Dissertation

Study of Biodiesel Production Technologies from Palm Oil Based on Life Cycle Assessment (LCA) and Exergy Analysis

Rosmeika

The Graduate School
Bogor Agricultural University
Bogor
2014
Hereby, I state that the dissertation entitled “Study of Biodiesel Production Technologies from Palm Oil Based on Life Cycle Assessment (LCA) and Exergy Analysis” is my own work, which has never previously been published in any university. All of incorporated originated from other published as well as unpublished papers are stated clearly in the text as well as in the references.

Bogor, April 2014

Rosmeika
F164100061
SUMMARY

ROSMEIKA. Study of Biodiesel Production Technologies from Palm Oil Based on Life Cycle Assessment (LCA) and Exergy Analysis. Supervised by ARMANSYAH H. TAMBUNAN, ARIEF SABDO YUWONO, and DYAH WULANDANI.

Concern over climate change is raising awareness on the need to use clean energy. Biodiesel (fatty acids methyl esters), which derived from triglycerides by transesterification with methanol, is recognized as an alternative fuel due to its renewability, sustainability and environmentally friendly. Biodiesel can be produced using a catalyst (catalytic) or without catalyst (non-catalytic). Several different methods of biodiesel production have been studied and proposed by many researchers. In order to maximize its associated environmental benefits and avoid as far as possible any potential negative effect, the increase in the use of biodiesel should be accompanied by a detailed analysis of their environmental impacts with a view to determining the benefits of such an increase in comparison with the use of fossil fuel. Accordingly, life cycle assessment (LCA) of the biodiesel production is indispensable to be conducted to evaluate its environmental impact. LCA is a tool for the analysis of the environmental burden of products at all stages of their life cycle and has been standardized in ISO 14040 series. However, its improvement is still required by incorporating exergy analysis into the method. Exergy is a thermodynamic function often chosen to complete LCA. Exergy (extractable energy), by definition, is the maximum amount of work in the form of material or energy in the interaction with its environment.

In this study, a non-catalytic biodiesel production with superheated methanol vapor (SMV) method was compared to the conventional alkali-catalyzed production method in terms of its environmental performance, exergy analysis, and Life Cycle Assessment (LCA). This study used the original data from several regions of Indonesia. Two scenarios of biodiesel production were evaluated. Scenario 1 is characterized by the absence of methane capture technology at the palm oil mill and utilization of industrial diesel oil (IDO) for boiler fuel at biodiesel plant, while, scenario 2 is characterized by the implementation of methane capture technology at palm oil mill and utilization of biomass waste for the boiler at biodiesel plant.

The result of Life Cycle Inventory (LCI) analysis shows that 1 kg of biodiesel is produced from about 1.046 kg of crude palm oil (CPO) or about 4.76 kg of fresh fruit bunch (FFB). The major water requirement for the production of biodiesel comes from oil palm plantation. The largest input from fertilizer is urea, although potassium and phosphorus are also significant contributors. The direct measurement of emissions from biodiesel plant was also discussed in this study. The results show that the concentration of SO$_2$, NO$_2$, PM, and O$_3$ pollutants emission from biodiesel plant was below the threshold, which means it did not influence the air quality around the biodiesel plant and did not endanger the surrounding population. Whereas, CO pollutant concentration from the biodiesel plant gave the negative impacts to the environment in the radius below 450 m
from the boiler stack (emission source). This implied that the safe distance of biodiesel plant site to the settlements area is in the radius of 450 m from the emission source.

The production of biodiesel through a catalytic transesterification method produced a large amount of wastewater that contains high contents of TSS, BOD, COD and oil & grease. The BOD/COD ratio was very low (below 0.1). Therefore, it could adversely affect if directly discharged into the environment without any treatment. Biodiesel plant that were studied, located in PUSPIPTEK, Serpong, Tangerang Selatan, within ± 600 m to the Cisadane Watershed. The results of the mass balance analysis for the contents of BOD and COD in Cisadane River stream that have been mixed with untreated wastewater from biodiesel plant showed an additional environmental burden with the increase of COD content from 12 mg/l to 29 mg/l. The form of appropriate engineering on aerobic and anaerobic processes in the waste water treatment plant (WWTP) before being discharged directly into the river is required in order to avoid the possible hazards.

The life cycle impact assessment (LCIA) result shows that the non-catalytic SMV method gives impact to higher greenhouse gas (GHG) emission and acidification, which was 1.7 kg CO₂ eq./kg biodiesel and 1.9E-03 kg SO₂ eq./kg biodiesel, respectively, and consume more energy (25 MJ/kg biodiesel) than the catalytic one when the biodiesel plant utilized fossil fuel as an energy source (scenario 1). The utilization of biomass waste as a substitute of fossil fuel can reduce the environment impact and total energy consumption for both methods. The implementation of methane capture system in palm oil mill also gave a big influence to GHG saving of biodiesel production. The implementation of methane capture system in the palm oil mill along with the utilization of biomass waste as an energy source in the biodiesel plant affected to the significant of GHG reduction in the SMV method (scenario 2).

The results of exergy analysis show that the exergy efficiency of non-catalytic SMV process was lower than the catalytic one, which was 92.61% and 95.37%, respectively, due to the high temperature requirement of the non-catalytic process. Heat recovery in SMV process should performed to reduce the irreversibility. The improvement of overall process in the non-catalytic SMV methods is required, especially in the methanol evaporation process to increase its exergy efficiency.

The SMV method can be made feasible by the utilization of biomass waste along its production line and the implementation of heat recirculation in the transesterification process.

Keywords: Palm Oil, Biodiesel, Superheated Methanol Vapor, Alkali-Catalyzed, Life Cycle Assessment, Exergy Analysis
RINGKASAN

ROSMEIKA. Kajian Teknologi Produksi Biodiesel Berbasis Minyak Sawit Berdasarkan Life Cycle Assessment (LCA) dan Analisis Eksergi. Dibimbing oleh ARMANSYAH H. TAMBUNAN, ARIEF SABDO YUWONO, dan DYAH WULANDANI.


Pada penelitian ini, proses produksi biodiesel non-katalitik dengan metode uap metanol superheated (Superheated methanol vapor/SMV) dibandingkan dengan metode produksi konvensional menggunakan katalis basa, dalam hal kinerja lingkungan, analisis eksergi dan Life Cycle Assessment (LCA). Penelitian ini menggunakan data original dari beberapa wilayah di Indonesia. Dua skenario produksi biodiesel dievaluasi. Skenario 1 ditandai dengan tidak digunakannya teknologi penangkapan metana di pabrik kelapa sawit dan pemanfaatan minyak solar industri (industrial diesel oil/IDO) untuk bahan bakar boiler di pabrik biodiesel, sementara, skenario 2 ditandai dengan penerapan teknologi penangkapan metana di pabrik kelapa sawit dan pemanfaatan limbah biomassa untuk boiler di pabrik biodiesel.

Hasil analisis LCI menunjukkan bahwa 1 kg biodiesel diproduksi dari sekitar 1.046 kg minyak mentah kelapa sawit/CPO atau sekitar 4.76 kg Tandan Buah Segar (TBS). Kebutuhan air utama untuk produksi biodiesel berasal dari berkebunan kelapa sawit. Urea (nitrogen) adalah input pupuk terbesar, meskipun kalium dan fosfor juga merupakan kontributor yang cukup signifikan. Pengukuran emisi dari pabrik biodiesel secara langsung, juga dibahas dalam penelitian ini. Hasil analisis menunjukkan bahwa konsentrasi polutan SO₂, NO₂, PM, dan O₃ dari pabrik biodiesel masih di bawah ambang batas, yang berarti tidak
mempengaruhi kualitas udara di sekitar pabrik biodiesel secara signifikan dan tidak membahayakan penduduk sekitarnya. Akan tetapi, konsentrasi polutan CO dari pabrik biodiesel memberikan dampak negatif terhadap lingkungan dalam radius di bawah 450 m dari cerobong asap boiler (sumber emisi). Ini berarti bahwa jarak aman dari lokasi pabrik dalam radius >450 m dari sumber emisi.

Produksi biodiesel melalui metode transesterifikasi katalitik menghasilkan sejumlah besar air limbah yang mengandung konsentrasi TSS, BOD, dan COD yang tinggi. Air limbah tersebut memiliki nilai rasio BOD/COD yang sangat rendah (di bawah 0.1). Oleh karena itu, air limbah tersebut dapat memberikan dampak negatif jika langsung dibuang ke lingkungan tanpa proses pengolahan terlebih dahulu. Pabrik biodiesel yang dikaji terletak di kawasan PUSPIPTEK, Serpong, Tangerang Selatan, yang berjarak ± 600 m dari Daerah Aliran Sungai Cisadane. Hasil analisis neraca massa untuk kandungan BOD dan COD di aliran Sungai Cisadane yang telah bercampur dengan air limbah yang tidak diolah dari pabrik biodiesel menunjukkan penambahan beban lingkungan yang ditandai dengan peningkatan kandungan COD dari 12 mg/l menjadi 29 mg/l. Untuk menghindari bahaya yang mungkin terjadi, diperlukan suatu teknik yang sesuai pada proses aerobik dan anaerobik dalam instalasi pengolahan air limbah (IPAL) sebelum air limbah tersebut dibuang langsung ke sungai.

Hasil kajian dampak lingkungan (LCIA) menunjukkan bahwa metode non-katalitik SMV menghasilkan dampak yang lebih tinggi untuk emisi gas rumah kaca dan pengasaman (acidification), yaitu sebesar 1.7 kg CO2 eq./kg biodiesel dan 1.9E-03 kg SO2 eq./kg biodiesel, secara berurutan, serta mengkonsumsi lebih banyak energi (25 MJ/kg biodiesel) dibandingkan metode katalitik ketika pabrik biodiesel menggunakan bahan bakar fosil sebagai sumber energi (skenario 1). Pemanfaatan limbah biomassa sebagai pengganti bahan bakar fosil bisa mengurangi dampak lingkungan dan konsumsi energi total untuk kedua metode tersebut. Penerapan teknologi penangkapan metana di pabrik kelapa sawit juga memberikan pengurang yang besar terhadap penghematan gas rumah kaca pada proses produksi biodiesel. Penerapan sistem penangkapan metana di pabrik kelapa sawit bersama dengan pemanfaatan limbah biomassa sebagai sumber energi di pabrik biodiesel berpengaruh signifikan terhadap pengurangan gas rumah kaca pada metode SMV (skenario 2).

Hasil analisis eksergi menunjukkan bahwa efisiensi eksergi pada proses non-katalitik SMV lebih rendah dibandingkan proses katalitik, yaitu sebesar 92.61% dan 95.37%, secara berurutan, hal ini disebabkan oleh kebutuhan suhu yang tinggi pada proses non-katalitik. Pemanfaatan panas dalam proses SMV perlu dilakukan untuk mengurangi nilai irreversibilitas tersebut. Perbaikan dalam keseluruhan proses metode SMV non-katalitik diperlukan, terutama dalam proses penguapan metanol untuk meningkatkan efisiensi eksergi-nya.

Metode SMV dapat menjadi layak dengan pemanfaatan limbah biomassa di sepanjang alur produksi biodiesel dan penerapan resirkulasi panas dalam proses transesterifikasi.

Kata kunci: Minyak Kelapa Sawit, Bahan Bakar Nabati, Superheated Methanol Vapor, Katalis Basa, Life Cycle Assessment, Analisis Eksergi
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STUDY OF BIODIESEL PRODUCTION TECHNOLOGIES FROM PALM OIL BASED ON LIFE CYCLE ASSESSMENT (LCA) AND EXERGY ANALYSIS

ROSMEIKA

A Dissertation
Submitted in partial fulfillment of the requirements for the Degree of Doctor in Agricultural Engineering Science

THE GRADUATE SCHOOL
BOGOR AGRICULTURAL UNIVERSITY
BOGOR
2014
The external assessor for closed examination are:
1. Dr. Ir. Lilik Pujantoro E.N., M.Agr.
2. Dr. Ir. Joelianingsih, MT.

The external assessor for open examination are:
1. Dr. Ir. Prastowo, M.Eng.
2. Dr. Ir. Soni S. Wirawan, M.Eng.
Dissertation title: Study of Biodiesel Production Technologies from Palm Oil Based on Life Cycle Assessment (LCA) and Exergy Analysis
Name: Rosmeika
Student Number: F164100061

Approved by,
Advisory Committee

Prof. Dr. Ir. Armansyah H. Tambunan
Chairman

Dr. Ir. Arief Sabdo Yuwono, M.Sc
Member

Dr. Ir. Dyah Wulandani, MSi
Member

Acknowledged by,
Chairman of Agricultural Engineering Science
Graduate Study Program

Dr. Ir. Wawan Hermawan, MS

Dean of Graduate School

Dr. Ir. Dahrul Syah, MSc.Agr

Date of Examination:
Date of Graduation:
PREFACE

Praise be to Allah SWT, The cherisher and sustainer of the worlds; God who has been giving blessing and mercy to me to complete the dissertation entitled “Study of Biodiesel Production Technologies from Crude Palm Oil Based on Life Cycle Assessment (LCA) and Exergy Analysis.”

This dissertation is submitted to fulfill one of the requirements to gain doctoral degree in Agricultural Engineering Science, Bogor Agricultural University.

In finishing this dissertation, I would like to give my best regards and gratitude to Prof. Dr. Ir. Armansyah H. Tambunan as the chairman of the advisory committee and all members of advisory committee: Dr. Ir. Arief Sabdo Yuwono, M.Sc and Dr. Ir. Dyah Wulandani, M.Si for all valuable assistance, support and their tireless and patient counsel. Thanks I gave to the Rector of Bogor Agricultural University (IPB), the Dean of The Graduate School of IPB, the Chairman of Agricultural Engineering Graduate Study Program, and all the lecturer and staff over all the facilities and assistance in studies and research. I would also thanks to the Indonesian Agency for Agricultural Research and Development for the opportunity to continuing study in The Graduate School Program, Bogor Agricultural University.

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I realize there are unintended errors in writing this dissertation. I really allow all readers to give their suggestion to improve its content in order to be made as one of the good examples for the next research.

Bogor, April 2014

Rosmeika
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LIST OF NOMENCLATURE

\[ \text{Exergy} \quad \text{kJ} \]

\[ \text{Chemical exergy} \quad \text{kJ} \]

\[ \text{Exergy at state 1 / exergy input} \quad \text{kJ} \]
Constituent average concentration for joint stream \( C_R \) mg/l
Constituent concentration at ‘i’ stream \( C_i \) mg/l
Heat capacity \( C_p \) kJ/kg K
Point concentration at receptor (x, y, z) \( C_{(x, y, z)} \) μg/m³
Energy \( E \) kJ
Gibbs free energy \( \bar{g} \) kJ/mol
Latent heat of vaporization \( \Delta H \) kJ/kg
Effective release height of emissions \( h \) m
Irreversibility \( I \) kJ
Constituent mass at ‘i’ stream \( M_i \) mg
Mass flow of a given pollutant from a source located at the origin \( m_p \) μg/s
Pressure \( P \) atm, bar, Pa
Pressure at the environment conditions \( P_0 \) atm, bar, Pa
Heat or input/output exergy related to heat \( q_i \) kJ
‘i’ stream discharge \( \dot{m}_i \) m³/s
Entrophy \( \Delta S \) kJ
Temperature \( T \) K
Temperature at the environment conditions \( T_0 \) K
Internal energy \( U \) kJ
Wind speed \( \bar{u} \) m/s
Work or exergy input/output related to work \( W \) kJ

**Greek symbols**

\( \sigma_y \) Standard deviation of plume concentration m
distribution in y plane
\( \sigma_z \) Standard deviation of plume concentration m
distribution in z plane

**LIST OF ABBREVIATIONS**

BCR Bubble Column Reactor
BDF Biodiesel Fuel
BOD Biochemical Oxygen Demand
BPPT *Badan Pengkajian dan Penerapan Teknologi*
CFP Carbon Footprint
CH₄ Methane
CO Carbon Monoxide
CO₂ Carbon Dioxide
COD Chemical Oxygen Demand
CPO Crude Palm Oil
EEA Exergy Accounting
EFB Empty Fruit Bunch
ELCA Exergetic Life Cycle Assessment
ExFA Exergy Flow Analysis
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>FLT</td>
<td>First Law of Thermodynamic</td>
</tr>
<tr>
<td>FFB</td>
<td>Fresh Fruit Bunches</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty Acid Methyl Ester</td>
</tr>
<tr>
<td>FFA</td>
<td>Free Fatty Acids</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>Gly</td>
<td>Glycerol</td>
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<tr>
<td>GWP</td>
<td>Global Warming Potential</td>
</tr>
<tr>
<td>HGF-B</td>
<td>High Grade Fertilizer Borate</td>
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<tr>
<td>IDEA</td>
<td>Inventory Database for Environmental Analysis</td>
</tr>
<tr>
<td>IDO</td>
<td>Industrial Diesel Oil</td>
</tr>
<tr>
<td>ISO</td>
<td>International Standard Organization</td>
</tr>
<tr>
<td>ISPO</td>
<td>Indonesian Sustainable Palm Oil</td>
</tr>
<tr>
<td>ISPU</td>
<td>Indeks Standar Pencemar Udara</td>
</tr>
<tr>
<td>JEMAI</td>
<td>Japan Environmental Management Association for Industry</td>
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<tr>
<td>LCA</td>
<td>Life Cycle Assessment</td>
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<tr>
<td>LCI</td>
<td>Life Cycle Inventory</td>
</tr>
<tr>
<td>LCIA</td>
<td>Life Cycle Impact Assessment</td>
</tr>
<tr>
<td>ME</td>
<td>Methyl Ester</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MiLCA</td>
<td>Multiple Interface Life Cycle Assessment</td>
</tr>
<tr>
<td>MOP</td>
<td>Muriate of Potash</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NOx</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td>NO2</td>
<td>Nitrogen Dioxide</td>
</tr>
<tr>
<td>N2O</td>
<td>Nitrous Oxide</td>
</tr>
<tr>
<td>O3</td>
<td>Ozone</td>
</tr>
<tr>
<td>PKO</td>
<td>Palm Kernel Oil</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PTPN</td>
<td>Perseroan Terbatas Perkebunan Nusantara</td>
</tr>
<tr>
<td>RFS</td>
<td>Renewable Fuel Standard</td>
</tr>
<tr>
<td>SCM</td>
<td>Supercritical Methanol</td>
</tr>
<tr>
<td>SLT</td>
<td>Second Law of Thermodynamic</td>
</tr>
<tr>
<td>SMV</td>
<td>Superheated Methanol Vapor</td>
</tr>
<tr>
<td>SOx</td>
<td>Sulphur Oxides</td>
</tr>
<tr>
<td>SO2</td>
<td>Sulphur Dioxide</td>
</tr>
<tr>
<td>STING</td>
<td>Simultaneous Reaction of Transesterification and Cracking</td>
</tr>
<tr>
<td>TG</td>
<td>Triglycerides</td>
</tr>
<tr>
<td>TSP</td>
<td>Triple Super Phosphate</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>UCO</td>
<td>Used Cooking Oil</td>
</tr>
<tr>
<td>UCOME</td>
<td>Used Cooking Oil Methyl Ester</td>
</tr>
<tr>
<td>US-EPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>WWTP</td>
<td>Waste Water Treatment Plant</td>
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</table>
CHAPTER I
INTRODUCTION

Background of the Research

Fossil fuel depletion, concern about environmental pollution, as well as the global warming issue, has increased the international interest on an alternative energy source. Biodiesel is a renewable energy source that could substitute fossil fuel. Biodiesel can be readily used with a certain blending ratio with the fossil diesel fuel in existing diesel engine without any major modifications to the engines because it has similar properties with petroleum diesel. Biodiesel can be degraded easily (biodegradable), non-toxic, contains no sulfur and aromatic compounds thus the combustion emissions are more environmentally friendly and does not increase the accumulation of carbon dioxide in the atmosphere, thereby it can reduce the global warming effects (Sheehan et al. 1998).

Biodiesel can be made from a variety of vegetable oils and fats with fatty acid ester composition. Palm oil is one of vegetable oils that are used as a biodiesel feedstock. Indonesia is the current leading global palm oil producer, thus palm oil based biodiesel is the most potential to be developed in Indonesia.

Biodiesel is mainly produced by transesterification process, a chemical reaction of any natural oil or fat with an alcohol such as methanol or ethanol. Methanol has been the most commonly used alcohol in the commercial production of biodiesel. Biodiesel can be produced using a catalyst (catalytic process) or without catalyst (non-catalytic process). Three types of catalysts, namely alkali, acid, and enzyme catalyst could be used in the catalytic process. Most of the methods on transesterification reaction are in the employing of alkali catalyst due to mild reaction conditions and high reaction rate. However, this method has some drawbacks such as difficulties in the recovery of glycerin, a need for removal of the catalyst and the energy intensive nature of the process. Furthermore, oil containing free fatty acids and/or water are incompletely transesterified using alkaline catalyst (Kusdiana and Saka 2001).

In order to eliminate the disadvantages resulted from the use of catalyst, non-catalytic transesterification methods have been proposed by many researchers; (1) supercritical methanol method, where the transesterification process is conducted at high temperature and high pressure (350-450°C, 43-65 MPa) (Kusdiana and Saka 2001), (2) simultaneous reaction of transesterification and cracking (STING) method, which is a complex reaction of transesterification, pyrolysis, cracking, and oxidation in supercritical methanol (Iijima et al. 2004), and (3) superheated methanol method, where the transesterification process is conducted at high temperature (290°C) but in atmospheric pressure (Yamazaki et al. 2007; Joelianingsih et al. 2008). Studies with various methods of biodiesel production processes have been conducted intensively because biodiesel can be feasible if it has a competitive price, an efficient production process, continuity of supply and assurance of appropriate quality standard. In addition, the development and utilization of biodiesel as an alternate to fossil fuels still require a more advanced technological development to increase their feasibility (Nigam and Singh 2011; Singh and Olsen 2011).
Selection of the proper process in producing biodiesel becomes a crucial decision, not only because of its cost and efficiency, but also the environmental impact factors. Accordingly, life cycle assessment (LCA) of the biodiesel production is indispensable to be conducted to evaluate its environmental impact. LCA is a systematic tool for assessing the environmental impacts associated with products, processes and activities (Ciambrone 1997) and has been standardized in ISO 14040 series. LCA is an environmental management approach that is increasingly being integrated into company and governmental decision making. At a conceptual level, it is called “life cycle thinking,” and approaches such as product stewardship and producer responsibility are built on this concept (Cowell 1999).

Efficient methods combining suitable indicators are needed to comprehend and assess the environment impacts. LCA is a method to compile a complete inventory, as well as to evaluate and to assess all relevant environmental impacts. Initially, the methods was developed for assessing the environmental impact of industrial plants and production processes (Haas 2001). In addition, the LCA is a tool that commonly used to analyze the energy savings and the reduction of greenhouse gas emissions, global environmental and energy audits that focus on the life cycle of a product, as well as the efficient use of resources such as land, water, energy and other natural resources. LCA can also be used to determine the global warming potential of each process in the biomass utilization.

However, LCA improvement is still required by incorporating exergy analysis into the method. The term exergy was introduced by Rant in the fifties. The concepts on which it is based, the first and second law of thermodynamics, were already established in the 19-th century (Cornelissen 1997). Exergy (extractable energy), by definition, is the maximum amount of work that can be done by a subsystem as it approaches thermodynamic equilibrium with its surroundings by a sequence of reversible processes (Bejan et al. 1996). Exergy can be used for analyzing the utilization of renewable and non-renewable energy in a system. Furthermore, it can be used as a tool to analyze the environmental quality degradation in the context of sustainable development (Dewulf and Van Langenhove 2006).

To determine the thermodynamic perfection of a system, not only processes that occur within the system will be taken into account, but also all kinds of interaction between energy and material flows outside the system’s boundaries. Only then the actual performance of the system and its impact on the environment can be evaluated. The irreversibility during the complete life cycle allows to evaluate the degree of thermodynamic perfection of the production processes and to conduct the assessment of the whole process chain (Cornelissen 1997).

Exergy is a thermodynamic function often chosen to complete LCA as it enables quantifying energetic efficiency of a process and takes into account the relation between the considered process and its environment. Exergy is more precisely based on the application of the first and second laws of thermodynamics and is a measure of energy quality (Portha 2008). Environmental impact associated with system and processes can often be decreased by reducing exergy losses (irreversibility), or correspondingly, increasing exergy efficiency.

Application of LCA and exergy analysis in the biodiesel production process technologies from palm oil is expected to anticipate the negative impact that
might be caused for realizing the environmentally friendly in biodiesel industry, to support the Indonesian Sustainable Palm Oil (ISPO) program, and to answer the European Community claim and US-EPA notification, which state that Indonesian biodiesel (esp. palm oil based biodiesel) has poor emission value and failed to meet the minimum 20% GHG emissions reduction threshold for renewable fuel under the Renewable Fuel Standard (RFS) program.

This report begins with giving background of the research (Chapter I) and reviewing the study of LCA and exergy analysis of palm oil biodiesel production (Chapter II). Goal and scope of this study and inventory analysis of palm oil Biodiesel production were identified in Chapter III. The purpose of the study, the boundary conditions, the assumptions, and the functional unit were defined in this chapter. Input and output data (raw materials, energy, products, waste, emissions to air and water) are collected for all the processes in the biodiesel production system. Calculations are then performed to estimate the total amounts of resources used in relation to the functional unit. Chapter IV discussed the analysis of direct measurement of emissions from biodiesel plant. Ambient air emissions and water pollutants were analyzed in this chapter. Chapter V described the life cycle impact analysis (LCIA) of palm oil biodiesel production and scenario for improvement.

In this chapter, the environmental burdens calculated in the inventory analysis are translated into environmental impacts. LCIA was divided in two general groups: 1) problem-oriented approaches, 2) damage-oriented methods (Azapagic 2006). This study was limited to the problem-oriented methods, which the environmental burdens are aggregated according to their relative contribution to the environmental effects. The impacts considered in this chapter were green house gasses (GHG), acidification, and eutrophication. The exergy analysis was described in Chapter VI. The final evaluation and discussions were presented in Chapter VII and the final conclusion of the research is shown in Chapter VIII.

Objective of the Research

The objective of this research is to study the influence of catalytic and non-catalytic (Superheated Methanol Vapor / SMV) method on the exergy and emission factor of palm oil based biodiesel production by using Life Cycle Assessment (LCA) and exergy analysis approach.

Benefits of the Research

a. To provide the information regarding with the life cycle assessment of palm oil biodiesel production process technologies (catalytic and SMV methods).
b. To identify areas where the technology of biodiesel production might be improved, in terms of environmental, energy, and exergy criteria.
c. To provide recommendations in choosing the most environmentally friendly technology in biodiesel production.
d. To provide original data and scientific analysis in responding to the heighten claims of international community that oil palm based biodiesel is far from environmentally friendly condition.
Boundaries of the Research

Actually, LCA is considering the impacts generated from “cradle to grave” of a product, process or activity. However, in regard with the limitation of data, time, and accessibility, this research was limited to these conditions:

a. The scope of the study was limited to “cradle to gate” LCA, which is from land preparation up to biodiesel production.

b. Direct measurement of emission and its analysis was limited to the analysis of air and water emissions from a biodiesel plant.

c. Parameter of ambient air emissions were based on the parameter of Air Pollutant Standard Index (Indeks Standar Pencemar Udara / ISPU), which were SO₂, NO₂, CO, PM, and O₃.

d. Exergy analysis was conducted only on the biodiesel production stage at biodiesel plant.

e. Impact analysis was limited to the characterization stage for greenhouse effect potential, acidification, and eutrophication.

All of the data used in life cycle inventory (LCI) was based on Indonesia condition.

Novelty of the Research

This research is the first LCA study in comparing the process of palm oil biodiesel production by conventional catalytic method with non-catalytic superheated methanol vapor (SMV) method.
CHAPTER II
A REVIEW ON LCA AND EXERGY ANALYSIS OF PALM OIL BIODIESEL PRODUCTION

Introduction

Biodiesel have become more attractive recently because of their environmental benefits and the fact that it is made from renewable resources. Biodiesel (monoalkyl esters of long-chain fatty acids) has a great potential as a substitute to fossil based diesel fuel. Substitution of conventional diesel fuel by biodiesel can have important benefits in terms of fossil energy saved and global warming emissions avoided.

Biodiesel can be produce by transesterification process, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol (Figure 2.1). Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a byproduct. (Zhang et al. 2003a; Zhang et al. 2003b).

Figure 2.1  A schematic representation of the transesterification of triglycerides (vegetable oil) with methanol to produce fatty acid methyl esters (biodiesel)

Transesterification reaction is controlled by three mechanisms: mass transfer, kinetic and equilibrium. The mass transfer becomes slow if the immiscibility of the two reactants (i.e. methanol and triglycerides) is poor. On the completion of the mass transfer, the ensuing process is controlled by the kinetic. Both kinetic and mass transfer of the reaction can be improved by increasing the reaction temperatures and vigorous mixing (Darnoko and Cheryan 2000).
Based on few criteria, palm oil is the most potential vegetable oil which can be used as raw material to manufacture biodiesel and on the other hand the usage of crude palm oil (CPO) consider to be the most wanted palm oil products for its cheap price and readiness for downstream processing (Alkabbashi et al. 2009). In the context of maximizing the environmental benefits and avoid as far as possible any potential negative effect, the increased use of biodiesel must be accompanied by a detailed analysis of its environmental impact with a purpose to determining the benefits of biodiesel utilization compared with the use of conventional diesel fuels. Life Cycle Assessment (LCA) method can be used to investigate the environmental sustainability of biodiesel production, since LCA can quantitatively assesses the environmental impact and the energy requirements of a product since its initial raw materials to its final disposal.

In addition to LCA, exergy analysis has also been proposed to assess process sustainability. The use of exergy analysis plays a very significant role in LCA as it enables identifying losses of useful energy. LCA can be used to calculate the environmental impact of a product or a process while exergy analysis can gives information about the thermodynamic efficiency of a process. Exergy analysis enables calculating exergy of streams (mass and heat fluxes) and the destroyed exergy in different units included in the overall process to find energetic efficiency (Portha et al. 2008).

This chapter reviews the LCA methodology and exergy analysis in the biodiesel production technologies. The purpose of this chapter is to give an overview on different technologies to produce biodiesel, and also an overview of LCA method and exergy analysis in their use to assess the biodiesel production.

**Production of Biodiesel**

Biodiesel can be produced using a catalyst (catalytic transesterification) or without catalyst (non-catalytic transesterification). Several different methods of biodiesel production has been studied and proposed by many researchers. The following discussions describe a brief review of these methods.

**Catalytic Transesterification**

Transesterification reactions can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Generally, alkali-catalyzed transesterification using sodium hydroxide (NaOH) or potassium hydroxide (KOH) as catalyst, and acid-catalyst transesterification using sulfuric acid (H₂SO₄) or phosphoric acid (H₃PO₄) as catalyst, while enzyme-catalyst transesterification utilizing lipase as catalyst. The selection of catalyst depends on the amount of free fatty acid (FFA) present in the oils or fats. Alkali-catalyst is used for oils/fats with FFA content less than 5%, while acid-catalyst is used for oils/fats with FFA content more than 5% (Joelianingsih et al. 2007). The FFA content of CPO is less than 5%, so the pre-treatment process is not required and a suitable catalyst used in the transesterification process is alkali-catalyst.
The biodiesel production by catalytic method started with the transesterification process, return of unreacted methanol, methyl ester purification from catalyst, and separation of glycerol as by product. Biodiesel reaction with the help of catalyst has an advantage that the reaction can be run faster. On the other hand, the purification process utilizes water by repeated washing, so the process is more wasteful of water. Biodiesel production by catalytic reaction has other problems including the process are relatively time consuming to purify the product and requires a rigorous stirring in the reaction due to the immiscible character of oil with methanol (Kusdiana and Saka, 2001).

Alkali-Catalyzed Transesterification

Alkali-catalyzed transesterification is most commercially used and the process is much faster than other type of catalyst (Ma and Hanna 1999; Zhang et al. 2003a; Bajpai 2006). A reaction temperature near the boiling point of the alcohol (e.g., 60°C for methanol) and a 6:1 molar ratio of alcohol to soybean oil were recommended (Freedman et al. 1984; Noureddini and Zhu 1997). Freedman et al. (1986); Darnoko and Cheryan (2000) studied the kinetics of the alkali-catalyzed system. Based on their results, approximately 90–98% of oil conversion to methyl esters was observed within 90 min.

Nakpong and Wootthikanokkhlan (2009) examined biodiesel production from the mixing of vegetable oil and used cooking oil (UCO) using alkali catalyst. Vegetable oil consists of jatropha oil, rosella oil, coconut oil, while the comparison between vegetable oil and UCO are 0.03-0.2 v/v. It was obtained that biodiesel production from the mixing of coconut oil and UCO has been met the standard of biodiesel characteristics except for low viscosity. The optimum ratio between the UCO with vegetable oil was 0.03 v/v. Alkabbashi et al. (2009) studied biodiesel production from Crude Palm Oil (CPO) using KOH as a catalyst. The study found that the optimal values of reaction time was 60 min, reaction temperature was 60°C, molar ratio of methanol to oil of 10:1 (m/m), catalyst dosage was 1.4 (%wt), and the best possible yield of biodiesel at the end of the reaction was 93.6%.

Acid-Catalyzed Transesterification

Production of biodiesel from raw materials that have low economic values and high FFA content is one of the alternatives to obtain a more competitive production costs compared to petroleum fuel. Currently, biodiesel production from raw materials consists of two stages in the process, because it requires pre-esterification process to reduce FFA levels down to below 5%. Raw materials that have relatively high FFA contents are more suitable by using acid catalyst for transesterification process, although transesterification by acid catalyst is much slower than that by alkali catalyst (Freedman et al. 1984; Ma and Hanna, 1999). Acid used for the transesterification process include sulfuric, phosphoric, hydrochloric, and organic sulfonic acids (Fukuda et al. 2001).
Freedman et al. (1984) investigated the transesterification of soybean oil with methanol using 1 wt.% concentrated sulfuric acid (based on oil). They found that at 65°C and a molar ratio of 30:1 methanol to oil, took 69 hour of reaction time to obtain more than 90% oil conversion to methyl esters. The kinetics of the acid-catalyzed transesterification with butanol was also investigated by Freedman et al. (1986). They stated that the forward and reverse reactions followed pseudo-first-order and second-order kinetics, respectively. Zhang et al. (2003a) used the acid-catalyzed process to produce biodiesel from waste cooking oil. The result showed that the acid-catalyzed process using waste cooking oil proved to be technically feasible with less complexity than the alkali-catalyzed process using waste cooking oil, thereby making it a competitive alternative to commercial biodiesel production by the alkali-catalyzed process.

Cardoso et al. (2008) evaluated the utilization of acid-catalyst to produce soybean oil biodiesel. Commonly, H$_2$SO$_4$ is utilized as the catalyst in the pre-esterification process. However, it has major drawbacks such as substantial reactor corrosion and the great generation of wastes, including the salts formed due to neutralization of the mineral acid. Therefore, Cardoso et al. (2008) evaluated the use of tin (II) chloride dihydrate (SnCl$_2$·2H$_2$O) as catalyst in the process of ethanalysis of oleic acid, which is the major component of several fats and vegetable oils feedstock. The SnCl$_2$ catalyst was shown to be as active as the mineral acid H$_2$SO$_4$. Its use has relevant advantages in comparison to mineral acids catalysts, such as less corrosion of the reactors as well as avoiding the unnecessary neutralization of products.

Studies of the acid-catalyzed system have been very limited in number. No commercial biodiesel plants to date have been reported to use the acid-catalyzed process. Despite its relatively slow reaction rate, the acid-catalyzed process offers benefits with respect to its independence from free fatty acid content and the consequent absence of pretreatment step. These advantages favour the use of the acid-catalyzed process when using waste cooking oil as the raw material (Zhang et al. 2003a).

**Enzym-Catalyzed Transesterification**

Alkali-catalyzed and acid-catalyzed methods are both sensitive to the presence of water and FFA. In addition, the reaction has several drawbacks, such as it is energy intensive, recovery of glycerol is difficult, the catalyst should be removed from the product and alkaline waste-water required treatment. To overcome those drawbacks, Masaru et al. (1999) developed a new enzymatic method of synthesizing methyl esters from plant oil and methanol in a solvent-free reaction system. Enzymatic reactions are insensitive to FFA and water content in oil, so it does not generate any waste materials. Enzymatic production of biodiesel fuel from waste oils therefore is strongly desirable (Fukuda et al. 2001; Watanabe et al. 2001). However, the degree of methanolysis was low in reaction systems, and the lipase catalyst could not be reused in spite of using immobilized enzyme. Shimada et al. (2002) clarified this problem with regards to the irreversible inactivation of the lipase by contact with insoluble methanol (MeOH). Based on this result, they developed a stepwise methanolysis system with immobilized
Candida antarctica lipase. Two-step batch methanolysis was most effective for the production of biodiesel fuel from waste oil. Shah et al. (2004) studied a method of production of biodiesel by lipase catalyzed transesterification of Jatropha oil. It was seen that immobilization of lipases and optimization of transesterification conditions resulted in more adequate yield of biodiesel compare with free enzyme, under the same conditions. Although enzymatic alcoholysis requires lower energy, the cost of lipase is still too high compared to alkaline catalyst.

**Non-catalytic Transesterification**

Several researchers have developed the technology of biodiesel production without using a catalyst (non-catalytic transesterification). The process of non-catalytic transesterification has several advantages such as not requiring the removal of FFA by refining or pre-esterification. Esterification or transesterification reaction can take place in the reactor so that the oils with high FFA content can be directly used (Joelianingsih et al. 2007). In addition, the separation and purification process become much simpler and environmentally friendly because of the absence of catalyst. However, non-catalytic transesterification typically utilizes a large excess of methanol with higher operating temperatures than the catalytic process (Kusdiana and Saka 2001; Demirbas 2002).

**Non-Catalytic Transesterification in Supercritical Methanol (SCM)**

Kusdiana and Saka (2001) and Demirbas (2002) have developed a method for biodiesel production with supercritical methanol (SCM). Non-catalytic SCM process was carried out at high temperature and high pressure, which is about 350-450°C and 43-65 MPa. Kusdiana and Saka (2001, 2004) studied a non-catalyst process in which vegetable oil was transesterified with supercritical methanol and found that the amount of water in the reaction does not affect the conversion of oil into biodiesel. Conversely, the presence of certain amount of water increases the formation of methyl esters and esterification of free fatty acids takes place simultaneously in one stage. The results showed that the reaction took only 4 min and a reaction temperature of 350°C with the molar ratio of methanol being 42 were considered as the best condition for a free-catalyst process of biodiesel fuel production.

SCM method at high temperature and pressure conditions provide improved phase solubility, decrease mass transfer limitations, provide higher reaction rates and make easier separation and purification steps. Besides, the SCM method is more tolerant to the presence of water and FFAs than the homogeneous base catalyst method, and hence more tolerant to various types of feedstocks (Abbaszaadeh et al. 2012). However, there is still question about the safety and energetic aspects because the SCM needs high pressure in order to keep methanol in the supercritical state. To overcome this disadvantage, they proposed a two-step preparation for biodiesel production by hydrolysis and methyl esterification to
reduce the temperature and pressures to 270 °C and 7 MPa, respectively (Saka et al. 2006).

**Simultaneous reaction of Transesterification and Cracking (STING)**

Iijima et al. (2004) have proposed a supercritical conditions (reaction parameters: T = 643–773 K; p = 20–60 MPa and residence time = 4–12 min) for producing an unconventional biodiesel fuel (mainly FAME, mono- and di-acyl glycerol) without yielding glycerin as a byproduct. It was called as simultaneous reaction of transesterification and cracking (STING). STING methods performed the complex reaction of transesterification, pyrolysis, cracking, and oxidation treated in Supercritical Methanol. The STING-process was applied for biodiesel production from animal fat. However, small size FAME was produced by the STING-process, kinetic viscosity could be lower than that of conventional biodiesel, and the production cost was still high. To overcome these drawbacks, enlargements of the plant are necessary.

**Superheated Methanol Vapor (SMV)**

To overcome the disadvantages of SCM and STING method, several researchers have studied the superheated methanol vapor (SMV) method, which transesterification process occurs at the atmospheric pressure. Yamazaki et al. (2007) studied non-catalytic biodiesel production process from sunflower oil using superheated methanol method. They have developed a bubble column reactor to produce FAME under around atmospheric pressure by blowing the superheated methanol vapor bubbles into oil (triglycerides) without using any catalysts. Kinetics of the non-catalytic transesterification of palm oil at atmospheric pressure has been reported by Joelianingsih et al. (2007). Joelianingsih et al. (2008) developed a new reactor for producing fatty acid methyl ester (FAME) by blowing the superheated methanol vapor bubbles continuously into vegetable oil.

**Life Cycle Assessment on Biodiesel Production**

Life Cycle Assessment (LCA) is an internationally renowned methodology for evaluating the global environmental performance of a product, process or pathway along its partial or whole life cycle, considering the impacts generated from “cradle to grave” (Gnansounou et al. 2009). The LCA methodology is standardized by the ISO 14040-14043 standards (ISO 1997, 1998, 2000a, 2000b). According to ISO 14040 (ISO 1997), the methodology comprises the following four phases (Figure 3.2):

1. goal and scope definition (defined by ISO 14040);
2. inventory analysis (defined by ISO 14041);
3. impact assessment (defined by ISO 14042); and
4. interpretation (defined by ISO 14043).
Goal and Scope Definition

The goal definition and scoping stage of LCA defines the purpose of the study, the expected product of the study, the boundary conditions, the assumption, and the functional unit. The goal and scope definition is very important since the study will be carried out according to the statements made in this phase. The functional unit is the unit of analysis defined for the study; it is defined according to the service delivered by the system under analysis. The functional unit provides a point of reference for the system inputs and outputs, assures equivalence that allows for meaningful comparisons between alternative systems, includes all factors involved in a decision, and identifies elements that all the items under the study have in common (Todd and Curran 1999).

Inventory Analysis

Life cycle inventory (LCI) analysis involves the collection of environmental burdens data necessary to meet the goal of the study. The input and output associated with the system in the process of biodiesel production identified and measured in unit function, including materials and energy used in the system, and emissions generated (Azapagic 2006). According to ISO 14041 (ISO 1998), the main steps of LCI are construction of flow diagrams, description of unit processes, data collection, calculation of flows and releases, validations of data, relating data to unit process, refining system boundaries, allocation of flows and emissions.
Impact Assessment

The third phase of LCA is life cycle impact assessment (LCIA). During the impact assessment phase, the environmental burdens calculated in the inventory analysis are translated into the related potential environmental impacts (or category indicators). The objective of phase is to present the environmental impacts of the system under analysis in a form that is useful for the purpose of the study and that can be understood by users of the study results (Cowell 1999).

Based on ISO 14042 key steps of a life cycle impact assessment are following three mandatory steps (SAIC 2006; Azapagic 2006):

1. Selection and Definition of Impact Categories - identifying relevant environmental impact categories (e.g., global warming, acidification, terrestrial toxicity).
2. Classification - assigning LCI results to the impact categories (e.g., classifying CO2 emissions to global warming).
3. Characterization - modeling LCI impacts within impact categories using science-based conversion factors. (e.g., modeling the potential impact of CO2 and methane on global warming).

A further optional three steps are also included within this phase:

1. Normalization - expressing potential impacts in ways that can be compared (e.g. comparing the global warming impact of CO2 and methane for the two options).
2. Grouping - sorting or ranking the indicators (e.g. sorting the indicators by location: local, regional, and global).
3. Weighting - emphasizing the most important potential impacts.

The last step of LCIA is evaluating and reporting LCIA results for gaining a better understanding of the reliability of the LCIA results.

Interpretation

The final phase of an LCA is Life cycle interpretation which is a systematic technique to identify, quantify, check, and evaluate information from the results of the life cycle inventory (LCI) and the life cycle impact assessment (LCIA), and communicate them effectively (SAIC 2006).

Sensitivity analysis is part of the interpretation step. Sensitivity analysis should be carried out before the final conclusions and recommendations of the study are made. Data availability and reliability are some of the main issues in LCA since the results and conclusions of an LCA study will be determined by the data used. Sensitivity analysis can help identify the effects of data variability, uncertainties and data gaps have on the final results of the study, and indicate the level of reliability of the final results of the study (Azapagic 2006).

The International Organization for Standardization (ISO) has defined the following two objectives of life cycle interpretation (ISO 1998):
1. Analyze results, reach conclusions, explain limitations and provide recommendations based on the findings of the preceding phases of the LCA and to report the results of the life cycle interpretation in a transparent manner.
2. Provide a readily understandable, complete, and consistent presentation of the results of an LCA study, in accordance with the goal and scope of the study.

The first comprehensive LCA of biodiesel production was published by Sheehan et al. (1998). They utilized the LCA method to compare biodiesel and petroleum diesel for use in an urban bus. Pleanjai et al. (2004) evaluate the environmental implications of palm oil biodiesel production in a life cycle perspective. Kiwjaroun et al. (2009) used LCA to compare the environmental performance of supercritical methanol process with the conventional alkali-catalyzed in producing palm oil biodiesel. It was found that the supercritical process generated a higher environmental impact and higher energy consumption. The supercritical methanol method needs high pressure in order to keep methanol in the supercritical state. However, there is still question about the safety and energetic aspects. Hasanudin (2010) studied the carbon footprint (CFP) and LCA on palm oil production in Indonesia. The results showed that the use of palm oil effluent into biogas as an energy source can reduce CO₂ emissions by 6.5 million tons per year. Nazir and Setyaningsih (2010) assessed the environmental impacts of Indonesian palm oil and jatropha biodiesel using the concept of life cycle thinking. Hidayatno et al. (2011) analyzed the potential environmental impact in the supply chain of palm oil biodiesel industries in Indonesia. Sekiguchi (2012) utilized LCA method to estimate GHG emission of Jathropha-based biodiesel fuel production by SMV method. Siregar (2013) compared emission and energy for biodiesel production from oil palm dan jatropha curcas in Indonesia using LCA as a method.

**Exergy analysis on Biodiesel Production**

Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics which provides an alternative and illuminating means of assessing and comparing processes and systems rationally and meaningfully. Exergy is defined as the maximum amount of work which can be produced by a stream of matter, heat or work as it comes to equilibrium with a reference environment (Dincer and Rosen 2007). The potential work is obtained through a reversible process. Exergy can be transferred between the systems and can be destroyed by irreversibility in the system. Exergy analysis has advantages compared to energy analysis, which are more accurate in determining the energy lost in the process or that discharged into the air, and be able to determine the quality of energy (Sugiyono 2000). Exergy has the characteristic that it is conserved only when all processes of the system and the environment are reversible. Exergy is destroyed whenever an irreversible process occurs (Dincer and Cengel 2001).

Talens et al. (2007) applied exergy flow analysis (ExFA) as an environmental assessment tool to account waste and emissions, determined the exergetic efficiency, compared substitutes and other types of energy sources in the process of biodiesel production. The result showed that the production process has
a low exergy loss. The exergy loss was reduce by using potassium hydroxide and sulphuric acid as process catalysts and it can be further minimised by improving the quality of the used cooking oil. Peiró et al. (2010) compared the production of 1 ton biodiesel from used cooking oil (UCO) and rapeseed oil using extended exergy accounting (EEA) method. The results showed that biodiesel production from UCO utilized source materials and energy, as well as less total investment and lower costs for environmental rehabilitation than rapeseed oil. On the other hand, UCOME require much longer working hours. Production of biodiesel from UCO used fewer resources than the production of biodiesel from rapeseed oil.

Exergetic life cycle assessment (ELCA) is a method that was developed based on a life cycle approach combined with the exergy analysis. This method is the development of life cycle assessment (LCA) method. ELCA was proposed by Cornelissen (1997). ELCA is use to account the exergy input required by the system. ELCA uses the concept of exergy from a life cycle approach to provide the natural basis for assessing efficiency of resource use. ELCA accounts also the renewables and non-renewables sources supplied to the system. ELCA can be also used for accounting for the depletion of natural resources (Peiró et al. 2009).

To illustrate the potential incorporation of LCA method and exergy analysis, Peiró et al. (2009) assessed the life cycle of biodiesel from used cooking oil (UCO) using LCA and ELCA method. The production of 1 ton of biodiesel was evaluated by LCA to assess the environmental impact and ELCA to account for the exergy input to the system. The result showed that the transesterification stage causes 68% of the total environmental impact.

**Conclusion**

Research on vegetable oil-based biodiesel has been widely applied and developed, including the research that aimed to evaluate the biodiesel production process and its environmental impact. However, the studies that aim to assess the life cycle of biodiesel by combining LCA method and exergy analysis are still rare. LCA in Indonesia is still not widely practiced. Several studies that have been done are still not integrated, thus the dataset of LCA inventory for Indonesia is not currently available. Incorporation of LCA methods and exergy analysis on biodiesel production was only performed by Peiró et al. (2009), which examined the life cycle of biodiesel from used cooking oil (UCO) with the catalytic method. Therefore, this study utilizes the methods of LCA and exergy analysis to analyze and compare the production of palm oil biodiesel by conventional (alkali-catalyzed transesterification) with non-catalytic superheated methanol vapor (SMV) method. This study will result in data on the exergy efficiency and the environmental impact associated with the biodiesel production with those two methods of transesterification process. This study can further be used as an en-trypoint to the ELCA study by combining the LCA method and exergy analysis in the unit.
CHAPTER III
GOAL & SCOPE DEFINITION AND
LIFE CYCLE INVENTORY OF PALM OIL BIODIESEL
PRODUCTION

Introduction

The Goal and scope definition is the phase in which the initial choices to determine the working plan of the entire LCA are made (Guinée et al. 2002). This phase defines and describes the product, process or activity, as well as establishes the context in which the assessment is to be made and identify the boundaries and environmental effects to be reviewed for the assessment. In this phase, the following items must be determined: the type of information that is needed to the decision-making process, how accurate the results must be, and how the results should be interpreted and displayed in order to be meaningful and usable (SAIC 2006). Without proper attention to these steps it is difficult to obtain a successful assessment (Searcy 2000).

The goal definition essentially provides the basis for scoping process. The scope describes the system to be studied and directs how much information is to be collected, in what categories, and to what levels of detail and quality (Todd and Curran 1999). In other word, it sets the boundaries, assumptions, limitations, and allocation procedures on which the rest of study will be based. In each case, the assumption, data and system boundaries may be different so that it is important that these are defined in accordance with the goal of the study. The goal and scope definition are very important since the study will be carried out according to the statements made in this phase (Roy et al. 2005).

In order to be able to compare the information in an objective fashion, it is important that a functional unit is identified during this stage of the LCA. The functional unit provides a point of reference for the system inputs and outputs, assures equivalence that allows for meaningful comparisons between alternative systems, includes all factors involved in a decision, and identifies elements that all the items under the study have common (Todd and Curran 1999). A functional unit, to which all the environmental impacts are related, has to be defined. The functional unit provides the study with a baseline to which criteria can be reference. The functional unit represents a quantitative measure of the output of products, or services which the system delivers. In comparative LCA studies, it is crucial that alternative systems are compared on the basis of an equivalent functional unit (Azapagic 2006).

The second phase of LCA is inventory analysis (life cycle inventory / LCI), which identifies inputs and outputs for each process or material and calculates the flows of materials, energy and emissions. Essentially, all the inventory analysis processes follow the basic laws of science and engineering with a good part of the effort focused on material and energy balances for each element within the system (Curran 1996). Life cycle inventory (LCI) analysis is a method to quantify the resources use, energy use and environmental releases associated with the system being evaluated (Azapagic 2006).
The design of LCI should be considered during the initial scoping of the study, because the inventory analysis should be in line with the requirements of the impact assessment stage (Todd and Curran 1999). In other words, the data requirements of this component are dependent on what is needed to perform the impact assessment. This fact should be reflected in the selection of the system boundaries. Only after the system boundaries have been clearly defined can the data collection process begin (Searcy 2000). Without an LCI, no basis exists to evaluate comparative environmental impacts or potential improvements. The level of accuracy and detail of the data collected is reflected throughout the remainder of the LCA process (SAIC 2006).

The data collection process is the main focus of the inventory analysis and it is often one of the most time consuming stages of the overall LCA study. The data to be collected is heavily dependent on how the system boundaries were defined. Data must be collected for all elements that have been designated under the system boundaries for review (Searcy 2000). According to Ciambrone (1997), LCA takes into consideration five types of outputs: airborne wastes, waterborne wastes; solid waste, products and co-products.

As with in any scientific study, it is important to consider data characteristics such as precision, accuracy, representativeness, consistency and reproducibility. Essentially, the higher the influence of the study will have on any decision being made, the higher the degree of rigor that is required for the data gathering (Todd and Curran 1999).

Life cycle inventory analyses can be used in various ways. They can assist an organization in comparing products or processes and considering environmental factors in material selection. In addition, inventory analyses can be used in policy-making, by helping the government develop regulations regarding resource use and environmental emissions (SAIC 2006).

The objective of this chapter was to define the boundaries, assumptions, limitations, and allocation procedures on palm oil biodiesel production, also to identify and quantify the environmental inputs and outputs associated with the production of palm oil biodiesel by conventional and SMV methods.

Methods

This research was conducted based on the standardized LCA tool with the incorporation of exergy analysis (Figure 3.1). According to the standard, LCA consist of the following phases: (1) Goal and Scope Definition, (2) Inventory Analysis, (3) Impact Assessment, and (4) Interpretation. This chapter describes only the first two steps.
Goal and Scope Definition

The goal of this study was to compare the energy consumption, exergy efficiency, and the environmental impacts of 1 kg palm oil based biodiesel production by catalytic and non-catalytic (SMV) method.

Around 1155 units of oil palm plantation has been established in Indonesia, owned by private companies, government and smallholder estates, scattered in 22 provinces (BPS 2012). This research was focused on the effect of technology used for biodiesel production, such that only big plantations (private and government estates) was studied without assessing the small plantations (smallholder estates), since small plantation is rarely own biodiesel plant.

Palm oil mill effluent (POME) is the largest source of greenhouse gases (GHG) in palm oil mill operation. During anaerobic digestion of POME in open ponds, methane gas is emitted to the atmosphere. In order to reduce GHG emissions, palm oil mill should implement methane capture technology for capturing and utilizing the methane gas, either for firing or electricity generation. Many palm oil mills in Indonesia have implemented the methane capture technology, even though it is not yet all of the mill, but the number is increasing due to the regulation of Indonesian Government. In this study, the effect of the implementation of methane capture technology was analyzed and discussed.

Transportation from nursery to plantation, from plantation to palm oil mill and from palm oil mill to biodiesel plant also considered. Many biodiesel plants are located in the same site with the palm oil mill; while others are located outside palm oil mill site with the average distance from the palm oil mill to the biodiesel plant is about 100 km.

The large scale biodiesel plants have already used biomass as an energy source along its production line. However, small scale biodiesel plants still utilize
the fossil fuel. This study investigated the effect of those two fuel types to the environmental impact of the biodiesel production.

**System Boundaries**

This research is systematized in four main groups: life cycle inventory of palm oil based biodiesel, direct measurement of emission at a biodiesel plant, life cycle impact assessment and scenario for improvement, and exergy analysis on biodiesel production technology. Each of the group is studied with different system boundary as shown in Figure 3.2. The study on life cycle inventory as well as impact assessment and scenario for improvement is bounded in the dashed line with legend 1. The data inventories were collected from many resources. Most of the emission data were obtained from plant reports and literature review. Two scenarios of biodiesel production were evaluated, as shown in Table 3.1. Scenario 1 is characterized by the absent of methane capture technology at the palm oil mill and utilization of industrial diesel oil (IDO) for boiler fuel at biodiesel plant. While, Scenario 2 is characterized by the implementation of methane capture technology at palm oil mill and the utilization of biomass waste (oil palm shell) for the boiler at biodiesel plant.

<table>
<thead>
<tr>
<th>Application of methane capture at palm oil mill</th>
<th>Type of fuel used at biodiesel plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>Not applied</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>Applied</td>
</tr>
</tbody>
</table>

Direct measurement of emission was conducted on a biodiesel plant using catalytic processing technology, as shown by the dashed line with legend 2. Data obtained from direct measurement is used for confirmation of data obtained from literature and to identify possible hazard generated by the biodiesel plant. Study on exergy analysis was conducted only on the biodiesel plant to identify the effect of alternative technology to the irreversibility and exergy efficiency of the biodiesel production process. The boundary is shown by the dashed line with legend 3.
Figure 3.2  LCA system boundary of biodiesel production technologies
One of the complexities of LCA lies in its multidisciplinary character. Following are characteristics of three spheres that are all required in an LCA (Hofstetter 1998 cited in Goedkoop et al. 2010):

- **Technosphere**: The modelling of technical systems, such as production processes, transport processes etc. Usually, uncertainties in technosphere are not greater than a factor 2, while almost all measurements are verifiable and repeatable. In this study, the data that included in the technosphere model were the data from palm oil mill and biodiesel plant (the process of biodiesel transesterification and direct measurement of emission).

- **Ecosphere**: The modelling of environmental mechanisms ("what happens with an emission?"). Uncertainties are often one to three orders of magnitude, and often verification is difficult or impossible. For example, one cannot test-run climate change and repeat this several times to get good measurements. In this study, the data that included in the ecosphere model were the data of biomass waste utilization in the biodiesel plant.

- **Valuesphere**: Dealing with subjective choices. This includes weighting of impact categories, but as we will see, values also play an essential role when an allocation procedure or a time horizon is selected. For example, in impact assessment it is important to choose whether the potential damage from heavy metals is integrated over just 100 years or over eternity. A valuesphere is typically in the area of social sciences. With valuespheres one cannot really speak of uncertainties, as a "single" truth does not exist. The result of impact assessment are the valuesphere model in this study.

**Life Cycle Inventory (LCI)**

The input and output associated with the system in the process of biodiesel production was identified and measured in functional unit of 1 kg biodiesel, including the generated emissions. The primary data were obtained from Oil Palm Plantation and Palm Oil Mill, in Banten Province, Indonesia. As an addition, secondary data from plant reports (Etika 2012; Harijana 2012; Situmorang 2012) and literature review (Ditjen PPHP 2006; BB Pengkajian 2008; Sastrosayono 2008; Sunarko 2009; Alloverung et al. 2010; Lubis and Widanarko 2011; Nazir and Setyaningsih 2010; Hasanudin 2010; Hidayatno et al. 2011; Pahan 2011; Furqon 2011; Sekiguchi 2012) are also used in the study. Since this study was devoted to the life cycle assessment of palm oil based biodiesel produced in Indonesia, original data is more preferred, which can only be obtainable from local publication, such as company report, report by related institution, field practice report conducted by students, etc., as listed above.

Catalytic transesterification experiment was conducted in a facility owned by Center for Design Engineering and Technology System (Engineering Center), Agency for Assessment and Application of Technology (Badan Pengkajian dan Penerapan Teknologi / BPPT), while the non-catalytic transesterification data was obtained from previous research (Joelianingsih et al. 2008; Sigalingging 2008; Furqon 2011; Sekiguchi 2012).

This study used ‘Multiple Interface Life Cycle Assessment (MiLCA)’ version 1.2.0, developed by Japan Industrial Environmental Management
The display of MiLCA-JEMAI software presents in Appendix 1. IDEA (Inventory Database for Environmental Analysis) is the standard equipment inventory database for MiLCA. IDEA format is created based on ISO TS 14048, with reference to the ILCD ecospold2 format. MiLCA software provide upstream inventory for all input materials and processes. The upstream conducts the mid-point impact assessment. Utilization of electricity from grid was corrected with actual data of Indonesia, which comprise 38.50% coal, 29.32% fossil fuels, 22.52% natural gas, 7.23% hydropower, and 2.44% geothermal (PT. PLN (Persero) Reports 2011). The following discussion describes the inventories data for each stage of CPO biodiesel production.

Result and Discussion

Oil Palm Plantation

Oil palms start to produce fruits 30 months after field planting. The typical commercial lifespan of an oil palm is 25 years, after which it is no longer commercially viable for harvesting. Water requirement for the oil palm plantation is mostly from the rain water in the 25 years’ lifetime of the plant. Oil palm productivity of the big plantations was 25 tons per hectare per year. Fertilizer is an important factor to increase the fresh fruit bunch (FFB) production. Weeding is performed within 1-1.5 months by applying herbicides to weeds. Insecticide is used in the nursery in case the seedlings are attacked by insects. Table 3.2 shows the inventories data for producing 1 kg FFB in the Indonesian oil palm plantation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>1.85E-02</td>
<td>kg</td>
</tr>
<tr>
<td>Water</td>
<td>1.26E+00</td>
<td>m³</td>
</tr>
<tr>
<td>Compound fertilizer</td>
<td>2.12E-03</td>
<td>kg</td>
</tr>
<tr>
<td>Urea</td>
<td>1.37E-02</td>
<td>kg</td>
</tr>
<tr>
<td>TSP</td>
<td>1.12E-02</td>
<td>kg</td>
</tr>
<tr>
<td>Rock phosphate</td>
<td>1.25E-02</td>
<td>kg</td>
</tr>
<tr>
<td>MOP</td>
<td>1.20E-02</td>
<td>kg</td>
</tr>
<tr>
<td>HGF-B</td>
<td>3.80E-05</td>
<td>kg</td>
</tr>
<tr>
<td>Kieserite</td>
<td>8.48E-03</td>
<td>kg</td>
</tr>
<tr>
<td>Paraquat</td>
<td>1.50E-04</td>
<td>kg</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>0.30E-04</td>
<td>kg</td>
</tr>
<tr>
<td>Diesel</td>
<td>4.21E-04</td>
<td>l</td>
</tr>
</tbody>
</table>

The fruit bunch is harvested manually by cutting bunches of fruit. The FFB must be immediately transported to the palm oil mill because the milling process of FFB should be implemented within eight hours after harvest to prevent the...
increase of FFA content. The transportation of FFB to palm oil mill utilized trucks, lorries or tractors. Approximately, 4.76 kg of FFB is needed to produce 1 kg biodiesel.

Palm Oil Production

Indonesia has about 608 palm oil mills (Ditjenbun 2012). The palm oil mills capacity are in the range of 30-75 tons per hour. The mills operate 16-24 hours per day. The FFB from oil palm plantation are weighed at the weight bridge and unloaded in the loading ramp. After unloading, FFB are sent to the sterilizer and cooked for 80-90 minutes with 2.0-2.8 kg/cm² steam at temperature of about 135°C. This process will generate palm oil mill effluent (POME) which is sent to wastewater treatment ponds. The sterilized FFB are delivered to stripping process to separate the sterilized fruits from bunch stalks. This processing step generates the empty fruit bunches (EFB), which are incinerated to produce bunch ash for fertilizer in oil palm plantation. The separated fresh fruits are digested to separate fruit from nut. Crude palm oil extraction is performed using screw press, and continues to clarification station for cleaning the CPO from impurities. The fiber and nuts from the screw press are separated in a cyclone. The fiber that passes out of the bottom of the cyclone is used as boiler fuel. Meanwhile, the nuts are processed to obtain the palm kernel oil (PKO) in the kernel treatment station. Table 3.3 shows the inventory data for producing 1 kg CPO in the Indonesian palm oil mill. Approximately, 1.04 kg of CPO is needed to produce 1 kg biodiesel.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFB</td>
<td>4.55E+00</td>
<td>kg</td>
</tr>
<tr>
<td>Water</td>
<td>2.90E-03</td>
<td>m³</td>
</tr>
<tr>
<td>HCl</td>
<td>2.00E-04</td>
<td>kg</td>
</tr>
<tr>
<td>NaOH</td>
<td>2.00E-04</td>
<td>kg</td>
</tr>
<tr>
<td>Diesel</td>
<td>6.30E-03</td>
<td>liter</td>
</tr>
<tr>
<td>Electricity</td>
<td>5.90E-02</td>
<td>kWh</td>
</tr>
<tr>
<td>EFB</td>
<td>1.05E+00</td>
<td>kg</td>
</tr>
<tr>
<td>PKO</td>
<td>1.32E-01</td>
<td>kg</td>
</tr>
<tr>
<td>Fiber</td>
<td>3.06E-01</td>
<td>kg</td>
</tr>
<tr>
<td>Shell</td>
<td>2.63E-01</td>
<td>kg</td>
</tr>
<tr>
<td>POME</td>
<td>3.35E+00</td>
<td>kg</td>
</tr>
</tbody>
</table>
Biodiesel Transesterification

Transesterification is a reaction of triglycerides is reacted with short-chain alcohols to form fatty acid methyl esters (FAME), known as biodiesel fuel. The stoichiometric ratio for the transesterification reaction requires three moles of methanol and one mole of triglyceride to yield three moles of fatty acid methyl ester and one mole of glycerol (Freedman et al. 1986).

The following discussion describes the catalytic and non-catalytic (SMV) transesterification process.

Catalytic Transesterification Process

This study used sodium hydroxide (NaOH) as a catalyst in the transesterification process. Figure 3.3 shows the batch process of catalytic transesterification to produce biodiesel at Engineering Center biodiesel plant. The catalyst (NaOH) was dissolved in methanol solution using a mixer / blade agitator, then the mixture is flowed to the reactor and palm oil is added into the reactor. The reaction temperature is 60-65°C. Biodiesel and glycerin is separated in a settling tank. Excess methanol is taken through a distillation process. Subsequently, glycerol as a byproduct still containing catalyst and soap is neutralized with a sulfuric acid solution, while biodiesel is purified using warm water and dried in a vacuum drying tank before it is sent to a storage tank. Material and energy input to the catalytic transesterification system for producing 1 ton of biodiesel per batch is shown in Figure 3.3. Three-dimensional layout of biodiesel plant in Engineering Center presents in Appendix 2.
Figure 3.3 The alkali-catalyzed process to produce palm oil biodiesel
Superheated Methanol Vapor of Non-catalytic Process (SMV)

The SMV method for biodiesel production has been proposed and studied by many researchers (Yamazaki et al., 2007; Joelianingsih et al. 2008; Furqon 2011; Sekiguchi 2012). Yamazaki et al. (2007) developed a new reactor to produce biodiesel by blowing superheated methanol gas continuously into oils without using any catalyst. The results showed that the maximum output rate of FAME occurred at reaction temperature of 290°C. The process has several advantages such as not requiring the removal of free fatty acid (FFA) by refining or pre-esterification prior to the process. Esterification or transesterification reactions can take place in a reactor, thus oils with high FFA content can be used directly. In addition, the processes of separation and purification products become more simple and environmentally friendly, due to the absent of catalyst. However, non-catalytic processes normally require a higher operating temperature than the catalytic one, and the reaction rate of biodiesel production is lower than that by catalytic process.

Joelianingsih et al. (2008) studied the kinetics of biodiesel production from refined palm oil by non-catalytic SMV transesterification using laboratory scale continuous low bubble column reactor (BCR). Joelianingsih (2008) also developed and tested a laboratory-scale continuous-flow BCR system for biodiesel production from refined palm oil by non-catalytic SMV transesterification and performed the scaling up of SMV process from a laboratory scale to the industrial scale, with the capacity of 1 ton biodiesel per hour, using HYSYS software. Sigalingging (2008) performed the energy and exergy analysis on CPO biodiesel production by catalytic and SMV methods. Tambunan et al. (2011) addresses heat recirculation in the SMV process by replacing the condenser with the counter flow heat exchanger. Sekiguchi (2012) performed a non-catalytic reaction process in a demonstration plant of SMV method with the production scale of 400 L biodiesel/day. Material and energy input to the non-catalytic SMV method for producing 1 ton of biodiesel is shown in Figure 3.4.
Figure 3.4 The superheated methanol vapor (SMV) process to produce 1 ton palm oil biodiesel
Conclusions

This research utilized the standardized LCA tool with the incorporation of exergy analysis. The goal of this research was to compare the energy consumption, exergy efficiency, and the environmental impacts of 1 kg palm oil based biodiesel production by catalytic and non-catalytic (SMV) method. Two scenarios of biodiesel production were evaluated. Scenario 1 is characterized by the absent of methane capture technology at the palm oil mill and utilization of industrial diesel oil (IDO) for boiler fuel at biodiesel plant. While, Scenario 2 is characterized by the implementation of methane capture technology at palm oil mill and the utilization of biomass waste for the boiler at biodiesel plant. This research is systematized in four main groups: life cycle inventory of palm oil based biodiesel, direct measurement of emission at a biodiesel plant, life cycle impact assessment and scenario for improvement, and exergy analysis on biodiesel production technology.

The life cycle inventory analysis has been performed in the production of palm oil biodiesel. 1 kg of biodiesel is produced from about 1.04 kg of CPO or about 4.76 kg of FFB. The major water requirement for the production of biodiesel comes from oil palm plantation. Urea (nitrogen) is the largest input from fertilizer although potassium and phosporus are also significant contributors.
CHAPTER IV
DIRECT MEASUREMENT OF EMISSIONS FROM BIODIESEL PLANT

Introduction

This chapter discusses the direct measurement of emissions from biodiesel plant. The emission was limited to the flue gas emitted from the boiler stack and water pollutant from the washing process in the biodiesel plant. One issue that caused by the combustion of fossil fuels in energy conversion devices is a decrease of ambient air quality. Therefore, in planning of a biodiesel plant establishment should be considered to the proper location in order to minimize the impact of environmental pollution that may endanger the population’s health near by the plant. The quantity of air pollutants that potentially released from the biodiesel plant should be considered, because high concentration of pollutants in ambient air will affect the recipients particularly humans, animals, plants, and materials or objects which are located in the pollutant sources environment.

The major emission sources associated with the operation of the biodiesel plant is emissions from the boiler stack (ERM 2007). Some air pollutants like nitrogen oxides (NOx), carbon monoxide (CO), sulfur dioxide (SO2), hydrocarbons (HC) and particulate matter (PM), generated from the combustion process from boiler providing steam and energy to the process, directly affects the environment and health risks (Cretu et al. 2010).

Pollution is the act that pollutes the environment that causes instability, disorder, harm or discomfort to the ecosystem, i.e. physical systems or living organisms. Air pollution is one of the major problems of urban environment as a consequence of economic development, urbanization, energy consumption, air and urban road transport and increasing number of urban population. Air pollution has been and continues to be a significant health hazard all over the world. Exposure to air pollution is an issue of concern due to the diversity of these pollutants, adverse effects were observed at different levels of air pollution, and a large number of people at risk. The effects of air pollution can sometimes be observed even when the pollution levels below the level indicated by the air quality guidelines (Brunekreef and Holgate 2002; Chen and Kan 2008; Cretu et al. 2010). Considering the fact that air pollutant has been associated with a series of adverse health effects, it is important to predict air pollution from the biodiesel plant stack. An easy and an inexpensive estimation can be performed through atmospheric dispersion modeling.

The other direct emission from biodiesel plant is wastewater. The catalytic production process would normally produce wastewater. Wastewater is generated from the washing process of methyl esters and glycerol. The contents in wastewater are mixture of methanol, fatty acids, oils and methyl esters that dissolved. Based on experiences from similar industries which contain these substances, such as wastewater from the palm oil industry, estimated the organic content expressed as COD (Chemical Oxygen Demands) is around 8000-10000 mg/L and BOD (Biochemical Oxygen Demands) is around 3000-4000 mg/L, the amount of waste produced about 2 m³ of wastewater per ton product (Syafila et al.
2007). Compared to the wastewater derived from fossil fuels production such as oil refining process (petroleum refinery) with organic content ranging between 300-600 mg/l COD, it appears that wastewater from biodiesel production has very high organic contents (Esmiralda 2010). If wastewater is not properly treated and discharged directly into the environment, it would affect the incidence of contamination. The next implication is pollution that would adversely affect the human life. Both anaerobic and aerobic wastewater treatment at the biodiesel plant showed less than the maximum results, so it still contains sufficiently high organic compound (Syafila et al. 2007).

The purpose of this study was to analyze the distribution of air pollutant (SO$_2$, NO$_2$, CO, PM and O$_3$) concentration from the biodiesel plant stack using Gaussian Dispersion Equation and to analyze the changes in the quality of water in Cisadane River due to wastewater disposal from biodiesel plant. The result of this study was expected to be used as a consideration in anticipation of possible negative impacts caused by biodiesel plants, and also provided recommendation and information about the safe distance of biodiesel plant site to the settlements area.

**Atmospheric Pollutants**

Sulfur dioxide (SO$_2$) emissions come from burning of sulfur-containing fossil fuels which may contain up to 6% sulfur. At relatively high concentrations, SO$_2$ causes severe respiratory problems (Badenhorst 2007); at sufficiently high concentrations, SO$_2$ exposure is harmful to susceptible plant tissue. SO$_2$ is also a source of acid rain, which is produced when SO$_2$ combines with water droplets to form sulfuric acid (H$_2$SO$_4$). Fine particles of H$_2$SO$_4$ will be binding in the lungs which can cause respiratory diseases. It can also heighten the risk of skin cancer due to sulfate and nitrate compounds into direct contact with skin. Another impact of acid rain include influence of surface water quality, dissolved heavy metals contained in the soil thus affecting the quality of ground water and surface water, and its corrosiveness damaging materials and buildings. SO$_2$ and other tropospheric aerosols containing sulfur are believed to affect the radiation balance of the atmosphere, which may cause cooling in certain regions (Cahyono 2007; Fardiaz 1992; Matthias et al. 2006).

Nitrogen oxides (NO$_x$) refers to the mixtures of nitric oxide (NO) and nitrogen dioxide (NO$_2$) that are formed when combustion causes the nitrogen and oxygen in the atmosphere to combine to form NO, some of which then oxidizes further to NO$_2$; combustion gases contain about 5 to 10% NO$_2$ mixed with NO. NO$_2$, the most toxic of the NO$_x$, causes damage to lung tissues at concentrations higher than usually found in ambient atmospheres (Ather et al. 2010). NO$_2$ is a noxious gas that can cause inflammation of the lungs and, at high concentrations, even death. In addition, NO$_x$ will react further with water and oxygen to form nitric acid (HNO$_3$). Like sulfuric acid (H$_2$SO$_4$), nitric acid is a very strong acid that easily corrodes or attacks many materials (Fardiaz 1992; Matthias et al. 2006; Pfafflin and Ziegler 2006). Nitric acid is also a component of acid rain.

Carbon monoxide (CO) is a product of incomplete combustion of any fuel. It is both a highly poisonous gas and the principal constituent of photochemical smog. CO is poisonous when inhaled because it combines with hemoglobin, the
oxygen-carrying substance in red blood cells and block it. Therefore, the lack of oxygen makes cells and tissues to die (Fardiaz 1992; Matthias et al. 2006; Pfafflin and Ziegler 2006; Currie et al. 2009).

Particulate matter (PM) is organic and inorganic compounds present in the atmosphere as both liquid and solid substances particles. Particulate matter emissions (soot and fly ash) can contribute to long-term respiratory problems. Its particles are extremely small, with the diameter between less than 2.5 micrometers (μm) and up to 10 micrometers, and may carry along small amounts of hazardous trace elements or potentially carcinogenic organic molecules. Particulate matter is also an aesthetic nuisance. Areas with high concentrations of air-borne particulate matter are more likely to experience fogs, because these particles are preferred nucleation sites for water droplets (Cretu et al. 2010; Fardiaz 1992; Matthias et al. 2006).

Ozone (O₃) is a secondary ambient air pollutant, which formed through reactions between nitrogen oxides and volatile organic compounds (which are found in auto emissions, among other sources) in heat and sunlight. Ozone may be either hazardous or beneficial, depending on its location in the atmosphere. Ozone is beneficial in the stratosphere as the “ozone layer,” because it absorbs UV radiation. However ground-level ozone is a pollutant and a primary cause of smog. In the presence of heat and sunlight, precursor compounds such as nitrogen oxides and volatile organic compounds react to form ground-level ozone. Exposure to ground-level ozone can induce a variety of health problems, because Ozone is a highly reactive compound that can damages tissue, reduces lung function, and sensitize the lungs to other irritants. Ground-level ozone can also damage plant life. In vegetation, the main damage occurs in foliage, with smaller effects on growth and yield (Artiola and McColl et al. 2006; Matthias et al. 2006; Currie et al. 2009).

The people most affected by air pollution are those who are situated downwind of the major sources. To prevent or minimize damages of atmospheric pollution, a method for predicting a concentration of atmospheric pollutants is urgently needed, which can rapidly and reliably detect and quantify air quality. The study on dispersion of air pollutants from a stack is an effort to develop an environmentally friendly industry.

**Water Quality**

Water is a basic need for every living thing that must be fulfilled. Water can cause direct or indirect effects on health depend on the stream quality. BOD and COD are a measure that is often used for measuring the water quality. Both of these measures are used to monitor the water quality by looking at the levels of oxygen contained therein. If oxygen levels in the water decreases as a result of decomposition of organic matter excess, then the water quality will be decline. Disruption of the water quality characterized by discoloration, odors and flavors, also the most severe is the disruption of the existing organisms in aquatic ecosystems. The explanations of the two indicators are as follows (Fardiaz 1992):
- **Biochemical Oxygen Demand (BOD)** indicates the amount of dissolved oxygen required by the living organisms to break down or oxidize the waste material in the water. BOD is expressed in the unit of milligrams per liter (mg/l) or milligrams per kilogram (mg/kg).
- **Chemical Oxygen Demand (COD)** is the concentration of dissolved oxygen in the wastewater that is required to decompose certain organic substances chemically due to difficulty destroyed by oxidation. Therefore, it takes a strong oxidizing reaction to becomes acidic. COD value is always greater than BOD values.

Water pollution occurs when a waterbody is adversely affected due to the addition of large amounts of materials to the water. The government regulation (PP No. 82 in the year of 2001) on the Management of Water Quality and Water Pollution Control, established the water quality into 4 (four) classes, namely:

- First class, which the allocation of water can be used for drinking water, and or other utilization that require the equal water quality to these usability;
- Second class, which the allocation of water can be used for infrastructure / recreation water facilities, freshwater aquaculture, animal husbandry, irrigation, and or other designation that require the equal water quality to these usability;
- Third grade, which the allocation of water can be used for freshwater aquaculture, animal husbandry, irrigation, and or other uses that require the equal water quality to these usability;
- Fourth grade, which the allocation of water can be used for irrigation, plantation and or other utilization that require the equal water quality to these usability.

Water quality standards based on the class division mentioned above presents in Table 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>10</td>
</tr>
</tbody>
</table>

In addition to the above mentioned parameters (BOD and COD), there are several other parameters that are also used in determining water quality, such as total suspended solids (TSS) and pH.

TSS is solid materials, including organic and inorganic, that are suspended in the water. These would include silt, plankton and industrial wastes. High concentrations of suspended solids can lower water quality by absorbing light. Waters then become warmer and lessen the ability of the water to hold oxygen necessary for aquatic life. Therefore, high concentration of TSS may adversely affect growth and reproduction rates of aquatic fauna and flora (Nasrullah *et al.* 2006).

The pH value of a water source is a measure of its acidity or alkalinity. The pH level is a measurement of the activity of the hydrogen atom, because the
hydrogen activity is a good representation of the acidity or alkalinity of the water. The pH scale ranges from 0 to 14, with 7.0 being neutral. Water with a low pH is said to be acidic, and water with a high pH is basic, or alkaline. Pure water would have a pH of 7.0. Low pH can cause the release of toxic elements and compounds from sediments into the water where they may be taken up by aquatic animals or plants. Changes in pH also influence the availability of plant nutrients, such as phosphate, ammonia, iron and trace metals, in the water. Acidic water can also cause problems for human consumption. While slightly acidic water is not dangerous, on its own, it can be quite dangerous when combined with other compounds. Water with a pH that is less than 6.5 can leach metal ions, including iron, manganese, copper, lead and zinc from plumbing fixtures and pipes. This, in return, can be quite dangerous. On the other end of the pH scale, water that has a pH greater than 8.0 can be difficult to disinfect. The World Health Organization recommends that the pH of the water be less than 8.0, because basic water does not allow for effective chlorination (Gray and Santini 1998; Addy et al. 2004).

**Water Quality of Cisadane River**

Wastewater sampling was conducted in biodiesel plant owned by Center for Design Engineering and Technology System (Engineering Center), Agency for Assessment and Application of Technology, Serpong that located in South Tangerang, Banten, Indonesia, which the polluted river is Cisadane River that located within ± 600 m from biodiesel plant. The upstream of Cisadane River comes from the north slope of Mount Kendeng (+1,764 m), Mount Perbakti (+1,699 m) and Mount Salak (+2,211 m), flowing northward through the mountains in West Java, passes Bogor, Tangerang City, and ended into the Java Sea. The river is approximately 140 km long with extensive watershed (DAS) ± 1,411 km². The primary tributaries are Ciapus, Cikideung, Cinangneng, Ciampea, Ciaruteun, Cianteun and Cikaniki which upstream near Parung Badak. Nearly 50% of Cisadane watershed is a mountainous area (BAPEDAL Banten Province 2004). From the publication data of Cisadane River discharge in the period of 2003 to 2008, it was known that the average annual discharge of Cisadane River is 65.78 m³/sec (Balai PSDA Cidurian Cisadane River Basin 2009 cited in Haryati 2010). Cisadane watershed can be seen in Figure 4.1.
The sufficient high of opacities values in the Cisadane River upstream reduces its water quality. The water quality in the middle part of Cisadane River has a very good value of total coliforms, but considerably less for dissolved oxygen. In the downstream of Cisadane River, water quality is affected by the high value of total coliforms and organic matter content (COD). The laboratory tests results which conducted by Sucofindo, indicated that the water of Cisadane River contains BOD of 5 mg/l and COD of 12 mg/l (Ersada 2011).

Methods

Air Pollution Dispersion

Pollutants dispersion in the air can be visualized by looking at the pattern of dispersion (plume) of smoke emitted by the stack continuously. The size of the plume carried by the wind will increase due to dispersion. Dispersion also leads to the decreases of pollutants concentration in the smoke along with the increase of the distance from the emission source.

Dispersion models use mathematical formulations to characterize the atmospheric processes that disperse a pollutant emitted by a source. Using observations and/or simulated meteorological fields, dispersion models can
predict concentrations at selected downwind receptor locations (Matthias et al., 2006). The Gaussian Dispersion Equation, a mathematical approximation that simulates the steady-state dispersion of pollutants from a continuous point source is given in equation 4.1 (Turner 1994; Matthias et al. 2006).

\[
C_{(x,y,z,h)} = \frac{m_p}{2\pi \sigma_y \sigma_z u} \times \exp \left( -\frac{y^2}{2\sigma_y^2} \right) \times \left[ \exp \left( -\frac{(z-h)^2}{2\sigma_z^2} \right) + \exp \left( -\frac{(z+h)^2}{2\sigma_z^2} \right) \right]
\]

(4.1)

Where:
- \( C \) = point concentration at receptor, in \( \mu g/m^3 \);
- \( (x, y, z) \) = ground level coordinates of the receptor relative to the source and wind direction, in meters;
- \( h \) = effective release height of emissions, in meters (m);
- \( m \) = mass flow of a given pollutant from a source located at the origin, in \( \mu g/s \);
- \( u \) = wind speed, in m/s;
- and \( \sigma_z \) = standard deviation of plume concentration distribution in \( y \) and \( z \) planes, in meters.

Value of \( \sigma \) in the above equation is estimated from several empirical formulas that connected \( \sigma \) with the distance of the wind flow and the stability conditions of the airflow (equation 5.2). The formulas were developed by Brookhaven National Laboratory (BNL).

\[
\sigma = ax^b \quad \text{and} \quad \sigma_z = cx^d
\]

(4.2)

Where \( a, b, c, \) and \( d \), are parameters that depend on the airflow stability conditions (Matthias et al. 2006). It is assumed that the total reflection of the plume at ground level (\( z = 0 \) conditions).

Gaussian dispersion model has been widely used for predicting pollutants dispersion and concentration (Laskarzewska and Mehrvar 2009; Cretu et al. 2010; Latha and Shanmugam 2010; Suryani et al. 2010; Teleaba and Mihai 2012).

**Ambient Air Pollutions**

The study was limited to a small scale biodiesel plant and used the data of emission from the boiler stack of biodiesel plant, then the distribution of pollutants concentration were analyzed using Gaussian model (equation 4.1). The air qualities were measured based on Air Pollutant Standard Index (Indeks Standar Pencemar Udara / ISPU) based on KEP 45 / MENLH / 1997 and Kep Ka. Bapedal No. 107 / 1997 (Appendix 3). ISPU is number that does not have a functional unit which describes the condition of ambient air quality in certain locations and times that based on the impact on human health, aesthetic values and other living things.

Pollutants concentration from the combustion of fossil fuel in boiler was directly measured from the boiler stack of a small scale biodiesel plant owned by Engineering Center located in the region of Research Centre for Science and
Technology, Serpong, South Tangerang Municipality, Indonesia. The plant capacity is 1.5 ton/day with a compact design and small size boiler for steam generator.

The simulated pollutant gases consist of five types, namely sulfur dioxide (SO$_2$), nitrogen dioxide (NO$_2$), carbon monoxide (CO), particulate matter (PM) and ozone (O$_3$). To obtain the concentration of pollutants distribution required the physical condition of the biodiesel plant, such as height and diameter of stack, gas velocity that emitted from stack, and also the meteorological condition data from the impact receiving area. The data included wind speed, wind direction, and atmospheric stability.

The meteorological condition data that were obtained from the first class of Geophysics Station in the Meteorology, Climatology, and Geophysics Agency Tangerang, on the official site of South Tangerang Municipality Government, were as follows: the wind speed average is 3.8 m/s, with the wind direction in January to April and November to December is to the West, while May to October is to the North (South Tangerang Municipality Government 2012).

The wind is one of the most important meteorological parameters for the transport and dispersion of air pollutants. The wind acts either by speed and direction, its influence on air pollution being high variable, depending on the source position. Generally, wind speed increases with altitude; the dispersion is being facilitated by the wind. More wind will be stronger; the pollution levels will be lower whereas, wind with a low speed supports the local accumulation of pollutants (Cretu et al. 2010).

**Water Pollution**

Effluents were collected from the washing stage at the biodiesel plant owned by Engineering Center for analysis of various physical and chemical parameters like TSS, pH, BOD, and COD. The water quality data of Cisadane River utilized the research data of Sucofindo in 2011, which stated that the water of Cisadane River contains BOD of 5 mg/l and COD of 12 mg/l (Ersada 2011). The flowrate (discharge) of the river was assumed to be the same and the average of Cisadane River discharge per year was 65.78 m$^3$/s (Balai PSDA Cidurian Cisadane River Basin 2009 cited in Haryati 2010).

To determine the pollution load capacity, the mass balance method was used and only BOD and COD parameters were assessed to determine the water quality of Cisadane River. Mathematical model using mass balance calculations can be used to determine the average concentration in the flow of downstream that comes from a point source or a non-sources point of pollution. This calculation can also be utilized to determine the percentage change in flow rate or pollutant load.

If multiple streams meet and generate final stream, or if the water quantity and the constituents mass calculated separately, then the mass balance analysis is needed to determine the quality of the final flow, which the calculation as in equation 4.3. (Kepmen LH No. 110 in the year of 2003 on Guidelines for Determination of Load Capacity of Water Pollution in Water Resource).
\[ C_R = \frac{\sum C_i q_i}{\sum q_i} = \frac{\sum M_i}{\sum q_i} \]  
\( (4.3) \)

where

- \( C_R \): constituent average concentration for joint stream (mg/l)
- \( C_i \): constituent concentration at ‘i’ stream (mg/l)
- \( q_i \): ‘i’ stream discharge (m³/s)
- \( M_i \): constituent mass at ‘i’ stream (mg)

**Result and Discussion**

**Ambien Air Pollution**

Based on the research that was conducted at the Engineering Center biodiesel plant, boiler stack emitted 25.362 µg/s SO₂ pollutant, 0.227 µg/s NO₂ pollutant, 178.478 µg/s CO, 0.187 µg/s PM pollutant, and 0.003 µg/s O₃ pollutant. The report of air quality analysis result is shown in Appendix 5.

The analysis result for pollutants concentration from biodiesel plant using Gaussian Dispersion Model (equation 4.1) is given in Table 4.2. The highest pollutant concentration value found at a radius of 25 m from the stack.

**Table 4.2 The value of pollutants concentration distribution**

<table>
<thead>
<tr>
<th>Distance by the wind direction, x (m)</th>
<th>SO₂</th>
<th>NO₂</th>
<th>CO</th>
<th>PM</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>69.418</td>
<td>0.623</td>
<td>488.516</td>
<td>0.511</td>
<td>0.007</td>
</tr>
<tr>
<td>50</td>
<td>27.196</td>
<td>0.244</td>
<td>191.390</td>
<td>0.200</td>
<td>0.003</td>
</tr>
<tr>
<td>100</td>
<td>8.920</td>
<td>0.080</td>
<td>62.775</td>
<td>0.066</td>
<td>0.001</td>
</tr>
<tr>
<td>200</td>
<td>2.772</td>
<td>0.025</td>
<td>19.508</td>
<td>0.020</td>
<td>0.000</td>
</tr>
<tr>
<td>300</td>
<td>1.387</td>
<td>0.012</td>
<td>9.763</td>
<td>0.010</td>
<td>0.000</td>
</tr>
<tr>
<td>400</td>
<td>0.848</td>
<td>0.008</td>
<td>5.964</td>
<td>0.006</td>
<td>0.000</td>
</tr>
<tr>
<td>500</td>
<td>0.578</td>
<td>0.005</td>
<td>4.067</td>
<td>0.004</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The results showed that based on the atmospheric dispersion modeling using Gaussian Dispersion Model, the distribution of concentrations in ambient air for parameter SO₂, NO₂, PM and O₃ are under the threshold. It means these pollutants didn’t affect to the air quality around the biodiesel plant, which based on the ISPU, a radius of 25 meters from the emission source (boiler stack) for these four pollutants, already in ‘good’ category, with the ISPU number below 50. At this air quality level, there was no adverse effects neither on the health of humans, animals, and plants, nor on the building and aesthetic value. Pollutants distribution model can be seen in Figure 4.2 – 4.5 for parameter SO₂ NO₂, PM and O₃, respectively.
Figure 4.2  SO$_2$ Pollutant distribution model

Figure 4.3  NO$_2$ Pollutant distribution model
Unlikely, the result of CO pollutant modeling showed that CO concentration in a radius of 100 m from the emission source was in the ISPU 'dangerous' category, which the concentration of CO was 62.775 µg/m$^3$ with ISPU number was higher than 500. Air quality level in this condition could harm the health of humans, animals, and plants, seriously. In a radius of 200 m from emission source, the concentration of CO was 19.508 µg/m$^3$ with ISPU number was 215, which
mean that it was in ‘extremely unhealthy’ category. At this air quality level, the concentration of CO could be harmful to the health of populations exposed. In a radius of 400 m from emission source, the concentration of CO was 5.964 µg/m³ with ISPU number was 60, which mean that it was in ‘medium’ category. The level of air quality in these conditions had no negative impact on human or animal health, but could affect to the sensitive plants that could cause injury to some plant species and could affect to the aesthetic value. The ‘good’ category was obtained at a radius of 450 m from the emission source. Pollutants distribution model for parameter CO can be seen in Figure 4.6.

Graphical illustration of simulated results from the biodiesel plant stacks are presented in Figure 4.7. The simulated results show that the CO concentration was much higher than SO₂, NO₂, PM, and O₃ concentrations. It observed that the concentrations of SO₂, NO₂, PM, and O₃ are below the Indonesian regulatory standards, whereas, due to the high concentrations of CO pollutant from the biodiesel plant, a simulated safety distance beyond 450 m from the plant is recommended for human settlement and activities.

The wind speed is one of the parameter that influence the transport and dispersion of air pollutants. The simulation results show that the increase of wind speed could caused the decrease of pollutant concentration, whereas the decrease of wind speed lead to the increase of pollutant concentration and broaden radius safety from emission source.
Figure 4.7 Pollutants concentration estimated by Gaussian Dispersion Model

The high concentration of CO pollutant was due to many incomplete combustion of fossil fuel in boiler. Incomplete combustion can also result in the reduction of boiler efficiency. In order to minimize the negative impacts of the air pollutants emitted from the biodiesel plant being studied, it is necessary to do the prevention attempt, such as installing the scrubber in the stack, maintaining the burner/boiler and doing periodic testing to keep it operating properly.

Boiler startup, shutdown, and load changes can cause the increase of CO emissions due to unstable combustion conditions. CO emissions are also sensitive to boiler operating conditions. Changes in operating conditions, such as rapid changes in load, can have a significant, though temporary, impact on emissions. During boiler startup, boiler itself is relatively cool, and the low air flow rates make it difficult to obtain good air/fuel mixing. For these reasons, CO emissions could radically increase when transient conditions occur during boiler startup and shutdown. Tuning of the combustion system and optimizing the boiler performance to maximize the combustion efficiency, can overcome this problem. Tuning of the combustion system and optimizing the boiler performance requires a visual check by an experienced boiler or stationary engineer to ensure that everything is in good working condition and set according to the manufacturer’s recommendations or the optimum settings developed for the particular boiler (US EPA 2010).

Juszczak (2002) stated that the increase in CO concentration is caused by two factors: temperature reduction in the combustion chamber and a considerable oxygen concentration increase. To avoid a radical increase of CO concentration, it is necessary to gradually reduce fuel stream as water temperature in the boiler approaches its maximum value.
Water Pollution

The analysis result of wastewater from washing stage in the biodiesel plant without any treatment present in Table 4.3.

Table 4.3  The analysis result of wastewater compare to the quality standard

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Result$^1$</th>
<th>Quality Standard$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSS</td>
<td>777 mg/l</td>
<td>300 mg/l</td>
</tr>
<tr>
<td>Chemical characteristics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>9</td>
<td>6 – 9</td>
</tr>
<tr>
<td>BOD</td>
<td>2808 mg/l</td>
<td>250 mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>150927 mg/l</td>
<td>500 mg/l</td>
</tr>
</tbody>
</table>

$^1$ Laboratorium analysis result (Appendix 4)

$^2$ Effluent quality standard for palm oil industry (KEP-51/MENLH/10/1995)

The results show that wastewater from the biodiesel production process is basic (alkaline) with a high content of TSS, BOD, and COD. The physical and chemical characteristics content of wastewater from washing stage were very high and has exceeded the effluent quality standard for palm oil industry (KEP-51/MENLH/10/1995, Appendix A.IV), except for pH content. However, the actual pH of the effluent has reached the threshold, so it could be said that this wastewater was very dangerous if discharged directly into the environment.

The ratio of BOD/COD has been used as a measure of biodegradability. The BOD/COD ratio gives a gross index of the proportion of the organic materials present which are aerobically degradable within a certain period of time. BOD is a measure of the oxidation occurring due to microbial activity while COD measures the highest extent of oxidation a material may undergo (Larson 2004). Low BOD/COD values (usually less than 0.1) indicate their resistance to conventional biological treatment (Koch et al. 2002).

The analysis result in table 4.3 shows that the BOD/COD ratios were below 0.10 (BOD/COD = 0.02) these results indicated that the diluent wasn’t very biodegradable. COD values were much higher compared with BOD indicated that most of the wastewater consists of oxidizable inorganic material. Low BOD/COD ratio also indicated that the wastewater is considered toxic to be discharged to natural water ways. Therefore, it requires appropriate treatment before discharge into the environment. Biological treatment of biodiesel wastewater is expected to be very difficult due to low BOD/COD ratio.

The mass balance analysis results of BOD and COD concentration in the Cisadane River stream after mixed with the wastewater of biodiesel plant without any treatment presents in Table 4.4.
Table 4.4 The BOD and COD concentration

<table>
<thead>
<tr>
<th>Stream</th>
<th>Discharge (m³/s)</th>
<th>BOD (mg/l)</th>
<th>COD (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>2808</td>
<td>150927</td>
</tr>
<tr>
<td>2</td>
<td>65.78</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>5</td>
<td>29</td>
</tr>
</tbody>
</table>

Stream 1: biodiesel plant wastewater condition  
Stream 2: Cisadane River condition  
Stream 3: stream 2 conditions after mixed with stream 1

Table 4.4 shows that the content of organic substances (BOD and COD) in Cisadane River already exceeded the drinking water quality standard (first class) which shown in Table 4.1. It means that Cisadane River has already been in polluted conditions (toxic).

Disposal of wastewater from the biodiesel plant if not being processed first the wastewater treatment plant (WWTP), would be very dangerous for the environment. The Cisadane River becomes more polluted with the addition of biodiesel plant wastewater. This can be seen in Table 4.4, which the addition of biodiesel plant wastewater into The Cisadane River had increased the COD content from 12 mg/l to 29 mg/l. This result indicated that the Cisadane River was in the third grade quality criteria, which the allocation of water can be used for freshwater aquaculture, animal husbandry, irrigation, or other uses that require the water quality equal to this usability. Unfortunately, it cannot be used either for drinking water or for infrastructure/recreation water facilities, because the high levels of COD concentrations are toxic to biological life and will affect the human health.

To be able to reduce BOD and COD content in order to meet the established quality standards required the form of appropriate engineering on aerobic and anaerobic processes in the WWTP. Due to COD content of biodiesel plant wastewater was very high (highly polluted), it needed the pre-treatment before being discharged into a biological treatment plant in order to decrease COD content and increase the BOD/COD ratio. The electrocoagulation (EC) process is possibly suitable for a primary treatment for biodiesel wastewater (Chavalparit and Ongwandee 2009). The EC process using an aluminum anode and graphite cathode is effective in reducing oil & grease and suspended solid by more than 95%, also reducing 55% of COD content in biodiesel processing wastewater. Daud et al. (2013) showed that coagulation and flocculation is a useful method in the treatment of biodiesel wastewater. Coagulation and flocculation are very effective in the suspended solids, oil and grease removal and moderately effective in the COD removal of the biodiesel wastewater.

Engineering center, which owned the biodiesel plant being studied, has the WWTP facilities to avoid hazards of wastewater from washing process in the production of biodiesel. Flow of wastewater treatment in Engineering Center presents in Figure 4.8.
Conclusions

The atmospheric dispersion modeling can be used to predict the downwind concentration of air pollutants emitted from stationery sources, such as biodiesel plant. The prediction result helps us to anticipate air pollution events that might pose a health hazard for the receptors. The distribution model result of pollutants concentration derived from the boiler stack of biodiesel plant using Gaussian Dispersion Model showed that the concentration of SO2, NO2, PM, and O3 was below the threshold, which means it did not influence the air quality around the biodiesel plant and did not endanger the surrounding population. Whereas, CO pollutant concentration from the biodiesel plant gave the negative impacts to the environment in the radius below 450 m from the boiler stack (emission source). This implied that the safe distance of biodiesel plant site to the settlements area is in the radius of 450 m from the emission source.

The production of biodiesel through a catalytic transesterification method produced a large amount of wastewater that contains high content of TSS, BOD, and COD. The BOD/COD ratio was very low (below 0.1). Therefore, it could adversely affect if directly discharged into the environment without any treatment. The results of the mass balance analysis for the content of BOD and COD in Cisadane River stream that have been mixed with untreated wastewater from biodiesel plant showed an additional environmental burden with the increase of COD content. The form of appropriate engineering on aerobic and anaerobic processes in the WWTP before being discharged directly into the river is required in order to avoid the possible hazards. Otherwise, the Cisadane River would entered the third grade of water quality criteria, which water cannot allocate for drinking water and water recreation infrastructure/facilities, but still can be utilize for freshwater aquaculture, animal husbandry, irrigation, and/or other uses that require similar water quality.
CHAPTER V
IMPACT ANALYSIS AND SCENARIO OF IMPROVEMENT

Introduction

The Life Cycle Impact Assessment (LCIA) phase of an LCA is the evaluation of potential impact to human health and environmental of the resources use and emission identified during the life cycle inventory (LCI). Impact assessment should address ecological and human health effects; it can also address resource depletion. A life cycle impact assessment attempts to establish a linkage between the product or process and its potential environmental impacts (SAIC 2006).

LCIA methods are divided in two general groups:

1. Problem-oriented approaches;
2. Damage-oriented methods.

In the problem-oriented methods the environmental burdens are aggregated according to their relative contribution to the environmental effects that they might cause. The impacts most commonly considered in the problem-oriented approach include resource depletion, global warming, ozone depletion, acidification, eutrophication, photochemical oxidant formation, human toxicity and ecotoxicity. Problem-oriented approaches are often referred to as ‘midpoint’ approaches because they link the environmental interventions from LCI somewhere at the intermediate position between the point of intervention and the ultimate damage caused by that intervention (Figure 5.1). Damage-oriented methods, on the other hand, model the ‘endpoint’ damage caused by environmental interventions to ‘areas of protection’, which include human health, natural and human-made environment (Azapagic 2006). This study is focused on the problem-oriented approaches (midpoint). The term midpoint is used to refer to the impact category, meaning that the impact is somewhere between the LCI result and the endpoint or broader impact category (Elcock 2007).

The objective of this chapter is to translate the inventory results (also termed environmental loads) obtained from the LCI of CPO biodiesel production into potential environmental impact.
Methods

Life Cycle Impact Assessment

Activities carried out in impact assessment stage were to analyze and quantify the environmental burden associated with the mass and energy flow in the biodiesel production process. The impact assessment was conducted using MiLCA software and based on the inventory data generated on LCI stage in Chapter III. The display of impact assessment in MiLCA-JEMAI software is presented in Appendix 6. The systems of palm oil biodiesel production by catalytic and non-catalytic SMV processes with MiLCA-JEMAI software are presented in Appendix 7 – 11.

The focused of environmental impacts to be evaluated in this study was limited to the GHG emission, acidification, eutrophication and energy consumption during the biodiesel production processes. GHG emission is the most widely discussed as environmental impact of biodiesel production and utilization. Characterization factor for predicting the GHG emission followed the greenhouse effect of 100-year time horizon. Acidification and eutrophication are also included in the impact assessment since they are also important environmental impact asserted by production and utilization of biodiesel. Energy consumption is included since the difference between SMV and catalytic method is mainly characterized by the process temperature which directly influences the energy consumption. This study evaluated two scenarios as explained before in the chapter III (Table 3.1).
Sensitivity Analysis

The LCI and the LCIA provide data about environmental emissions and impacts. To use these results for process, product, or design changes, or for other purposes, decision makers need to understand the reliability and validity of the information. Analyses to assess the robustness of the results and conclusions include the sensitivity analysis. Sensitivity analysis identifies and checks the effect of critical data on the results. It can be conducted by systemically changing the input parameters. Input parameters for which only a small change leads to a major change in results would be identified as the most sensitive, and critical in terms of requirement for more accurate data (Elcock 2007). On the basis of sensitivity analysis, one can suggest steps to improve the technology/process involved (Singh et al. 2010).

LCA depends on data availability and reliability. Therefore, it requires sensitivity analysis to identify the effect of data variability, uncertainty, and the deficiencies in final results which leads to determination of reliability. The analysis was conducted to display the GHG emission sensitivity of biodiesel production with the catalytic method in scenario 1. The GHG emission sensitivity analysis was performed by tornado diagrams. Tornado diagrams graphically display the result of single-factor sensitivity analysis. This lets one evaluate the risk associated with the uncertainty in each of the variables that affect the outcome. Single-factor analysis means that we measure the effect on the outcome of each factor, one at a time, while holding the others at their nominal (or base) value (Taylor 2009). In this study, the interval of the variables, one at a time, was ±20%.

Result and Discussion

Environmental Emissions

The environmental emission of CPO biodiesel is shown in Table 5.1. The atmospheric emission is related to the energy consumption pattern. The highest value was obtained when biodiesel plant utilized fossil fuel as energy source (scenario 1). The substitution of energy source by biomass waste can reduce the environmental emission both for catalytic and SMV method (scenario 2). The utilization of biomass waste as an energy source made environmental load of SMV method lower than the catalytic one. The implementation of methane capture system in palm oil mill and transportation in each stage also influence the environmental load among the biodiesel production process.

The source of water emissions among the biodiesel production process are fertilizer, herbicide, and pesticide that leached into water bodies. Besides, waste water from palm oil mill and biodiesel plant also contributes to water emission. The non-catalytic SMV method contributes lower water emission than catalytic methods due to the absence of catalyst in the process. However, the catalytic process generates waste water from washing process to purify methyl ester from catalyst.
Table 5.1 Environmental emissions in producing 1 kg CPO biodiesel

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Catalytic Scenario 1</th>
<th>Catalytic Scenario 2</th>
<th>SMV Scenario 1</th>
<th>SMV Scenario 2</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.41E-01</td>
<td>6.35E-01</td>
<td>1.20E+00</td>
<td>1.16E+00</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>Atmospheric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.99E-02</td>
<td>4.88E-04</td>
<td>2.05E-02</td>
<td>4.65E-04</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.16E-04</td>
<td>1.14E-04</td>
<td>1.21E-04</td>
<td>1.21E-04</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>N₂O</td>
<td>6.11E-10</td>
<td>6.11E-10</td>
<td>6.03E-10</td>
<td>6.03E-10</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>SO₂</td>
<td>4.43E-04</td>
<td>2.79E-04</td>
<td>1.25E-03</td>
<td>2.58E-04</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>SOₓ</td>
<td>4.33E-05</td>
<td>3.64E-05</td>
<td>8.30E-05</td>
<td>3.46E-05</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>NO₂</td>
<td>1.77E-09</td>
<td>1.77E-09</td>
<td>1.73E-09</td>
<td>1.73E-09</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>NOₓ</td>
<td>4.63E-04</td>
<td>3.99E-04</td>
<td>7.71E-04</td>
<td>3.81E-04</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>HCl</td>
<td>1.17E-10</td>
<td>1.17E-10</td>
<td>1.05E-10</td>
<td>1.05E-10</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>Water emission</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>4.50E-07</td>
<td>4.50E-07</td>
<td>4.42E-07</td>
<td>4.42E-07</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>P total</td>
<td>2.23E-13</td>
<td>2.23E-13</td>
<td>2.00E-13</td>
<td>2.00E-13</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>N total</td>
<td>1.34E-07</td>
<td>1.34E-07</td>
<td>1.20E-07</td>
<td>1.20E-07</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>NH₃</td>
<td>5.54E-10</td>
<td>5.54E-10</td>
<td>4.97E-10</td>
<td>4.97E-10</td>
<td>kg/kg BDF</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>3.06E-14</td>
<td>3.06E-14</td>
<td>3.00E-14</td>
<td>3.00E-14</td>
<td>kg/kg BDF</td>
</tr>
</tbody>
</table>

Life Cycle Impact Assessment

The difference on the environmental impact between catalytic and SMV methods occurred only at the biodiesel plant, since the CPO passed through the same treatment before entering the biodiesel plant and both processes use the same raw material with nearly the same amount.

1. GHG Emission

Figure 5.2 shows the comparison of each scenario’s impact on GHG emission generation. In scenario 1 of the catalytic transesterification process, the palm oil mill stage presented highest GHG emission among other stages. The main contribution was from methane release from open digesting tanks of POME treatment. However, in the SMV process, biodiesel plant stage contributed the highest GHG emission among other stages due to high requirement of energy to provide high temperature in the transesterification process. In scenario 2, when palm oil mill have implemented the methane capture system and biodiesel plant have utilized the biomass waste as the energy source, oil palm plantation stage contributed highest GHG emission for both catalytic and SMV methods. The main contributions were from the utilization of fertilizer, herbicide and pesticide.
Figure 5.2 Process contribution of each scenario to GHG emission

**Acidification**

Figure 5.3 shows that in scenario 1, biodiesel production at biodiesel stage in the SMV method contributed the highest acidification effect. The contribution was mainly from the IDO combustion to generate power and steam in the transesterification process. Acidification effect reduced with the substitution of IDO to biomass as energy source (scenario 2). Most of palm oil mills in Indonesia have utilized the biomass waste as the energy source; therefore contribution to acidification effect is expectedly low.

The electricity consumption also contributed to the acidification effect. Indonesian grid electricity is generated from a mix of hydro (7.23 %), geothermal (2.44 %), coal (38.50 %), petroleum (29.32 %), and natural gas (22.52 %) (PT. PLN (Persero) Reports 2011). The electricity productions from coal, petroleum and natural gas have high impacts on acidification.
3. Eutrophication

The eutrophication of each scenario is presented in Figure 5.4. This impact category is mainly borned by substances containing nitrogen and phosphate. The nitrate emissions from leachate contribute to eutrophication (Goedkoop 1995). Therefore, oil palm plantation contributed the highest eutrophication effect due to the utilization of chemical fertilizer in this stage.
Figure 5.4 Process contribution of each scenario to eutrophication

Table 5.2 shows that the SMV method of biodiesel processing technology contributed to higher GHG emission and acidification when the plant utilized fossil fuel as energy source compared to the catalytic method (scenario 1). This phenomenon due to the higher temperature required for the SMV method. Nevertheless, the result of the GHG emission by the SMV method corresponded to a 46% reduction in comparison with that of petrodiesel production, which is 3.26 kg CO₂/kg product. Sekiguchi et al. (2012) also stated that biodiesel production with the SMV method could reduce 45% of the GHG emission over the petrodiesel production. Starting from the year 2017, the EU sustainability standard requires a 50% reduction. The GHG savings of biodiesel production by the catalytic method over diesel fuel was 64%. It means that palm oil based biodiesel is a sustainable fuel and more environmentally friendly compared to diesel fuel.

<table>
<thead>
<tr>
<th>Impact</th>
<th>Catalytic scenario 1</th>
<th>Catalytic scenario 2</th>
<th>SMV scenario 1</th>
<th>SMV scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHG emission (kg-CO₂eq.)</td>
<td>1.2E+00</td>
<td>5.7E-01</td>
<td>1.7E+00</td>
<td>5.5E-01</td>
</tr>
<tr>
<td>Acidification (kg-SO₂eq.)</td>
<td>8.2E-04</td>
<td>6.0E-04</td>
<td>1.9E-03</td>
<td>5.7E-04</td>
</tr>
<tr>
<td>Eutrophication (kg-phosphate eq.)</td>
<td>3.5E-08</td>
<td>3.5E-08</td>
<td>3.2E-08</td>
<td>3.2E-08</td>
</tr>
</tbody>
</table>
The substitution of energy source to biomass waste (scenario 2) will further reduce the environment impact both for catalytic and SMV transesterification methods. This energy source substitution made the SMV method contributed almost equal environmental impact to the catalytic method. The implementation of methane capture system in palm oil mill also gave a big influence to the environmental impact. Irvan et al. (2012) reported that methane concentration in biogas from digestion of POME in PTPN II Sumatera Utara Indonesia was approximately 65%. Yacob et al. (2005) reported that 5.5 kg of methane will be emitted from every ton of POME. Therefore, the methane capture system can achieve substantial GHG reduction, which can be seen in Figure 5.2 and Table 5.2. The implementation of methane capture system could reduce the GHG emission in the palm oil mill stage, significantly.

The GHG emissions of biodiesel production by different scenarios compared with the conventional alkali-catalytic process is presented in Table 5.3. The GHG savings over catalytic process ranges from -49.6 to 53.2%. The negative sign of GHG savings means an increase to the GHG emission. As mentioned before, higher GHG emission by SMV method is due to higher temperature requirement compared to the catalytic one. The implementation of methane capture in palm oil mill still gave a negative sign of GHG savings over catalytic method in scenario 1, if biodiesel production conducted in the SMV method. The reduction of GHG emissions by the SMV method was obtainable by the substitution of fossil fuel to biomass waste in the biodiesel plant. The highest GHG savings was performed with the combination of methane capture implementation in the palm oil mill stage and biomass utilization in the biodiesel plant stage both for catalytic and SMV methods, with approximately 50% of GHG saving over catalytic process in scenario 1.

Table 5.3 GHG emissions of biodiesel production from palm oil under different scenarios

<table>
<thead>
<tr>
<th>Scenario</th>
<th>GHG (kg-CO₂ eq.)</th>
<th>% reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic fossil fuel utilization and without methane capture implementation (scenario 1)</td>
<td>1.2E+00</td>
<td></td>
</tr>
<tr>
<td>with methane capture implementation</td>
<td>6.9E-01</td>
<td>41.0</td>
</tr>
<tr>
<td>with biomass utilization</td>
<td>1.1E+01</td>
<td>10.3</td>
</tr>
<tr>
<td>with methane capture implementation and biomass utilization (Scenario 2)</td>
<td>5.7E-01</td>
<td>51.1</td>
</tr>
<tr>
<td>Non-Catalytic fossil fuel utilization and without methane capture implementation (scenario 1)</td>
<td>1.8E+00</td>
<td>-49.6</td>
</tr>
<tr>
<td>with methane capture implementation</td>
<td>1.3E+00</td>
<td>-8.5</td>
</tr>
<tr>
<td>with biomass utilization</td>
<td>1.0E+00</td>
<td>12.0</td>
</tr>
<tr>
<td>with methane capture implementation and biomass utilization (Scenario 2)</td>
<td>5.5E-01</td>
<td>53.2</td>
</tr>
</tbody>
</table>
4. Energy Consumption

The total energy consumption is shown in Figure 5.5. The utilization of energy resources in the biodiesel plant was the most influential on the results. The SMV method consumed higher nonrenewable energy than catalytic method when the biodiesel plant utilized fossil fuel as an energy source for increasing the temperature (scenario 1). Process temperature for SMV is 290 °C while that for catalytic method is 60 °C. However, as in scenario 2, when biomass waste was used to substitute fossil fuel for increasing the temperature, the nonrenewable energy consumption of SMV method decreased to almost equal with the catalytic method.

Heat supply in SMV method of non-catalytic process is very important since it requires high temperature process. Accordingly, utilization of biomass waste for heat supply in the SMV method is recommended in order to significantly reduce the nonrenewable energy consumption. If the utilization of biomass waste as energy source can be regarded as internal flow of energy, then it implies to the reduction of energy input to the system. Reduction of energy consumption for catalytic method also occurred when biomass waste was applied, even though it is not as significant as for the SMV method, since catalytic transesterification process did not require high temperatures.

In order to overcome the high energy consumption in the SMV method, Joelianingsih (2008) proposed the substitution of evaporator, superheated and condenser function in the SMV process by four heat exchangers. The heat balance of the biodiesel production process was determined using HYSYS software. The simulation result showed that heat recirculation by heat exchangers could reduce
about 55% of energy consumption in biodiesel production with the SMV method. Tambunan et al. (2012) performed heat recirculation in the SMV process. The results presented that heat recovery in the SMV process could increase about 18% of energy ratio in biodiesel production.

**Sensitivity Analysis**

Tornado diagram was utilized to display the sensitivity of GHG emission in this study. The tornado diagram further below demonstrates that the parameters with the largest bars are the most influential.

Figure 5.6 presents the most influential eight parameters to the GHG emission. It demonstrates that a change in diesel consumption during the biodiesel production will be the most significant contribution to the GHG emission followed by the application of urea and kieserite fertilizers in oil palm plantation. A change in triple superphosphate (TSP) application and electricity consumption are also influential but not as critically as the diesel consumption and the application of urea and kieserite fertilizers.

![Figure 5.6 The sensitivity of GHG emission](image)

**Interpretation**

The non-catalytic SMV method contributed highest environmental impact (GHG emission and acidification effect) and consumed the largest amount of energy in scenario 1, when palm oil mill have not implemented the methane capture system and biodiesel plant still utilized industrial diesel oil (IDO) for
boiler fuel. The implementation of methane capture system and substitution of fossil fuel to biomass waste have reduced the environmental impact and energy consumption of the SMV method (Scenario 2).

Conclusions

The life cycle impact assessment has been performed to determine the influence of catalytic and non-catalytic SMV methods on palm oil biodiesel production process to the environmental impact. It was found that the SMV method contributed the highest environmental impact (GHG emission and acidification effect) if palm oil mill have not implemented the methane capture system and biodiesel plant still used industrial diesel oil (IDO) for boiler fuel (scenario 1). The GHG emission and acidification was 1.7 kg CO$_2$ eq./kg biodiesel and 1.9E-03 kg SO$_2$ eq./kg biodiesel, respectively. The SMV method in scenario 1 also consumed the largest amount of energy for increasing the process temperature. The utilization of biomass waste as a substitute of fossil fuel was reduced the environmental impact and energy consumption of the SMV method (Scenario 2). The heat recirculation in the SMV process can also reduce the total energy consumption of biodiesel production. The utilization of biomass waste along biodiesel production line and the implementation of heat recirculation in the transesterification process were highly recommended to create a biodiesel production process become more efficient and environmentally friendly, especially if the SMV method will be adopted.
CHAPTER VI
EXERGY ANALYSIS

Introduction

The energy output/input ratio in biodiesel production life cycle can be an important factor for the feasibility evaluation of biodiesel production since higher energy content of the output compared to the energy content of the input means higher energy conversion efficiency. However, output/input ratio alone is not enough to indicate the conversion effectiveness. There is a measure of availability of the energy input, as well as the output, which has to be considered in order to express the effectiveness. Besides, utilization of fossil energy as input to the energy production will jeopardize renewability of biodiesel itself. Measuring the renewability of an energy resource is also questionable if based only on energy balance stipulated by the first law of thermodynamics (FLT). Thereby, exergy analysis is indispensable for evaluation of the energy production.

Exergy is often confounded with energy. According to Dincer and Rosen (2007), energy analysis is the traditional method of assessing the way energy is used in some physical or chemical process with transfer and/or conversion of energy. This usually entails performing energy balances and evaluating energy efficiencies. However, an energy balance provides no information on the quality degradation of energy or resources during a process.

The exergy method of analysis overcomes the limitations of the FLT. The concept of exergy is based on both the FLT and the Second Law of Thermodynamic (SLT). Exergy analysis clearly indicates the locations of energy degradation in a process and can therefore lead to improved operation or technology, also can quantify the quality of heat in a waste stream. A main aim of exergy analysis is to identify meaningful (exergy) efficiencies and the causes and true magnitudes of exergy losses. Table 6.1 presents a general comparison of both energy and exergy (Dincer and Cengel 2001).

Exergy is a measure of distance from thermodynamic equilibrium. It is not a conserved quantity (like energy) but it is possible to construct an exergy balance for any energy or materials transformation process, accounting for inputs, process losses, useful products and wastes (Ayres et al. 1996).

The exergy of a system (relative to the assumed reference environment) depends on system temperature, pressure and composition; the first two contribute to thermo-mechanical exergy, and the third is the effect of composition to chemical exergy. Exergy analysis can identify areas in which technical and other improvements should be undertaken, and indicate the priorities, which should be assigned to conservation measures, efficiency improvements and optimizations. Exergy is an excellent concept to describe the utilization of energy and material resources in systems (Wall 2011).
Table 6.1  Comparison of energy and exergy

<table>
<thead>
<tr>
<th>ENERGY</th>
<th>EXERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>• is dependent on the parameters of matter or energy flow only, and</td>
<td>• is dependent both on the parameters of matter or energy flow and on</td>
</tr>
<tr>
<td>independent of the environment parameters.</td>
<td>the environment parameters.</td>
</tr>
<tr>
<td>• has the values different from zero (equal to mc² upon Einstein’s</td>
<td>• is equal to zero (in dead state by equilibrium with the environment).</td>
</tr>
<tr>
<td>equation).</td>
<td>• is governed by the FLT for reversible processes only (in irreversible</td>
</tr>
<tr>
<td>• is governed by the FLT for all the processes.</td>
<td>processes it is destroyed partly or completely).</td>
</tr>
<tr>
<td>• is limited by the SLT for all processes (incl. reversible ones).</td>
<td>• is not limited for reversible processes due to the SLT.</td>
</tr>
<tr>
<td>• is a measure of quantity only.</td>
<td>• is work or ability to produce work.</td>
</tr>
<tr>
<td></td>
<td>• is always conserved in a reversible process, but is always consumed in</td>
</tr>
<tr>
<td></td>
<td>an irreversible process.</td>
</tr>
<tr>
<td></td>
<td>• is a measure of quantity and quality due to entropy.</td>
</tr>
</tbody>
</table>

Exergy analysis enables calculating exergy of streams (mass or heat fluxes) and the destroyed exergy in different units included in the overall process to find energetic inefficiency (Portha et al. 2008). Exergy of a system is divided into four components: kinetic exergy associated with relative motion; potential exergy associated with gravitational or electromagnetic field differentials; physical exergy from pressure and temperature differentials; and chemical exergy arising from differences in chemical composition (Szargut 1988 cited in Ayres et al. 1996; Kotas 1995).

The objective of this study was to evaluate and discuss the irreversibility and exergy efficiency of palm oil based biodiesel production by catalytic and non-catalytic SMV methods.

Methods

This study concerned only on exergy analysis during the transesterification process at the biodiesel plant, and the analysis limited up to the conversion process without assessing the separation and methanol recovery process. The catalytic method utilized catalyst to accelerate the transesterification process. Therefore, it needs the washing process to purify the product from catalyst. This process also concerned in this study.

The exergy associated with a specified state of a system is the sum of two contributions: the thermomechanical contribution (physical exergy) and the chemical contribution (chemical exergy). A closed system was assumed both for catalytic and non-catalytic SMV processes, the kinetic and potential exergy were ignored. Schematic of transesterification process presents in Figure 6.1.
The exergy balance for a closed system is developed by combining the closed system energy and entropy balances (Moran and Shapiro 2006). The form of energy balance express in equation (6.1).

\[
\Delta E = Q - W
\]  

(6.1)

where \( W \) and \( Q \) represent, respectively, work and heat transfers between the system and its surroundings. These interactions do not necessarily involve the environment. \( \Delta E \) is the energy change of the system, equal to the sum of the energy changes of the closed system and the environment. The energy of the closed system initially is denoted by \( E \), which includes the kinetic energy, potential energy, and internal energy of the system. The kinetic and potential energy can be ignore in the system, the energy of the closed system when at the dead state would be just its internal energy, \( U \). Accordingly, equation (6.1) can be expressed as equation (6.2).

\[
\Delta U = Q - W
\]  

(6.2)

The form of entropy balance express in equation (6.3)

\[
\Delta S = \frac{Q}{T} + \sigma_g
\]  

(6.3)
\( T \) denotes the temperature on the system boundary where \( Q \) is received and the term \( \sigma \) accounts for entropy produced by internal irreversibilities.

The first step in deriving the exergy balance, multiply the entropy balance by the temperature \( T_0 \) and subtract the resulting expression from the energy balance, as in equation (6.4) (Moran and Shapiro 2006):

\[
\Delta U - T_0 \Delta S = Q \left( 1 - \frac{T_0}{T} \right) - W - T_0 \sigma_g \quad (6.4)
\]

The closed system exergy balance results as in equation (6.5)

\[
\Delta B = Q \left( 1 - \frac{T_0}{T} \right) - W - T_0 \sigma_g \quad (6.5)
\]

The equations above are the thermomechanical contribution of exergy, also called as physical exergy, where \( \Delta B \) is the change in exergy between two states \( (B_2 - B_1) \). State 1 was in the form of triglyceride and methanol, state 2 was in the form of FAME and glycerol, which can be obtained by calculating its internal exergy (chemical exergy).

Chemical exergy, \( B_{ch} \), is the work that can be obtained by taking a substance at \( T_0 \) and \( P_0 \), to the state defined by the environmental reference composition. It represents exergy that nature has spent or should have spent to create the resource, respectively the waste. The chemical exergy in this study was approached by a chemical exergy of a hydrocarbon, \( C_aH_b \), which the reaction given by

\[
C_aH_b + \left( a + \frac{b}{4} \right) O_2 \rightarrow aCO_2 + \frac{b}{2} H_2O
\]

The chemical exergy of each element that contributed to the transesterification process can be calculated by the equation (6.6) (Bejan et al. 1996; Moran and Shapiro 2006).

\[
B_{ch} = \left[ \bar{g}_f + \left( a + \frac{b}{4} \right) \bar{g}_{O_2} - a \bar{g}_{CO_2} - \frac{b}{2} \bar{g}_{H_2O(l)} \right] (T_0, P_0) + \left( aB_{chCO_2} + \frac{b}{2} B_{chH_2O(l)} - \left( a + \frac{b}{4} \right) B_{chO_2} \right) \quad (6.6)
\]

The specific Gibbs functions are evaluated at the temperature \( T_0 \) and pressure \( P_0 \) of the environment as in equation (6.7).

\[
\bar{g}(T_0, P_0) = \bar{g}_f^0 + \left[ \bar{g}(T_0, P_0) - \bar{g}(T_{ref}, P_{ref}) \right] \quad (6.7)
\]
where $\bar{g}_f$ is the Gibbs function of formation. For the special case where $T_0$ and $P_0$
are the same as $T_{\text{ref}}$ and $P_{\text{ref}}$, respectively, the second term on the right of Eq. 6.7
vanishes and the specific Gibbs function is just the Gibbs function of formation.
Finally, note that the underlined term of Equation (6.6) can be written more compactly as $-\Delta G$: the negative of the change in Gibbs function for the reaction, regarding each substance as separate at temperature $T_0$ and pressure $P_0$.

Exergy efficiency (second law of thermodynamics) in each subsystem can be written as in equation (6.8) (Cengel and Boles 2007).

$$\eta = 1 - \frac{l}{B_1} = 1 - \frac{T_0 \Delta S_{gen}}{B_1} \quad (6.8)$$

where $l$ is the irreversibility which is the multiplication of dead state temperature ($T_0$) and entropy generated by the process ($\Delta S_{gen}$). $B_1$ is exergy at state 1 (kJ) in each subsystem.

Exergy is evaluated with respect to a reference environment. The reference ambient air is at 27°C and 100 kPa, for temperature and pressure, respectively.

**Result and Discussion**

**Comparison of Exergy Efficiency of Catalytic and SMV Methods**

Exergy is a measure of energy quality or energy availability to perform work, and the calculation uses environmental parameters as a reference. Exergy analysis included both exergy consumed in production processes due to energy use and due to materials used. The differences between catalytic and non-catalytic SMV methods are conducted at the exergy transfer accompanying heat, since SMV method required high temperature in the process, and the exergy transfer accompanying work, since no mechanical work in the SMV method, hence the catalytic method utilized mechanical work in the mixing process of methanol and catalyst. Mass balances to produce 1 kg biodiesel in the catalytic and SMV process are shown in Table 6.2 and 6.3, respectively. Mechanical energy in catalytic process is 3.55 kJ/kg biodiesel.

Exergy balance analysis provides the amount of energy availability to run a process and also provides the irreversibility value at each unit. The change of exergy of a system will change exergy transfer and exergy destruction.

Table 6.4 represents the total exergy balance of palm oil biodiesel production. The result shows the total irreversibility of the non-catalytic SMV process was higher than the catalytic one due to high temperature requirement of the non-catalytic SMV process. Irreversibility represents the internal exergy loss in the process as the loss of quality of materials and energy due to dissipation (Prins et al. 2003). The irreversibility is influenced by several factors, which are: the mass transfer between phases, environment temperature, and heat transfer. The heat recirculation is needed to reduce the irreversibility and to make the process more sustainable, especially if the SMV methods will be adopted.
Table 6.2  Mass balance to produce 1 kg biodiesel in the catalytic process

<table>
<thead>
<tr>
<th></th>
<th>NaOH mass (kg)</th>
<th>NaOH temperature (K)</th>
<th>MeOH mass (kg)</th>
<th>MeOH temperature (K)</th>
<th>CPO mass (kg)</th>
<th>CPO temperature (K)</th>
<th>ME mass (kg)</th>
<th>ME temperature (K)</th>
<th>Gly mass (kg)</th>
<th>Gly temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>input</td>
<td>0.008</td>
<td>300</td>
<td>0.314</td>
<td>300</td>
<td>1.046</td>
<td>303</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>output</td>
<td>0.008</td>
<td>338</td>
<td>0.202</td>
<td>338</td>
<td>0.012</td>
<td>338</td>
<td>1.000</td>
<td>338</td>
<td>0.110</td>
<td>338</td>
</tr>
</tbody>
</table>

Table 6.3  Mass balance to produce 1 kg biodiesel in the SMV process

<table>
<thead>
<tr>
<th></th>
<th>MeOH mass (kg)</th>
<th>MeOH temperature (K)</th>
<th>CPO mass (kg)</th>
<th>CPO temperature (K)</th>
<th>ME mass (kg)</th>
<th>ME temperature (K)</th>
<th>Gly mass (kg)</th>
<th>Gly temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>input</td>
<td>5.551</td>
<td>308</td>
<td>1.041</td>
<td>308</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>output</td>
<td>5.445</td>
<td>563</td>
<td>0.001</td>
<td>563</td>
<td>1.000</td>
<td>563</td>
<td>0.107</td>
<td>563</td>
</tr>
</tbody>
</table>
The discrepancy amount of exergy change between catalytic and non-catalytic SMV methods was due to the difference of triglyceride and methanol consumption, and also the difference of glycerol production in the production of 1 kg biodiesel. The exergy change between two states can be evaluated based on its internal exergy (chemical exergy).

The chemical exergy in a material is the least possible amount of exergy that has to be consumed to create and maintain the chemical structure of the material in certain surroundings (Hovelius 1999). The catalyst in the catalytic process was assumed can be recycled after the washing process, so it was not taken into account in the chemical exergy. The result of chemical exergy balance of CPO biodiesel production presents in Table 6.5.

Table 6.5  Chemical exergy balance to produce 1 kg biodiesel

<table>
<thead>
<tr>
<th>Catalytic</th>
<th>State 1 (kJ)</th>
<th>State 2 (kJ)</th>
<th>SMV</th>
<th>State 1 (kJ)</th>
<th>State 2 (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPO</td>
<td>41645.77</td>
<td>41460.18</td>
<td>CPO</td>
<td>41460.18</td>
<td>40014.60</td>
</tr>
<tr>
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<td>Methanol (g)</td>
<td>2393.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biodiesel</td>
<td>40014.60</td>
<td>Biodiesel</td>
<td>40014.60</td>
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<tr>
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<td>glycerol</td>
<td>2019.89</td>
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</table>

Figure 6.2 represents the total exergy efficiency of palm oil biodiesel production. The result shows the total exergy efficiency of the non-catalytic SMV process was lower than the catalytic one, again, due to high temperature requirement of the non-catalytic SMV process. Therefore, the improvement of the SMV process is indispensable to be conducted.
Figure 6.2 Total exergy efficiency to produce 1 kg biodiesel

Exergy Analysis of the Non-catalytic SMV Method

In order to identify the critical area in the transesterification process of non-catalytic SMV method, exergy analysis also conducted in each subsystem of the process being evaluated.

Transesterification process in the non-catalytic SMV method occurred by passing methanol vapor up to superheated conditions (290°C) in reactor that has been loaded by palm oil and conditioned at a temperature of 290°C with semi-batch system. Evaporator works to increase the methanol temperature and change it to vapor phase, further the temperature of methanol steam upgraded to the level of superheated in the superheater sub-systems. In reactor occurred the reaction between palm oil in the liquid phase with methanol in the superheated vapor phase at a temperature of 290°C. As a result of the exothermic nature of the reaction, the reactor also got the addition of heat energy from the chemical reaction of biodiesel formation. Mass balances to produce 1 kg biodiesel in each subsystem of the SMV process are shown in Table 6.6 – 6.8.

Table 6.6 Mass balance to produce 1 kg biodiesel in evaporator of the SMV process

<table>
<thead>
<tr>
<th></th>
<th>Evaporator 1</th>
<th>Evaporator 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass (kg)</td>
<td>5.55</td>
<td>5.55</td>
</tr>
<tr>
<td>temperature (K)</td>
<td>308</td>
<td>423</td>
</tr>
<tr>
<td>input</td>
<td></td>
<td></td>
</tr>
<tr>
<td>output</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass (kg)</td>
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<td>5.55</td>
</tr>
<tr>
<td>temperature (K)</td>
<td>423</td>
<td>473</td>
</tr>
</tbody>
</table>
Table 6.7  Mass balance to produce 1 kg biodiesel in superheater of the SMV process

<table>
<thead>
<tr>
<th></th>
<th>Superheater 1</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH</td>
<td>MeOH</td>
</tr>
<tr>
<td>mass (kg)</td>
<td>temperature (K)</td>
<td>mass (kg)</td>
</tr>
<tr>
<td>input</td>
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<td>473</td>
</tr>
<tr>
<td>output</td>
<td>5.55</td>
<td>523</td>
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</tbody>
</table>

Table 6.8  Mass balance to produce 1 kg biodiesel in reactor of the SMV process

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<thead>
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<th>Gly</th>
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<td>mass (kg)</td>
<td>temperature (K)</td>
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<tr>
<td>output</td>
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<td>563</td>
<td>0.001</td>
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</table>
The exergy balance in each subsystem of the non-catalytic SMV process presented in Appendix 12-14 (Furqon 2011). The analysis result of exergy balance of the non-catalytic SMV process shows that the methanol evaporation process in the evaporator 1 contributed the highest irreversibility compared to other processes (Table 6.9). The evaporator 1 works to transform methanol into a vapor phase. The different temperature levels and mass transfer between phases were the main source of irreversibility in evaporator. It can be said that evaporator is the key component for improvements.

<table>
<thead>
<tr>
<th>Subsystem</th>
<th>Exergy Input (kJ)</th>
<th>Exergy Output (kJ)</th>
<th>Irreversibility (kJ)</th>
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</thead>
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<td>2802.07</td>
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<td>Evaporator 2</td>
<td>434.52</td>
<td>343.54</td>
<td>90.98</td>
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<td>Superheater 1</td>
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<td>590.22</td>
<td>111.22</td>
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<tr>
<td>Superheater 2</td>
<td>863.26</td>
<td>777.91</td>
<td>85.35</td>
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<tr>
<td>Reactor</td>
<td>1501.91</td>
<td>1162.95</td>
<td>338.96</td>
</tr>
</tbody>
</table>

As mentioned before at chapter V, Joelianingsih (2008) proposed the substitution of evaporator, and superheated functions in the SMV process by four heat exchangers. The heat balance of the biodiesel production process was determined using HYSYS software. The simulation result showed that heat recirculation by heat exchangers could reduce about 55% of energy consumption in biodiesel production with the SMV method. Tambunan et al. (2012) performed heat recirculation in the SMV process. The results presented that heat recovery in the SMV process could increase about 18% of energy ratio in biodiesel production. Those methods, which performed by Joelianingsih (2008) and Tambunan et al. (2012), can be implemented in order to reduce the irreversibility and to increase the exergy efficiency of SMV methods.

Conclusions

Exergy analyses of the palm oil biodiesel production technologies were accomplished in this study. The exergy analysis result shows that the exergy efficiency of non-catalytic SMV method was lower than the catalytic method. This condition occurred because the irreversibility of the non-catalytic SMV process was higher than the catalytic one due to high temperature requirement of the non-catalytic SMV process. Heat recirculation is needed to increase the exergy efficiency of both methods and to make the process more sustainable, especially if the SMV methods will be adopted. The improvement of overall process in the SMV methods is required, especially in the methanol evaporation process to reduce the irreversibility and increase the exergy efficiency. Exergy analysis is a useful concept for improving the efficiency of biodiesel production.
CHAPTER VII
GENERAL DISCUSSION

The global search for cleaner energy sources has led to the development of biodiesel. Biodiesel is a renewable energy source that could substitute fossil fuel. Biodiesel can be degraded easily (biodegradable), non-toxic, has a better cetane numbers than petroleum diesel, contains no sulfur and aromatic compounds thus the combustion emissions are more environmentally friendly and does not increase the accumulation of carbon dioxide in the atmosphere, thereby it can reduce the global warming effects (Sheehan et al. 1998).

Biodiesel can be produced by transesterification of natural oils or fats with short-chain alcohol, mainly methanol. Transesterification reaction can be performed with or without catalysts. Three types of catalysts, namely alkali, acid and enzyme catalyst, could be used in the transesterification process. On the other hand, three methods of non-catalytic process have been studied by many researchers; (1) supercritical methanol (SCM), (2) simultaneous reaction of transesterification and cracking (STING), and (3) superheated methanol vapor (SMV) methods.

Selecting an appropriate process for biodiesel production is crucial decision, between these two fundamental approaches, catalytic and non-catalytic, especially from the environmental point of view. Assessment of environmental impact and energy consumption during its life cycle are indispensable to assess better technology, and thereby to select the best one, for the biodiesel production. Thorough life cycle assessment (LCA) of the biodiesel production can provide information on the most critical path of the process that gives impact to the environment. Further, assessment on possible alternative process and input could give the suggestion for improvement to the conventional way. However, LCA, based on the first law of thermodynamics (FLT), which is provides no information on the degradation of energy or resources during a process and does not quantify the usefulness or quality of the energy and mass stream of system and exiting as products and wastes. Using exergy as the unified baseline is able to overcome the problems. Exergy analysis clearly indicates the locations of energy degradation in a process and can therefore lead to improved operation or technology, also can quantify the quality of heat in a waste stream (Dincer and Cengel 2001).

The objective of this research is to study the influence of catalytic and non-catalytic (Superheated Methanol Vapor / SMV) method on the exergy and emission factor of palm oil based biodiesel production by using Life Cycle Assessment (LCA) and exergy analysis approach.

In this study, LCA method was conducted to calculated the environmental impact of palm oil biodiesel, while exergy analysis gave information about the thermodynamic efficiency and irreversibility of palm oil biodiesel. This study is based on the standardized LCA tool with the incorporation of exergy analysis. Two scenarios of biodiesel production were evaluated, that can be seen in Table 3.1.

Life cycle inventory (LCI) is the heart of LCA. LCI have quantified resources use, energy use, and environmental releases throughout the biodiesel life cycle. 1 kg of biodiesel is produced from about 1.04 kg of CPO or about 4.76
kg of FFB. The major water requirement for the production of biodiesel comes from oil palm plantation. Urea (nitrogen) is the largest input from fertilizer although potassium and phosphorus are also significant contributors. Palm oil mill effluent (POME) represents the single largest source of methane emission in the operation of palm oil mill. POME is generated mainly from the extraction of the palm oil, the washing process and the cleaning of the mill. During the anaerobic digestion of POME in open ponds, methane gas is emitted to the atmosphere and could have adverse effects to the environment. In order to address this problem, the palm oil mill should implement the methane capture system. Methane may be captured in its pure form or as a component of biogas. The harvested biogas can be used as energy in the mills for the milling process (Vijaya et al. 2008). Moreover, the POME sludge can be utilized as an organic fertilizer in the oil palm plantation.

In Chapter IV, the direct measurements of emissions from biodiesel plant were discussed. The emission was limited to the flue gas emitted from the boiler stack and water pollutant from the washing process in the biodiesel plant. The atmospheric dispersion modeling was used to predict the downwind concentration of air pollutants emitted from biodiesel plant. The results showed that the concentration of SO₂, NO₂, PM, and O₃ pollutants emission from biodiesel plant was below the threshold, which means it did not influence the air quality around the biodiesel plant and did not endanger the surrounding population. Whereas, CO pollutant concentration from the biodiesel plant gave the negative impacts to the environment in the radius below 450 m from the boiler stack (emission source). The high concentration of CO pollutant was due to many incomplete combustion of fossil fuel in boiler. Boiler startup, shutdown, and load changes can causes the increase of CO emissions due to unstable combustion conditions. CO emissions are also sensitive to boiler operating conditions. Changes in operating conditions, such as rapid changes in load, can have a significant, though temporary, impact on emissions. In order to minimize the negative impacts of the air pollutants emitted from the biodiesel plant being studied, it is necessary to do the prevention attempt, such as installing the scrubber in the stack, maintaining the burner/boiler and doing periodic testing to keep it operating properly. Furthermore, tuning of the combustion system, optimizing the boiler performance to maximize the combustion efficiency, and gradually reducing fuel stream as water temperature in the boiler approaches its maximum value can overcome the high concentration of CO pollutant.

The production of biodiesel through a catalytic transesterification method produced a large amount of wastewater that contains high contents of TSS, BOD, and COD. The BOD/COD ratio was very low (below 0.1). Therefore, it could adversely affect if directly discharged into the environment without any treatment. The results of the mass balance analysis for the contents of BOD and COD in Cisadane River stream, which located within ± 600 m from biodiesel plant, that have been mixed with untreated wastewater from biodiesel plant showed an additional environmental burden with the increase of COD content. The form of appropriate engineering on aerobic and anaerobic processes in the WWTP before being discharged directly into the river is required in order to avoid the possible hazards. Otherwise, the Cisadane River would entered the third grade of water quality criteria, which water cannot allocate for drinking water & recreation water.
infrastructure/facilities, but still can be utilize for freshwater aquaculture, animal husbandry, irrigation, and/or other uses that require similar water quality.

GHG emission, acidification, and eutrophication are the impacts categories under consideration in this study. Energy consumption is included since the difference between SMV and catalytic method is mainly characterized by the process temperature which directly influences the energy consumption.

The LCIA result shows that the SMV method contributed the highest environmental impact (GHG emission and acidification effect) if palm oil mill have not implemented the methane capture system and biodiesel plant still used industrial diesel oil (IDO) for boiler fuel (scenario 1). The GHG emission and acidification was 1.7 kg CO$_2$ eq./kg biodiesel and 1.9E-03 kg SO$_2$ eq./kg biodiesel, respectively.

Gases that trap heat in the atmosphere are called greenhouse gases (GHG). For each GHG, a Global Warming Potential (GWP) has been calculated to reflect how long it remains in the atmosphere, on average, and how strong it absorbs energy. Gases with a higher GWP absorb more energy, per pound, than gases with a lower GWP, and thus contribute more to warming Earth (US EPA 2014). In scenario 1 of the catalytic transesterification process, palm oil mill stage presented highest GHG emission among other stages. The main contribution was from methane release from open digesting tanks of POME treatment. Methane (CH$_4$) is a powerful greenhouse gas, with GWP is 25 times greater than that of CO$_2$. The implementation of methane capture system can achieve substantial GHG emission reduction (scenario 2). In the SMV process (scenario 1), biodiesel plant stage contributed the highest GHG emission among other stages due to high requirement of energy to provide high temperature in the transesterification process. The utilization of biomass waste as the energy source in biodiesel plant has reduced the GHG emission (scenario 2). In scenario 2, oil palm plantation stage contributed highest GHG emission for both catalytic and SMV methods. The main contributions were from the utilization of fertilizer, herbicide and pesticide. The sensitivity analysis result shows that the change in diesel consumption during the biodiesel production will be the most significant contribution to the GHG emission.

The result of the GHG emission by the catalytic and non-catalytic SMV methods corresponded to 64% and 46% reduction, respectively, in comparison with that of diesel production for scenario 1. The percentage of reduction was increased in scenario 2. It means that palm oil based biodiesel is more environmentally friendly compared to diesel fuel.

Acidification is the process of being converted into an acid or becoming acid. Acidifying pollutants have a wide variety of impacts on soil, groundwater, surface waters, biological organisms, ecosystems and materials (buildings). Examples include fish mortality, forest decline and crumbling of building materials. The major acidifying pollutants are SO$_2$, NO$_x$ and NH$_3$ (Guinée et al. 2002). In scenario 1, biodiesel production at biodiesel stage in the SMV method contributed the highest acidification effect. The contribution was mainly from the IDO combustion to generate power and steam in the transesterification process. Acidification effect reduced with the biomass substitution to IDO (scenario 2). The electricity consumption also contributed to the acidification effect. The Indonesian grid electricity is generated from a mix of hydro, geothermal, coal,
petroleum and natural gas. The electricity productions from coal, petroleum and natural gas have high impacts on acidification.

Eutrophication covers all potential impacts of excessively high environmental levels of macronutrients, the most important of which are nitrogen (N) and phosphorus (P). Nutrient enrichment may cause an undesirable shift in species composition and elevated biomass production in both aquatic and terrestrial ecosystems. In addition, high nutrient concentrations may also render surface waters unacceptable as a source of drinking water. In aquatic ecosystems increased biomass production may lead to a depressed oxygen level, because of the additional consumption of oxygen in biomass decomposition (measured as BOD) (Guinée et al. 2002). Urea (nitrogen) is the largest input from fertilizer in the oil palm plantation. Therefore, the oil palm plantation contributed the highest eutrophication effect. LCI and LCIA of 1 kg palm oil biodiesel production for scenario 1 present in Figure 7.1.

![Figure 7.1 LCI and LCIA of 1 kg palm oil biodiesel production (scenario 1)](image)

The SMV method in scenario 1 consumed the largest amount of energy for increasing the process temperature. Figure 7.1 shows that non-catalytic SMV method required 13.74 MJ energy in transesterification process (70% energy
conversion was assumed), much higher than the catalytic one. The utilization of biomass waste as a substitute of fossil fuel was reduced the energy consumption of the SMV method (Scenario 2).

The exergy analysis result shows that the exergy efficiency of non-catalytic SMV method was lower than the catalytic method, which was 92.61% and 95.37%, respectively. This condition occurred because the irreversibility of the non-catalytic SMV process was higher than the catalytic one, again, due to high temperature requirement of the non-catalytic SMV process. The irreversibility of the SMV process is influenced by several factors, which are: the mass transfer between phases, environment temperature, fluid friction, and heat transfer. The heat recirculation could decrease the irreversibility, which lead to the increase of exergy efficiency of biodiesel production, especially if the SMV methods will be adopted. The methanol evaporation process in the evaporator 1 of the non-catalytic SMV process (Figure 3.4) contributed the highest irreversibility, which was 2802.07 kJ/kg biodiesel. The evaporator 1 works to transform methanol into a vapor phase. The improvement of non-catalytic SMV process is indispensable to be conducted, especially in the methanol evaporation process, since this will lead to the largest improvement to the biodiesel production efficiency in the non-catalytic SMV method.

LCA and exergy analysis are complementary tools that can be used together in providing solutions to analyze processes and to determine environmental impact, irreversibility, and exergy efficiency of biodiesel production. The LCIA result shows that in scenario 1 non-catalytic SMV method gave higher GHG emission than catalytic method. Methanol evaporation process contributed highest GHG emission in the SMV process, which was 0.77 kg CO₂ eq./kg biodiesel, while the transesterification process in BCR was 0.12 kg CO₂ eq./kg biodiesel. This result was in line with the exergy analysis result, which also indicated that the SMV method contributed higher irreversibility (lower exergy efficiency) than the catalytic one, and methanol evaporation process also gave the highest contribution to the irreversibility. Based on those results, the concepts of LCA and exergy analysis, the minimisation of life cycle irreversibility, can be applied to improve the palm oil biodiesel production process technologies in term of environmental impact and exergy efficiency.
CHAPTER VIII
FINAL CONCLUSIONS AND SUGGESTIONS

Conclusions

This dissertation led to the following conclusions:

1. The LCA method have been performed to assess the life cycle of palm oil biodiesel production technologies in this study. The LCI results showed that 1 kg of biodiesel was produced from about 1.04 kg of CPO or about 4.76 kg of FFB.

The concentration of SO$_2$, NO$_2$, PM, and O$_3$ emissions from biodiesel plant was below the threshold. Whereas, CO pollutant concentration was over the threshold and gave the negative impacts on the environment in the radius less than 450 m from the boiler stack (emission source). This implied that the safe distance of biodiesel plant site to the settlements area is in the radius of 450 m from the emission source.

The wastewater from washing stage in the biodiesel plant is basic (alkaline) with a high content of TSS, BOD, and COD, and has exceeded the effluent quality standard for palm oil industry. Therefore, it requires the form of appropriate engineering on aerobic and anaerobic processes in the WWTP before being discharged directly into the river. The mass balance analysis result indicated that the discharged of untreated wastewater from biodiesel plant would gave an additional environmental burden with the increase of COD content in the river.

The non-catalytic SMV method contributed the highest environmental impact (GHG emission and acidification effect) and consumed the largest amount of energy due to high temperature requirement in scenario 1. It can be reduced with the implementation of the methane capture system in the palm oil mill and the substitution of fuel oil with biomass waste (scenario 2).

Palm oil based biodiesel is more environmentally friendly compared to diesel fuel. It was shown with the reduction of GHG emission was up to 64% and 46% for the catalytic and non-catalytic SMV methods, respectively in scenario 1. The percentage of reduction was increased in scenario 2.

The total exergy efficiency of non-catalytic SMV process was lower than the catalytic one, which was 92.61% and 95.37%, respectively. The methanol evaporation process contributed the highest irreversibility, which was 2802.07 kJ/kg biodiesel. The improvement of non-catalytic SMV process is indispensable to be conducted, especially in the methanol evaporation process, since this will lead to the largest improvement to the biodiesel production efficiency in the non-catalytic SMV method.

The utilization of biomass waste along biodiesel production line and the implementation of heat recirculation in the transesterification process were highly recommended to create a biodiesel production process become more efficient and environmentally friendly, especially if the SMV method will be adopted.
Suggestions

1. In future work, research should be conducted the ‘cradle to grave’ LCA, included the assessment of land use change and utilization of biodiesel in transportation and/or industrial sectors.
2. The inventory data should be consisting of more Indonesian database.
3. In future work, the research of LCA biodiesel production should also considered the production factors such as length of time required and production cost in the transesterification process, so it can help decision makers in selecting the appropriate technology in the addition to the environment and exergy point of view.

Recommendation

The LCA studies of palm oil biodiesel in Indonesia should be organize to strengthen the inventory data in order to clarify the European Community claim and the US-EPA notification. This study results can be part of that inventory data.

Acknowledgement

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Masaru K, Taichi S, Takeshi M, Kazuhiro B, Akihiko K, Yuji S, Hideo N, Fumiki
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Vegetable Oil and Used Cooking Oil. *As. J. Energy Env.* 10(04): 221-229.

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International Conference on “Sustainable Energy and Environment (SEE)”.*
1-3 December 2004, Hua Hin, Thailand.


APPENDICES
# Appendix 1 The display of MiLCA-JEMAI software

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<th>Case study</th>
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Appendix 2  The 3D layout of biodiesel plant with capacity of 1.5 ton per day in Engineering Center (Courtesy of Engineering Center)


### Appendix 3  Air Pollutant Standard Index (Indeks Standar Pencemar Udara / ISPU)

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<tr>
<th>Index Number</th>
<th>Category</th>
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<th>NO₂ (1 hours) µg/m³</th>
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<td>SO₂ ≤ 80</td>
<td>*)</td>
<td>CO ≤ 5</td>
<td>PM₁₀ ≤ 50</td>
<td>O₃ ≤ 120</td>
</tr>
<tr>
<td>51 - 100</td>
<td>Medium</td>
<td>80 &lt; SO₂ ≤ 365</td>
<td>*)</td>
<td>5 &lt; CO ≤ 10</td>
<td>50 &lt; PM₁₀ ≤ 150</td>
<td>120 &lt; O₃ ≤ 235</td>
</tr>
<tr>
<td>101 - 199</td>
<td>Unhealthy</td>
<td>365 &lt; SO₂ &lt; 800</td>
<td>*)</td>
<td>10 &lt; CO &lt; 17</td>
<td>150 &lt; PM₁₀ ≤ 350</td>
<td>235 &lt; O₃ ≤ 400</td>
</tr>
<tr>
<td>200 - 299</td>
<td>Extremely unhealthy</td>
<td>800 ≤ SO₂ &lt; 1600</td>
<td>1130 ≤ NO₂ &lt; 2260</td>
<td>17 ≤ CO &lt; 34</td>
<td>350 ≤ PM₁₀ &lt; 420</td>
<td>400 ≤ O₃ &lt; 800</td>
</tr>
<tr>
<td>≥ 300</td>
<td>Dangerous</td>
<td>SO₂ ≥ 1600</td>
<td>NO₂ ≥ 2260</td>
<td>CO ≥ 34</td>
<td>PM₁₀ ≥ 420</td>
<td>O₃ ≥ 800</td>
</tr>
</tbody>
</table>

*) There is no index to be reported at low concentrations with short-term exposure.
Appendix 4 The report of wastewater quality analysis result
Appendix 5 The report of air quality analysis result

<table>
<thead>
<tr>
<th>NO. PARAMETER YANG DIANALISIS</th>
<th>METODE ANALISIS</th>
<th>SATUAN</th>
<th>Tanggal</th>
<th>Jam</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitrogen Dioksida (NO&lt;sub&gt;x&lt;/sub&gt;)</td>
<td>Saltzman</td>
<td>mg/m³</td>
<td>0.2503</td>
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<tr>
<td>2</td>
<td>Sulfur Dioksida (SO&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>Parameasian</td>
<td>mg/m³</td>
<td>1.8550</td>
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<tr>
<td>3</td>
<td>Total Oxidant (NOx)</td>
<td>Chemiluminescent</td>
<td>mg/л</td>
<td>0.0325</td>
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<tr>
<td>4a</td>
<td>Karbon Monoksida (CO) Maximun</td>
<td>Flue Gas Analyzer</td>
<td>mg/m³</td>
<td>385.5690</td>
</tr>
<tr>
<td>4b</td>
<td>Karbon Monoksida (CO) Rata-Rata</td>
<td>Flue Gas Analyzer</td>
<td>mg/m³</td>
<td>128.4710</td>
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<tr>
<td>5</td>
<td>PM10</td>
<td>Gravimetrik</td>
<td>mg/л</td>
<td>0.205</td>
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</tbody>
</table>

数据分析

报告日期：2012年7月6日

采样地点：

采样时间：2012年7月6日

报告机构：

PUSAT PENELITIAN LINGKUNGAN HIDUP
LEMBAGA PENELITIAN DAN PENGABDIAN KEPADA MASYARAKAT
INSTITUT PERTANIAN BOGOR

DATA LABORATORIUM
No. : 1812/43/PLH-IPB/2012
Contoh Uji : Udara
Biaya Analisis : 20.000
Dept. Teknik Mesin & Bioisien

Tanggal msuk contoh : 06 Juli 2012
Tanggal Analisis : 25 Juli 2012

LAPORAN ANALISIS

<table>
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<tr>
<th>Ref. Agenda</th>
<th>METODE ANALISIS</th>
<th>SATUAN</th>
<th>Tanggal</th>
<th>Jam</th>
<th>LOKASI</th>
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<td>1012</td>
<td>EOG-894</td>
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</table>

Pengadaan disampaikan setelah remahatnya 30 hari setelah tanggal dilibatkan certifier
Complaint should be submitted within 30 days since the release date of certificate

F.10.3
Edi : 10.12. Rev. : 0.00 Tgl 11.06.10

PPLH-LPPM, IPB
Gedung PPLH Lantai 2-4, J. Lingkar Akademil, Kampus IPB Darmaga, Bogor 16680
Alamat Surat : P.O. Box. 263 Bogor 16091
Telepon : (0251) 8621 085, 8621 262, Faksimili : (0251) 8621 134
E-mail : pplh@ipb.ac.id, pplh-ipb@indo.net.id | Website : https://www.ipb.ac.id/pplh
Appendix 6 The display of impact assessment in MiLCA-JEMAI software
Appendix 7  The system of palm oil biodiesel production by catalytic process with MiLCA_JEMAI software (Oil palm plantation stage)
Appendix 8 The system of palm oil biodiesel production by catalytic process with MILCA_JEMAI software (Palm oil mill stage)
Appendix 9  The system of palm oil biodiesel production by catalytic process with MiLCA_JEMAI software (Biodiesel plant stage)
Appendix 10 The system of palm oil biodiesel production by non-catalytic SMV process with MiLCA_JEMAI software (Oil palm plantation stage)
Appendix 11 The system of palm oil biodiesel production by non-catalytic SMV process with MiLCA_JEMAI software (Palm oil mill and biodiesel plant stage)
Appendix 12 Exergy balance in the evaporator of non-catalytic SMV process
(Furqon 2011)

- Energy Balance

\[ Q_a = \left( \dot{m}_1 C_{pf} (T_{sat} - T_1) + \dot{m}_1 h_{fg} + \dot{m}_2 C_{pg} (T_2 - T_{sat}) \right) \]

- Entropy Balance

\[ \Delta S_{gen} = \dot{m}_1 C_{pf} \ln \left( \frac{T_{sat}}{T_1} \right) + \frac{\dot{m}_1 h_{fg}}{T_{sat}} + \dot{m}_2 C_{pg} \ln \left( \frac{T_2}{T_{sat}} \right) \]

- Exergy Balance

\[ Q_a - T_0 \Delta S_{gen} = \left( \dot{m}_1 C_{pf} (T_{sat} - T_1) + \dot{m}_1 h_{fg} + \dot{m}_2 C_{pg} (T_2 - T_{sat}) \right) \\
- T_0 \left( \dot{m}_1 C_{pf} \ln \left( \frac{T_{sat}}{T_1} \right) + \frac{\dot{m}_1 h_{fg}}{T_{sat}} + \dot{m}_2 C_{pg} \ln \left( \frac{T_2}{T_{sat}} \right) \right) \]
Appendix 13  Exergy balance in the superheater of non-catalytic SMV process (Furqon 2011)

- Energy Balance
  \[ Q_b = \dot{m}_3 C_{pg} (T_3 - T_2) \]

- Entropy Balance
  \[ \Delta S_{gen} = \dot{m}_3 C_{pg} \ln \frac{T_3}{T_2} \]

- Exergy Balance
  \[ Q_b - T_0 \Delta S_{gen} = (\dot{m}_3 C_{pg} (T_3 - T_2)) - T_0 \left( \dot{m}_3 C_{pg} \ln \frac{T_3}{T_2} \right) \]
Appendix 14  Exergy balance in the bubble column reactor of non-catalytic SMV process (Furqon 2011)

- Energy Balance

\[ Q_c + \Delta H_{\text{reaksi}} = \dot{m}_4 C_{pg}(T_4 - T_3) \]

- Entropy Balance

\[ \Delta S_{\text{gen}} = \dot{m}_4 C_{pg} \ln \frac{T_3}{T_4} - \frac{\Delta H_{\text{reaksi}}}{T_4} \]

- Exergy Balance

\[ Q_c + \Delta H_{\text{reaksi}} \left( 1 - \frac{T_0}{T_4} \right) - T_0 \Delta S_{\text{gen}} = \left( \dot{m}_4 C_{pg}(T_4 - T_3) \right) - T_0 \left( \dot{m}_4 C_{pg} \ln \frac{T_4}{T_3} \right) \]
BIOGRAPHY

Rosmeika, S.TP, M.Sc. (author) was born in Bogor, West Java on May 3rd, 1979. In 1997, she was graduated from SMUN 3 Bogor and continued her under graduate study in Agricultural Engineering Major, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University and graduated in 2001.

In 2002, she was starting work as research engineer in Indonesian Center for Agricultural Engineering Research and Development, Agency of Agricultural Research and Development, Ministry of Agriculture. In 2007, she continued her study in Master Degree Program in Agricultural Engineering of Gadjah Mada University, Yogyakarta and was graduated in 2009. In 2010, she got a scholarship from Indonesian Agency of Agricultural Research and Development, Ministry of Agriculture, to continuing study in Agricultural Engineering Science, Bogor Agricultural University.

Some scientific works that were part of writer’s dissertation that have been published and under review process, including:


- Exergy Analysis of CPO Biodiesel Production Technologies. Peer-review improvement in Jurnal Teknologi Industri Pertanian.


