# LIFE CYCLE ASSESSMENT OF BIOETHANOL PRODUCTION FROM FEEDSTOCKS IN THAILAND

BY

THANAPAT CHAIREONGSIRIKUL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF
ENGINEERING (ENGINEERING TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
THAMMASAT UNIVERSITY
ACADEMIC YEAR 2015

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A Thesis Presented

By

Thanapat Chaireongsirikul

Submitted to

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# Abstract

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B.Eng, Sirindhorn International Institute of Technology

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An analysis of mass balance, energy performance, and environmental impact assessment were performed to evaluate bioethanol production in Thailand. Thailand is an agricultural country, Thai government plans to increase the use of alternative energy to 20 percent by 2022. One of the primary campaigns is to promote a bioethanol production from abundant biomass resources such as bitter cassava, molasses and sugarcane. The bioethanol production is composed of three stages: cultivation, pretreatment, and bioethanol conversion. All of mass, material, fuel, and energy were calculated to determine the environmental impact of three bioethanol production: bioethanol productions from cassava, bioethanol production from molasses, and bioethanol production from rice straw. Environment impacts in this thesis are climate change, human toxicity, fresh water toxicity, terrestrial toxicity, eutrophication, and acidification. In addition, to better evaluate the impact assessment of each bioethanol production options, we scored the impact severity using LCA normalization. The results showed that bioethanol production from cassava has the best environmental performance. Cassava-based bioethanol production contributes less impact when compared to the other processes.



**Keywords**: Life cycle assessment, Bioethanol Production, Biofuel

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# Introduction

## 1.1 Introduction

Biodiesel is one of the most promising biofuels today and considered as an alternative diesel. It plays a significant role in transportation sector since the oil price has been increasing. Biodiesel can be derived from a wide range of biomass sources such as plant residue, animal residue and organic waste. Biodiesel has gained an increasing public and academic attention driven by worldwide effort to reduce conventional gasoline consumption in transport sector because of an uncertainty in diesel production and an effort to reduce its negative environmental impacts [1]. Bioethanol gains the most attention today due to its popularity in the international markets. Bioethanol can be produced from various biological sources and various processes such as hydration and fermentation. It is usually used as a gasoline additive to increase octane number and improve vehicle emission performance [2].

Nowadays, Thailand is facing an energy crisis due to a continually escalated crude oil price and a heavy reliance on imported oil. As a result, Thai government has encouraged the development of domestic bioethanol production for a sustainable energy supply. The main purpose for promoting Bioethanol as an alternative source of energy is its environmental friendly property which mitigates environmental impacts and helps the country rely less upon the imported oil. Since 2004, Thai government has promoted Bioethanol which is derived from cane molasses, cassava, and sugar cane in order to substitute the conventional gasoline [3]. Promotional strategy is to mix ten percent of ethanol content in gasoline and remove methyl tertiary butyl ether (MTBE), an additive, and this diesel is called "E10," which was introduced in 2004. After E10 had penetrated the market, E20, 20% ethanol blend, was later introduced in 2008. In 2007, there were seven ethanol plants with the total installed capacity of 955,000 liter/day, comprising 130,000 liter/day cassava ethanol and 825,000 liter/day molasses ethanol. The amount of gasohol consumption in the country increased from 3.5 million liters/day in 2006 to 7.4 million liters/day in 2008 and is likely to grow continuously in the foreseeable years [4]. The research of energy performance and environmental impacts of bioethanol production is still inaccurate and insufficient. Some studies have paid less attention on environmental impacts. Thus, Life cycle assessment is used to observe life-cycle span of products through several life stages such as cultivation, harvesting, production, production, and transportation. It is a standardized method to evaluate the environmental impacts arising from the entire life of product and process and can appropriately be applied to evaluating Bioethanol processes.

## 1.2 The potential feedstock for Bioethanol production in Thailand

Thailand is known as an "agricultural country" whose economy relies much upon exporting agricultural products. Thai export is very successful internationally especially in rice market. In 2008, the agricultural area per total area was 0.392 and increased to 0.412 in 2012 [5]. According to availability, the most well-known agricultural products are rice, sugarcane and cassava. Thailand is ranked as the world's 6th largest rice producer but the 3rd largest rice exporter. Thailand is also the world's largest cassava producer and exporter contributing about 70% of the world market share. It is the second leading sugar exporter though still relatively small as compared to the outstanding sugarcane producer Brazil [47]. The wastes from these economic crops can be used as a biomass source to produce Bioethanol in Thailand such as rice straw, sugarcane molasses, and cassava chip. All of these wastes become the primary raw materials in bioethanol production.

### 1.2.1 Cassava chip

Cassava is one of the most important economic crops in Thailand. It was the first commercially planted in southern region of Thailand. Later, as demand from domestic market escalated, planting area extended to the other provinces especially in the northeastern region.

Cassava is a starch crop which can be classified into two types: sweet cassava and bitter cassava. Sweet cassava is used for consumption as it contains low hydrocyanic acid content [6]. On the other hand, the bitter type is poisonous due to the high level of hydrocyanic acid content. It is not suitable for consumption or animal feed. Therefore, its use lies in the production of some certain types of products such as cassava pellet, cassava chip, and bioethanol. The chip of cassava can be used to produce bioethanol by advanced processes such as simultaneous saccharification and fermentation [3].

Thailand had an average production quantity of cassava during 2007-2008 around 26.98 million tons, which was processed for domestic consumption at about 7.68 million tons. The remaining of 19.30 million tons could be used to produce ethanol at around 2,702 million liters per year [7].

### 1.2.2 Molasses

Sugar cane is a hardy crop that is cultivated in tropical and sub-tropical regions for sugar production with by-products such as molasses and bagasse. It is considered as one of the most important economic crops in Thailand. Generally, the cultivation area is located in the non-irrigation area especially in the northeastern part of Thailand [3].

Molasses is a black viscous by-product, used in Bioethanol production. Molasses is produced in two forms: blackstrap and syrup. Syrup molasses is edible. It can use as sweetener by mixing it with a corn syrup. On the other hand, Blackstrap molasses is not edible and is used as an animal additive or to produce ethanol [8].

Thailand had an average production quantity of sugar cane during 2007- 2011 around 68.67 million tons, of which 25 million tons were used to produce sugar for domestic consumption. The remaining of 43.67 million tons of sugarcane could be used to produce ethanol at around 3,057 million liters per year [7].

### 1.2.3 Rice

In Thailand, rice has been the staple food for Thai people since the ancient time. Thai people eat both glutinous and non-glutinous rice, prepared as meals, snacks, desserts and drinks [9]. Rice is being cultivated in the total area of approximately 61 million rais (97.6 billion $m^3$) annually. The by-product of rice cultivation is rice straw which can also be used to produce other agricultural products such as animal feed, diesel, etc. According to Thailand's research fund, the estimated maximum production of rice straw is 32,200 kg annually [10]. Normally, rice straw is used for combustion but it can also be used directly in fermentation process because it contains high content of starch. Therefore, production of Bioethanol can be achieved by the use of rice straw which is an abundant by-product in Thailand as a feedstock.

## 1.3 Problem Statement and Significance

Bioethanol is seen as a clean alternative to fossil diesels. Bioethanol can be produced from 3 types of feedstock; Sugar-based crops (sugarcane, sugar beet, sweet sorghum), Starchy crops (corn, wheat, cassava) or Lignocelluloses crops (switchgrass, miscantus, poplar). It was promoted by the Ministry of Energy who proposed to increase the use of bioethanol to 20% by 2022 [2]. Bioethanol can be used as a primary diesel in industrial sector or used as an additive by blending it with gasoline. Therefore, it presents a good opportunity to conduct an in-depth study about bioethanol production in Thailand.

From the previous studies, the research groups have investigated the environmental assessment and energy performance of bioethanol productions from molasses [11-13] and cassava chip [14-17] in Thailand. The studies are mainly based on the information from interviews, and on-site inspection. The energy performance and environmental assessment were calculated to observe the performance of bioethanol production. However, there is some certain degree of reservation in terms of information accuracy and the suitability of the primary raw material for bioethanol production in Thailand. Therefore, this study aims to assess all of the material flow, energy flow of the bioethanol production from various types of feedstock, which are available in Thailand, such as cassava chip, molasses and rice straw. This research is a comparative study of bioethanol productions from 3 different sources, cassava chip, molasses, and rice straw, in Thailand.

This study is divided into 4 parts. The first part of the study focuses on the mass analysis of bioethanol production from the cradle, which mainly involves the cultivation of crops to the final stage of bioethanol production. The mass analysis includes material (chemicals, pesticide, and fertilizer) and diesel input. The second part of study focuses on the energy performance of bioethanol production process. The amount of energy used in each stage was calculated as a total energy used. Third part of the study investigates environmental assessment, calculated based on LCA, which is divided into six categories including global warming, human toxicity, freshwater toxicity, terrestrial toxicity, acidification, and eutrophication. Finally, the last part of the study recommended the proper feedstock by LCA normalization to provide to provide the most environmental friendly process for bioethanol production.

## 1.4 Objectives of the study

The objectives of study are as follows:
1. To study present the full-chain of mass and energy analysis of bioethanol production in Thailand.
2. To assess the environmental impact of bioethanol production from cassava chip, molasses, and rice straw on life cycle approach.
3. To determine the proper process in term of environmental impact of bioethanol production in Thailand.

## 1.5 Scope of study

The scopes of study are as follows:
1. Cradle to gate evaluation including fertilizer, herbicide, chemical input, fuel used, primary raw material, and final product.
2. Energy performance which mainly embraces energy consumption in cultivation, pre-treatment, and bioethanol production.
3. Environmental assessment based on LCA, which is divided in to 6 categories: global warming, human toxicity, freshwater toxicity, terrestrial toxicity, acidification, and eutrophication.
4. The data were obtained from journal, literature, LCA database, and Aspen plus simulation.
5. Basis of this study is 1,000 L of 99.7 vol% bioethanol production.

# Chapter 2

# Literature Review

From previous study, the research groups have investigated the environmental assessment and energy performance of bioethanol productions from molasses [11-13] and cassava chip [14-17] in Thailand. Although there is no rice straw-based bioethanol production in Thailand, rice straw shows the potential to be a feedstock to produce bioethanol due to the abundantly rice cultivation in Thailand. Literature reviews are mainly based on methodology of LCA and overview of bioethanol production in Thailand.

## 2.1 Life cycle assessment

LCA is defined as the evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle. Thus, LCA is a tool for the analysis of the environmental burden of products at all stages in their life cycle – from the first stage to final disposal.

Life Cycle Assessment (LCA) had its beginnings in the 1960's. Concerns over the limitations of raw materials and energy resources sparked interest in finding ways to cumulatively account for energy use and to project future resource supplies and use. First publication was introduced by Harold Smith. He reported his calculation of cumulative energy requirements for the production of chemical intermediates and products at the World Energy Conference in 1963. Later in the 1960's, global modeling studies published in The Limits to Growth [41] and A Blueprint for Survival [42] resulted in predictions of the effects of the world's changing populations on the demand for finite raw materials and energy resources. In 1969, researchers initiated an internal study for The Coca-Cola Company that laid the foundation for the current methods of life cycle inventory analysis in the United States [43]. First life cycle inventory analysis is a comparison of different beverage container. Coca-Cola aimed to used container which had the least affected the supply of natural resources. At that time, life cycle inventory was very popular.

Since solid waste became a worldwide issue in 1988, LCA again emerged as a tool to observe environmental problems. As interest in all areas affecting resources and the environment grows, the methodology for LCA is again being improved. Researchers have been expanding the methodology of LCA which lead to another point of evolution of LCA methodology [44].

In 2002, the United Nations Environment Program (UNEP) joined forces with the Society of Environmental Toxicology and Chemistry (SETAC) to launch a new international partnership called "Life Cycle Initiative". It is consisted of three programs that change the methodology to be more practical.The Life Cycle Management (LCM) program improves skills of decision-makers by producing information materials, establishing communities for sharing best practice, and carrying out training programs in all parts of the world. The Life Cycle Inventory (LCI) program improves global access to transparent, high quality life cycle data in web-based information systems. The Life Cycle Impact Assessment (LCIA) program increases the quality and global reach of life cycle indicators by promoting the exchange of views among experts whose work results in a set of widely accepted recommendations [43].

Most important, a cradle-to-grave analysis involves a 'holistic' approach, bringing the environmental impacts into one consistent framework, wherever and whenever these impacts have occurred, or will occur. One fundamental reason for choosing such an approach is related to the fact that the final consumption of products happens to be the driving force of the economy. Therefore, this final consumption offers core opportunities for indirect environmental management along the whole chain or network of unit processes related to a product [18].

The Main Applications of LCA are:
1. Analyzing the origins of problems related to a particular product,
2. Comparing improvement variants of a given product,
3. Designing new products, and
4. Choosing between a numbers of comparable products.

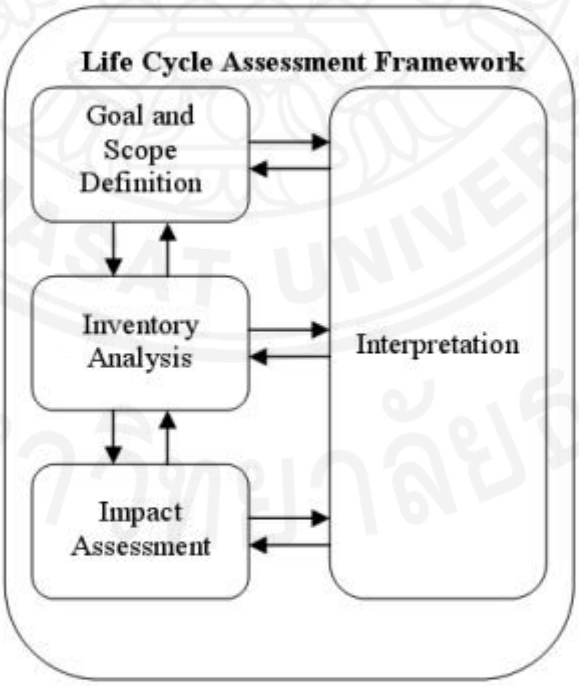


Figure 2.1 Life Cycle Assessment Framework
Source: Heijungs, R et al. (1992)

Figure 2.1 is shown the general framework of Life cycle assessment. LCA conduct start from setting up the goal and definition of work. The objective and the detail of the study need to be clarified in this step. Inventory analysis is a second step in the framework. After, goal, objective, and scope were setting up in the first part. Researcher need to determine the amount of mass flow, energy flow, labor, and cost. All of these factor will affect the last part which is impact assessment where researcher need to bring all of the factors and data from the second part to calculated for the impact in each categories such as global warming, acidification, toxicity, or land used.

### 2.1.1 Impact assessment

Impact assessment is the phase in which the set of results of the inventory analysis. It is further processed and interpreted in terms of environmental impacts and societal preferences. To this end, a list of impact categories is defined, and models for relating the environmental interventions to suitable category indicators for these impact categories are selected. The actual modeling results are calculated in the characterization step, and an optional normalization serves to indicate the share of the modeled results in a worldwide or regional total. Finally, the category indicator results can be grouped and weighted to include societal preferences of the various impact categories [18]. According to LCA handbook, impact categories are depletion of abiotic resources, depletion of biotic resources, climate change, stratospheric ozone depletion, human toxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, freshwater sediment ecotoxicity, marine sediment ecotoxicity, photo-oxidant formation, acidification, and eutrophication.

### 2.1.2 LCA nomalization

LCA normalization offered a reference situation of a load on the environment of each environmental impact category. Normalization makes it possible to translate abstract impact score of each for every impact categories into relative contributions of the product to the reference situation [25]. Normalization can also be used to check for inconsistencies, to provide and communicate information on the relative significance of the category indicator results and to prepare for additional procedures such as weighting and interpretation [40] impact score of different impact categories [45].

Normalized values can be calculated by dividing the indicator results from characterization by normalization factors connected to the reference information. These factors are usually various in different assessment methods including CML 2002, Eco-indicator-99, and etc.

## 2.2 Bioethanol production in Thailand

History of bioethanol production in Thailand began in the late 1970s and further emphasized in the early to mid-2000s, Thailand realized the need for development of a domestic transportation diesel production process. Thai Government began to develop their own domestic bioethanol strategy to lessen the reliance upon imported oil [19]. Appendix A provides a timeline detailing the history of bioethanol production in Thailand [20].

In 2003, the Thai government developed three strategies to address their oil import problem as follow:
1. Increase renewable diesel and the efficiency of diesel utilization.
2. Secure alternative oil sources.
3. Increase the value of energy sources.

As a result of these strategies, since 2005, the number of gasohol station had dramatically increased across the country to nearly 4,200 stations which accounted for 23% of the country's total gas stations by 2009 [21]. Ethanol production and gasohol consumption in Thailand had also continued to increase in 2008.

### 2.2.1 Cassava-based bioethanol production

In cultivation stage, major farming activities include land preparing, planting, fertilizing, weeding, and harvesting [22]. Sweet cassava and bitter cassava are obtained from cultivation stage. Sweet cassava has low hydrocyanic acid compared to the bitter one. Therefore, the sweet type can be directly sold to the market. Bitter cassava cannot be used as food. However, it does contain high level of starch so it can be used as a food source for bacteria in fermentation process to produce bioethanol.

In Pre-treatment stage, major activities are chopping, sun-drying, and turning chip by tractor. After being harvested, cassava roots are readily converted to dried chip using simple chopping machine [22]. One kg of cassava root can be converted to 410 gram of cassava chip [23].

In bioethanol production stage, the processes in this stage consist of milling, mixing and liquefaction, saccharification, fermentation and dehydration. The main product is 99.7 vol% of ethanol [22]. The fermentation of 1,000 litres of bioethanol requires 2,500 kg of dried chips [23]. The residue mass from distillation process is called "thick slop" and can be used as a fertilizer or animal feed.

From previous work, there are only a few publications, which related to the bioethanol production from cassava chip in Thailand. T.L.T Nguyen (2006) studied about the full chain of energy analysis of diesel ethanol in Thailand. The paper shows the overall material input and output of the processes including amount of herbicide used, amount of fertilizer used, amount of energy used in each stage. K.Sriroth (2006) also studied about the bioethanol production from cassava chip. He argues that there are a several step in bioethanol production from cassava chip including grinding, slurry, liquefaction, saccharification, fermentation, distillation and dehydration. The material balance of cassava-based process which obtained from literature is shown in Figure 2.2. The processes in this bioethanol conversion are milling, mixing, liquefaction, fermentation, distillation and dehydration. It shows that it required 362,100 kg of cassava chip to produce 150,000 L of bioethanol. It required water around 1,258 ton per day or per 150,000 L. So, this information can be used to calculate the amount of material required if the basis is 1,000 L of bioethanol.

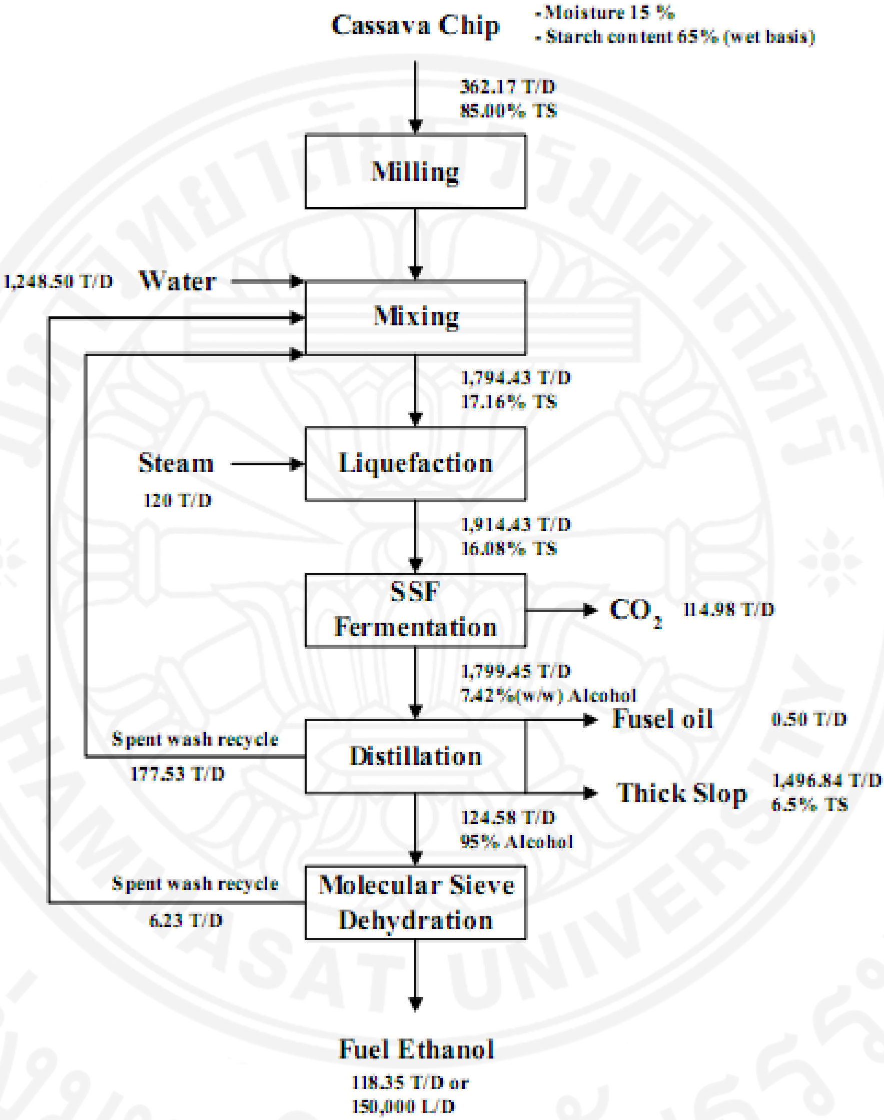


Figure 2.2 Material balance of Cassava chip-based bioethanol production
Source: Department of alternative energy development and efficiency (2006)

### 2.2.2 Molasses-based bioethanol production

Sugarcane crop rotation generally takes two to five years: one new planting followed by one to four ratoons. Steps involve at this stage include land preparation, planting, crop maintenance and harvesting [11]. Sugar cane crop which is about one year old is ready to be harvested and processed into sugar. Only cane stalks are cut and collected from the field whereas the trash left is either open burned or ploughed back into soil [24].

In pre-treatment stage, cane stalk from sugarcane cultivation is ready for sugar milling. Sugar milling involves a series of stages namely crushing, clarifying, boiling, seeding, and centrifuging to extracting sugar crystal from the cane [11].

There are two by-products from sugar milling process; molasses and bagasse. Normally, bagasse can be used to produce a stream or electricity by combustion. However, bagasse can also be used to produce bioethanol. But, in this work, molasses from sugarcane is the only feedstock used to produce bioethanol.

In bioethanol production stage, the process consists of 2 main steps: First, molasses in fermentation with yeast yields diluted alcohol. Second, the fermented mash is passing through the distillation column and then dehydration system to produce 99.7 vol% alcohols [11]. The residue mass from distillation process called "Thick slop" can be used as a fertilizer or animal feed.

From the previous work, there are several publications, which related to the bioethanol production from the molasses. Department of alternative energy development and efficiency (2006) shows the overall mass balance of the bioethanol production from molasses. It is including the amount of mass flow in each stage in bioethanol production step, allocation of wastes which produce within the process, and the amount of mass, which require producing 1,000 L bioethanol. Nguyen, T.L.T (2008) also presents the full chain of energy analysis of diesel ethanol from cane molasses in Thailand. The study show the amount of herbicide used, amount of fertilizer used, and amount of energy used in each stage from cradle to product. Sathitbun-anan S (2011) also studied about the assessment of energy saving potentials in sugar processing. The study show the amount of energy used of sugar milling process. The result from this paper had shown that sugar milling processes required 1,360 kW-h of electricity and 42,325 MJ from combustion. While the Figure 2.3 show some material balance of molasses-based bioethanol production. The processes in this bioethanol conversion are mixing, fermentation, distillation and dehydration. It shows that it required 532,450 kg of molasses to produce 150,000 L of bioethanol. It required water around 987.64 ton per day or per 150,000L. So, this information can be used to calculate the amount of material required if the basis is 1,000 L of bioethanol in the same method as calculated in cassava-based process.

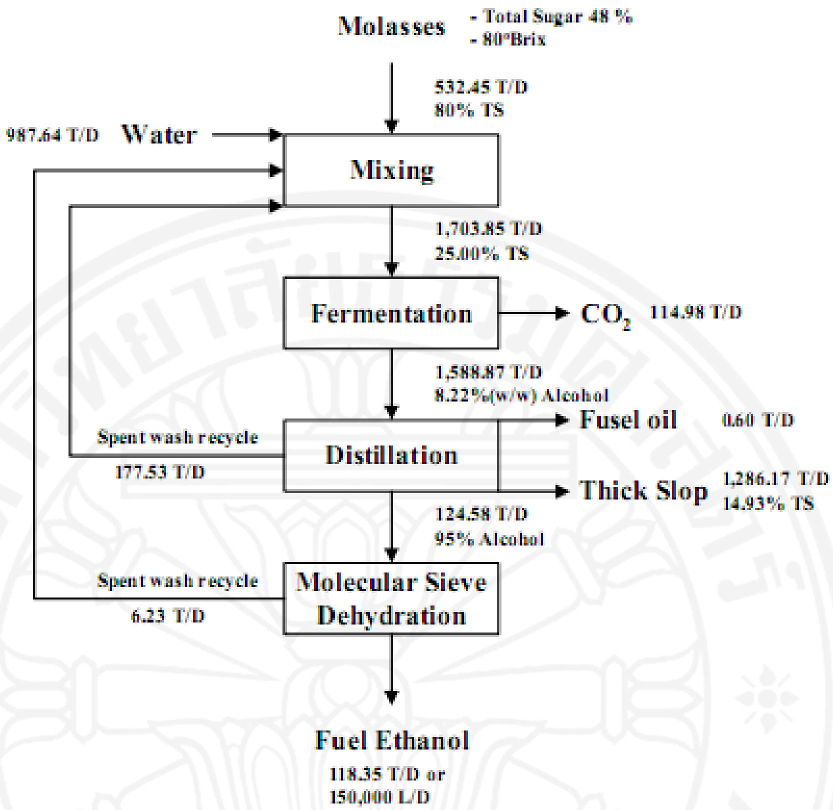


Figure 2.3 Material balance of Molasses-based bioethanol production
Source: Sriroth K et al. (2012)

### 2.2.3 Rice straw-based bioethanol production

Rice is grown in bunded fields with ensured irrigation for one or more crops a year. Farmers generally try to maintain 5–10 centimeters (cm) of water ("floodwater") in the field. In general, irrigated rice farms are small, with the majority takes up the land of from 0.5 to 2 acres. In many humid tropical and subtropical areas, irrigated rice is grown as a monoculture with two or even three crops a year [25].

Harvesting is the process of collecting the mature rice crops from the field. Depending on the variety, a rice crop usually reaches maturity at around 115-120 days after the seed has been planted. Harvesting activities include cutting, stacking, handling, threshing, cleaning, and hauling. Good harvesting methods help maximize grain yield and minimize grain damage and deterioration [14].

In pretreatment stage, major activities are cleaning, husk removing and straw removing. After being harvested, rice must be milled in order to produce brown rice. Two main by-products in this stage are husk and straw. Rice husk can be used as a diesel in direct combustion while rice straw can be used as a lignocelluloses-based feedstock in fermentation process. The Straw to Grain Ratio (SGR) is 0.75 [26].

In bioethanol production stage, the processes in this stage consist of several steps including decrystallization, chromatographic separation, fermentation, distillation and dehydration. To produce 1,000 L of 99.7 vol% of ethanol, 4,640 kg of rice straw is required in pre-treatment step [46].

From previous studied, there are no publication that work on the bioethanol production from rice straw in Thailand. But author adopted the process from Vietnam which has a similar geography to Thailand and there is some database, which showed the overall mass or ratio of mass required such as government database, and herbicide/pesticide provider website. Pathak H (2012) studied about the low carbon technologies for agriculture of rice and wheat. The paper showed the mass balance and energy require in rice cultivation stage. N.Q.Diep (2012) also studied about bioethanol production from rice straw. He showed the full balance of material and energy in cultivation and rice milling stage. S. M. Amin Salehi (2012) studied about the bioethanol production by using sodium carbonate pretreatment. In this paper, author showed the material balance in bioethanol production step. The paper also showed the energy consumption in this fermentation process. K.L Kadam (1999) shown the material balance of concentrated acid process which available in Figure 2.4. The main step in this processes are hydrolysis, separation, chromatographic separation, evaporation, fermentation and dehydration. The product from concentrated acid is 99.7 vol% of bioethanol. Therefore, this information can be used as a reference in order to calculated for the amount of material required when producing 1,000 L of ethanol.

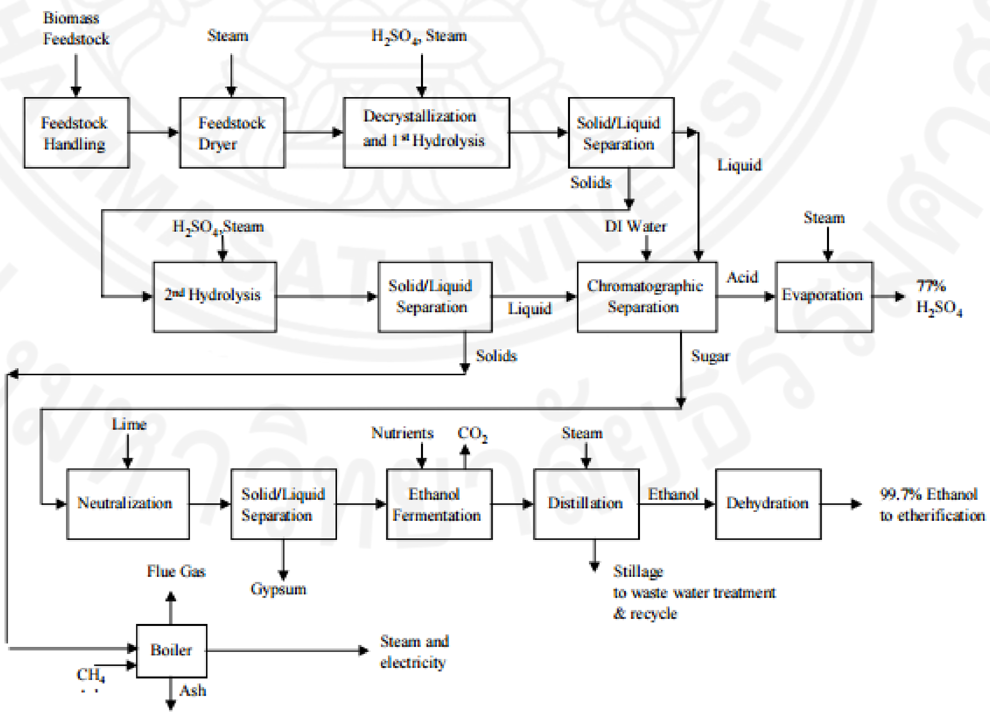


Figure 2.4 Concentrated Acid Process diagram
Source: K.L. Kabam et al. (1999)

# Chapter 3

# Methodology

This section shows all methods that were used to obtain the data of material balance, energy balance, environmental assessments, and LCA for the bioethanol production in Thailand. In this work, Cassava-based, Molasses-based, and Rice straw-based bioethanol production are used to observe the environmental performance of each process. The scope of this study covers from the cultivation stage of raw material to bioethanol production step. The calculations involved in this research are mass balance, energy balance, aspen simulation, life cycle assessment, toxic allocation, normalization and weighting.

## 3.1 Feedstocks of interest

In this study, agricultural wastes including cassava chip, molasses and rice straw were used as a feedstock for bioethanol production. Cassava chip and molasses are biomass, which have already been used to produce bioethanol in Thailand. For rice, there is no currently bioethanol production from this feedstock. Therefore, this research tried to study about the potential of bioethanol production from rice straw in Thailand.

Figures below are the feedstock used to produce bioethanol in Thailand:

Cassava Chip

Molasses

Potential feedstock which can be used to produce bioethanol in Thailand:

Rice Straw

Figure 3.1 Feedstocks in this study

### 3.2 System process

The overall system boundaries of bioethanol production derived from cassava chip, molasses and rice straw are shown in Figure 3.2, 3.3 and 3.4, respectively. The system boundaries were set to observe the mass flow and energy consumption from cradle to gate. The process starts with the cultivation process of cassava, sugarcane and rice. This process involves planting, and harvesting. The study excludes the impact of pesticide production and transportation. The second stage is pre-treatment of feedstock. The major activity in this stage is sugar milling for molasses-based bioethanol production, cassava chip production for cassava-based bioethanol production and rice milling for rice straw-based bioethanol production. The last stage is bioethanol production which embodies fermentation, hydration and distillation.

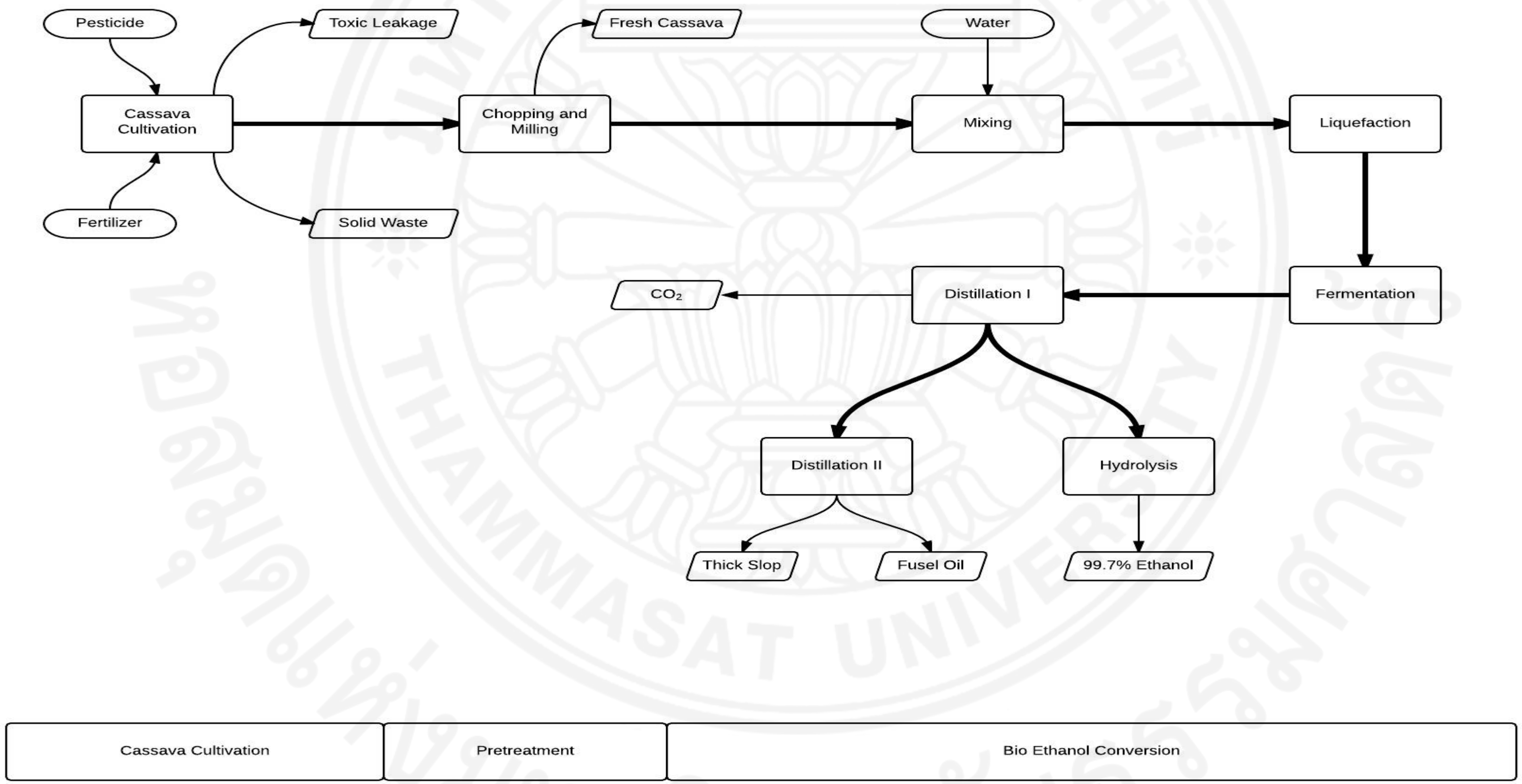


Figure 3.2 System boundary of bioethanol production from cassava chip

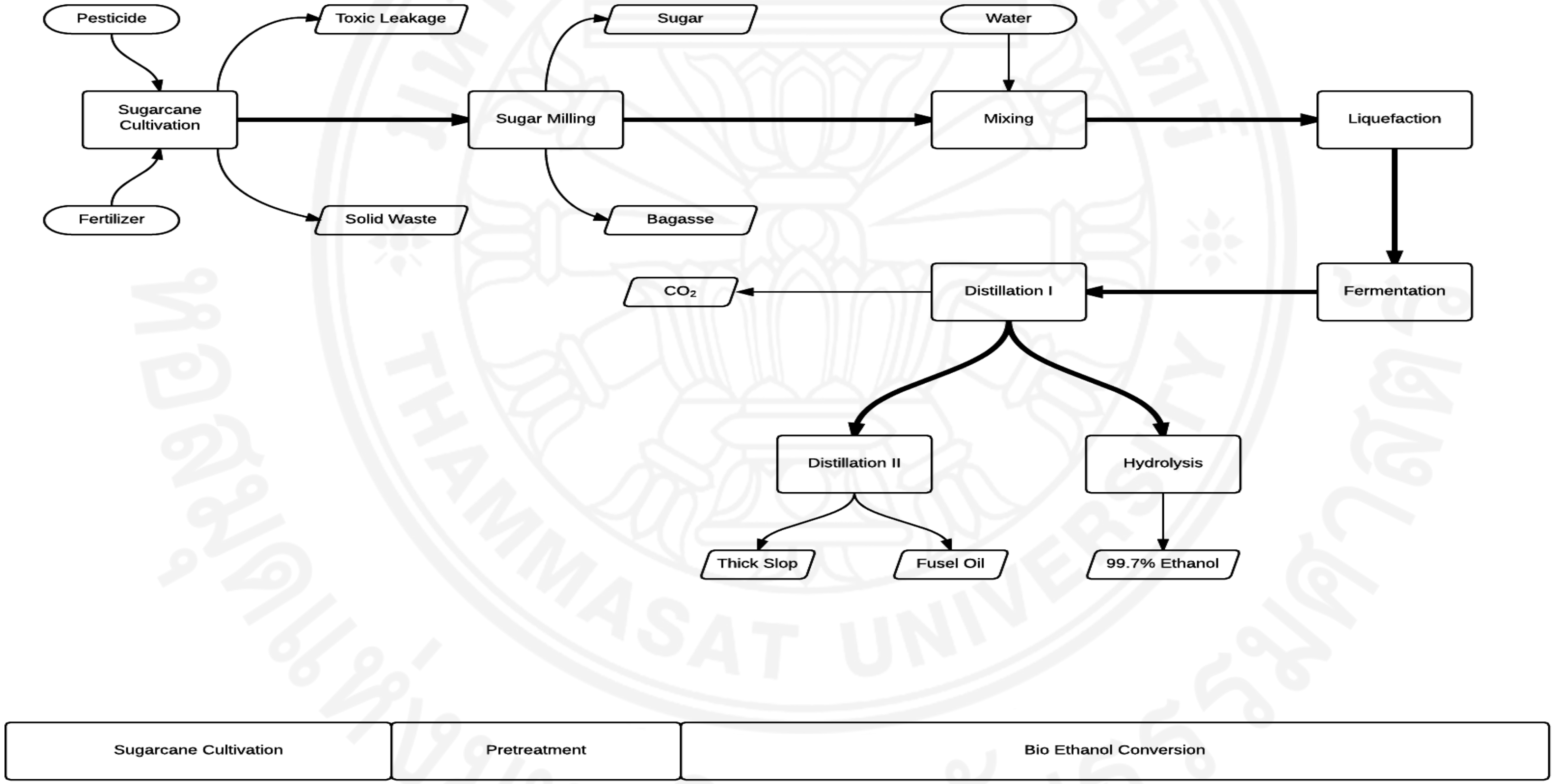


Figure 3.3 System boundary of bioethanol production from molasses

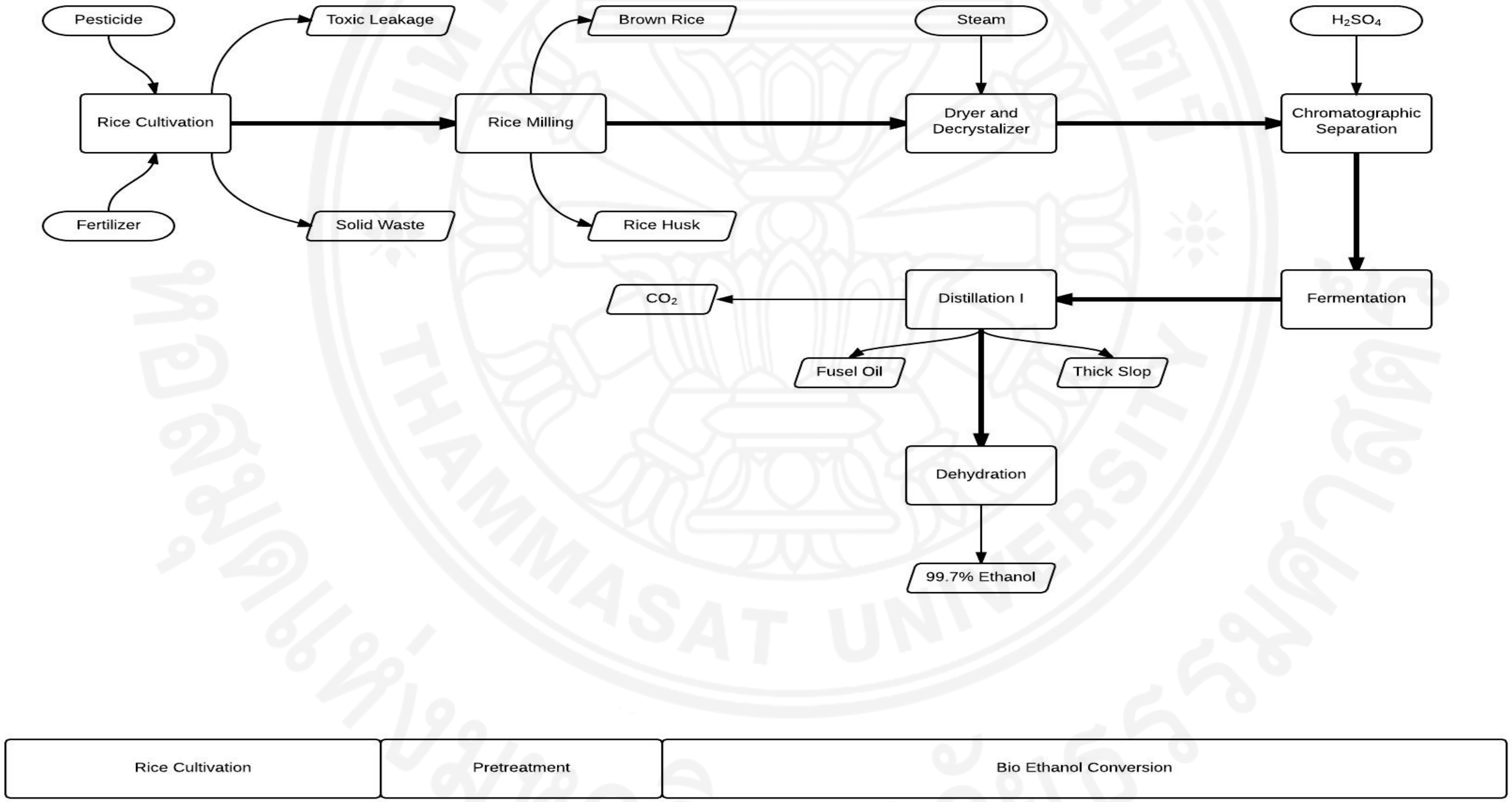


Figure 3.4 System boundary of bioethanol production from rice straw

### 3.3 Mass analysis

Mass Analysis was used to analyze the flow of material including fertilizer, herbicide, chemical, and diesel used. The analysis was conducted from the first stage, where the primary raw material is cultivated, to the last process, where ethanol is produced.

From the previous studies, many research groups already undertook mass analysis of bioethanol production from cassava chip, and molasses. However, this study will investigate material flow in deeper details, in order to obtain reliable data. The study will also identify the flow of chemical substance, the flow of fertilizer the flow of herbicide, the accumulation of toxic substance in plant and the leakage of toxic substance into environment, as well as the flow of waste and by-product of bioethanol production process. In addition, all of the mass analysis data are available in Appendix K-S and W-Y.

### 3.4 Energy analysis

Energy is an aggregation of heat of diesel combustion and energy used for fermentation, extraction, production and distillation. The major activities are bioethanol production, distillation, fermentation, pre-treatment, and refining. The procedure of estimating the energy used in each stage is shown in Table 3.1. As for thermal heat, the unit of thermal energy is in MJ while the unit of electricity is in kW-h.

Table 3.1 Data source for performing LCA

| Item | Sub-Item | Type of data | Information source | | |
|---|---|---|---|---|---|
| | | | Molasses | Cassava Chip | Rice Straw |
| Mass Analysis | Overview Mass Balance | Secondary data | [12] | [14],[15] | [17],[45],[48] |
| | Estimate Herbicide used | Secondary data and Calculation | [27] | [28],[29] | [30] |
| | Estimate Fertilizer used | Secondary data and Calculation | [31] | [32] | [33] |
| | Estimate Toxic Leakage | Secondary data and Calculation | [34] | [34] | [34] |
| Energy Analysis | Energy consumption in cultivation | Secondary data, | [11],[13] | [16],[35] | [36], |
| | Energy consumption in pre treatment | Secondary data | [11],[13] | [16],[35] | [36],[37],[45] |
| | Energy consumption in ethanol-production | Secondary data and Aspen simulation | [11],[13] | [16],[35] | [17],[45] |

### 3.5 Aspen plus simulation

In this research, aspen simulation is used to determine the amount of energy consumption in distillation column in bioethanol production stage. The simulation had been done by using the extractive RFRAC. Additional substance, ethylene glycol, is used as an extractive agent in order to enhance the efficiency of the separation between ethanol and water. In addition, all information of simulations is available in table 3.2 and 3.3. The table show about the separation information such as feed flow rate, extractive agent flow rate, production of ethanol rate, thermodynamic properties of each stream, purity of stream and etc. The simulation was performed under NRTL thermodynamic property.

Table 3.2 Simulation results for cassava-based bioethanol production

| | **Feed Stream** | **Ethylene Stream** | **Product Stream** | **Water Stream** |
|---|---|---|---|---|
| Substream: MIXED | | | | |
| Mole Flow (kmol/sec) | | | | |
| Water | 0.000672 | 0.000000 | 0.000011 | 0.000661 |
| Ethanol | 0.004733 | 0.000000 | 0.003960 | 0.000774 |
| Ethylene Glycol | 0.000000 | 0.002784 | 0.000001 | 0.002783 |
| Total Flow (kmol/sec) | 0.005406 | 0.002784 | 0.003971 | 0.004218 |
| Total Flow (kg/sec) | 0.230167 | 0.172819 | 0.182671 | 0.220314 |
| Total Flow (cum/sec) | 0.000285 | 0.000159 | 0.000249 | 0.000229 |
| Temperature (K) | 298.00 | 333.15 | 351.46 | 390.00 |
| Pressure (N/sqm) | 202,650.00 | 202,650.00 | 101,325.00 | 202,650.00 |
| Vapor Frac | 0.00 | 0.00 | 0.00 | 0.00 |
| Liquid Frac | 1.00 | 1.00 | 1.00 | 1.00 |
| Solid Frac | 0.00 | 0.00 | 0.00 | 0.00 |
| Enthalpy (MJ/kmol) | 278.51 | -453.47 | -270.26 | -384.83 |
| Enthalpy (MJ/kg) | -6.54 | -7.31 | -5.88 | -7.37 |
| Enthalpy MW | -1.51 | -1.26 | -1.07 | -1.62 |
| Entropy (kJ/kmol-K) | -321.50 | -434.26 | -323.84 | -341.73 |
| Entropy (kJ/kg-K) | -7.55 | -7.00 | -7.04 | -6.54 |
| Density (kmol/cum) | 18.97 | 17.51 | 15.95 | 18.44 |
| Density (kg/cum) | 807.94 | 1,087.03 | 733.73 | 962.99 |
| Average MW | 42.58 | 62.07 | 46.00 | 52.23 |
| Liq Vol 60F (cum/sec) | 0.00 | 0.00 | 0.00 | 0.00 |
| *** ALL PHASES *** | | | | |
| Mole Frac | | | | |
| Water | 0.124 | 0.000 | 0.003 | 0.157 |
| Ethanol | 0.876 | 0.000 | 0.997 | 0.183 |
| Ethylene Glycol | 0.000 | 1.000 | 0.000 | 0.660 |
| Mass Flow (kg/sec) | | | | |
| Water | 0.012 | 0.000 | 0.000 | 0.012 |
| Ethanol | 0.218 | 0.000 | 0.182 | 0.036 |
| Ethylene Glycol | 0.000 | 0.173 | 0.000 | 0.173 |

Table 3.3 Simulation results for molasses-based bioethanol production

| | **Feed Stream** | **Ethylene Stream** | **Product Stream** | **Water Stream** |
|---|---|---|---|---|
| Substream: MIXED | | | | |
| Mole Flow (kmol/sec) | | | | |
| Water | 0.000646 | 0.000000 | 0.000011 | 0.000635 |
| Ethanol | 0.004733 | 0.000000 | 0.003957 | 0.000776 |
| Ethylene Glycol | 0.000000 | 0.002761 | 0.000001 | 0.002760 |
| Total Flow (kmol/sec) | 0.005379 | 0.002761 | 0.003969 | 0.004171 |
| Total Flow (kg/sec) | 0.229694 | 0.171357 | 0.182557 | 0.218495 |
| Total Flow (cum/sec) | 0.000284 | 0.000158 | 0.000249 | 0.000227 |
| Temperature (K) | 298.00 | 333.15 | 351.46 | 389.84 |
| Pressure (N/sqm) | 202,650.00 | 202,650.00 | 101,325.00 | 202,650.00 |
| Vapor Frac | 0.00 | 0.00 | 0.00 | 0.00 |
| Liquid Frac | 1.00 | 1.00 | 1.00 | 1.00 |
| Solid Frac | 0.00 | 0.00 | 0.00 | 0.00 |
| Enthalpy (MJ/kmol) | -278.48 | -453.47 | -270.26 | -385.11 |
| Enthalpy (MJ/kg) | -6.52 | -7.31 | -5.88 | -7.35 |
| Enthalpy (MW) | -1.50 | -1.25 | -1.07 | -1.61 |
| Entropy (kJ/kmol-K) | -322.33 | -434.26 | -323.84 | -342.74 |
| Entropy (kJ/kg-K) | -7.55 | -7.00 | -7.04 | -6.54 |
| Density (kmol/cum) | 18.91 | 17.51 | 15.95 | 18.38 |
| Density (kg/cum) | 807.60 | 1,087.03 | 733.73 | 962.63 |
| Average MW | 42.70 | 62.07 | 46.00 | 52.38 |
| Liq Vol 60F cum/sec | 0.00 | 0.00 | 0.00 | 0.00 |
| *** ALL PHASES *** | | | | |
| Mole Frac | | | | |
| Water | 0.120 | 0.000 | 0.003 | 0.152 |
| Ethanol | 0.880 | 0.000 | 0.997 | 0.186 |
| Ethylene Glycol | 0.000 | 1.000 | 0.000 | 0.662 |
| Mass Flow (kg/sec) | | | | |
| Water | 0.012 | 0.000 | 0.000 | 0.011 |
| Ethanol | 0.218 | 0.000 | 0.182 | 0.036 |
| Ethylene Glycol | 0.000 | 0.171 | 0.000 | 0.171 |

### 3.6 Impact assessment

Impact Assessment focuses mainly on the environmental impacts of processes throughout the life cycle. The material balance and energy balance were conducted to calculate the amount of solid waste, toxic substance emission and by-product of life cycle of cassava, sugarcane, and rice.

For example, pesticide used in agricultural stage, carbon dioxide emission from processing, effect of waste from fermentation. All of the calculation was perform under 6 impact categories which are climate change, human toxicity, fresh water toxicity, terrestrial toxicity, eutrophication, and acidification. Impact assessment calculation are based on [18], and [38]

#### 3.6.1 Climate change

Climate change is defined as the impact of human emission on radiative forcing of the atmosphere. (3.1) is equation to calculate climate change. The indicator result is expressed in kg of the reference substance [11]. $GWP_{100}$ is a Global Warming Potential, constant over 100 years of substance i which can be obtain from Appendix F.

$$\text{Climate Change} = GWP_{100,i} \times m_i \qquad (3.1)$$

#### 3.6.2 Human toxicity

This impact category covers the impact on human health. (3.2) is an equation to calculate human toxicity. The indicator result is expressed in kg of equivalent substance [7]. $HTP_{100,i}$ is a Human Toxicity Potential over 100 years of substance i which can be obtain from Appendix G.

$$\text{Human Toxicity} = HTP_{100,i} \times m_i \qquad (3.2)$$

#### 3.6.3 Ecotoxicity

This impact can be divided into two sub categories. First is fresh water aquatic ecotoxicity which refers to an impact of toxic substance on fresh aquatic life. (3.3) is an equation to calculate fresh water aquatic ecotoxicity. Another sub-category is terrestrial ecotoxicity which refers to the impact of toxic substance on the terrestrial ecosystem. (3.4) is an equation to calculate terrestrial ecotoxicity. The indicator result of this category is expressed by equivalent substance in kg. $FAETP_i$, and $TETP_i$ stand for Fresh water aquatic ecotoxicity potential of substance I and Terrestrial Ecotoxicity Potential of substance I, respectively. Constants are available in Appendix G [11].

$$\text{Fresh Water Aquatic Ecotoxicity} = FAETP_i \times m_i \qquad (3.3)$$

$$\text{Terrestrial Ecotoxicity} = TETP_i \times m_i \qquad (3.4)$$

### 3.6.4 Acidification

Acidification has a wide variety of impacts on soil, groundwater, surface waters, biological organism, ecosystem and building. Acidification can be calculated by equation (3.5). The indicator result is expressed in kg of equivalent substance [11]. $AP_i$ is Acidification Potential of substance i which can be obtain from Appendix I.

$$\text{Acidification} = AP_i \times m_i \qquad (3.5)$$

### 3.6.5 Eutrophication

Eutrophication embraces all potential impacts of excessively high environmental levels of macro nutrients such as nitrogen and phosphorus. Nutrient enrichment can cause an undesirable shift in elevated biomass production in both aquatic and terrestrial ecosystem**.** Eutrophication can be calculated by equation (3.6). The indicator result is expressed in kg of equivalent substance [11]. $EP_i$ is Eutrophication Potential of substance i which can be obtain from Appendix H.

$$\text{Eutrophication} = EP_i \times m_i \qquad (3.6)$$

## 3.7 Toxic allocation

Toxic substance allocation is used to analyze the flow of toxic substance in the cultivation stage. The toxic substance flow is calculated by the water-octanol partition coefficient, which determines the amount of toxic substance accumulated in plant and amount of toxic leaked to environment [39]. Toxic substance allocation can be calculated by equation (3.7). The result is expressed in the percentage of toxic leakage to environment. Constant K, $B_v$, and Percentage accumulation can be obtained from Appendix B and C [34].

$$\log B_v = 1.588 - (0.578 \log K) \qquad (3.7)$$

where, $B_v$ is the calculated soil to plant biotransfer factor above-ground plant part ($10^{-6}$g $g^{-1}$ DW plant over $10^{-6}$g $g^{-1}$ DW soil)

K is the octanol-water partition coefficient for chemical (dimensionless)

### 3.8 LCA normalization

In this work, BRE ecopoints is used as a normalize model to weighing and translate the data from the impact categories to the reference situation. The calculation takes to account the following 6 impact categories:

1. Climate Change
2. Human Toxicity
3. Fresh water Toxicity
4. Terrestrial Toxicity
5. Acidification
6. Eutrophication

BRE ecopoints are calculated by multiplying the normalized data by the weighting factor for each impact category and the ecopoints in each category are summarized to get a single ecopoint score. Table 3.4 is BRE ecopoint weighting factor for LCA normalization which adopted from Appendix J.

Table 3.4 BRE ecopoints weighting factor for LCA normalization

| Environmental Profile Methodology 2008 | |
|---|---|
| Impact category | Weighting factor (%) |
| Climate change | 21.6 |
| Acidification | 0.05 |
| Ozone depletion | 9.1 |
| Terrestrial ecotoxicity | 8 |
| Photochemical ozone creation | 0.2 |
| Fossil diesel depletion | 3.3 |
| Human toxicity | 8.6 |
| Freshwater ecotoxicity | 8.6 |
| Eutrophication | 3 |
| Mineral resource extraction | 9.8 |
| Water extraction | 11.7 |
| Waste disposal | 7.7 |
| Nuclear waste | 8.2 |
| Total | 100 |

However, this work focused on only 6 main impact categories which are climate change, human toxicity, freshwater toxicity, terrestrial toxicity, acidification and eutrophication. Therefore, factors from Table 3.4 need to be adjust in order to make the result more reliable. The calculation of adjusted factor is done by create a new ratio which includes only 6 categories that study in this work. The calculation is shown as below.

Example 3.1

| Impact Categories | Weighting Factor (%) |
|---|---|
| Climate change | 21.6 |
| Human toxicity | 0.05 |
| Freshwater Ecotoxicity | 8 |
| Terrestrial Ecotoxicity | 8.6 |
| Acidification | 8.6 |
| Eutrophication | 3 |
| Total | 49.85 |

Therefore, the new weighting scores are calculated as follows.

Climate change: New weighting score = 21.6/49.85 =43.33%
Human toxicity: New weighting score = 8.6/49.85 =17.25%
Freshwater toxicity: New weighting score = 8.6/49.85 =17.25%
Terrestrial toxicity: New weighting score = 8/49.85 =16.05%
Acidification: New weighting score = 0.05/49.85 =1%
Eutrophication: New weighting score = 3/49.85 =6.02%

So, the new weighting factors are listed in Table 3.5. Factors in Table 3.5 are used to indicate the importance of each category. For example, climate change's weighting factor is 43.33%. Therefore, climate change is the most important category among 6 categories.

Table 3.5 New weighting factor including 6 impacts categories.

| Impact Categories | Weighting Factor (%) |
|---|---|
| Climate change | 43.33 |
| Human toxicity | 17.25 |
| Freshwater Ecotoxicity | 17.25 |
| Terrestrial Ecotoxicity | 16.05 |
| Acidification | 1 |
| Eutrophication | 6.02 |
| Total | 100 |

# Chapter 4

# Result and Discussion

In this chapter, the calculations are manipulated for mass balance, energy balance, flow of toxic substance, impact assessment, and normalization based on the examples and parameters shown in Chapter 3. The raw data required for the calculations are obtained from databases and literature review. Material balance represents the full chain of mass flow of the materials such as fertilizer, chemical substances, waste, and product from the cultivation stage to bioethanol production stage. As well, Energy balance interprets the entire channels of energy consumption within each process. The energy balance is carried out using both secondary data and Aspen simulation. The energy results are shown in both kW-h of electricity and MJ of coal combustion. Flow of toxic substance gives the amount of toxic substance flow or leakage into the environment. This is necessary to be calculated for the impact assessment, of each impact category. In addition, normalization provides a comparative measure for each impact category with respect to reference values.

## 4.1 Bioethanol production from cassava chip

### 4.1.1 Material balance of Cassava-based Bioethanol production

Initially, the material balance calculations are performed to determine the amount of pesticides and fertilizer used during the cultivation stage of cassava production. 19,300 kg of cassava is required to produce 1,000L of 99.7 vol% ethanol. The total land area required to cultivate 19,300 kg of cassava can be calculated from the total required feedstock divided by the average cassava cultivation rate. The average cassava cultivation rate is available in Appendix T. Thereafter, the amount of pesticide and fertilizer can be determined by multiplying the total cassava cultivation land area with the amount of pesticides and fertilizer required per land area. The amount of pesticides and fertilizer required per land area is available in Appendix U. Example 4.1 shows the calculation of the amount of pesticide and fertilizer required to produce 1,000L of 99.7 vol% ethanol

<u>Example 4.1</u>

At first, calculate the cultivation area required to produce 1,000L of 99.7 vol% ethanol.

19,300 kg of cassava is required to produce 1,000L of 99.7 vol% ethanol (Both sweet and bitter)

| | |
|---|---|
| Average production rate of cassava cultivation | = 3,600 kg/rai |
| Area required for cassava cultivation | = 19,300 kg/3,600 (kg/ rai) |
| | = 5.3611 rai (Appendix T) |

Secondly, calculate the amount of herbicides used in cassava cultivation

| | |
|---|---|
| From Appendix U: Alachlor used | = 0.625 kg /rai |
| Total Alachlor used in cassava cultivation | = 0.625 kg/rai * 5.3611 rai |
| | = 3.35 kg |

Then, calculate the amount of fertilizer used in cassava cultivation

| | |
|---|---|
| From Appendix X: Fertilizer used per rai | = 25 kg |
| Total fertilizer | = 25 kg * 5.3611 rai |
| | = 134.02 kg |

| | |
|---|---|
| From Appendix Y: Percentage of Ammonium sulfate in fertilizer | = 34% |
| Therefore: Total ammonium sulfate used | = 134.02 * 0.34 |
| | = 45.56 kg |

Table 4.1 indicates inputs and outputs for the cassava cultivation stage in the cassava-based ethanol production. It provides an overview of materials in the cassava cultivation stage of bioethanol production from cassava chips such as raw materials, pesticides, fertilizer, and chemicals. The numbers in this table are based on the literature, databases, and calculations as shown above. The unit of measurement for inputs and outputs is kg.

Table 4.1 Direct Material input/output associated with cassava-based ethanol production in cassava cultivation stage

| Material | Unit | Input | Output |
|---|---|---|---|
| Cassava Cultivation | | | |
| Cassava seed | kg | 21.86 | |
| Alachlor | kg | 3.35 | 1.62 |
| Metalachlor | kg | 3.62 | 1.97 |
| Diuron | kg | 1.21 | 0.62 |
| Oxyfuorfen | kg | 1.02 | 0.13 |
| Paraquat | kg | 2.01 | 0.03 |
| Glysophate | kg | 8.04 | 0.25 |
| Fluazifop-p-butyl | kg | 0.70 | 0.39 |
| Haloxyfop-R-methyl ester | kg | 0.64 | 0.43 |
| Fenoxaprop-P-Ethyl | kg | 0.75 | 0.56 |
| Quizalofop-P-Ethyl | kg | 0.94 | 0.67 |
| Fertilizer | | | |
| Ammonium Sulfate | kg | 45.56 | |
| Potassium Chloride | kg | 87.11 | 0.36 |
| Diammonium Phosphate | kg | 22.11 | |
| Monoammonium Phosphate | kg | 14.07 | |
| Cyanide | kg | | 0.65 |
| Cassava (Sweet) | kg | | 13,507 |
| Cassava (Bitter) | kg | | 5,793 |

The results in Table 4.1 show that there are several types of pesticides such as Glysophate, Alachlor, Metalachlor, and Paraquat, used in the cassava cultivation process. Pesticides and chemicals output can be considered as a toxic leakage. The leakage of toxic components to environment causes serious effects such as toxicity, and eutrophication. Therefore, the amount of pesticides and fertilizer leakage will be used for calculations in impact assessment section. Calculations are performed for cassava chips production stage and ethanol production stage using the data in Table 4.1.

According to Table 4.1, the amount of required cassava seed for the production of 1,000 L of ethanol is around 21.86 kg. The production of sweet cassava and bitter cassava, are around 13,520 kg and 5,790 kg, respectively. Bitter cassava is used as a primary raw material in cassava chip production. The outputs such as main product, by-products, and wastes in cultivation stage can be used as an input to the cassava chip production. As well, the output of cassava chip production can also be used as the starting material in the bioethanol production stage. Table 4.2 shows Mass balance of these 2 stages.

Table 4.2 Direct Material input/output associated with cassava-based ethanol production in cassava chip production and ethanol production

| Material | Unit | Input | Output |
|---|---|---|---|
| Cassava Chip Production | | | |
| Cassava (Bitter) | kg | 5,793 | |
| Cassava Chip | kg | | 2,457 |
| Cassava Peeling | kg | | 3,336 |
| Ethanol Production | | | |
| Cassava Chip | kg | 2,457 | |
| Water | kg | 9,920 | |
| 99.7 vol% Ethanol | L | | 1,000 |
| Fusel Oil | kg | | 3 |
| Thick Slop | kg | | 640 |
| Stillage | kg | | 9,340 |
| Carbon Dioxide | kg | | 0,760 |

Table 4.2 shows the direct material input/output associated with cassava-based ethanol. Bitter cassava is converted to cassava chips in this process. The cassava chips production of 2,410 kg is around 41% of the bitter cassava input. The bioethanol production consists of pretreatment, liquefaction, fermentation and distillation. Cassava chips are used as a sugar source in the fermentation process. Cassava chips are mixed with water at a ratio of 4:1. Bioethanol is produced in a fermenter and separated as the light key component in the distillation process. In addition, there are by-products produced in this stage such as thick slop, fusel oil and stillage.

### 4.1.2 Energy balance of Cassava-based Bioethanol production

The simulation results in ASPEN PLUS software and the secondary data obtained from literature are utilized for energy balance calculations. Simulation provides reliable approximations for the actual scenario in addition to the secondary data available in the literature.

The simulation of distillation process in ASPEN PLUS software provides the amount of energy consumption in bioethanol production stage. The distillation column is an extractive column which has been designed to feed extra compound in order to promote the ability of the separation between water and ethanol. The simulation flowsheet is shown in Figure 4.1.

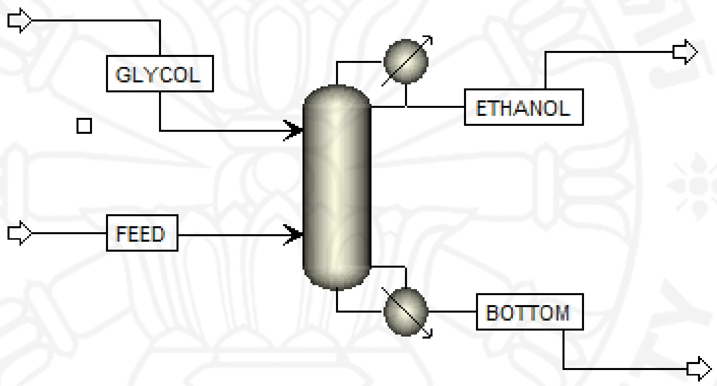


Figure 4.1 Overview of simulation by using Aspen plus (Cassava-based)

Reflux ratio, feed stage of ethylene glycol and feed stage of ethanol-water mixture are fixed parameters for the simulation. The amount of ethylene glycol is varied in order to obtain 99.7 vol% of bioethanol as the product. Table 4.3 shows the stream balance of the extractive distillation in cassava-based bioethanol production.

Table 4.3 Stream input/output of the extractive distillation in cassava-based bioethanol production

| Stream | Input (kg/hr) | Output (kg/hr) |
|---|---|---|
| Feed (Ethanol+Water Mixture) | 829 | N/A |
| Ethylene glycol (Extractive agent) | 622 | N/A |
| 99.7 vol% of Ethanol | N/A | 782 |
| Bottom Liquid (Water+Ethlylene glycol mixture) | N/A | 793 |

According to Table 4.3, the amount of the ethylene glycol input is around 622 kg/hour. The amount of feed input is approximately around 830 kg for cassava-based bioethanol production.

The energy consumption in the extractive column can be classified into to 2 parts such as, hot heat duty ($Q_H$) and cold heat duty ($Q_c$). Hot heat duty ($Q_H$) represents the energy consumption in the reboiler and cold heat duty ($Q_C$) is energy consumption in the condenser. The Hot heat duty of the extractive column is 1,931.68 MJ, and the cold heat duty is 465.15 kW-h.

According to the secondary data available in the literature, the amount of energy consumption for the bioethanol production can be classified into usage of electricity and combustion energy from diesel and coal. Diesel consumption for the cassava based bioethanol production process can be obtained from the literature review. Diesel is mainly consumed for the cultivation of raw material and the pre-treatment process. The diesel consumption in litres is converted to MJ and combined with the amount of coal combustion in the same unit (MJ) in order to figure out the total combustion energy as shown in the following example. The toxic emission in the bioethanol production process due to combustion of diesel and coal is estimated later. Example 4.2 shows amount of diesel used in cassava-based bioethanol production in combustion energy unit (MJ)

<u>Example 4.2</u>
Calculate amount of diesel used in cassava-based bioethanol production and convert it into combustion energy unit (MJ).

Total Diesel used = 11.26+12.14 = 23.4 L
Convert energy from diesel to MJ: Energy (MJ) = Diesel used * Heating Value
= 23.4 L * 32 MJ/L
= 748.8 MJ
Energy from coal (MJ) = 2,332.82 MJ
Therefore: Total Combustion energy = 748.8 + 2,332.82
= 3,081.62 MJ

Table 4.4 shows the combustion energy values obtained from the above calculation and literature for the different stages of entire bioethanol production process.

Table 4.4 Energy balance of cassava-based ethanol production

| Process | Energy Source | | |
|---|---|---|---|
| | Combustion energy | | Electrical energy |
| | Coal (MJ) | Diesel (MJ) | Electricity (kW-h) |
| Cultivation | N/A | 388.48 | N/A |
| Pretreatment | N/A | 360.32 | N/A |
| Ethanol Production | 2,332.82 | N/A | 554.42 |
| Total | 3081.62 | | 554.42 |

The result shows that cassava cultivation requires 12.41 L of diesel for cultivation and 11.26 L of diesel in cassava chip production. In bioethanol production stage, the electrical energy requirement is 554.42 kW-h and coal combustion energy is 2,332.82 MJ. These energy consumptions are mainly due to fermenter and distillation column.

**4.1.3 Flow of substances of Cassava-based Bioethanol production**

This part is focused to determine the amount of toxic substances accumulated in soil due to the bioethanol production process. Calculation is based on the octanol water partition function which indicates the solubility of toxic substance in water and octanol. Appendix C shows the percentage of toxic substance accumulation in both soil and plant root. The total amount of toxic substance used is multiplied by the percentage of toxic substance accumulation available in Appendix C. The result of this calculation can be used in the impact assessment later. The calculation is shown in Example 4.3.

<u>Example 4.3</u>
Calculate amount of toxic leakage to environment using octanol water partition function.

| | |
|---|---|
| Input amount of Alachlor in cassava cultivation | = 3.35 kg |
| From Appendix C: Soil accumulation of Alachlor | = 48.304 % |
| Therefore: Leakage of Alachlor in cassava cultivation | = 3.35 x 0.48304 |
| | = 1.6181 kg of Alachlor |

Table 4.5 shows the Flow of toxic substances and toxic leakage to the environment from cassava-based ethanol production in cassava cultivation stage calculated as per the above example. The unit of toxic substance input and leakage is represented in kg.

Table 4.5 Total toxic leakage from chemicals used in cassava cultivation

| Material/Substance | Input Amount (kg) | Leakage (kg) |
|---|---|---|
| Alachlor | 3.35 | 1.62 |
| Metalachlor | 3.62 | 1.97 |
| Diuron | 1.21 | 0.62 |
| Oxyfuorfen | 1.02 | 0.13 |
| Paraquat | 2.01 | 0.03 |
| Glysophate | 8.04 | 0.25 |
| Fluazifop-p-butyl | 0.7 | 0.39 |
| Haloxyfop-R-methyl ester | 0.64 | 0.43 |
| Fenoxaprop-P-Ethyl | 0.75 | 0.55 |
| Quizalofop-P-Ethyl | 0.94 | 0.67 |
| Potassium Chloride | 87.11 | 0.36 |

According to Table 4.5, the leakage of toxic substance mainly involves pesticide and fertilizer used in the cultivation stage. In cassava-based bioethanol production, leakage includes pesticide (Alachlor, Metalachlor, Diuron, Oxyfuorfen, Paraquat, Glysophate, Fluazifop-p-butyl, Haloxyfop-r-methyl ester, Fenoxaprop-p-ethyl) and fertilizer (Ammonium sulfate, Potassium chloride, Diammoniumhydrogenorthophosphate, Monoammoniumphosphate). The largest amounts of leakage are Alachlor and Metalachor.

### 4.1.4 Material analysis of Cassava-based Bioethanol production

Table 4.6 summarizes the material requirement for the cassava-based ethanol production in order to produce 1,000 L of bioethanol. The material amounts are indicated in kg.

Table 4.6 Total starting material to produce 1,000 L of bioethanol from cassava-based bioethanol production

| Material | Amount (kg) |
|---|---|
| Cassava Chip | 2,414 |
| Water | 9,920 |
| Total Herbicide | 22.28 |
| Total Fertilizer | 168.85 |

Table 4.6 points out that 2,414 kg of cassava chips, 9,920 kg of water, 22.28 kg of total herbicides and 168.85 kg of total fertilizer are required to produce 1000 L of cassava based bioethanol.

### 4.1.5 Pollutant emission of Cassava-based Bioethanol production

Pollutants release from 2 main sources i.e. coal combustion and electricity. The total energy obtained from coal combustion in this process is available in section 4.1.2. Appendix E provides the amount of toxic gases emission when 1 GJ of energy is produced from coal combustion. Therefore, the toxic gases emission due to coal combustion in cassava-based bioethanol production can be determined. Calculation for $CO_2$ emission is shown in Example 4.4.

<u>Example 4.4</u>

At First, Calculate the amount of toxic gas emission from coal combustion

| | |
|---|---|
| Total Combustion energy | = 3,081 MJ |
| From Appendix E: $CO_2$ emission from combustion | = 75.8 kg/GJ |
| | = 0.0758 kg/ MJ |
| Then, the total $CO_2$ emission from coal | = 0.0758 kg/MJ * 3,081 MJ |
| | = 233.58 kg of $CO_2$ |

Secondly, the total energy obtained from electricity in this process is also available in section 4.1.2. Appendix D indicates the toxic gases emission when producing 1 TJ of electricity. Therefore, the toxic gases emission due to coal combustion in cassava-based bioethanol production can be determined. Calculation for $CO_2$ emission is shown in Example 4.5.

Example 4.5

Calculate amount of toxic gas emission from electricity

| | |
|---|---|
| From Appendix D: $CO_2$ emission for producing 1TJ of electricity | = 229,380 kg |
| From unit production: 1 TJ | = $2.77 \times 10^5$ kW-h |
| Total electricity consumption | = 554.42 kW-h |
| Then: $CO_2$ emission when producing 554.42 kW-h | = 459.1 kg of $CO_2$ |

Then, the total amount of toxic gases emission from the cassava-based bioethanol production is the summation of the amount that emit from coal combustion and electricity. Calculation for $CO_2$ emission is shown in Example 4.6.

Example 4.6

Calculate the total amount of toxic emission

| | |
|---|---|
| $CO_2$ emission from coal combustion | = 223.58 kg |
| $CO_2$ emission from electricity | = 459.10 kg |
| Total Emission of $CO_2$ | = 233.58 + 459.10 kg |
| | = 692.68 kg of $CO_2$ |

Table 4.7 shows the emission of different pollutants from the cassava-based ethanol production process to produce 1,000 L of bioethanol. The values for different pollutants were calculated as per the example calculation shown for $CO_2$. There are six main toxic gasses in Table 4.7. There are $CH_4$, CO, $CO_2$, $N_2O$, $NO_2$, and $SO_2$

Table 4.7 Total pollutant emission from cassava-based bioethanol production

| Pollutants | Emission (kg) |
|---|---|
| $CH_4$ | 6.01 |
| CO | 0.19 |
| $CO_2$ | 459.1 |
| $N_2O$ | 0.01 |
| $NO_2$ | 1.47 |
| $SO_2$ | 5.89 |

Note: Based on the production of 99.7 vol% bioethanol

Table 4.7 clearly indicates that $CO_2$, which is the main contributor to global warming, is the highest pollutant emission amounts to 459.10 kg $CO_2$. The results also show that $NO_2$ and $SO_2$ which are the main acidifying pollutants have been released moderately around 1.47 and 5.89 kg respectively. The other pollutants are released in traceable amount.

### 4.2 Bioethanol production from molasses

At first, the material balance calculations are performed to determine the amount of pesticides and fertilizer used during the cultivation stage of sugarcane production. 78,540 kg of sugarcane is required to produce 1,000 L of 99.7 vol% bioethanol. The calculation is the same procedure available in section 4.1.1. Example 4.7 shows the calculation of the amount of pesticide and fertilizer required to produce 1,000L of 99.7 vol% ethanol

<u>Example 4.7</u>

At first, calculate the cultivation area required to produce 1,000L of 99.7 vol% ethanol.

78,540 kg of Sugarcane is required to produce 1,000L of 99.7% vol% ethanol.

| | |
|---|---|
| Average production rate | = 20,000 kg/rai |
| Then: Area required | = 78,540kg/20,000(kg/rai) |
| | = 3.927 rai (Appendix T) |

Secondly, calculate the amount of herbicide used in sugarcane cultivation

| | |
|---|---|
| From Appendix V: Antrazine used | = 0.42 kg /rai |
| Then: Total Atrazine used | = 0.42 kg/rai * 3.927 rai |
| | = 1.65 kg |

Then, calculate the amount of fertilizer used in sugarcane cultivation

| | |
|---|---|
| From Appendix X: Fertilizer used per rai | = 33.3 kg |
| Then: Total fertilizer | = 33.3 kg * 3.927 rai |
| | = 130.88 kg |
| From Appendix Y: Percentage of Ammonium sulfate in fertilizer | = 34% |
| Therefore: Total ammonium sulfate used | = 130.88 * 0.34 |
| | = 45.50 kg |

Table 4.8 shows inputs and output for the sugarcane cultivation stage in the molasses based ethanol production. It provides an overview of material flow in sugarcane cultivation such as raw materials, pesticides, fertilizer, and chemical. The numbers in Table 4.8 are based on the literature, databases, and calculations as shown in Example 4.7. The unit measurement for inputs and outputs is kg.

### 4.2.1 Material balance of Molasses-based Bioethanol production

Table 4.8 Direct Material input/output associated with molasses-based ethanol production in sugarcane cultivation stage

| Material | Unit | Input | Output |
|---|---|---|---|
| Sugarcane Cultivation | | | |
| Sugarcane Seed | kg | 11.38 | |
| Antrazine | kg | 1.65 | 0.83 |
| Diuron | kg | 3.77 | 1.95 |
| Alachlor | kg | 1.18 | 0.57 |
| Metribuzin | kg | 2.83 | 0.98 |
| Pendimethalin | kg | 0.79 | 0.63 |
| Ametryn | kg | 1.65 | 0.80 |
| Oxyfuorfen | kg | 0.38 | 0.05 |
| Metalachlor | kg | 1.18 | 0.64 |
| 2,4-D | kg | 0.63 | 0.32 |
| Asulam | kg | 2.83 | 0.52 |
| 2,4-D sodium salt | kg | 2.28 | 1.16 |
| Paraquat | kg | 1.18 | 0.02 |
| Fertilizer | | | |
| Ammonium Sulfate | kg | 44.50 | |
| Potassium Chloride | kg | 32.72 | 0.45 |
| Diammonium Phosphate | kg | 21.59 | |
| Monoammonium Phosphate | kg | 13.74 | |
| Sugarcane | kg | | 78,540 |

The result in Table 4.8 show that there are several type of pesticide used in sugarcane cultivation i.e. Antrazine, Diuron, Alachlor, etc. Pesticide and chemical output in sugarcane cultivation are toxic leakage. The leakage of these substances will be used to calculate in impact assessment section.

According to Table 4.8, the amount of require sugarcane seed for the production of 1,000 L of 99.7 vol% bioethanol is 11.38 kg. The production of sugarcane is 78,540 kg. Sugarcane is used as a primary raw material in sugar milling process. The output such as main product, by-product, and wastes in cultivation stage can be used as an input to the sugar milling process. Also, the main output of sugar milling process, which is molasses can be used as the main starting material in fermentation process of bioethanol production. Table 4.9 shows mass balance of these 2 stages.

Table 4.9 Direct Material input/output associated with molasses-based ethanol production in sugar milling and ethanol production

| Material | Unit | Input | Output |
|---|---|---|---|
| Sugar Milling | | | |
| Sugarcane | kg | 78,540 | |
| Bagasse | kg | | 19,400 |
| Sugar | kg | | 5,533 |
| Molasses | kg | | 3,549 |
| Ethanol Production | | | |
| Molasses | kg | 3,549 | |
| Water | kg | 6,584 | |
| 99.7 vol% Ethanol | L | | 1,000 |
| Fusel Oil | kg | | 4 |
| Thick Slop | kg | | 1,280 |
| Carbon Dioxide | kg | | 760 |

Table 4.9 examines the direct flow of material associated with molasses-based ethanol production. Sugarcane is converted to be sugar and molasses in this process. The molasses to sugar ratio (MSR) is 2:3. Therefore, the total amount of molasses obtained from sugar milling is 3,549 kg.

The bioethanol production stage consists of several steps such as pretreatment, liquefraction, fermentation and distillation. Molasses is used as a main sugar source for in bioethanol production. Molasses are mixed with water at a ratio 1:2.18. Bioethanol is produced via the fermentation and separated as the light key component in the distillation process. Moreover, there are 3 by-products in this stage such as stillage, thick slop, and fusel oil.

### 4.2.2 Energy balance of Molasses-based Bioethanol production

The simulation results in ASPEN PLUS software and secondary data obtained from literature are utilized for energy balance calculation. Simulation is used to increase reliability for the actual scenario in addition to the secondary data available in the literature.

The simulation of distillation process in ASPEN PLUS software provides the amount of energy consumption and material flow in bioethanol production stage. The distillation column is an extractive column. It is designed to feed extra compound in order to enhance an ability of separation between water and ethanol. The simulation flow sheet is shown in Figure 4.2.

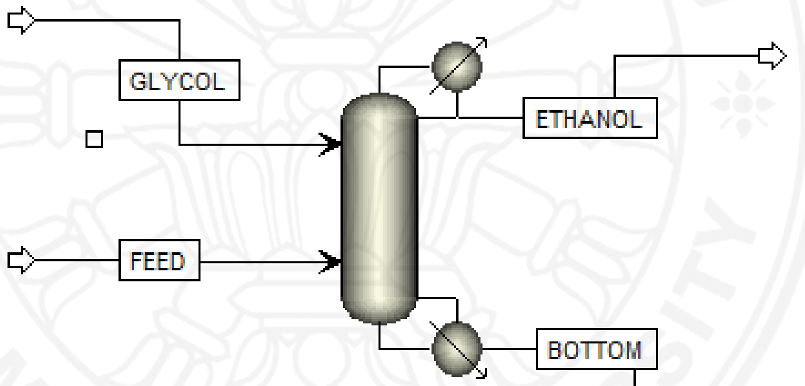


Figure 4.2 Overview of simulation by using Aspen plus (Molasses-based)

Reflux ratio, feed stage of ethylene glycol and feed stage of ethanol-water mixture are fixed parameters for the simulation. The amount ethylene glycol is varied in order to obtain 99.7 vol% of bioethanol as the product. Table 4.10 show the stream balance of the extractive distillation in molasses-based bioethanol production.

Table 4.10 Stream input/output of the extractive distillation bioethanol in molasses-based bioethanol production

| Stream | Input (kg/hr) | Output (kg/hr) |
|---|---|---|
| Feed (Ethanol+Water Mixture) | 827 | N/A |
| Ethylene glycol (Extractive agent) | 617 | N/A |
| 99.7 vol% of Ethanol | N/A | 782 |
| Bottom Liquid (Water+Ethlylene glycol mixture) | N/A | 786 |

According to Table 4.10, the amount of the ethylene glycol input is around 617kg/hour. The amount of feed input is approximately around 830 kg for molasses-based bioethanol produce.

The energy consumption in the extractive column can be classified into 2 parts i.e. got hear duty ($Q_H$) and cold heat duty ($Q_C$). Hot heat duty ($Q_H$) represents the energy consumption in the reboiler. On the other hand, cold heat duty ($Q_C$) is energy consumption in the condenser. The energy consumption of extractive column are 1,928.94 MJ and 464.85 kW-h of coal combustion and electricity respectively.

According to the secondary data available in literature, the amount of energy consumption for the bioethanol production can be classified into 2 types; usage of electricity and combustion energy from diesel and coal. The diesel consumption for the cassava based bioethanol production process can be obtained from literature review. Diesel is mainly consumed for the cultivation of raw material and the pre-treatment process. The consumption of diesel in liters is converted to MJ and combined with the amount of coal combustion in the same unit (MJ) in order to figure out the total combustion energy. The calculation is the same procedure available in section 4.1.2. Example 4.8 shows amount of diesel used in molasses-based bioethanol production in combustion energy unit (MJ)

<u>Example 4.8</u>

Calculate amount of diesel used in molasses-based bioethanol production and convert it into combustion energy unit (MJ).

Total Diesel used = 26.39 L

Convert energy from diesel to MJ: Energy (MJ) = Total Diesel used * Heating Value

= 26.39 L * 32 MJ/L

= 844.48 MJ

Energy from coal (MJ) = 2,332.82 MJ

Therefore: Total Combustion energy = 844.48+42,325.20+2,248.81

= 45,418.49MJ

Table 4.11 shows the combustion energy values obtained from the above calculation and literature for the different stages of entire bioethanol production process.

Table 4.11 Energy balance of molasses-based ethanol production

| Process | Energy Source | | |
|---|---|---|---|
| | Combustion energy | | Electrical energy |
| | Coal (MJ) | Diesel (MJ) | Electricity (kW-h) |
| Cultivation | N/A | 844.48 | N/A |
| Pretreatment | 42,325.20 | N/A | 1,360 |
| Ethanol Production | 2,248.81 | N/A | 568.2 |
| Total | 45,418.49 | | 1,928.20 |

The result shows that sugarcane cultivation requires 844.48 MJ of diesel for planting, 42,325.2 MJ for sugar milling process and 2,248.81 MJ for bioethanol production. The electrical energy required is 1,360 and 568.2 kW-h in sugar milling and bioethanol production process respectively.

### 4.2.3 Flow of substances of Molasses-based Bioethanol production

This part is focused to determine the amount of toxic leakage to soil in sugarcane cultivation. Calculation is based on the octanol water partition function which is shown in section 3.5.1. The percentage of toxic substance accumulation in both soil and plan root is available in Appendix C. The result of this calculation can be used in impact assessment later. The calculation is shown in Example 4.9.

<u>Example 4.9</u>

Calculate amount of toxic leakage to environment using octanol water partition function

| | |
|---|---|
| Input amount of Atrazine in sugarcane cultivation | = 1.65 kg |
| From Appendix C: Soil accumulation of Atrazine | = 50.037 % |
| Therefore: Leakage of Atrazine | = 1.65 x 0.50037 |
| | = 0.8256 kg of Atrazine |

Table 4.12 shows the Flow of toxic substances and toxic leakage to the environment from molasses-based ethanol production in cassava cultivation stage calculated as per the above example This table is calculated by using the calculation method which shown in Example 4.9. The unit of toxic substance input and leakage is represented in kg.

Table 4.12 Total leakage of chemical used in sugarcane cultivation

| Material/Substance | Input Amount (kg) | Leakage (kg) |
|---|---|---|
| Atrazine | 1.65 | 0.83 |
| Diuron | 3.77 | 1.95 |
| Alachlor | 1.18 | 0.57 |
| Metribuzin | 2.83 | 0.98 |
| Pendimethalin | 0.79 | 0.63 |
| Ametryn | 1.65 | 0.8 |
| Oxyfuorfen | 0.38 | 0.05 |
| Metalachlor | 1.18 | 0.64 |
| 2,4-D | 0.63 | 0.32 |
| Asulam | 2.83 | 0.52 |
| 2,4-D sodium salt | 2.28 | 1.16 |
| Paraquat | 1.18 | 0.18 |
| Potassium Chloride | 32.72 | 0.45 |

According to Table 4.12, the leakage of toxic substance mainly involves pesticide and fertilizer used in cultivation stage. In molasses-based bioethanol production, leakage includes pesticide (Atrazine, Diuron, Alachlor, Metribuzin), and fertilizer (Ammonium sulfate, Potassium chloride, Diammonium hydrogenorthophosphate, Monoammoniumphosphate). The largest amounts of leakage are Diuron and Metribuzin.

**4.2.4 Material analysis of Molasses-based Bioethanol production**

Table 4.13 shows the summary of the material requirement for the molasses-based ethanol production in order to produce 1,000 L of bioethanol. The material amounts are represented in kg.

Table 4.13 Total starting material to produce 1,000 L of bioethanol from molasses-based bioethanol production

| Material | Amount (kg) |
|---|---|
| Molasses | 3,549 |
| Water | 6,584 |
| Total Herbicide | 20.35 |
| Total Fertilizer | 112.55 |

Table 4.13 shows the amount of material requirement in summary. 3,549 kg of molasses, 6,584 kg of water, 20.35 kg of total herbicides and 112.55 kg of total fertilizer are required to produce 1000 L of molasses based bioethanol.

### 4.2.5 Pollutant emission of Molasses-based Bioethanol production

Pollutant emissions are mainly come from 2 main sources; coal combustion and electricity. The total energy obtained from coal combustion is available in section 4.2.2. Appendix E provides the amount of toxic gasses emission when 1 TJ of energy is produced from coal combustion. The calculation's methodology is the same as shown in section 4.1.5. The calculation is shown in Example 4.10.

<u>Example 4.10</u>

Calculate the amount of toxic gas emission from coal combustion

| | |
|---|---|
| Total Combustion energy | = 45,418 MJ |
| From Appendix E: $CO^2$ emission from combustion | = 76 kg/GJ |
| | = 0.076 kg/ MJ |
| Then $CO_2$ emission from combustion | = 0.076kg/MJ*45,418 MJ |
| | = 3442.72 kg of $CO_2$ |

Secondly, the total energy obtained from electricity in this process is also available in section 4.12. Appendix D indicates the amount of gaseous emission when producing 1 TJ. The following example is used the same method as shown in Example 4.5. The calculation is shown in Example 4.11.

<u>Example 4.11</u>

Calculate amount of toxic gas emission from electricity

From Appendix D: $CO_2$ emission when producing 1 TJ of electricity = 229,380 kg

From unit production: 1 TJ of electricity = $2.77 \times 10^5$ kW-h

Total electricity consumption = 1,928.20 kW-h

Then: $CO_2$ emission when producing 1,928.20 kW-h

= 229,380 kg * ($1,928.20/2.77 \times 10^5$)

= 1,596.71 kg of $CO_2$

Then the total amount of toxic gasses emission from the molasses-based bioethanol production is the summation of the amount that emit from coal combustion and electricity. Example calculation for $CO_2$ emission is shown in Example 4.12.

<u>Example 4.12</u>

Calculate the total amount of toxic emission

$CO_2$ emission from coal combustion = 3,442.72 kg

$CO_2$ emission from electricity = 1,596.71 kg

Therefore: Total Emission of $CO_2$ = 3,442.72 + 1,596.71 = 5,039.43 kg of $CO_2$

Table 4.14 shows the emission of several pollutants from molasses-based bioethanol production. The amounts of emissions were obtained from the calculation shown in Example 4.11. There are $CH_4$, CO, $CO_2$, $N_2O$, $NO_2$, and $SO_2$.

Table 4.14 Total pollutant emission from molasses-based bioethanol production

| Pollutants | Emission (kg) |
|---|---|
| $CH_4$ | 20.93 |
| CO | 1.11 |
| $CO_2$ | 5,039.43 |
| $N_2O$ | 0.04 |
| $NO_2$ | 10.33 |
| $SO_2$ | 33.68 |

Note: Based on the production of 99.7 vol% bioethanol

Table 4.7 clearly indicates that CO2, which is the main contributor to global warming, is the highest pollutant emission amounts to 459.10 kg $CO_2$. The results also suggest that NO2 and SO2 which are the main source of acidification, have been release moderately around 10.33 and 33.68 kg. As well, $CH_4$ is emitted from the process around 20.93. The other pollutants are released in traceable amounts.

## 4.3 Bioethanol production from rice straw

Initially, the material balance calculations are completed to determine the amount of toxic substance used in the cultivation stage of sugarcane production. 8,230 kg of paddy rice is required to produce 1,000 L of 99.7 vol% bioethanol. The calculation is the same method which in section 4.1.1. Example 4.13 shows the calculation of the amount of pesticide and fertilizer required to produce 1,000L of 99.7 vol% ethanol

Example 4.13

At first, calculate the cultivation area required to produce 1,000L of 99.7 vol% ethanol.

8,234 kg of Rice is required to produce 1,000L of 99.7 vol% ethanol.

| | |
|---|---|
| Average production rate | = 1,000 kg/rai |
| Then: Area required for rice cultivation | = 8,234 kg / (1,000 kg/ rai) |
| | = 8.234 rai (Appendix T) |

Secondly, calculate the amount of herbicide used in sugarcane cultivation

| | |
|---|---|
| From Appendix W: Dimethenamid used | = 0.05 kg /rai |
| Then: Total Atrazine used in rice cultivation | = 0.05 kg/rai * 8.234 rai |
| | = 0.41 kg |

Then, calculate the amount of fertilizer used in sugarcane cultivation

From Appendix X: Fertilizer used per rai = 30 kg

| | |
|---|---|
| Then: Total fertilizer | = 30 kg * 8.234 rai |
| | = 247.02 kg |

From Appendix Y: Percentage of Ammonium sulfate in fertilizer = 34%

| | |
|---|---|
| Then: ammonium sulfate from fertilizer | = 247.02 * 0.34 |
| | = 83.98 kg |
| From Appendix X: Extra Nutrient | = 205.85kg |
| Therefore: total amount of ammonium sulfate | = 205.85 +83.98 |
| | =289.83 kg |

Table 4.15 shows inputs and output for the rice cultivation stage in the rice straw based ethanol production. It shows an overview of material balance in rice cultivation i.e. raw materials, pesticides, fertilizer, and chemical. The values in Table 4.15 are based on the literature, databases, and calculations as shown in Example 4.12. The unit measurement for inputs and outputs is kg.

### 4.3.1 Material balance of Rice straw-based Bioethanol production

Table 4.15 Direct Material input/output associated with rice straw-based ethanol production in rice cultivation stage

| Material | Unit | Input | Output |
|---|---|---|---|
| Rice Cultivation | | | |
| Rice seed | kg | 81 | |
| Dimethenamid | kg | 0.41 | 0.17 |
| Thiobencarb | kg | 5.76 | 4.05 |
| Butachlor | kg | 2.47 | 1.81 |
| Pretilachlor | kg | 2.47 | 1.69 |
| Oxadiargyl | kg | 0.82 | 0.55 |
| Pendimethalin | kg | 2.74 | 2.21 |
| Thiobencarb | kg | 16.47 | 11.56 |
| 2,4-D | kg | 16.47 | 8.38 |
| Glufosinate ammonium | kg | 1.24 | 0.02 |
| Quizalofop-P-Ethyl | kg | 0.82 | 0.61 |
| Fertilizer | | | |
| Ammonium Sulfate | kg | 289.83 | |
| Potassium Chloride | kg | 61.75 | 0.63 |
| Diammonium Phosphate | kg | 40.75 | |
| Monoammonium Phosphate | kg | 25.93 | |
| Paddy Rice | kg | | 8,230 |

The results in Table 4.15 indicated the amount of toxic substance leakage such as Dimethenamid, Thiobencarb, and Butachlor, used in the rice cultivation process. Pesticides and chemicals output can be considered as a toxic leakage. The leakage of toxic components to environment causes serious environmental effect. The amount of pesticides and fertilizer leakage will be used for calculations later. Calculations are performed for further material balance in rice milling stage and ethanol production stage using the data in Table 4.15.

According to Table 4.15, the amount of rice seed input for the production of 1,000 L of 99.7 vol% bioethanol is 81 kg. The production of paddy rice is 8,230 kg. Paddy rice is used as a main starting material in rice milling process. The by-product of rice milling process i.e. rice straw, can be used as the input in bioethanol conversion stage due to its sugar content. Mass balance of rice milling and bioethanol conversion are shown in Table 4.16

Table 4.16 Direct Material input/output associated with rice straw-based ethanol production in milled rice production and ethanol production

| Material | Unit | Input | Output |
|---|---|---|---|
| Rice Milling | | | |
| Paddy Rice | kg | 8,230 | |
| Rice straw | kg | | 3,520 |
| Unmilled rice | kg | | 4,710 |
| Ethanol Production | | | |
| Rice straw | kg | 3,520 | |
| Water | kg | 7,52 | |
| 99.7 vol% Ethanol | L | | 1,000 |
| Hydrocarbon Waste | kg | | 1,950 |
| Furfural | kg | | 0.541 |
| Methane | kg | | 15.41 |
| Nitrous Oxide | kg | | 4.56 |
| Carbon Monoxide | kg | | 4.13 |
| Carbon Dioxide | kg | | 6.24 |

Table 4.16 shows the direct material input/output associated with rice straw based bioethanol production. Paddy rice is converted to milled rice in this process. By-product in this stage is rice straw. Rice straw can be used as a starting material in bioethanol conversion. The bioethanol conversion consists of a several step such as chromatographic separation, fermentation, distillation, and hydration.

### 4.3.2 Energy balance Rice straw-based Bioethanol production

Energy balance is used to represent the overview of energy consumption in rice straw process. There are 2 main sources of energies i.e. electrical energy and combustion energy from coal. Diesel, which considered being combustion energy, is mainly consumed for the cultivation of raw material and the pretreatment process. The diesel consumption in Liters is converted to MJ and combined with the amount of coal combustion for an easy comparison. Example 4.14 is the method to figure out the total combustion energy.

<u>Example 4.14</u>

Calculate amount of diesel used in molasses-based bioethanol production and convert it into combustion energy unit (MJ).

Total Diesel used = 23.47 L

Convert energy from diesel to MJ: Energy (MJ) = Total Diesel used * Heating Value

= 23.47 L * 32 MJ/L

= 751.04 MJ

Energy from coal (MJ) = 2,332.82 MJ

Therefore: Total Combustion energy = 751.04 + 16,023 +11,447

= 28,221.04 MJ

Table 4.17 shows the combustion energy values obtained from the Example 4.13 and literature for the different stages of entire bioethanol production process.

Table 4.17 Energy balance of rice straw-based ethanol production

| Process | Energy Source | | |
|---|---|---|---|
| | Combustion energy | | Electrical energy |
| | Coal (MJ) | Diesel (MJ) | Electricity (kW-h) |
| Cultivation | N/A | 751.04 | N/A |
| Pretreatment | 16,023 | N/A | N/A |
| Ethanol Production | 11,447 | N/A | 948.6 |
| Total | 28,221.04 | | 948.6 |

The result shows that rice cultivation required 751.04 MJ of diesel for rice plantation. It required 16,023 MJ of coal combustion in pretreatment stage. In bioethanol production, the electrical energy requirement is 948.6 kW-h and coal combustion energy is 11,447 MJ. These energy consumptions are mainly due to the fermenter and distillation column.

### 4.3.3 Flow of substances Rice straw-based Bioethanol production

This part is focused to determine the amount of toxic substance accumulated in soil due to the bioethanol production process. Calculation is based on the octanol water partition function which indicates the solubility of toxic substance in water and octanol. The percentage of toxic substance accumulated in soil is available in Appendix C. The result of this calculation can be used in an impact assessment later. The calculation is shown in Example 4.15.

<u>Example 4.15</u>
Calculate amount of toxic leakage to environment using octanol water partition function
Input amount of Dimethenamid in rice cultivation = 0.41 kg
From Appendix C: Soil accumulation of Dimethenamid = 42.155 %
Therefore: Leakage of Dimethenamed = 0.41x0.42155
= 0.1728 kg of Dimethenamed

Table 4.18 Total leakage of chemicals used in rice cultivation

| Material/Substance | Input Amount (kg) | Leakage (kg) |
|---|---|---|
| Dimethenamid | 0.41 | 0.17 |
| Thiobencarb | 22.23 | 15.61 |
| Butachlor | 2.47 | 1.81 |
| Pretilachlor | 2.47 | 1.69 |
| Oxadiargyl | 0.82 | 0.55 |
| Pendimethalin | 2.74 | 2.21 |
| 2,4-D | 16.47 | 0.38 |
| Glufosinate ammonium | 1.24 | 0.02 |
| Quizalofop-P-Ethyl | 0.82 | 0.61 |
| Potassium Chloride | 61.75 | 0.63 |

According to Table 4.18, the leakage of the toxic substance mainly involves pesticide and fertilizer (Dimethenamid, Thiobencarb, Butachlor, Pretilachlor, Oxadiargyl, Pendimethalin) and fertilizer (Ammonium sulfate, Potassium chloride, Diammonium hydrogenorthophosphate, Monoammoniumphosphate). The largest amount of toxic leakage is Thiobencarb.

### 4.3.4 Material analysis of Rice straw-based Bioethanol production

Table 4.19 summarizes the material requirement for the rice-straw based ethanol production in order to produce 1,000 L of bioethanol. The material amounts are indicated in kg.

Table 4.19 Total starting material to produce 1,000 L of bioethanol from rice straw-based bioethanol production

| Material | Amount (kg) |
|---|---|
| Rice Straw | 3,526 |
| Water | 7,521 |
| Total Herbicide | 49.67 |
| Total Fertilizer | 418.26 |

Table 4.19 shows that 3,526 kg of rice straw, 7,521 kg of water, 49.67 kg of herbicide, and 418.26 kg of fertilizer are required to produce 1,000L of cassava based bioethanol.

### 4.3.5 Pollutant emission of Rice straw-based Bioethanol production

Pollutants emitted from 2 main sources i.e. coal combustion and electricity. The amount of toxic gasses emission when1 GJ is produced from coal combustion is available in Appendix E. Therefore, the amount of toxic release from coal combustion can be determined. The example is shown in a following calculation.

<u>Example 4.16</u>
Calculate the amount of toxic gas emission from coal combustion
Total Combustion energy of rice straw-based ethanol production = 28,221.04 MJ
From Appendix E: $CO_2$ emission from combustion = 75.8 kg/GJ
= 0.0758 kg/ MJ
Then $CO_2$ emission from combustion of rice straw-based bioethanol production
= 0.0758 kg/MJ * 28,221.04 MJ
= 2,139.15 kg of $CO_2$

Secondly, the total energy obtained from electricity in this process is also available in section 4.1.2. Appendix D indicates the toxic gasses emission when producing 1 TJ of electricity. Therefore, the toxic gases emission due to electricity in rice straw based bioethanol production can be determined. Calculation is shown in Example 4.17.

<u>Example 4.17</u>
Calculate amount of toxic gas emission from electricity
From Appendix D: $CO_2$ emission when producing 1 TJ of electricity = 229,380 kg
From unit production: 1 TJ of electricity = $2.77 \times 10^5$ kW-h
Total electricity consumption = 948.6 kW-h

Then: $CO_2$ emission when producing 948.6 kW-h
= 229,380 kg * (948.6/2.77 x $10^5$)
= 785.52 kg of $CO_2$

Then, the total amount of toxic emission is the summation of the amount of toxic that comes from coal combustion and electricity as shown in Example 4.18.

<u>Example 4.18</u>

Calculate the total amount of toxic emission

| | |
|---|---|
| $CO_2$ emission from coal combustion | = 2,139.15 kg |
| $CO_2$ emission from electricity | = 785.52 kg |
| Therefore: Total Emission of $CO_2$ | = 2,139.15 + 785.52 |
| | = 2,924.67 kg of $CO_2$ |

Table 4.20 shows the emission of different pollutants from the rice straw based ethanol production process to produce 1,000 L of bioethanol. The amounts of emissions were obtained from the calculation shown in Example 4.11. There are $CH_4$, CO, $CO_2$, $N_2O$, $NO_2$, and $SO_2$

Table 4.20 Total pollutant emission from rice straw-based bioethanol production

| Pollutants | Emission(kg) |
|---|---|
| $CH_4$ | 10.3 |
| CO | 0.62 |
| $CO_2$ | 2,924.67 |
| $N_2O$ | 0.02 |
| $NO_2$ | 5.96 |
| $SO_2$ | 18.8 |

Note: Based on the production of 99.7 vol% bioethanol

Table 4.20 clearly shows that $CO_2$, is the highest pollutant emission amounts that release to atmosphere. The result also show the moderate amount of acidifying gas such as $NO_2$ (5.96 kg) and $SO_2$ (18.8 kg). $CH_4$, which is considered to be greenhouse gas, is also released moderately around 10.3 kg. The other pollutants are release in a traceable amount.

### 4.4 Material comparison

Material comparison is performed to determine the amount of pesticides and fertilizer used, water consumption, starting materials, and products arising within the processes.

Table 4.21 Total of starting material input required to produce 1,000 L of 99.7 vol% Ethanol

| Process | Material | Amount (kg) |
|---|---|---|
| Cassava | Cassava Chip | 2,414 |
| | Water | 9,920 |
| | Total Herbicide | 22.28 |
| | Total Fertilizer | 168.85 |
| Sugarcane | Molasses | 3,549 |
| | Water | 6,584 |
| | Total Herbicide | 20.35 |
| | Total Fertilizer | 112.55 |
| Rice | Rice Straw | 3,526 |
| | Water | 7,521 |
| | Total Herbicide | 49.67 |
| | Total Fertilizer | 418.26 |

Material comparisons between 3 bioethanol production processes are shown in Table 4.21. It provides the summary of total material required such as starting material, water, herbicide, and fertilizer. This numbers in this table are based on the calculation in section 4.1.4, 4.2.4, and 4.3.4 respectively. According to Table 4.21, the amount of starting material required in cassava chip bioethanol production process is the lowest. The amount of required cassava chip for producing bioethanol production is around 2,414 kg. The amount of water consumption in molasses based bioethanol production is the lowest. The amount of required water for producing bioethanol production is around 6,584 kg. As well, the amount of herbicide and fertilizer in in molasses based bioethanol production is the lowest. The values are 20.35 kg of herbicide and 112.55 of fertilizer respectively.

Table 4.21 clearly shows that cassava based bioethanol production has potential to be a best choice for bioethanol production according to the material requirement. The result also shows that the lowest water consumption process is sugarcane bioethanol production process because it has ability to survive in drought environment. For the herbicide and fertilizer, the lowest herbicide and fertilizer requirement is molasses-based bioethanol production. However, this calculation is not including the severity of each toxic substance.

## 4.5 Energy comparison

Energy comparison is performed to determine the amount of energy consumption in three different bioethanol production processes. Energy consumption in process can be classified into 2 source; coal combustion and electricity.

Table 4.22 Total of amount of energy required to produce 1,000 L of 99.7 vol% Ethanol.

| Processes | Energy | |
|---|---|---|
| | Combustion Energy (MJ) | Electricity (kW-h) |
| Cassava-based | 3,081.62 | 554.42 |
| Molasses-based | 45,418.49 | 1,928.2 |
| Rice straw-based | 28,221.04 | 948.6 |

Energy comparisons between 3 bioethanol production processes are shown in Table 4.21. It provides the total energy usage for production of 99.7 vol% 1,000 L bioethanol production. The result shows that the energy consumption in cassava-based bioethanol production is the lowest. It required 3,081.62 MJ of combustion energy and 554.42 kW-h of electricity. On the other hand, the amount of energy usage in molasses based bioethanol production is the highest. The result show that molasses-based bioethanol production had been used energy in a huge amount. The energy requirements are 45,418.49 MJ of combustion energy and 1,928.2 kW-h of electricity. The result also shows that the cassava-based bioethanol production required only 6.78% and 10.91% of total biomass combustion energy compare to molasses-based bioethanol production and rice straw-based bioethanol production respectively. The main reason is the simplicity of the process.

## 4.6 Environmental impact assessment and comparison

This part is focused to determine the environmental impact using BRE ecopoint. The calculation is in 6 different categories which are global warming, human toxicity, fresh water toxicity, terrestrial toxicity, acidification and eutrophication. The result from section 4.1.3, 4.1.5, 4.2.3, 4.2.5, 4.3.3, and 4.3.5 are used for the calculation of environmental impact assessment. BRE ecopoints can be determined by the multiplying the toxic leakage with the characterize factors in each categories. Characterize factors are available in Appendix D-H. Thereafter, the summation of BRE ecopoints is used to determine the most proper bioethanol production process. Example 4.19 shows the calculation of the BRE ecopoints.

Example 4.19

Global warming impact of cassava-based bioethanol production

From Table 4.8: Total emissions of toxic gases are:

| Pollutants | Emission (kg/1000L) |
|---|---|
| $CH_4$ | 6.01 |
| CO | 0.19 |
| $CO_2$ | 459.10 |
| $N_2O$ | 0.01 |
| $NO_2$ | 1.47 |
| $SO_2$ | 5.89 |

From Appendix F: GWP factor for characterizing climate gases are:

| Substance | $GWP_{100}$ ( kg $CO_2$ eq /kg) |
|---|---|
| $CH_4$ | 21 |
| $CO_2$ | 1 |
| $N_2O$ | 310 |

Therefore, we can calculate amount of $CO_2$ equivalent by using formula (1) from page 18.

| Substance i | Mass (kg) | $GWP_{100}$ (kg $CO_2$ eq/kg) | $CO_2$ Equivalent (kg) |
|---|---|---|---|
| $CH_4$ | 6.01 | 21 | 126.21 |
| CO | 0.19 | N/A | N/A |
| $CO_2$ | 459.10 | 1 | 459.10 |
| $N_2O$ | 0.01 | 310 | 3.10 |
| $NO_2$ | 1.47 | N/A | N/A |
| $SO_2$ | 5.89 | N/A | N/A |
| | | **Total** | 588.41 |

Therefore, the total impact assessment of cassava-based bioethanol production in global warming category is equal to 558.41equivalent $CO_2$ kg.

Table 4.23 Environmental impact assessment of bioethanol production

| Impacts | Equivalent Unit | Cassava-based | Molasses-based | Rice Straw-based |
|---|---|---|---|---|
| | | Amount (kg/1000L) | Amount (kg/1000L) | Amount (kg/1000L) |
| Global warming | Carbon dioxide eq | 588.41 | 5491.36 | 3,147.17 |
| Human toxicity | Triethylene glycol eq | 0.01 | 0.26 | 0.26 |
| Freshwater toxicity | Triethylene glycol eq | 177,178.88 | 661,417.91 | 1,521,710.48 |
| Terrestrial toxicity | Triethylene glycol eq | 16,077.68 | 59,386 | 139,696 |
| Acidification | Sulfur dioxide eq | 7.33 | 43.80 | 24.64 |
| Eutrophication | Sulfate eq | 34.41 | 19.34 | 188.21 |

Table 4.23 clearly shows the summary of environmental impact assessment in 6 different options i.e. global warming, human toxicity, freshwater toxicity, terrestrial toxicity, acidification, and eutrophication.

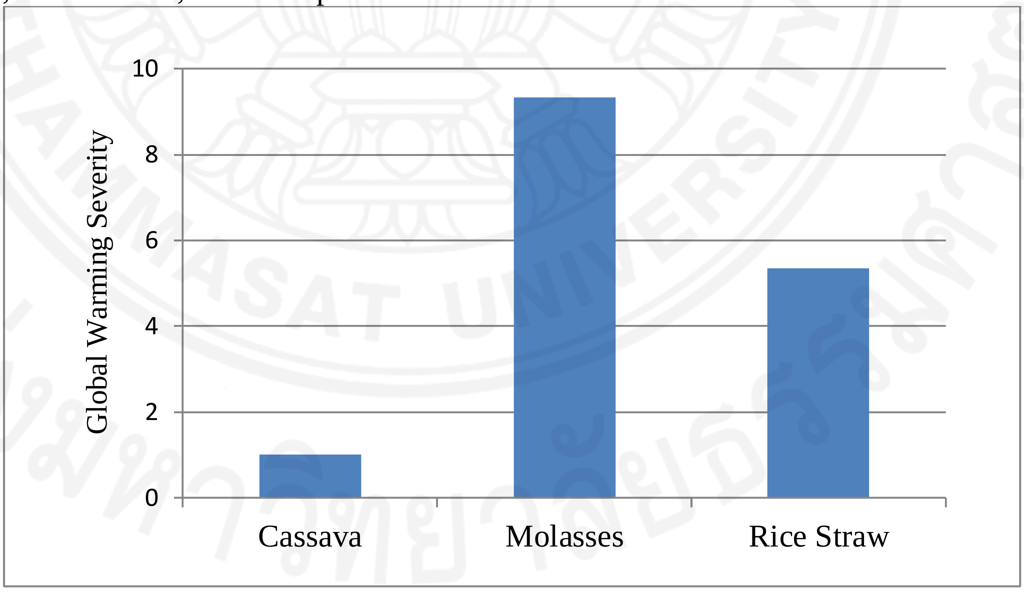


Figure 4.3 Comparison of global warming's severity magnitude

The calculation of global warming is based on the emission of greenhouse gas as shown in Figure 4.3. The result show that the value of global warming’s severity magnitude of molasses-based bioethanol production is the highest according to the amount of greenhouse gases emission. On the other hand, the lowest contribution of greenhouse gas is cassava-based bioethanol. Cassava-based bioethanol production contributes 588.41 kg of carbon dioxide equivalent. The main $CO_2$ contributor in cassava-based production is from the coal combustion, used in distillation process.

The amount of the greenhouse gasses in emission of molasses-based bioethanol production is 5,491.36 kg of carbon dioxide equivalent. The amount of greenhouse gasses emission in molasses-based bioethanol production is 9.33 times compared to cassava-based bioethanol production. It reflects the amount of electricity usage in sugar milling process and amount of coal consumption for combustion processes. Rice straw-based bioethanol production contributes. The amount of greenhouse gasses emission in rice straw-based bioethanol production is 5.34 times compared to cassava-based bioethanol production. The main contributors of rice straw-based bioethanol production are mainly come from coal combustion in distillation process.

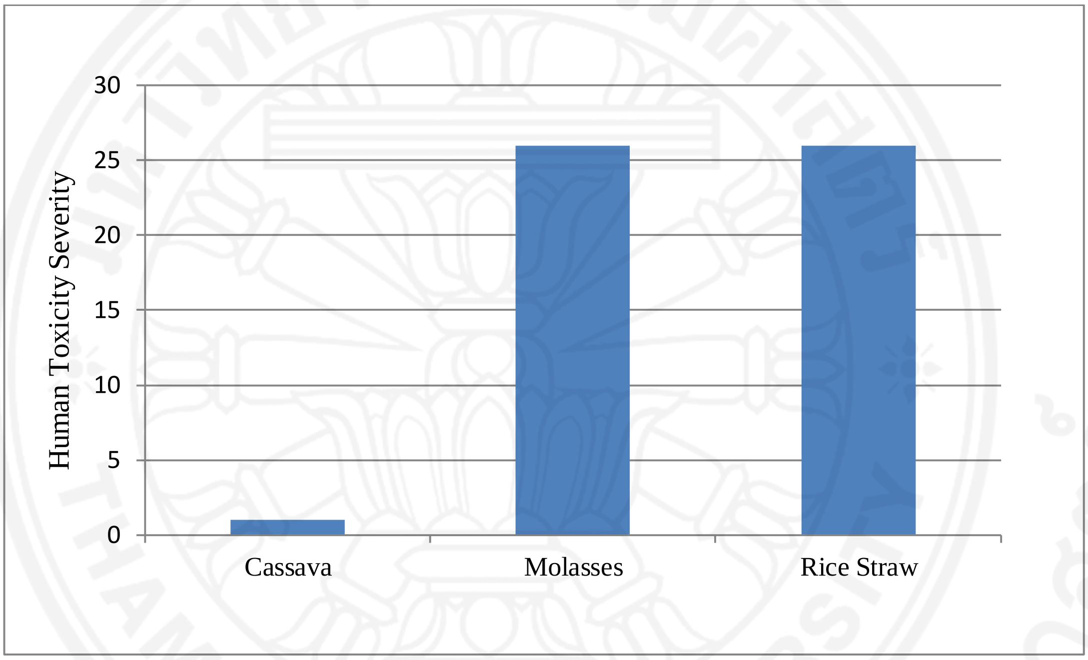


Figure 4.4 Comparison of human toxicity's severity

For toxicity, the study divides toxicity into 3 sub categories: human toxicity; freshwater toxicity; and terrestrial toxicity. Figure 4.4 shows the impact assessment of human toxicity. The unit is represented in a triethylene glycol equivalent. The result shows that cassava-based bioethanol production contributed the lowest amount of toxic substance. The amount of the toxic leakage in cassava-based bioethanol production is only 0.01 kg of triethylene glycol. The result also shows that the human toxicity severity of molasses-based bioethanol production and rice-straw based bioethanol production are equivalent. The values of these 2 processes are 0.26. It reflects the severity of the chemical which used in cultivation process of molasses-based bioethanol production and rice straw-based bioethanol production. The main contributor are atrazine, 2,4-D, metribuzin in sugarcane cultivation of molasses based-bioethanol production and thiobencarb, pendimethalin in rice cultivation of rice straw-based bioethanol production. Figure 4.4 also indicated that the severity magnitude of molasses-based and rice straw-based bioethanol production is around 26 times compared to cassava-based bioethanol production. This number indicates a huge difference in terms of ratio.

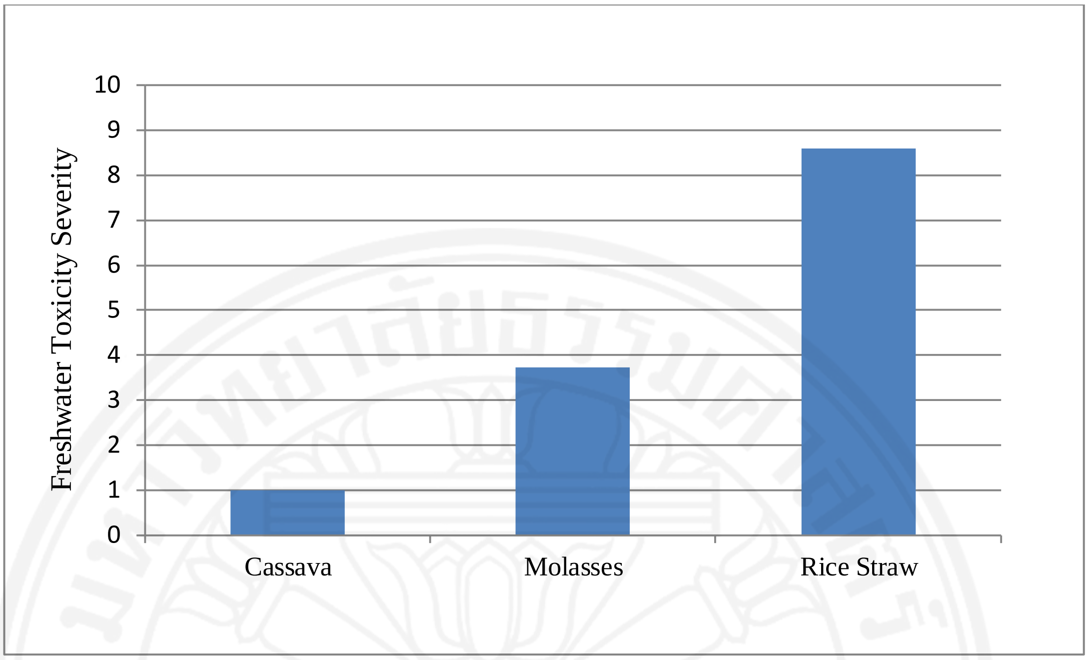


Figure 4.5 Comparison of freshwater toxicity's severity

Figure 4.5 shows the impact assessment of freshwater toxicity. The unit is represented in a triethylene glycol equivalent. The result shows that cassava-based bioethanol production contributed the lowest amount of toxic substance to the freshwater body. The amount of the toxic leakage of cassava-based bioethanol production in freshwater is 177,178.9 kg of triethylene glycol due to the usage of alachlor, and metachlor. As for molasses-based bioethanol production, the amount of toxic substance released to freshwater is 661,417.91 kg or equal to 3.73 times compare to cassava-based bioethanol production. The main reason is the usage of diuron. The amount of the toxic substance released in freshwater of rice-based bioethanol production is the highest. 1,521,710.48 kg of triethylene glycol equivalent is released in to the freshwater that considered as a worst scenario. The result also shows that rice straw-based bioethanol production affect freshwater ecosystem more than cassava based-bioethanol production 8.58 times.

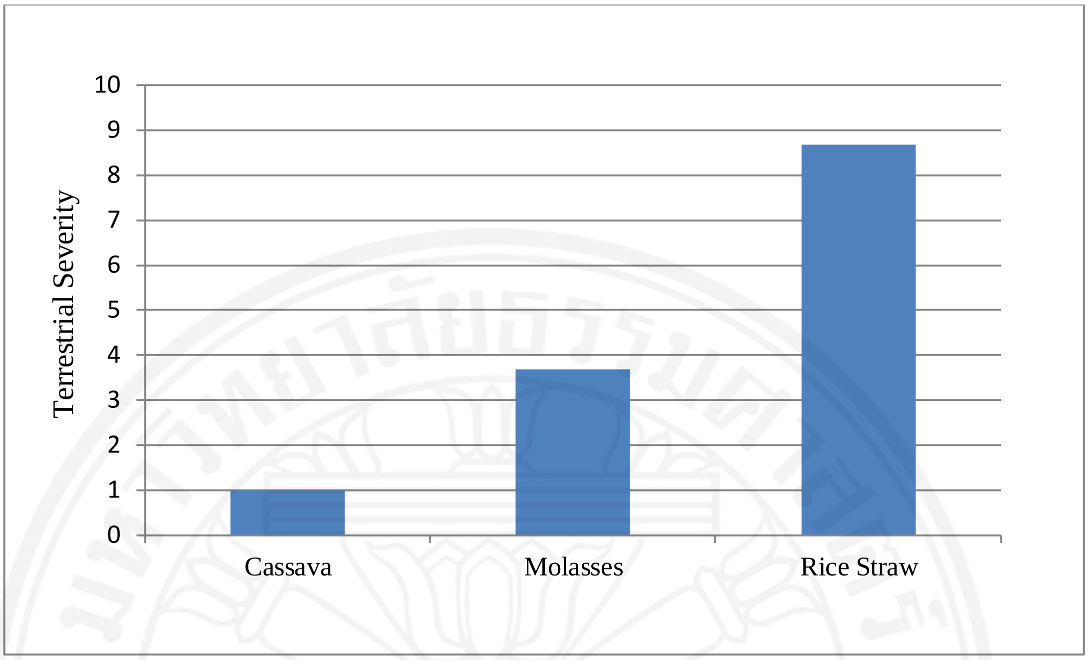


Figure 4.6 Comparison of terrestrial toxicity's severity

Last category of toxicity is terrestrial toxicity. Figure 4.6 shows the impact assessment of terrestrial toxicity which represented in triethylene glycol equivalent unit. The amount of triethylene glycol equivalent released from cassava-based bioethanol production is the lowest. The contribution of cassava-based bioethanol production is 16,077 kg of triethylene glycol equivalent. The main contributor is mainly from herbicide used in cultivation stage such as alachlor, and metachlor. The amount of toxic substance released from molasses-based bioethanol production is 59,386 kg of triethylene glycol equivalent. The main contributors are duiron and pendimethalin usage in sugarcane cultivation. The most severe process in terrestrial toxicity is rice straw-based bioethanol production. The amount of triethylene glycol equivalent release is 139,696 kg. The main contributor is mainly come from the usage of thiobencarb. The result also shows that the amount of triethylene glycol equivalent release in molasses-based bioethanol production and rice straw-based bioethanol production is 3.69 times and 8.86 times respectively compared to cassava-based bioethanol production.

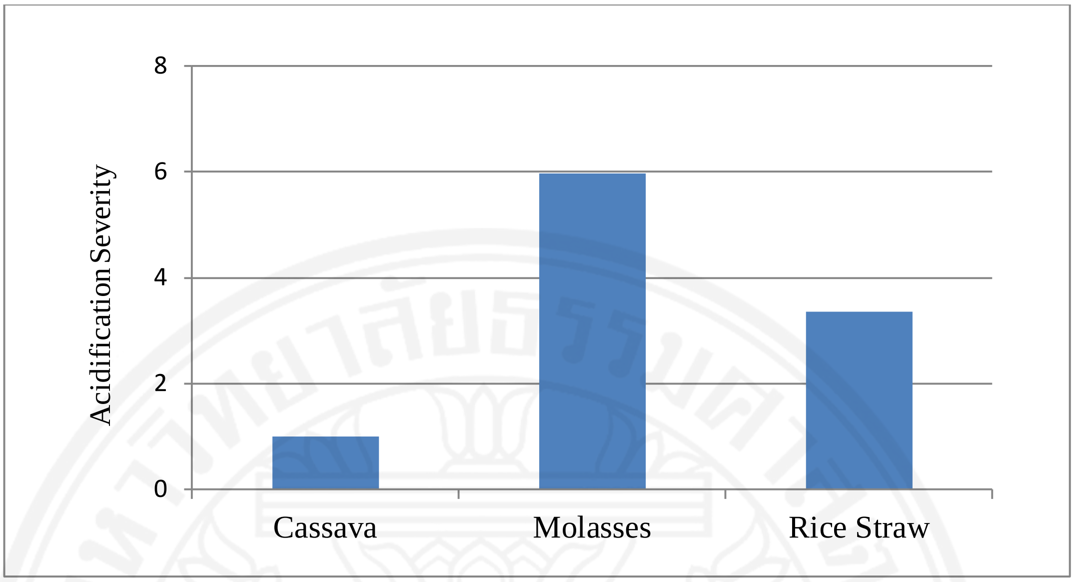

Figure 4.7 Comparison of acidification's severity

Impact assessment also examines the impact of acidifying substances. The study of acidification is calculated from the amount of acidifying substance released from the bioethanol production process. The main contributor in this category is the coal usage in the bioethanol production. According to Figure 4.7, the amount of acidifying substance in cassava-based bioethanol production is the lowest. 7.33 kg of sulfur dioxide releases from cassava-based bioethanol production. The emission of acidifying substance from molasses based bioethanol production is 43.8 kg or 5.97 times compared to cassava-based bioethanol production. The result also shows the amount of sulfur dioxide equivalent released from rice straw-based bioethanol production. The emission of acidifying substance in rice straw based bioethanol production is 24.64 which equal to 3.36 times compare to cassava-based bioethanol production.

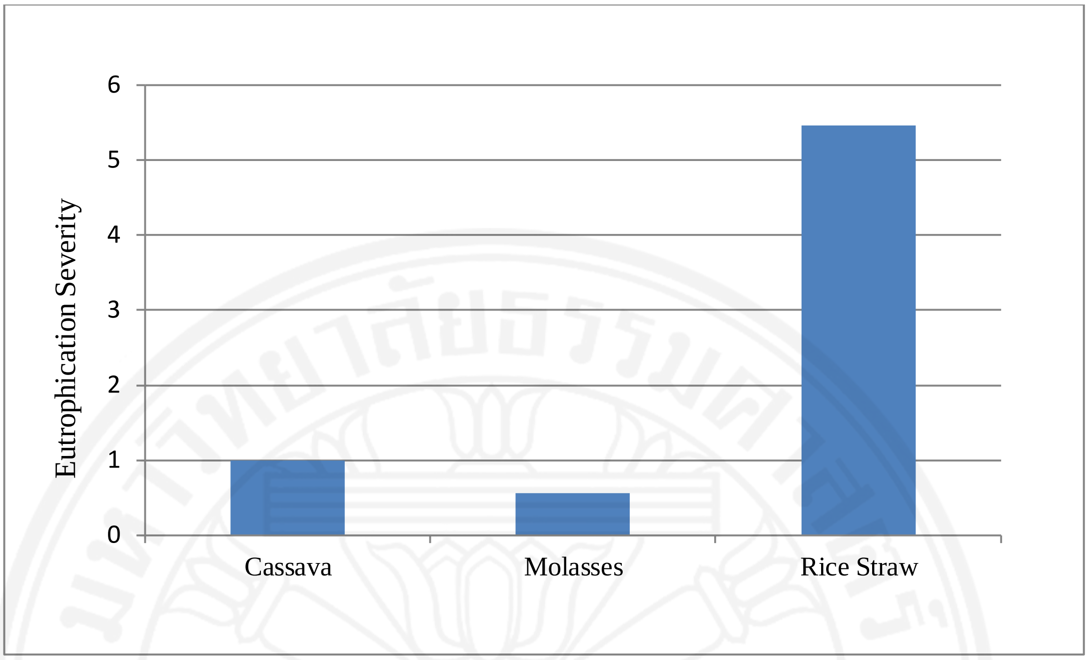

Figure 4.8 Comparison of eutrophication's severity

Last impact assessment is the study of eutrophication. Eutrophication is a study of potential impact of excessively high environmental levels of macro nutrients in water body. According to Figure 4.8, the amount of sulfate equivalent released of cassava-based bioethanol production is 34.41 kg of sulfate. The amount of sulfate equivalent released from molasses-based bioethanol production is the lowest. The contribution of molasses based bioethanol production is around 19.34 kg of sulfate equivalent. The result insists that the amount of sulfate equivalent released from rice straw based bioethanol production is the highest. It values around 188.2 kg. The result also show that cassava-based bioethanol production is 2 times higher compared to molasses-based bioethanol production. As well, the amount of sulfate equivalent in rice straw-based bioethanol production is 5.46 times higher compared to molasses-based bioethanol production.

## 4.7 LCA normalization and environmental comparison

In this part, LCA normalization is performed to determine the most appropriate method for bioethanol production. The results from Table 4.23 are converted into one single score. The calculation are acquired by manipulation of each reference intervention with applicable characterization factor for all impact categories i.e. climate change, human toxicity, freshwater toxicity, terrestrial toxicity, acidification, and eutrophication. The characterize factors are available in Table 3.5. Example 4.19 shows the calculation of LCA normalization as a following method.

Example 4.20
From Table 3.5

| Impact Categories | Weighting Factor (%) |
|---|---|
| Climate change | 43.33 |
| Human toxicity | 17.25 |
| Freshwater Ecotoxicity | 17.25 |
| Terrestrial Ecotoxicity | 16.05 |
| Acidification | 1 |
| Eutrophication | 6.02 |
| Total | 100 |

We can calculate BRE ecopoints Score of cassava by multiplying weighting factor to Impact ratio. These impact ratios is come from the ratio of equivalent unit release from cassava-based in each category divided by the lowest equivalent unit release in each category.

| Impact Categories | Weighting Factor (%) | Impact Ratio | BRE Ecopoints |
|---|---|---|---|
| Climate change | 43.33 | 1 | 43.33 |
| Human toxicity | 17.25 | 1 | 17.25 |
| Freshwater Ecotoxicity | 17.25 | 1 | 17.25 |
| Terrestrial Ecotoxicity | 16.05 | 1 | 16.05 |
| Acidification | 1 | 1 | 1 |
| Eutrophication | 6.02 | 1.77 | 10.65 |
| | | Total | 105.53 |

Therefore, Cassava-based Ecopoints is 105.53.

Table 4.24 Result of LCA normalization of bioethanol production processes

| Bioethanol Production Processes | Ecopoints Score |
|---|---|
| Cassava-based | 105.53 |
| Molasses-based | 988.34 |
| Rice Straw-based | 1,029.12 |

According to table 4.24, the result clearly shows that the ecopoint score of cassava-based bioethanol production is the lowest. It scored 105.53. Ecopoint score of molasses-based bioethanol production is 988.34. The main impact category that affected the ecopoint of molasses-based bioethanol productions are human toxicity, and acidification. The result also indicated that the ecopoint score of rice straw-based bioethanol production is the highest. Therefore, rice straw-based bioethanol production becomes the worst process in term of environmental impact. The main impact category that affected the ecopoint of rice straw-based bioethanol productions are global warming, human toxicity, fresh water toxicity, terrestrial toxicity, and eutrophication. The result insisted that the cassava-based bioethanol production contributed only 10.6% and 10.2% compared to molasses-based bioethanol production and rice straw based-bioethanol production respectively.

# Chapter 5

## Conclusions and Recommendations

Nowadays, Biodiesel is considered as an alternative diesel. Since, the oil price has been increasing; Biodiesel has gained an increasing public and academic attention driven by worldwide effort. The main purpose is to reduce conventional gasoline consumption in transport sector. Biodiesel can be produce from various processes. One of them is bioethanol from yeast fermentation.

In Thailand, Thai government has encouraged the development of domestic bioethanol production for a sustainable energy supply. Thai government has promoted Bioethanol which is derived from cane molasses, cassava, and sugar cane in order to substitute the conventional gasoline. The research of energy performance and environmental impacts of bioethanol production in Thailand is still inaccurate and insufficient. Therefore, it is a good opportunity to observe its life-cycle span through several life, evaluate the environmental impacts arising from the entire life of product and process and can appropriately be applied to evaluating Bioethanol processes.

Nowadays, an effort to minimize environmental impacts has turned to be one of the most significant topics of research interest. Green diesel becomes more attractive due to its impact on the environment. Therefore, this research aims to study and evaluate bioethanol production from various feedstock including cassava chip, molasses and rice straw. The objectives of this study is to study the flow of mass, examine the energy consumption, and explore the environment impact in bioethanol production from molasses, bioethanol production from cassava and bioethanol production from rice straw in Thailand. This study also determines the best environment friendly process of bioethanol production in Thailand using LCA normalization.

This study is divided into 4 steps. The first step of the study focuses on the mass analysis of bioethanol production from the first stage, which mainly involves the cultivation, to the last stage, which is an ethanol production. The mass analysis includes material (chemical, pesticide, fertilizer) and diesel input. The second step of study highlights the energy performance of bioethanol production process. The amount of energy used in each stage was calculated as a total energy used. Third step of the study investigates environmental assessment, calculated based on LCA, which is divided into six categories: global warming, human toxicity, freshwater toxicity, terrestrial toxicity, acidification, and eutrophication. Finally, the last step of the study determines the best bioethanol process using LCA normalization.

In this study, agricultural wastes including cassava chip, molasses and rice straw were used as a feedstock for bioethanol production. Author uses life cycle assessment to assess all of the stages involved in the entire product life cycle which are cultivation, distillation, production, and purification. Author also uses LCA normalization to determine the best environmental performance in three bioethanol production processes including cassava -based, molasses-based, and rice straw-based.

The functional unit of this study is 1,000 L of 99.7 vol% ethanol production. The assumption on this basis renders a justifiable result, especially when comparisons are involved, even though there are differences in the pathway of bioethanol production processes. In addition, most of the data were secondary data from literature review, database, and calculation. The data are based on conditions and settings in Thailand including plant cultivation, fertilizer used, pesticide used and energy consumption. The assumptions are there is no transportation activity arising in the product life span, no labor cost and no pesticide used in the cultivation stage.

From the result, the study of mass balance shows the amount of material required such as fertilizer, herbicide, feedstock and water. For the amount of feedstock used in bioethanol production, cassava-based bioethanol production required least amount of feedstock. It required only 2,414 kg of cassava chip. For molasses-based and rice straw based, they required 3,549 kg of molasses and rice straw 3,526 kg of rice straw respectively. Water required in cassava chip-based process is the highest. It required 9,920 kg of water. Water requirement is only 6,584 kg in molasses-based process and 7,521 kg in rice-straw based process. In herbicide and fertilizer aspect, rice straw-based required the highest amount of herbicide and fertilizer. It required around 49.67 kg of herbicide and 418.26 kg of fertilizer. The requirement of herbicide and fertilizer in molasses-based and cassava chip-based reduce to ½-¼. It required only 22.28 kg of herbicide and 168.85 kg of fertilizer in cassava chip-based. For molasses-based process, herbicide required is around 20.35 kg and fertilizer required is only 112.55 kg.

From the result, the study of impact assessment indicates that cassava-based bioethanol production contributes only a moderate degree of severity magnitude in each impact categories. The rice straw-based bioethanol production is the process with the highest severity magnitude, ranking number 1 in 4 out of 6 impact categories which are human toxicity, freshwater toxicity, terrestrial toxicity and acidification. The study found that the major contribution of global warming in molasses-based bioethanol production is mainly from the amount of coal used in combustion. This also affects the amount of $SO_x$ and $NO_x$ released, which may lead to high potential of acidification. On the other hand, in toxicity category, the result show that Thiobencarb is the most hazardous pesticide used in rice cultivation. The degree of hazard of Thiobencarb is relatively high compared to pesticides used in other processes such as Diuron, atrazine in sugarcane cultivation and Alachlor, Metalachlor in cassava cultivation. Therefore, the implication might call for the attempt to find other substitutable substance to replace the usage of atrazine in order to reduce the potential impact on toxicity.

For molasses-based bioethanol production, the impact assessment shows that molasses-based bioethanol production ranks number 1 in 2 out of 6 categories which are global warming and eutrophication. The major contributor is the usage of energy in sugar milling process. The result also shows that the amount fertilizer used in sugarcane cultivation causes a serious problem in eutrophication.

The result from impact assessment is used to in LCA normalization in order to make an ease comparison. In this part, author used BRE-ecopoints model to determine the best environmental performance processes. The process that has the highest ecopoints score is molasses-based bioethanol production. It scored 988.34 ecopoints. Rice straw-based bioethanol production has 1029.12 ecopoints. Cassava-based bioethanol production has 105.53 ecopoints. The main reason that make cassava-based become the most environmental friendly process is the amount of greenhouse gases that contributed to the environment. It contributed only 10.7% compared to molasses-based bioethanol production and 18.7% compared to rice straw based bioethanol production. Beside the effect of greenhouse gases emission, freshwater toxicity is also considered as a point that make become best environmental performance process. Freshwater toxicity equivalent value are only 26.7% and 11.6% compared to molasses-based and rice straw based bioethanol production. Therefore, the most environmental friendly process is cassava-based bioethanol production.

For material and energy comparison, the result from this section also support that cassava-based bioethanol production is the best process compare to the others. Starting material required to produce 1,000L of bioethanol in cassava-based bioethanol production is a lot lower compare to the other 2 processed. Moreover, cassava- based bioethanol production required the lowest amount of energy compare to the other 2 processes. Especially in combustion energy category, cassava-based bioethanol production required less than 10% of the total energy required in molasses-based bioethanol production and rice straw-based bioethanol production.

The result of this study could lead to the development of an entire process which should minimize the negative impact to our environment. For instance, in the case of atrazine used in sugarcane cultivation; although atrazine is a common pesticide, which is used in sugarcane cultivation, the study suggests that substituted pesticide or biological treatment should replace atrazine. This could help the molasses-based bioethanol production becomes more environmentally friendly.

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# Appendices

# Appendix A

## History of bioethanol production in Thailand

| Year | Description of Event |
|---|---|
| 1985 | HRH King Bhumipol requested a study of the cost of producing alcohol from sugarcane for alternative diesel, and an ethanol facility opened in the Royal Chitralada Palace. However, the cost of bioethanol production was found to still be much higher than CG. |
| 1994 | Royal Chitrlada Project (RCP) investigated ethanol production from sugarcane with a capacity of 900 litres/batch and 15 automobiles of various makes and models. |
| 1996 | HRH Princess Mahajakree Sirindhorn opened the first gasohol, E10, filling station in the Palace. |
| 1999 | Dr. Dennis Shuetzel, Director of Ford Motor Company, visited the Ministry of Science and Technology to discuss a collaborative effort in research of ethanol as a transportation diesel. The National Metal and Materials Technology Center was requested to test the viability of E10 gasohol in light trucks with Ford. |
| 2001 | The National Ethanol Committee was established under the Ministry of Science and Technology (MOST) and then transferred to the Ministry of Industry (MOI), now known as The National Biodiesels Committee under the Ministry of Energy (MOE). |
| 2002 | The Thai government set up the specifications for commercialization of gasohol. |

# Appendix B

## Bulk density and octanol-water partition coefficient of herbicide

| BV Calculation | Bulk density (g $ml^{-1}$) | Log K | Bv |
|---|---|---|---|
| 2,4-D | 4.120 | 2.810 | 0.964 |
| 2,4-D sodium salt | 4.120 | 2.810 | 0.964 |
| Alachlor | 1.110 | 2.630 | 1.070 |
| Ametryn | 1.180 | 2.630 | 1.070 |
| Asulam | 1.530 | 0.150 | 4.488 |
| Atrazine | 1.190 | 2.750 | 0.999 |
| Butachlor | 1.080 | 4.500 | 0.363 |
| Dimethenamid | 1.200 | 2.200 | 1.372 |
| Diuron | 1.500 | 2.870 | 0.932 |
| Fenoxaprop-P-Ethyl | 1.320 | 4.580 | 0.347 |
| Fluazifop-p-butyl | 1.200 | 3.180 | 0.779 |
| Glufosinate Ammonium | 1.320 | -4.010 | 49.689 |
| Glysophate | 1.710 | -3.200 | 31.112 |
| Haloxyfop-R-methyl ester | 1.370 | 4.000 | 0.485 |
| Metalachlor | 6.670 | 3.050 | 0.840 |
| Metribuzin | 1.260 | 1.650 | 1.886 |
| Oxadiargyl | 1.410 | 3.950 | 0.499 |
| Oxyfuorfen | 1.170 | -0.600 | 6.923 |
| Paraquat | 1.500 | -4.500 | 65.957 |
| Pendimethalin | 1.170 | 5.200 | 0.242 |
| Pretilachlor | 1.080 | 4.080 | 0.463 |
| Quizalofop-P-Ethyl | 1.360 | 4.610 | 0.341 |
| Thiobencarb | 1.160 | 4.230 | 0.424 |

# Appendix C

## Toxic substance allocation during cultivation stage

| BV Calculation | Plant Accumulation (%) | Soil Accumulation (%) |
|---|---|---|
| 2,4-D | 49.096 | 50.904 |
| 2,4-D sodium salt | 49.096 | 50.904 |
| Alachlor | 51.696 | 48.304 |
| Ametryn | 51.696 | 48.304 |
| Asulam | 81.777 | 18.223 |
| Atrazine | 49.963 | 50.037 |
| Butachlor | 26.639 | 73.361 |
| Dimethenamid | 57.845 | 42.155 |
| Diuron | 48.229 | 51.771 |
| Fenoxaprop-P-Ethyl | 25.745 | 74.255 |
| Fluazifop-p-butyl | 43.781 | 56.219 |
| Glufosinate Ammonium | 98.027 | 1.973 |
| Glysophate | 96.886 | 3.114 |
| Haloxyfop-R-methyl ester | 32.651 | 67.349 |
| Metalachlor | 45.639 | 54.361 |
| Metribuzin | 65.346 | 34.654 |
| Oxadiargyl | 33.290 | 66.710 |
| Oxyfuorfen | 87.378 | 12.622 |
| Paraquat | 98.506 | 1.494 |
| Pendimethalin | 19.504 | 80.496 |
| Pretilachlor | 31.643 | 68.357 |
| Quizalofop-P-Ethyl | 25.415 | 74.585 |
| Thiobencarb | 29.798 | 70.202 |

# Appendix D

## Air emission for electricity production via gasoline. The data relate to a functional unit of 1 TJ net electricity delivered from power plant

| Substance | Quantity (kg) |
|---|---|
| Cd | 0.0158 |
| $CH_4$ | 3007 |
| CO | 75.15 |
| $CO_2$ | 229,380 |
| Hg | 0.00101 |
| $N_2O$ | 5.53 |
| $NH_3$ | 0.224 |
| $NO_x$ | 504.6 |
| PAH | 0.00534 |
| Pb | 0.136 |
| $SO_2$ | 2,359.4 |

Source: Department of agriculture

# Appendix E

## Emission factor for combustion in stationary installation

| Discharge substance | Discharge amount (kg/GJ) |
|---|---|
| SO2 | 0.38 |
| NOx | 0.15 |
| CO | 0.013 |
| CO2 | 75.8 |

Source: Bureau of Rice Research and Development

# Appendix F

## $GWP_{100}$ factor for characterizing climate gases

| Substance | $GWP_{100}$ ( kg $CO_2$ eq /kg) |
|---|---|
| $CH_4$ | 21 |
| $CO_2$ | 1 |
| $N_2O$ | 310 |

Source: James Sangster (1989)

# Appendix G

## HTP, FAETP and TETP factor for characterizing eco-toxicity release, for infinite time horizon and global scale

| Substance | HTP (kg of Triethylene glycol eq/kg) | MAETP (kg of Triethylene glycol eq/kg) | TETP (kg of Triethylene glycol eq/kg) |
|---|---|---|---|
| 2,4-D | 0.0244 | 293.9 | 43.29 |
| 2,4-D sodium salt | 0.0244 | 293.9 | 43.29 |
| Alachlor | 0.0041 | 125,034 | 11,504 |
| Ametryn | 0.00108 | 74,570.18 | 913.34 |
| Asulam | N/A | 353.6 | 32.54 |
| Atrazine | 0.2511 | 113,880.25 | 2,010.85 |
| Butachlor | 0.00003 | N/A | N/A |
| Dimethenamid | 0.007 | 230,351 | 21,195 |
| Diuron | 0.00323 | 98,434.85 | 9,057.26 |
| Fenoxaprop-P-Ethyl | 0.00309 | 94,325 | 8,679 |
| Fluazifop-p-butyl | 0.0015 | 47,909 | 4,408 |
| Glufosinate Ammonium | 0.009 | 946.41 | 87.08 |
| Glysophate | 0.00001 | 1,898.32 | 2,063.19 |
| Haloxyfop-R-methyl ester | 0.00062 | 19,042 | 1,752 |
| Metalachlor | 0.0036 | 110,115 | 10,132 |
| Metribuzin | 0.0005 | 15,542 | 1,430 |
| Oxadiargyl | 0.000021 | N/A | N/A |
| Oxyfuorfen | 0.0034 | 104,607 | 9,625 |
| Paraquat | 0.00141 | 9,134.11 | 9,933.32 |
| Pendimethalin | 0.024 | 750,051 | 69,014 |
| Pretilachlor | 0.000018 | N/A | N/A |
| Quizalofop-P-Ethyl | 0.00017 | 23,566.16 | 31.97 |
| Thiobencarb | 0.005 | 159,638 | 14,688 |

Source: Norris GA (2001)

## Appendix H

## Alternative generic EP factors for characterizing acidifying releases to the air

| Substance | EP (kg of SO2 eq/kg) |
|---|---|
| Ammonium Sulfate | 1 |
| Diammonium Hydrogenorthophosphate | 1.66 |
| Monoammonium Phosphate | 1.33 |

Source: Huijbregts, M.A.J, (2000)

## Appendix I

## Alternative generic AP factors for characterizing acidifying releases to the air

| Substance | AP (kg of SO2 eq/kg) |
|---|---|
| $SO_2$ | 1 |
| $NO_2$ | 0.98 |
| $NH_3$ | 1.88 |

Source: Huijbregts, M.A.J, (2000)

# Appendix J

## BRE ecopoints weighting factor for LCA normalization

| Environmental Profile Methodology 2008 | |
|---|---|
| Impact category | Weighting factor (%) |
| Climate change | 21.6 |
| Acidification | 0.05 |
| Ozone depletion | 9.1 |
| Terrestrial Ecotoxicity | 8 |
| Photochemical ozone creation | 0.2 |
| Fossil diesel depletion | 3.3 |
| Human toxicity | 8.6 |
| Freshwater Ecotoxicity | 8.6 |
| Eutrophication | 3 |
| Mineral resource extraction | 9.8 |
| Water extraction | 11.7 |
| Waste Disposal | 7.7 |
| Nuclear waste | 8.2 |
| Total | 100 |

## Appendix K

## Total Mass Balance of Cassava-based bioethanol production in cassava cultivation stage

| In | | Out | |
|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Cassava seed | 21.86 | Cassava (Bitter) | 5,793 |
| Alachlor | 3.35 | Alachlor | 0.49 |
| Metalachlor | 3.62 | Metalachlor | 0.59 |
| Diuron | 1.21 | Diuron | 0.19 |
| Oxyfuorfen | 1.02 | Oxyfuorfen | 0.04 |
| Paraquat | 2.01 | Paraquat | 0.01 |
| Glysophate | 8.04 | Glysophate | 0.08 |
| Fluazifop-p-butyl | 0.70 | Fluazifop-p-butyl | 0.12 |
| Haloxyfop-R-methyl ester | 0.64 | Haloxyfop-R-methyl ester | 0.13 |
| Fenoxaprop-P-Ethyl | 0.75 | Fenoxaprop-P-Ethyl | 0.17 |
| Quizalofop-P-Ethyl | 0.94 | Quizalofop-P-Ethyl | 0.21 |
| Potassium Chloride | 87.11 | Potassium Chloride | 25.69 |
| Ammonium Sulfate | 45.56 | Ammonium Sulfate | 13.66 |
| Diammonium Hydrogenorthophosphate | 22.11 | Diammonium Hydrogenorthophosphate | 0.00 |
| Monoammonium Phosphate | 14.07 | Monoammonium Phosphate | 0.00 |
| Cyanide | N/A | Cyanide | 0.65 |
| **Out (By Product)** | | **Product** | |
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Alachlor | 1.62 | Cassava (Sweet) | 13,518 |
| Metalachlor | 1.97 | Alachlor | 1.13 |
| Diuron | 0.62 | Metalachlor | 1.38 |
| Oxyfuorfen | 0.13 | Diuron | 0.44 |
| Paraquat | 0.03 | Oxyfuorfen | 0.09 |
| Glysophate | 0.25 | Paraquat | 0.02 |
| Fluazifop-p-butyl | 0.39 | Glysophate | 0.18 |
| Haloxyfop-R-methyl ester | 0.43 | Fluazifop-p-butyl | 0.27 |
| Fenoxaprop-P-Ethyl | 0.56 | Haloxyfop-R-methyl ester | 0.30 |
| Quizalofop-P-Ethyl | 0.70 | Fenoxaprop-P-Ethyl | 0.39 |
| Potassium Chloride | 0.36 | Quizalofop-P-Ethyl | 0.49 |
| Ammonium Sulfate | 0.00 | Potassium Chloride | 61.06 |
| Diammonium Hydrogenorthophosphate | 22.11 | Ammonium Sulfate | 29.98 |
| Monoammonium Phosphate | 14.07 | Diammonium Hydrogenorthophosphate | 0.00 |
| Cyanide | N/A | Monoammonium Phosphate | 0.00 |
| | | Cyanide | 0.15 |

# Appendix L

## Total Mass Balance of Cassava-based bioethanol production in cassava chip production

| **In** | | **Out** | | **Out (By Product)** | |
|---|---|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Cassava (Bitter) | 5,793 | Cassava Chip | 2,414 | Cassava peeling | 3,349 |
| Alachlor | 0.49 | Alachlor | 0.20 | Alachlor | 0.29 |
| Metalachlor | 0.59 | Metalachlor | 0.25 | Metalachlor | 0.34 |
| Diuron | 0.19 | Diuron | 0.08 | Diuron | 0.11 |
| Oxyfuorfen | 0.04 | Oxyfuorfen | 0.02 | Oxyfuorfen | 0.02 |
| Paraquat | 0.01 | Paraquat | 0 | Paraquat | 0.01 |
| Glysophate | 0.08 | Glysophate | 0.03 | Glysophate | 0.05 |
| Fluazifop-p-butyl | 0.12 | Fluazifop-p-butyl | 0.05 | Fluazifop-p-butyl | 0.07 |
| Haloxyfop-R-methyl ester | 0.13 | Haloxyfop-R-methyl ester | 0.05 | Haloxyfop-R-methyl ester | 0.08 |
| Fenoxaprop-P-Ethyl | 0.17 | Fenoxaprop-P-Ethyl | 0.07 | Fenoxaprop-P-Ethyl | 0.1 |
| Quizalofop-P-Ethyl | 0.21 | Quizalofop-P-Ethyl | 0.09 | Quizalofop-P-Ethyl | 0.12 |
| Potassium Chloride | 25.69 | Potassium Chloride | 10.76 | Potassium Chloride | 14.93 |
| Ammonium Sulfate | 13.66 | Ammonium Sulfate | 5.72 | Ammonium Sulfate | 7.94 |
| Cyanide | 0.65 | Cyanide | 0.27 | Cyanide | 0.38 |

# Appendix M

## Total Mass leakage from 1,000 L of 99.7 vol% ethanol in Cassava-based bioethanol production

| Material/Substance | Amount (kg) |
|---|---|
| Fusel oil | 3 |
| Thick slop | 649.8 |
| Stillage | 9,347.20 |
| Carbon dioxide | 766.5 |

# Appendix N

## Total Mass Balance of Molasses-based bioethanol production in sugarcane cultivation stage

| In | | Out | | Out (By Product) | |
|---|---|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Sugarcane Seed | 11.382 | Sugarcane | 7,854 | Atrazine | 0.83 |
| Atrazine | 1.65 | Atrazine | 0.82 | Diuron | 1.95 |
| Diuron | 3.77 | Diuron | 1.82 | Alachlor | 0.57 |
| Alachlor | 1.18 | Alachlor | 0.61 | Metribuzin | 0.98 |
| Metribuzin | 2.83 | Metribuzin | 1.85 | Pendimethalin | 0.64 |
| Pendimethalin | 0.79 | Pendimethalin | 0.15 | Ametryn | 0.80 |
| Ametryn | 1.65 | Ametryn | 0.85 | Oxyfuorfen | 0.05 |
| Oxyfuorfen | 0.38 | Oxyfuorfen | 0.33 | Metalachlor | 0.64 |
| Metalachlor | 1.18 | Metalachlor | 0.54 | 2,4-D | 0.32 |
| 2,4-D | 0.63 | 2,4-D | 0.31 | Asulam | 0.52 |
| Asulam | 2.83 | Asulam | 2.31 | 2,4-D sodium salt | 1.16 |
| 2,4-D sodium salt | 2.28 | 2,4-D sodium salt | 1.12 | Paraquat | 0.02 |
| Paraquat | 1.18 | Paraquat | 1.16 | Ammonium Sulfate | 0 |
| Ammonium Sulfate | 44.50 | Ammonium Sulfate | 44.50 | Potassium Chloride | 0.45 |
| Potassium Chloride | 32.72 | Potassium Chloride | 32.27 | Diammonium Hydrogenorthophosphate | 21.59 |
| Diammonium Hydrogenorthophosphate | 21.59 | Diammonium Hydrogenorthophosphate | 0 | Monoammonium Phosphate | 13.74 |
| Monoammonium Phosphate | 13.74 | Monoammonium Phosphate | 0 | | |

# Appendix O

## Total Mass Balance of Molasses-based bioethanol production in sugar milling process

| In | | Out | | Out (By Product) | |
|---|---|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Sugarcane | 7,854 | Molasse | 3,549 | Bagasse | 19,398 |
| Atrazine | 0.82 | Atrazine | 0.1 | Sugar | 5,533 |
| Diuron | 1.82 | Diuron | 0.23 | Cane Stalk | 500.6 |
| Alachlor | 0.61 | Alachlor | 0.08 | Atrazine | 0.72 |
| Metribuzin | 1.85 | Metribuzin | 0.23 | Diuron | 1.59 |
| Pendimethalin | 0.15 | Pendimethalin | 0.02 | Alachlor | 0.53 |
| Ametryn | 0.85 | Ametryn | 0.11 | Metribuzin | 1.62 |
| Oxyfuorfen | 0.33 | Oxyfuorfen | 0.04 | Pendimethalin | 0.13 |
| Metalachlor | 0.54 | Metalachlor | 0.07 | Ametryn | 0.74 |
| 2,4-D | 0.31 | 2,4-D | 0.04 | Oxyfuorfen | 0.29 |
| Asulam | 2.31 | Asulam | 0.29 | Metalachlor | 0.47 |
| 2,4-D sodium salt | 1.12 | 2,4-D sodium salt | 0.14 | 2,4-D | 0.27 |
| Paraquat | 1.16 | Paraquat | 0.14 | Asulam | 2.02 |
| Ammonium Sulfate | 44.5 | Ammonium Sulfate | 2.93 | 2,4-D sodium salt | 0.98 |
| Potassium Chloride | 32.27 | Potassium Chloride | 4.01 | Paraquat | 1.02 |
| | | | | Ammonium Sulfate | 41.57 |
| | | | | Potassium Chloride | 28.26 |

# Appendix P

## Total Mass leakage from 1,000 L of 99.7 vol% ethanol in molasses-based bioethanol production

| Material/Substance | Amount (kg) |
|---|---|
| Fusel oil | 4 |
| Thick slop | 1,280 |
| Stillage | 5,304 |
| Carbon dioxide | 766.5 |

# Appendix Q

## Total Mass Balance of Rice straw-based bioethanol production in rice cultivation stage

| In | | Out | | Out (By Product) | |
|---|---|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Rice seed | 59.00 | Paddy Rice | 8,234 | Dimethenamid | 0.17 |
| Dimethenamid | 0.41 | Dimethenamid | 0.24 | Thiobencarb | 15.61 |
| Thiobencarb | 22.23 | Thiobencarb | 6.62 | Butachlor | 1.81 |
| Butachlor | 2.47 | Butachlor | 0.66 | Pretilachlor | 1.69 |
| Pretilachlor | 2.47 | Pretilachlor | 0.78 | Oxadiargyl | 0.55 |
| Oxadiargyl | 0.82 | Oxadiargyl | 0.27 | Pendimethalin | 2.21 |
| Pendimethalin | 2.74 | Pendimethalin | 0.53 | 2,4-D | 8.38 |
| 2,4-D | 16.47 | 2,4-D | 8.09 | Glufosinate ammonium | 0.03 |
| Glufosinate ammonium | 1.24 | Glufosinate ammonium | 1.21 | Quizalofop-P-Ethyl | 0.61 |
| Quizalofop-P-Ethyl | 0.82 | Quizalofop-P-Ethyl | 0.21 | Ammonium Sulfate | 0 |
| Ammonium Sulfate | 289.83 | Ammonium Sulfate | 289.83 | Potassium Chloride | 0.63 |
| Potassium Chloride | 61.75 | Potassium Chloride | 61.12 | Diammonium Hydrogenorthophosphate | 40.75 |
| Diammonium Hydrogenorthophosphate | 40.75 | Diammonium Hydrogenorthophosphate | 0 | Monoammonium Phosphate | 25.93 |
| Monoammonium Phosphate | 25.93 | Monoammonium Phosphate | 0 | Monoammonium Phosphate | 25.93 |

# Appendix R

## Total Mass Balance of Rice straw-based bioethanol production in rice milling process

| In | | Out | | Out (By Product) | |
|---|---|---|---|---|---|
| Material/Substance | Amount (kg) | Material/Substance | Amount (kg) | Material/Substance | Amount (kg) |
| Paddy Rice | 8,234 | Rice Straw | 3,526 | Unmilled rice | 4,708 |
| Dimethenamid | 0.24 | Dimethenamid | 0.10 | Dimethenamid | 0.14 |
| Thiobencarb | 6.62 | Thiobencarb | 2.84 | Thiobencarb | 3.78 |
| Butachlor | 0.66 | Butachlor | 0.28 | Butachlor | 0.38 |
| Pretilachlor | 0.78 | Pretilachlor | 0.34 | Pretilachlor | 0.44 |
| Oxadiargyl | 0.27 | Oxadiargyl | 0.12 | Oxadiargyl | 0.15 |
| Pendimethalin | 0.53 | Pendimethalin | 0.23 | Pendimethalin | 0.30 |
| 2,4-D | 8.09 | 2,4-D | 3.47 | 2,4-D | 4.62 |
| Glufosinate ammonium | 1.21 | Glufosinate ammonium | 0.52 | Glufosinate ammonium | 0.69 |
| Quizalofop-P-Ethyl | 0.21 | Quizalofop-P-Ethyl | 0.09 | Quizalofop-P-Ethyl | 0.12 |
| Ammonium Sulfate | 289.83 | Ammonium Sulfate | 124.04 | Ammonium Sulfate | 165.26 |
| Potassium Chloride | 61.12 | Potassium Chloride | 26.19 | Potassium Chloride | 34.93 |

## Appendix S

## Total Mass Balance of Rice straw-based bioethanol production in bioethanol production

| Material/Substance | Amount (kg) |
|---|---|
| Furfural | 0.51 |
| HMF | 1.54 |
| Solid Waste | 1.95 |
| Benzene | 0.44 |
| Methane | 15.42 |
| Nitrous Oxide | 4.56 |
| Sulfure Oxide | 1.37 |
| Carbon monoxide | 4.14 |
| Carbon dioxide | 6.25 |

## Appendix T

## Total land used in cultivation stage of bioethanol productions

| **Bioethanol Production** | **Total starting material (kg)** | **Production rate (kg/ rai)** | **Total Land Use (rai)** |
|---|---|---|---|
| Cassava | 19,300 | 3,600 | 5.3611 |
| Sugarcane | 78,540 | 20,000 | 3.927 |
| Rice | 8,234 | 1,000 | 8.234 |

## Appendix U

## Total Herbicide used in cassava cultivation stage of bioethanol productions

| Herbicide | Duration | kg/rai | kg used |
|---|---|---|---|
| Alachlor | Pre-Emergence | 0.625 | 3.350 |
| Metalachlor | Pre-Emergence | 0.675 | 3.618 |
| Diuron | Pre-Emergence | 0.225 | 1.206 |
| Oxyfuorfen | Pre-Emergence | 0.191 | 1.023 |
| Paraquat | Post-Emergence | 0.375 | 2.010 |
| Glysophate | Post-Emergence | 1.500 | 8.041 |
| Fluazifop-p-butyl | Post-Emergence | 0.130 | 0.696 |
| Haloxyfop-R-methyl ester | Post-Emergence | 0.120 | 0.643 |
| Fenoxaprop-P-Ethyl | Post-Emergence | 0.140 | 0.750 |
| Quizalofop-P-Ethyl | Post-Emergence | 0.175 | 0.938 |

## Appendix V

## Total Herbicide used in sugarcane cultivation stage of bioethanol productions

| Herbicide | Duration | kg/rai | kg used |
|---|---|---|---|
| Atrazine | Pre-Emergence | 0.420 | 1.649 |
| Diuron | Pre-Emergence | 0.640 | 2.513 |
| Alachlor | Pre-Emergence | 0.300 | 1.178 |
| Metribuzin | Pre-Emergence | 0.720 | 2.827 |
| Pendimethalin | Pre-Emergence | 0.200 | 0.785 |
| Ametryn | Pre-Emergence | 0.420 | 1.649 |
| Oxyfuorfen | Pre-Emergence | 0.096 | 0.376 |
| Metalachlor | Pre-Emergence | 0.300 | 1.178 |
| 2,4-D | Pre-Emergence | 0.160 | 0.628 |
| Asulam | Post-Emergence | 0.720 | 2.827 |
| 2,4-D sodium salt | Post-Emergence | 0.580 | 2.277 |
| Diuron | Post-Emergence | 0.320 | 1.256 |
| Paraquat | Post-Emergence | 0.300 | 1.178 |
| Ametryn | Post-Emergence | 0.240 | 0.942 |

# Appendix W

## Total Herbicide used in rice cultivation stage of bioethanol productions

| Herbicide | Duration | kg/rai | kg (used) |
|---|---|---|---|
| Dimethenamid | Pre-Emergence | 0.050 | 0.411 |
| Thiobencarb | Pre-Emergence | 0.700 | 5.763 |
| Butachlor | Pre-Emergence | 0.300 | 2.470 |
| Pretilachlor | Pre-Emergence | 0.300 | 2.470 |
| Oxadiargyl | Post-Emergence | 0.100 | 0.823 |
| Pendimethalin | Post-Emergence | 0.300 | 2.470 |
| Thiobencarb | Post-Emergence | 2.000 | 16.468 |
| 2,4-D | Post-Emergence | 2.000 | 16.468 |
| Glufosinate ammonium | Post-Emergence | 0.150 | 1.235 |
| Quizalofop-P-Ethyl | Post-Emergence | 0.100 | 0.823 |

# Appendix X

## Total fertilizer used in cultivation stage of bioethanol productions

| Fertilizer | Fertilizer used (kg/Rai) | Fertilizer used (kg) |
|---|---|---|
| **Cassava** | | |
| 15-15-15 | 25 | 134.02 |
| Potassium Chloride | 10 | 53.611 |
| **Sugarcane** | | |
| 15-15-15 | 33.33 | 130.88 |
| **Rice** | | |
| 15-15-15 | 30 | 247.02 |
| Ammonium Sulfate | 25 | 205.85 |

# Appendix Y

## Composition of 15-15-15 fertilizer

| Component | Composition (%) |
|---|---|
| Ammonium Sulfate (34) | 34 |
| Potassium Chloride (25) | 25 |
| Diammonium Hydrogenorthophosphate (16.5) | 16.5 |
| Monoammonium Phosphate (10.5) | 10.5 |
| Other | 14 |