EXERGY ANALYSIS OF JATROPHA AND MICROALGAL BIODIESEL PRODUCTION PLANTS

BY

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ABBREVIATIONS

AFU	Average fuel use per working hour (l/h)
AREA	Operating area (ha)
B5	Biodiesel blend with petro-diesel (5% biodiesel, 95% petro-diesel)
B10	Biodiesel blend with petro-diesel (10% biodiesel, 90% petro-diesel)
ED	Specific direct energy use (fuel) for field operation (MJ/ha)
JME	Jatropha methyl ester
LABEN	Labour energy (MJ/ha),
LABENF	Labour energy factor (MJ/h)
LABOUR	Number of working labourers
MME	Microalgae methyl ester
OECD	Organization for Economic Co-operation and Development
PEU	Specific energy value per liter of fuel (MJ/l)
R & D	Research and Development
RU	Runs (number of application in the considered field operation)
TIME	Operating time (hr)
UCOME	Used Cooking Oil methyl ester

SYMBOLS

C_i	Final concentration
C_{io}	Initial concentration
C_p	Specific heat capacity (kJ/kmol.K)
D^{int}	Internal exergy loss
D^{ext}	External exergy loss
E^{pu}	Produced utilizable exergy;

E^{c}	Consumed exergy.
En_{in}^{net}	Net energy into a system (MJ)
$E^{\sim}$	Exergy content
E^{tr}	Transformed exergy
$Ex_{destroyed}$	Total exergy destroyed, MJ
$Ex_{efficiency}$	Exergy efficiency
$Ex_{de\text{-}activation}$	Exergy of activation energy used during treatment of wastes (MJ)
$Ex_{emissions}$	Exergy of wastes (MJ)
Ex_{fossil}	Exergy non-renewable energy resources (MJ)
$Ex_{product}$	Exergy of the product
Ex_{total}	Total exergy (MJ)
Ex_{i}	Exergy of ith component (MJ/kg)
$Ex_{ch,i}^{0}$	Standard chemical exergy of *i*th component (MJ/kg)
$Ex_{ch,i}$	Chemical exergy of *i*th component (MJ)
$Ex_{ph,i}$	Physical exergy of *i*th component (MJ)
$Ex_{ch,mixtures}$	Exergy of mixtures (MJ)
Ex_{ch,H_2O}^{0}	Standard chemical exergy of water (MJ/kg)
$Ex_{kin,i}$	Kinetic Exergy (MJ)
$Ex_{pot,i}$	Potential Exergy (MJ)
h	Specific working hours per run (h/ha)
H	Specific enthalpy (kJ/kg)
H_0	Specific enthalpy at T_0, p_0 (kJ/ kg)
I	Irreversibility (MJ)
m_i	Mass of *i*th component (kg)

N_i	Number of moles of component *i*
p_i	Pressure of *i*th component (kPa)
p_0	Reference pressure =1atm = 101.3kPa
q	Quality of joule (work)
Q	Heat flux (J)
R	Ideal gas constant = 8.314 J/mol.K
S	Specific entropy (kJ/kgK)
S_0	Specific entropy at T_0, p_0 (kJ/kgK)
$S_{generation}$	Entropy generation (MJ/K)
T	Temperature (K)
T_0	Reference temperature = 273.15K
μ_i	Chemical potential of *i*th component (kJ/mol^2)
v_{H_2O}	Mole fraction of water
W_{in}	Net energy into a system
W_{lost}	Lost work (MJ)
ΔG_{fo}	Standard Gibbs free energy of formation (kJ/mol), (kJ/kg)
β	Ratio of chemical exergy to the lower heating value (LHV) or dry organic substances (dimensionless)
λ_i	Mole fraction of *i*th component

ANALISIS EXERGY LOJI PENGHASILAN BIODIESEL JATROPHA DAN MICROALGAAL

ABSTRAK

Anggaran simpanan minyak mentah menunjukkan puncak pengeluaran akan berlaku pada 2047 pada kadar 83 juta tong sehari berbanding kira-kira 98 milion tong/hari pada 2010. Oleh itu, penyelidikan dan pembangunan yang dilaksanakan kini menjurus ke arah pengeluaran mampan biotenaga terutamanya biodiesel cecair yang boleh menggantikan bahan api fosil cecair dalam masa terdekat. Dalam kajian ini, parameter prestasi termodinamik loji pengeluaran metil ester jatropha (JME) dan metil ester mikroalga (MME) telah ditentukan dan dibandingkan. Analisis exergy yang diambilkira dalam kajian ini adalah berdasarkan tiga parameter prestasi termodinamik iaitu kemusnahan exergy, kecekapan exergy dan potensi peningkatan termodinamik. Keputusan analisis exergy yang diperolehi selepas proses simulasi dengan perisian Aspen plus menunjukkan bahawa bagi kilang pengeluaran biodiesel dengan kapasiti satu ton yang menggunakan jatropha dan mikroalga sebagai bahan mentah, 64% dan 44% daripada tenaga yang berguna (tersedia untuk melakukan kerja) yang terdapat dalam sumber-sumber input dimusnahkan masing-masing untuk menghasilkan produk akhir (biodiesel dan gliserin). 58% dan 30% daripada tenaga berguna yang musnah bagi loji penghasilan MME dan JME masing-masing adalah akibat pembebasan hasil sampingan dan sisa ke alam sekitar. Penghasilan jumlah entropi dalam unit operasi loji penghasilan MME dan JME adalah 494 MJ/K dan 419 MJ/K masing-masing. Walau bagaimanapun, kecekapan proses untuk loji penghasilan MME dan JME adalah 36% dan 56% masing-masing. Prestasi peningkatan termodinamik bagi logi penghasilan MME dan JME pula adalah 98% dan 86% masing-masing daripada jumlah exergy yang musnah. Petunjuk diperbaharui adalah 0.44 dan 0.34 untuk loji penghasilan MME dan JME masing-masing. Unit penyarian minyak bagi kedua-dua loji mengalami kemusnahan exergy yang tertinggi iaitu 132,648 MJ dan 115,161 MJ untuk loji pengeluahan MME dan JME masing-masing. Oleh itu, bagi setiap tan microalgal dan jatropha biodiesel yang dihasilkan, 38% dan 39% masing-masing daripada exergy input ke dalam unit pengeluaran minyak adalah dimusnahkan. Walau bagaimanapun, unit transesterification mencatatkan kerugian exergy paling rendah iaitu 5% dan 2% daripada exergy sumber input untuk loji pengeluaran MME dan JME masing-masing. Keputusan ini menunjukkan bahawa analisis exergy berdasarkan hanya unit transesterification tidak boleh menjustifikasikan kemungkinan termodinamik proses pengeluaran biodiesel. Menurut kajian ini, loji pengeluaran MME dan JME adalah secara termodinamik tidak terlaksana memandangkan nisbah exergy jumlah keluaran kepada masukan bagi kedua-dua loji adalah jauh kurang daripada 1 (iaitu 0.36 dan 0.56 untuk loji pengeluaran MME dan JME masing-masing). Oleh itu, pelaksanaan kaedah kecekapan tenaga yang dibincangkan dalam tesis ini boleh membantu meningkatkan prestasi kilang-kilang pengeluaran

EXERGY ANALYSIS OF JATROPHA AND MICROALGAL BIODIESEL PRODUCTION PLANTS

ABSTRACT

Estimates of crude oil reserves show that its exhaustion will occur in 2047 at a rate of 83 million barrels per day compared to an extraction rate of approximately 98 million barrels/day in 2010. As a result of this, present research and developments are geared towards sustainable production of liquid biofuels especially biodiesel to replace fossil based liquid fuel in the near future. In this study, thermodynamic performance parameters of jatropha methyl ester (JME) and microalgae methyl ester (MME) production plants are determined and compared. The exergy analyses results obtained after process simulation with Aspen Plus software show that for 1 ton biodiesel production plant which utilizes jatropha and microalgae as feedstock, 64% and 44% of the useful energy (available to do work) embedded in the input resources are destroyed respectively in order to obtain the final products (biodiesel and glycerin). 58% and 30% of the destroyed useful energy for MME and JME production plants respectively are as a result of emissions or wastes into the environment. The total entropy generations occurring in the unit operations of MME and JME production plants are 494 MJ/K and 419 MJ/K respectively. Renewability indicators were 0.44 and 0.34 for MME and JME production plants respectively. The oil extraction units for both plants recorded the highest exergy losses of 132,648 MJ and 115,161 MJ for MME and JME production plants respectively. For every ton of microalgal and jatropha biodiesel produced, 38% and 39% of the input exergy into the oil extraction unit is destroyed respectively. On the other hand, the transesterification units recorded the lowest exergy loss of 5% and 2% of the exergies of input resources for MME and JME production plants respectively. These results indicate that the exergy analysis of only the transesterification unit cannot justify the thermodynamic feasibility of biodiesel production processes. According to this study, MME and JME production plants are not thermodynamically feasible since the ratios of total exergies of outputs to inputs for both plants are far less than 1 (i.e. 0.36 and 0.56 for MME and JME production plants respectively). Therefore, the implementation of energy efficiency methods which are discussed in this thesis may help improve the performances of these production plants.

CHAPTER ONE

INTRODUCTION

1.1 Non-Renewable Energy Resources: Profile

1.1.1 World's Fossil Fuel Production and Consumption Data

According to the report of the International Energy Agency (IEA, 2010a) in its World Energy Outlook 2010, the global demand for energy is said to increase by not less than 50% over the next 20 years as a result of increased population growth and rapid industrialization in most parts of the world. Fossil fuel, currently forming about 82% of the world's total energy, has been the main source of energy in the world since the late 1930's (IEA, 2010a). Coal is estimated to have world's reserves of approximately 835 billion metric tons as at January, 2010 with a consumption rate of approximately 203 metric tons per second. It is however predicted to get depleted by May, 2140 (RES, 2010)**.** The estimated total world's reserve of natural gas as at January, 2010 was approximately 172×10^{12} m^3 with an approximate consumption rate of 92653 m^3/s. It is however projected to get exhausted by September 2068 (RES, 2010). Liquid fuel is reported to be consumed more than any other fuel in the world. However, estimates of crude oil reserves (1.2 trillion barrels in January, 2010) show that its exhaustion will occur in 2047 at a rate of 83 million barrels per day compared to an extraction rate of approximately 98 million barrels/day in 2010 (IEA, 2010a). However, these statistics are the proven energy reserves; real reserves may be larger.

This information predicts a huge threat to the world's energy sector if an alternative energy source is not sought. Even though fossil fuel forms larger part of the world's energy share in terms of production and consumption, their increasingly high prices coupled with their gradual depletion and negative impacts on the environment limit their frequent utilization. This has increased the resurgence in developing new energy which would last. Renewable energy resources would completely serve as a potential replacement for fossil fuel in the near future though its share is currently only 13.5% of the world's primary energy (IEA, 2010a; EIA, 2011). For the past nine years, there has been a tremendous increase in growth rate (to reach 3.6% by 2035) for renewable energy production and consumption (EIA, 2011) whilst fossil fuel production has been recording a sharp decrease in growth rate. **Figure 1.1** shows the growth rate of renewable and non-renewable energy sources from 2000 to 2009.

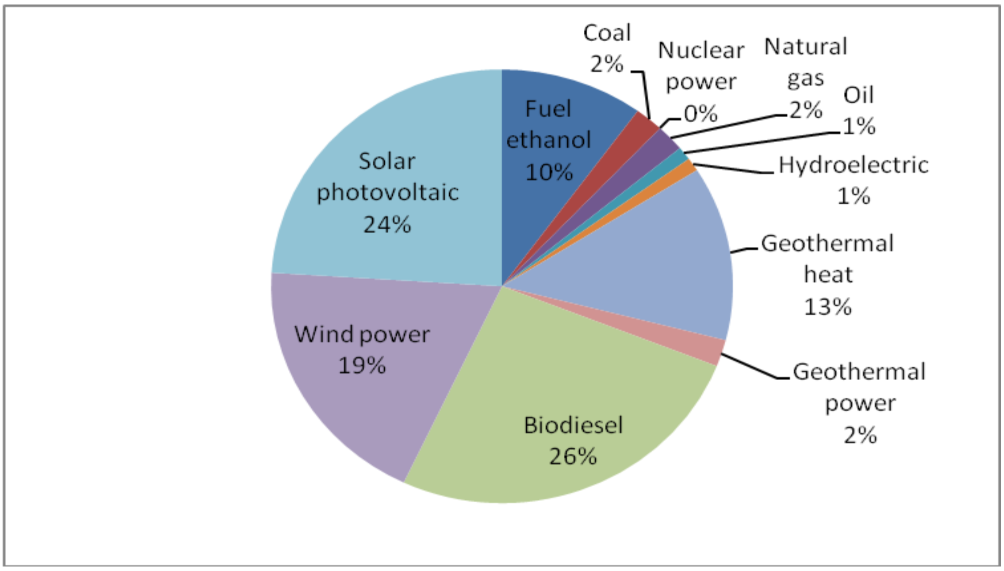

Figure 1.1: The world's energy production growth rate by source from 2000 to 2009 (IEA, 2010a; EPI, 2010)

Figure 1.1 shows a clear indication of gradual fall in the supply and consumption rate of crude oil (the most consumed liquid fuel now), thus the need for a better replacement. Biodiesel however, shows the highest growth rate hence a better option for crude oil replacement in the near future. Since liquid fuel is consumed rapidly in most parts of the world, the focus of research and development in biofuels must be geared towards efficient methods of production and improvement performance assessments. More cost-effective and energy-efficient potential renewable energy sources must be tapped as energy demand keeps increasing because as global energy intensity is ameliorating, there would be little room left for complacency. Energy efficiency in production processes therefore should be improved across all sectors.

1.1.2 Impacts of fossil fuel use on thermodynamic efficiency of a process

Energy use within economic establishments and production plants is usually a corporate key performance indicator and this is directly linked to the energy efficiency of the plant. Any production process which is energy intensive records high destruction of useful energy (exergy) leading to thermodynamic inefficiencies of the process (Ayres 2002; Ayres, 2007). The cost of energy in most industries range from 20% to 80% of the variable cost (Ayres, 2002; Doldersum, 1998; El-Sayed *et al.*, 1970) and therefore the reduction of energy intensity of any company would increase its sustainability (Ayres *et al.*, 2002). Without energy-efficiency improvements, final energy use in 2006 for instance would have been 63% higher in the Organization for Economic Co-operation and Development (OECD) than it was in the early 1970's (IEA, 2010b). In most chemical and other manufacturing industries, fossil fuel is the main source of energy yet its impacts on the environment and process efficiency is negative. The implementation of energy efficiency methods coupled with the reduction of CO_2 emissions fulfill both the environmental and thermodynamic sustainability of an industry (De Swaan *et al.,* 2004; Dewulf *et al.*, 2001; Rosen, 2002).

Energy efficiency or demand-side management programs are reported to possess the lowest capital, lowest risk, and usually the shortest lead time for making substantive reductions in an organization's carbon emissions (Ayres *et al.,* 1998; De Meester *et al.,* 2006; De Vries, 1999). For instance, by combining proper equipment maintenance and upgrades with appropriate insulation, air sealing, thermostat settings and etc., energy use for heating and cooling can also reduce environmental emissions from 20% to 50% (De Vries, 1999). Also, switching from fossil fuel to renewable energy resources can help minimize negative environmental impacts. Efficiency improvement implies the reduction in energy intake (hence reduction in fossil fuel use) which further leads to the reduction in CO_2 emissions because whenever the use of fossil fuels is reduced at any point between the production of the fuel (e.g. production of biodiesel) and the delivery of the desired service (e.g. combustion of biodiesel), there are minimal emissions. Therefore, energy use can be reduced in order to improve the efficiency of individual devices (such as refrigerators, industrial boilers, pumps, motors etc.). This can be achieved for instance by using the correct motor size for the task and using energy that is not currently utilized such as waste heat.

Carbon dioxide emissions from any process contribute to exergy of wastes (resulting from the dissipative effect production) into the environment, consequently adding to exergy destruction and exergy inefficiency. The destruction of order in any system is a form of environmental damage (Dewar, 2005) which includes excess heat as wastes into the environment which contains harmful substances; and this would subsequently reduce the exergy efficiency of the system. Fossil fuel possesses the characteristics of causing environmental damage hence a major contributor to carbon dioxide emission and exergy loss due to wastes into the environment (Crutzen *et al.*, 2008; Dewulf *et al.*, 2005; Gaggioli, 1983; Georgescu-Roegen, 1971) leading to the reduction in energy and thermodynamic efficiencies. As exergy efficiency approaches 100%, positive environmental impact gets to zero since exergy is converted from one form to another without degradation (internal loss or waste emissions), and sustainability approaches infinity because the process approaches reversibility.

The most carbon-intensive and the fastest growing carbon-emitting source of fossil fuels is coal with a total CO_2 emission of 12.5 billion metric tons in 2007 (IEA, 2010a). According to the report by the International Energy Outlook 2010 (IEA, 2010a), CO_2 emissions from the combustion of coal are projected to increase by 46% in 2035**.** However, contributions of CO_2 emissions from liquid fuels and natural gas are 11.3 billion metric tons and 5.9 billion metric tons respectively in 2007 and these are estimated to increase by 0.9% and 1.3% per year by 2035 respectively (IEA, 2010; CDIAC, 2001).

Fossil fuels are also implicated in increased levels of atmospheric methane (CH_4) and nitrogen oxide (NO_x), (Crutzen *et al.*, 2008) although they are not the major source of these gases. About 50% of the (NO_x) in the atmosphere and 70% of the sulphur dioxide in the atmosphere are direct results of emissions released when coal is burned (Marland *et al.*, 2010; Crutzen *et al.*, 2008; Linnhoff *et al.*, 1982)**.** These contributions together with carbon emissions have been increasing the earth's average surface temperature between $0.5\text{-}1.1^0$F ($0.3\text{-}0.6^0$C) (IEA, 2010a). The use of renewable energy resources as blends with fossil fuel (B5, B10 and etc) to facilitate fuel reformation can result in substantial environmental benefits. The adoption of energy efficient methods, however, can help alleviate the toll on environmental and human health. The projected emissions of CO_2 from fossil fuels would be much lower if carbon capture and storage became economical. **Figure 1.2** shows the trend in the global CO_2 emissions from the combustion of fossil fuel sources from 1990 to 2009.

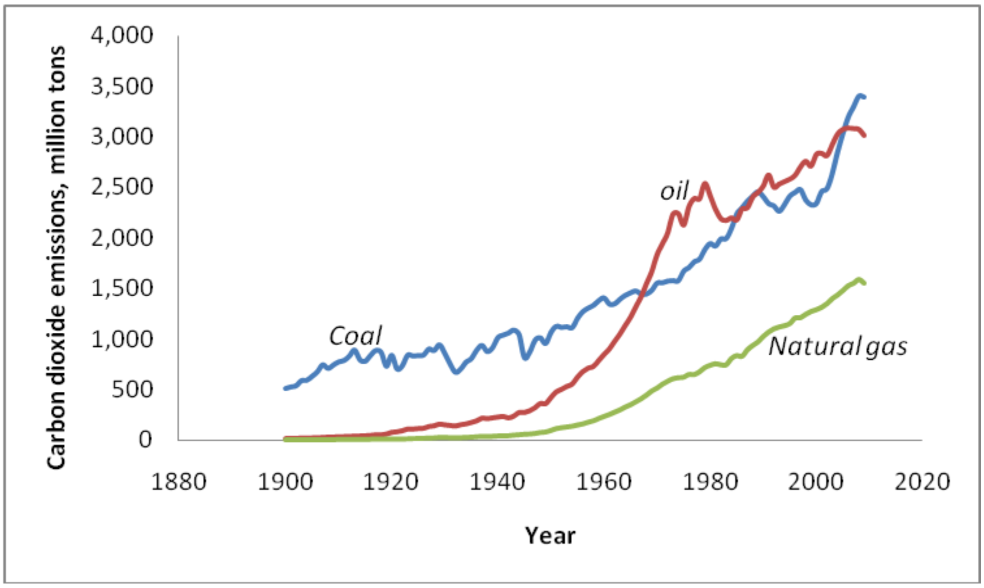

Figure 1.2: World's CO_2 emissions from fossil fuel use
(Marland *et al.*, 2010; CDIAC, 2010; EPI, 2010)

1.2 World Biodiesel Profile and Development

1.2.1 Impacts of biodiesel production and consumption on energy efficiency

Notwithstanding the increasing trends in global financial crisis, fluctuations in crude oil prices and slow progress with climate policies, renewable energy developments in the past years have been tremendously increasing. Renewable energy (such as hydropower, solar energy, wind power, biofuels, geothermal, tidal, and energy from biomass) however, formed only about 13.5% of the total energy mix as at January, 2010 (IEA, 2010a). The world's total biodiesel production was

11 million metric tons in 2008 and this number increased to 20 million metric tons in 2010 (IEA, 2010a). The global biodiesel market is therefore projected to reach 84 million metric tons by 2016, with an annual average growth rate of over 30% (IEA, 2010a; EIA, 2011). The world consumes about 3.8 million metric tons of biodiesel each year and this is estimated to reach 28 million metric tons by 2015 (IEA, 2010a; CDIAC, 2010). This data indicates that there is a high possibility of biodiesel providing as much as 20% of the total capacity of all on-road diesels used in the world by 2020. In Malaysia for instance, as at 2008, the total installed biodiesel production capacity was about 10.2 million tons (Puah *et al.,* 2008; MPOB, 2008; Lim & Teong, 2010). **Figure 1.3** shows the production capacities of biodiesel in the world from 1990 to 2010 (CDIAC, 2010). As biodiesel production increases year by year, energy efficiency methods and improvements must be considered in the research and development process since fossil fuel is consumed or used in large quantities in the production of biodiesel (since presently, fossil fuel use is inevitably utilized in production processes).

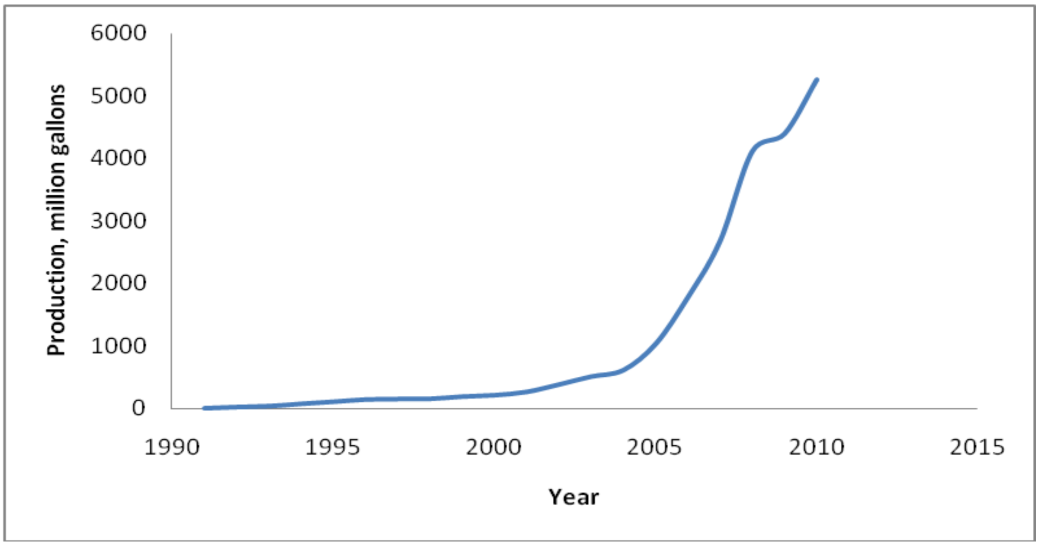

Figure 1.3: World's biodiesel production from 1991 to 2010
(Licht, 2006; EPI, 2010)

Biodiesel, a liquid biofuel, is a fatty acid methyl (or ethyl) ester derived from vegetable oils and animal fats (Mittelbach & Koncar, 1998). Vegetable oils can directly be used as liquid fuels in diesel engines without major modifications but due frequent engine breakdown resulting from the high viscosity of the oils, they are made to undergo chemical reactions in order to reduce the viscosity through processes such as transesterification, pyrolysis, emulsification and etc. (Pramanik, 2003).

Although biodiesel is gradually replacing the conventional liquid fuel as major potential transportation fuel in future, current major drawbacks and debates which are being addressed include the high cost of the biodiesel, the food verses fuel delineation, the emission of nitrogen oxide on combustion, transportation difficulties, the poor performance of biodiesel in cold conditions compared to petroleum diesel due to its higher cloud and pour points (Levine *et al.,* 2010). These problems may be rectified by choosing the right feedstock and technology to achieve sustainability.

Biodiesel currently is mostly used as a blend with petrodiesel. Whilst it has been found that 100% biodiesel without any blend of petrodiesel (B100) eliminates almost 90% of air toxics, a blend of 20% of biodiesel (B20) with petrodiesel reduces the air toxins by about 20–40% (Joshi *et al.,* 2007; Marland, 2010; Pramanik, 2003). Also, the emission of NOx and SO_2 can also be reduced by almost 20% when biodiesel blends are used (Joshi *et al.,* 2007; Crutzen *et al.,* 2008). B100 and B20 are also found to reduce CO_2 emissions by more than 75% and 15% respectively over petroleum diesel (Balat, 2007; Radich, 2004)**.**

Biodiesel on combustion is found to reduce CO_2 emissions significantly by 70% compared to fossil fuel (REN21, 2010). On an energy basis, carbon trading has the potential to benefit biodiesel producers immensely in that it has about 92% of the energy content of petroleum diesel and saves about 6.5 kg of CO_2 emissions **(**Marticorena *et al.,* 2009; Sabine, 2004). The production and consumption of significant quantities of zero-emitting renewables could help mitigate the negative environmental impacts of fossil fuel use.

1.2.2 Non-Edible Feedstocks for Biodiesel Production

1.2.2(a) Jatropha curcas L. as a Second Generation Biodiesel feedstock

One of the ways to reduce the dependency on edible oil to make biodiesel is to use non-edible oils. Second generation biodiesel feedstocks are the non-edible oils from energy crops mostly with higher free fatty acids (FFA) such as jatropha (*Jatropha curcas L.*), castor beans, karanj (*Pongamia pinnata*), rubber seed (*Ficus elastic*), sea mango, camelina, seashore mallow, mustard, *Carapa procera*, jojoba, kusum, neem (Gui *et al.*, 2008; Heller, 1996; Gubitz *et al.*, 1999)**.** These crops easily survive on marginal agricultural lands where many other crops may not grow hence the problem of competition with food for land is solved. Jatropha in particular has an added advantage over other oil sources in that it is a drought-resistant plant capable of surviving in abandoned and fallowed agricultural land with an oil yield more than 4.5 tons/ha in the first year (Achten *et al.,* 2008; Henning, 1998). However, for increased oil yield (between 4.5- 15 tons/ha from 1st to 4th year of cultivation), proper soil management including fertilizer applications and irrigation must be used (Achten *et al.,* 2008). Therefore, the potential of using jatropha as a feedstock for biodiesel production has attracted much attention nowadays in most countries of the world.

Jatropha curcas L. is a small deciduous tree which originates from Mexico and Central America which has found its way in most tropical countries of the world especially Asian countries (Heller, 1996). Under normal conditions, the plant will fruit once a year. However, for higher yields, it may require 625-750 mm rainfall (Henning, 1998; Achten *et al.*, 2008) at productivity between 1.5 and 6 tons/ha/year (Tewari, 2007)**.** After 5 years of cultivation, depending on the genetic variety of seeds or cuttings used, the climatic conditions as well as the management technologies used, *Jatropha curcas L.* may yield 2-5 tons of dry seed/ha/year (Tewari, 2007)**.** Jatropha trees are productive for up to 30-40 years. With about 2,200 jatropha trees planted on a hectare of land, a yield around 7 tons of seeds per year can be obtained (Henning, 1998; Achten *et al.,* 2008). The seeds and oil from jatropha plant are non-edible due to the presence of phorbol esters, trypsin inhibitors, lectins, phytates which are considered to be toxins (Tewari, 2007)**.** The seeds have been analysed to contain about 35 to 40% oil i.e. 1.75 tons oil/ha after extraction (Henning, 1998; Achten *et al.*, 2008; Tewari, 2007; Gubitz *et al.*, 1999). The kennel however contains about 50 to 60% oil content by weight. Upon critical analysis of *J. curcas* seeds, it has been reported (Gubitz *et al*, 1999) that they contain 6.6% moisture, 18.2% protein, 38.0% fat, 17.3% carbohydrates, 15.5% fibre and 4.5% ash. The oil also contains about 21% saturated fatty acids and 79% unsaturated fatty acids (Gubitz *et al.,* 1999). *J. curcas* oil is found to be more environmentally safe, cost effective and has a high potential of being a substitute for petroleum diesel and kerosene. When the oil is converted to biodiesel, the properties are much enhanced thus excellent to replace fossil based fuels (Pramanik, 2003; Tewari, 2007).

The unique properties of *J. curcas* oil and its biodiesel make it a highly potential replacement of fossil based liquid fuel. The specific gravities of *J. curcas* oil and petroleum diesel are 0.9180 and 0.8410 respectively. Calorific values, flash points, cetane numbers and sulphur weights of *J. curcas* oil and petroleum diesel are 41 MJ/kg and 45 MJ/kg, >130^{o}C and 64^{o}C, 51 and 50, 0.13% and 1.2% respectively

(Gubitz *et al.,* 1999; Rosenblum, 2000; Radich, 2004). The higher flash point of *J. curcas* oil gives it certain advantages over petroleum diesel like greater safety during storage, handling and transport.

By the end of 2009, over 1 million hectares of land in India had undergone *Jatropha curcas L*. plantation purposely for commercial biodiesel production (Gubitz *et al*., 1999). This is the largest land size of *Jatropha curcas L*. cultivation in a single country as of 2010, which can replace 20% of India's diesel consumption by 2011 (Rosenblum, 2000). In Malaysia for example, there is a tremendous growth in biodiesel production from jatropha and over 500,000 hectares of land are under *Jatropha curcas L*. cultivation (Jayed *et al.,* 2009**).** In Africa, most countries including Ghana, Benin, Mali, South Africa and etc. have huge hectares of land undergoing *Jatropha curcas L*. cultivation for biodiesel production in commercial quantities. Globally, the number of companies producing biodiesel from *J. curcas* oil increased from 60 in 2005 to 224 in 2008 (CJR, 2010). **Figure 1.4** shows the estimated and projected share of jatropha biodiesel in the global biodiesel production from 2009 to 2015.

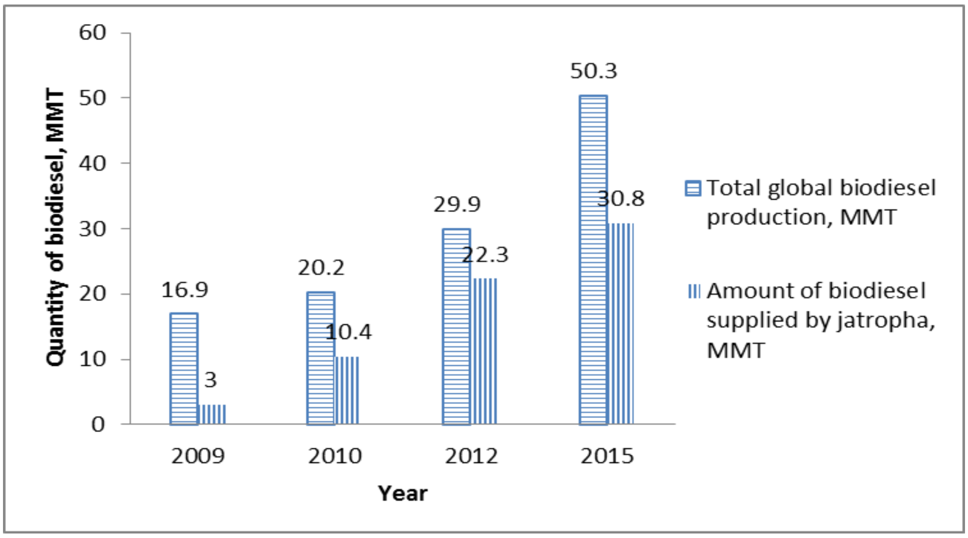

Figure 1.4: Projected share of jatropha biodiesel in the world’s total biodiesel production (CDIAC, 2010; EPI, 2010)

The energy balance of *Jatropha curcas L.* cultivation is reported to be positive (Tobin & Fulford, 2005). However, in the view point of energy use in terms of irrigation, transportation and etc., the energy balance may be negative. It has been reported by Kritana and Shabbir that the net energy consumption in producing 1 GJ of jatropha methyl ester is 0.884 GJ when screw press, solar fruit drying and alkali transesterification is employed (Kritana & Shabbir, 2006). This means that almost 90% of the energy in jatropha biodiesel is used to produce it. These data indicate that jatropha biodiesel production is energy intensive. This study aims at establishing the thermodynamic feasibility (input to output exergy) of jatropha and microalgal biodiesel production plants.

1.2.2(b) Energy security: The potential of microalgae for biodiesel production

The production of the algae biomass and subsequent conversion into fuel should consume less energy than that of inherent value of its biofuel in order to make it thermodynamically and economically sustainable (Patzek & Pimentel, 2005). Only a cost effective biofuel will compete effectively with conventional fuels at the world market (Haas, 2005). In algae biofuel production, these factors are influenced by the cell density and growth rate of the algal culture, which are in turn controlled in large part by photobioreactor configuration, nutrient supply (Benemann *et al.,* 1980), and oil extraction equipment design.

Microalgae can be cultivated under difficult agro-climatic conditions and are able to produce byproducts such as fats and oils, sugars and etc. (Chisti, 2007). It also has a high possibility to uptake industrial sources of CO_2 (it needs more than 2 tons of CO_2 to produce 1 ton of microalgae biomass). With this unique pollution-control characteristic and the large quantity of oil yield per hectare of land, it is considered to have an extraordinary potential for commercial cultivation as feedstock for the production of biodiesel (US DOE, 2009**).** The high preference of microalgae to all other biofuel feedstocks for biodiesel is due to its less complex structure, fast growth rate, CO_2 sequestration and high oil content of between 58,700-136,900 litre/ha/year (Chisti, 2007**).** Previous researches have concluded that microalgae may be up to 40 times more productive as a biodiesel feedstock in terms of oil yield per unit area (between 14,000-28,000 l/ha/yr) than conventional terrestrial crops (~4752 l/ha/yr for palm oil, ~2151 l/ha/yr for coconut oil, ~954 l/ha/yr for rapeseed oil and ~680 l/ha/yr for jatropha curcas oil) (Sheehan *et al.,* 1998; Dar, 2006). However, according to the research conducted by U.S. Department of Energy Aquatic Species Program, the costs of algae production and processing are very high (averagely US$ 3.78/liter and US$ 6.11/liter algal biodiesel for cultivation in ponds and photobioreactors respectively) and thus the use of algae as a feedstock for biodiesel is not attractive (US DOE; Sheehan *et al.*, 1998; YouCho project report, 2010). Notwithstanding these findings, the Aquatic Species Program close-out report concluded that algal wastewater treatment might be effectively combined with algae biodiesel production in order to reduce the cost (Sheehan *et al.*, 1998). Third generation biofuel feedstocks, specifically microalgae does not directly affect human food chain and can be grown in places which are not suitable for food crop production. This makes it high potential feedstock for biodiesel production.

On the other hand, there are some drawbacks of using microalgae for biodiesel which include a negative net energy ratio due to the high energy consumption for water pumping, CO_2 distribution, mixing and harvesting, oil extraction as well as the biodiesel production processes (Li *et al.,* 2008; Peralta *et al.,* 2010; SBI Energy, 2010). Such an energy intensive production needs a critical attention on how to minimize internal and external exergy losses due to the generation of entropy resulting from irreversibilities. There is also the problem of instability of the culture resulting in photo saturation, photo inhibition and photo acclimation due to difficulty in maintaining a particular species of microalgae (Chisti, 2007**).** This instability results in entropy generation leading to exergy destruction.

In 2010, the world's market size for algae cultivation and subsequent production of biodiesel was estimated at US$ 271 million and expected to show an annual growth rate of nearly 43% (SBI Energy, 2010) with the cultivation technology sales holding most of the total algae biofuels production technologies market (SBI Energy, 2010). Before the year 2000, there were roughly 10 companies worldwide pursuing the development of algae biofuels as their sole business area or in relation to other business operations such as algae production or renewable fuels (SBI Energy, 2010**).** By 2009, the number of companies involved in the development and implementation of algae biofuels technologies had grown to over 60 worldwide. Most of these companies are operating on pilot basis. Different technologies of cultivating microalgae are employed by these companies. For instance, U.S. is forecasted to represent over 82% of the global market for open pond algae cultivation systems from 2010-2015, while the E.U and Asian markets are expected to claim 11% and 7% respectively (US DOE, 2009). **Figure 1.5** shows the percentage of worldwide technologies used in microalgae cultivation (SBI, 2010**).**

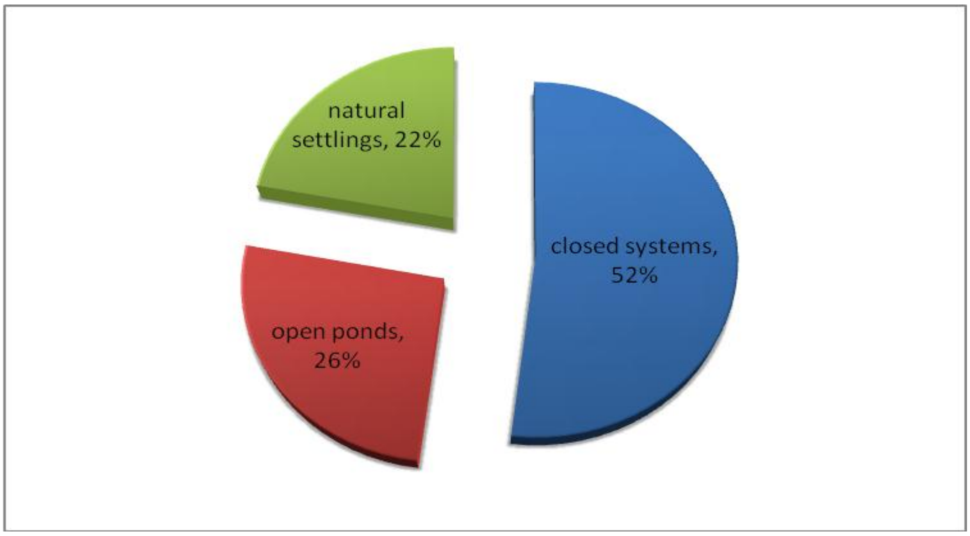

Figure 1.5: Worldwide technologies being used for algae biofuel production companies (SBI Energy, 2010).

Closed systems like photobioreactors are commonly used by most algal production industries hence energy and exergy efficiency improvements on photobioreactors must be assessed. This study considers photobioreactor for algae cultivation.

1.3 Exergy and sustainable development

1.3.1 Thermodynamic and exergy analyses of a process

Because most of the industrial processes are mainly energy conversion processes, sustainable development coupled with the efficient use of resources is vital for sound economic growth of every nation. Presently, the focus on environmental safety is gradually shifting towards energy efficiency in industrial processes. Exergy analysis which is synonymous to thermodynamic analysis is a suitable scientific concept in the work towards sustainable energy development (Bejan *et al.*, 1996; Ayres, 2007; De Swaan *et al.,* 2004).

Exergy refers to the maximum portion of an energy form in a reversible process that can be transformed into work. In other words, the usable energy in a system or resource is called exergy and can be measured as the total of the free energies within the system. Exergy is based on the applications of both the first and second laws of thermodynamics.

The first law of thermodynamics explains the fact that in a system, energy is neither created nor destroyed, which means energy is always conserved. In other words, the total amount of energy and matter involved in a process is never consumed hence a reversible process (Bridgman, 1943; Callen, 1960). In reality however, no process takes place in accordance with this law but in almost all processes, there is the generation of entropy leading to the destruction of exergy. Hence, the thermodynamic feasibility study by taking into account the contribution of energy alone is not sufficient as it does not capture the irreversible nature of each process due to the entropy losses.

The exergy value of a steady stream of fluid entering or leaving any part of a process is the minimum amount of energy or work that can be obtained from that stream in bringing it to equilibrium with its environment (Keenan, 1951; Sussman, 1980; Szargut *et al.*, 1988; Kotas, 1985; Dewar, 2005). This is expressed mathematically by **Equation 1.1:**

$$Ex_{ph} = (H - H_0) - T_0(S - S_0) \qquad \textbf{(1.1)}$$

This equation is similar to Gibbs' free energy expression except that for physical exergy, the reference temperature is the system's environmental temperature (since it has to be in equilibrium with its surrounding) which is often taken as 25^0C.

With real (irreversible) processes there is always an increase in entropy. This extra entropy (exergy loss) is either released into the environment or destroyed within the process (Georgescu-Roegen, 1971; Keenan, 1951; Gibbs, 1873). Though entropy generation is unavoidable in a process, it can be minimized to a higher extent in such a way that the ratio of the total exergy of the product to the total exergy of the inputs can be between 0.80 and 0.99 for a thermodynamically sustainable production. **Figure 1.6** shows the relationship between the thermo-mechanical exergy (physical exergy) and entropy. **Figure 1.6** again illustrates the variation of temperature change with entropy change of a process. The diagram illustrates that, below a certain temperature, entropy generation is unavoidable hence resulting in exergy destruction.

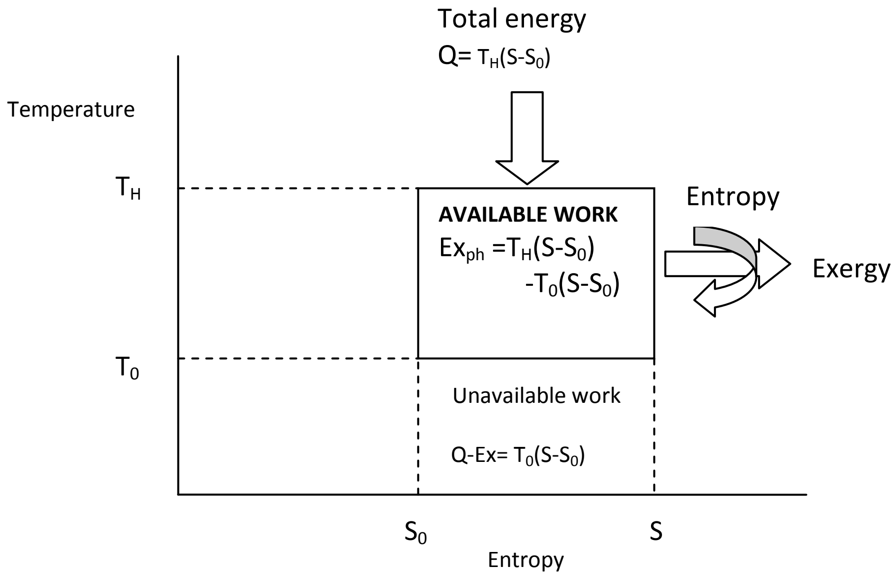

Figure 1.6: Carnot cycle between temperature change and entropy (Bejan, 1997)

The sustainability of an industrial process is characterized by three main factors namely social, economic and environmental aspects (Rucker & Gruhn, 1999; Ayres *et al.*, 2007; Berthiaume *et al.*, 1987; De Swaan *et al.*, 2004). Thermodynamic efficiency assessment combines both the economic and environmental aspects of sustainability (Valero *et al.,* 1986). The second law of thermodynamics is used to describe the quality and quantity of energy as well as its degradation within a system (Bejan *et al.,* 1996; Ayres *et al.,* 1998; Ayres & Ayres, 1998; Fiorini & Sciubba, 2005**).** The application of this law allows the true thermodynamic efficiencies of industrial processes to be assessed (Gaggioli, *et al.,* 1983), the primary causes of their inefficiencies to be established (Ahern, 1980; Ayres *et al.,* 2007) and the costs of obtaining their internal flows and productions to be assigned in a more comprehensive way (Ayres *et al.,* 2007; De Swaan *et al.,* 2004; Doldersum, 1998).

Exergy concept and tools are essential to the creation of a new engineering paradigm towards sustainable energy development. There are most at times controversies when the expressions such as ‘energy consumption’, ‘energy saving’ and ‘energy conservation’, are used to implicitly refer to ‘energy’ as intense energy available from fossil fuel. If energy is always conserved in a process, then it would not be logic to talk about ‘energy conservation’. The quantity that is actually consumed in a process is exergy not energy (Wall, 1977; Wepfer *et al.,* 1979). Exergy helps to articulate the amount of resources that is consumed in any industrial process by quantifying the exergy loss occurring in each unit operation. Both Exergy and entropy, clearly define the resources consumed and the waste generated. Exergy quantifies the effect of energy and matter dissipation (entropy) whilst entropy quantifies the state of dispersion i.e. the degree to which energy and matter are dispersed in a particular process (Gibbs, 1873; Asada *et al.,* 1999; Gaggioli, 1983; Olawale & Adefila, 1998).

The responsible use of biofuels should consider the issues of resource availability and utilization, economic investment and environmental impacts.

Resource use (materials and energy) and environmental impact studies are accounted for in physical or equivalent units (tons, joules, kg equivalent of CO_2 and etc.) whereas economic investments are accounted for in monetary units (Ayres & Ayres, 1998; Ayres *et al.*, 1998; Seader, 1982; Tsatsaronis, 1999b). Chapter two of this thesis gives a detailed explanation of the concept of exergy and thermodynamic analyses as well as their applications by various researches.

1.4 Problem Statement

Liquid fuel such as gasoline, petro-diesel and etc., is reported to be consumed more than any other fuel in the world. However, estimates of crude oil reserves show that its exhaustion will occur in 2047 at a rate of 83 million barrels per day compared to an extraction rate of approximately 98 million barrels/day in 2010 (IEA, 2010a)**.** Biodiesel, a non-exhaustible bio-liquid presents a better option to replace fossil based liquid fuel in the near future. *Jatropha curcas L.* and microalgae have gained international acceptance as potential feedstock for biodiesel production. Microalgae have significantly higher areal productivity and their growth in saline media or in photobioreactors on large scale do not compete with agriculture for the very limited land and fresh water resources. Also, biodiesel from *Jatropha curcas L.* presently forms about 50% of the total share of world's biodiesel production with over 300 companies involved. Moreover, environmental assessments of the various emissions from biodiesel produced via these feedstocks are approximately half of those from petroleum diesel. Hence the complete substitution of the world's petroleum diesel usage by biodiesel from *Jatropha curcas L.* and microalgae would lead to a reduction in greenhouse gas emissions of approximately 25 metric tons CO_2-eq per annum

(Sabine, 2004). It is in this view that this study considers *Jatropha curcas L.* and microalgae (*Chlorella sp.*) as the biodiesel feedstock for the exergy analysis.

The focus of sustainable development is gradually shifting towards thermodynamic efficiencies in industrial processes (Ayres *et al.*, 1998; De Meester *et al.*, 2006). Energy resource consumption has been shown to be the principal cost of many energy-intensive chemical processes, such as biodiesel production (Talens *et al.*, 2010) from *Jatropha curcas L.* and microalgae. Due to this, the vision of energy-intensive process design has been to reduce energy consumption hence a decrease in capital cost. The problem that arises with biodiesel production either domestically or commercially becomes more difficult when there is the lack of expertise to adopt technologies that minimize energy losses. Previous researches on exergy analysis of biodiesel production plants are focused on only the transesterification unit (Peralta *et al.*, 2010; Sorguven *et al.,* 2010; Talens *et al.,* 2007). However, the results from this unit alone cannot justify the thermodynamic feasibility of biodiesel production plants. Feedstock cultivation and oil extraction are reported to be energy intensive, and in any energy intensive process, there is great destruction of exergy reducing the efficiency of the plant. It is in this respect that this study objectively assesses the feasibility of biodiesel production plants via exergy analysis so as to help locate possible improvement potentials within the plants.

This study presents a comparative exergy analyses of the biodiesel production processes simulated with Aspen Plus software (Aspen Tech., 2004) to assess the thermodynamic feasibility (ratio of output exergy to input exergy must be very close to 1 for a thermodynamically feasible production) of the plants.

1.5 Research Objectives

- To simulate microalgal methyl ester (MME) and jatropha methyl ester (JME) production processes in Aspen plus software for thermodynamic properties.
- To assess the thermodynamic feasibility of biodiesel production processes from *Jatropha curcas L.* and microalgae using thermodynamic efficiency assessment tool (Exergy Analysis).
- To locate major unit operations within the production plants where there is high exergy destruction.
- To suggest improvement options for a sustainable MME and JME production plants.
- To compare the renewability of microalgae and jatropha biodiesel production plants.

1.6 Scope and Limitations of the study

This study uses standard chemical exergy data from literature (Szargut, 1989; Rivero & Garfias, 2006), experimental results (Undocumented results of USM School of Chemical Engineering Environmental Research Laboratory work ; Kian *et al.*, 2011) and industrial data (Chisti, 2007; Ugwu *et al.*, 2008; Xu *et al.*, 2006; Brian, 2011; Tredici, 1999; Gubitz *et al.*, 1999; Mendoza *et al.*, 2007; Tobin & Fulford, 2005; Achten *et al.*, 2008) on microalgal and jatropha biodiesel production processes. The mathematical analyses were done based on thermodynamic properties (entropy and enthalpy values) which were obtained from Aspen plus software version 2006 (Aspen Tech., 2006).

1.7 Thesis Organization

This thesis comprises five major chapters with headings Introduction, Literature review, Research Methodology, Results and discussions and Conclusion.

Chapter one gives an introduction to the main subject (exergy and sustainable development) under study. It begins with the overview of fast depletion of fossil based fuel and their impacts on energy efficiency of a production plant. This chapter again gives a summary of the development of biodiesel from jatropha and microalgae hence their potential of replacing fossil fuel. Thermodynamics and exergy analysis are also discussed and related to the production of biodiesel with the overview of some publications done on exergy analysis for process improvement. This chapter finally gives the problem statement and outlines the objectives of this study.

Chapter two presents the literature review on exergy analysis including the three main thermodynamic performance parameters (exergy destruction, exergy efficiency and thermodynamic improvement potential). The differences between energy, entropy and exergy are clearly discussed in this chapter. The conversion processes of jatropha and microalgae into biodiesel are also reviewed. An overview of the renewability indicator which predicts the renewability of a production plant is also given in this chapter.

Chapter three outlines and elaborates on the major steps or methodology employed in this study. These steps include the definition of system boundary, simulation of MME and JME production processes in Aspen plus, estimation of chemical exergy of all inputs and output streams, calculations of physical exergy using the generated thermodynamic properties obtained from Aspen plus and finally carrying out exergy balance on the whole plants.

Chapter four presents the results from the exergy analysis done on both the MME and JME production plants based on the system boundary given in **chapter three**. This chapter further discusses the results and suggests improvement options in biodiesel production plants. The flow diagrams obtained from the simulation with Aspen plus are given. The calculations of the chemical and physical exergies of every stream in the MME and JME production plants are given. Summary of exergy balance calculations are also presented and compared with results of other studies.

Chapter five summarizes the results of this study and gives possible recommendations for future studies related to exergy analysis of MME and JME production plants.

CHAPTER TWO

LITERATURE REVIEW

This chapter gives an overview of thermodynamics and exergy analyses of industrial processes. The concepts of energy, entropy and exergy are explained and their differences clearly defined. Reviews on the thermodynamic performance parameters determined in this work are given. Overview of the case studies (jatropha and microalgal biodiesel production processes) for the exergy analysis are also elaborated in this chapter.

2.1 Thermodynamic Concepts: Energy, Entropy and Exergy

2.1.1 Comparison of energy and exergy as applied to industrial processes

The differences between energy and exergy have not been clearly stated in most research papers. Energy is a physical quantity which cannot be destroyed but conserved for all processes and it is dependent on properties of only matter or energy flows and independent on environmental properties based on the first law of thermodynamics. Energy analysis has been criticized in most cases because it does not quantify the quality of resource consumption in a production process. Energy balance provides no information on the degradation of energy resources during a process (Sorguven & Ozilgen 2010; Valero *et al.*, 1986; Wall, 1977). Moreover, it does not quantify the usefulness or quality of the various energy and material streams flowing through a system as well as those existing as products and wastes.