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Feasibility study of microalgal and jatropha biodiesel production plants: Exergy analysis approach

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ABSTRACT

The exergy analyses performed in this study are based on three thermodynamic performance parameters namely exergy destruction, exergy efficiency and thermodynamic improvement potentials. After mathematical analysis with Aspen Plus software, the results showed that 64% and 44% of the total exergy content of the input resources into microalgal methyl ester (MME) and jatropha methyl ester (JME) production plants were destroyed respectively for 1 ton of biodiesel produced. This implies that only 36% and 56% (for MME and JME production plants respectively) useful energy in the products is available to do work. The highest and lowest exergy destructions were recorded in the oil extraction units (38% and 39% of the total exergy destroyed for MME and JME plants respectively) and transesterification units (5% and 2% of total exergy destroyed for MME and JME plants respectively) respectively for 1 ton biodiesel produced. Since sustainable biodiesel production depends on cultivation of feedstock, oil extraction and transesterification processes, exergy analysis which is carried out on only the transesterification unit cannot justify the thermodynamic feasibility of the whole biodiesel production plant unless a complete thermodynamic assessment has been done for the whole plant. Thus, according to this study which considers all the biodiesel production processes, MME and JME production plants are not thermodynamically feasible.

1. Introduction

Though liquid fuel such as gasoline, petro-diesel etc., is reported to be consumed more than any other fuel in the world, the 2010 global production or supply of crude oil (of about 72 million barrels/day) was less than the global demand (about 86 million barrels/day) [1]. Again, the peak of extraction of crude oil is predicted to occur in 2047 [2] implying that world's energy security based on liquid fossil fuel cannot be completely assured in the next 50 or less years.

Biodiesel, a non-exhaustible liquid biofuel therefore presents a better option to replace fossil based liquid fuel in the near future. Microalgae have significantly higher areal productivity (between 58,700–136,900 L/ha/year) [3] 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. By the year 2009, the number of companies involved in the development and implementation of algae biofuels technologies had increased to over 60 worldwide [4]. Biodiesel from *Jatropha curcas* oil presently forms about 50% of the total share of world's biodiesel production with over 300 companies involved [4]. These data illustrates the potential of microalgal and jatropha biodiesel as reliable sources of liquid biofuels to replace fossil based liquid fuel in the near future. Thus, the production processes of the methyl esters from these feedstocks must well be analysed with respect to resource consumption in order to ascertain the sustainability of the production plants and suggest improvements for their performances.

Nowadays, sustainable energy development has been the issue of discussion concerning the production of biofuels since fossil fuel is consumed in large quantities during biofuels production. Energy resource consumption has been found to be the principal cost of many energy-intensive chemical processes such as biodiesel production [5] from jatropha and microalgae. Due to this, the vision of energy-intensive process designs has been to reduce energy consumption so as to decrease its capital and operational costs. The

Abbreviations: JME, jatropha methyl ester; MME, microalgae methyl ester; UCOME, used cooking oil methyl ester; LABEN, labour energy (MJ/ha); LABOUR, number of working labourers; TIME, operating time (h); AREA, operating area (ha); LABENF, labour energy factor (MJ/h); ED, specific direct energy use (fuel) for field operation (MJ/ha); AFU, average fuel use per working hour (l/h); PEU, specific energy value per litre of fuel (MJ/l); RU, runs (number of application in the considered field operation).

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Symbols

h	Specific working hours per run (h/ha)
Ex_{tot}	Total exergy (MJ)
$Ex^0_{ch,i}$	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)
ΔG_{fo}	Standard Gibbs free energy of formation (kJ/mol), (kJ/kg)
Ex_{dest}	Total exergy destroyed, MJ
S_{gen}	Entropy generation
R	Ideal gas constant = 8.314 J/mol K
T	Temperature
T_0	Reference temperature = 273.15 K
p_i	Pressure of *i*th component (kPa)
p_0	Reference pressure = 1atm = 101.3 kPa
v_i	Number of moles of component *i*
H	Specific enthalpy (kJ/kg)
H_0	Specific enthalpy at T_0, p_0 (kJ/kg)
S	Specific entropy (kJ/kgK)
S_0	Specific entropy at T_0, p_0 (kJ/kgK)
Q	Heat flux (W/m^2)
C_p	Specific heat capacity (kJ/kmol K)
m_i	Mass of *i*th component (kg)
Ex_i	Exergy of ith component (MJ/kg)
C_i	Final concentration
C_{io}	Initial concentration

problem that arises with biodiesel production either small or large scale becomes more difficult when there is lack of expertise to adopt technologies that would minimize exergy losses. Previous researches on exergy analysis of biodiesel production plants [6–8] are focused on only the transesterification unit unlike in this study which takes into account feedstock cultivation, oil extraction and methanol recovery processes. Peralta et al. [6] used Aspen Plus to analyse the exergetic efficiency of biodiesel production from microalgae. Their study concentrated on only the transesterification and methanol recovery units which resulted in 79% exergetically efficient production system. Sorguven, and Ozilgen [7] also concluded that algae-biodiesel-carbon dioxide cycle provides a positive amount of useful work. For a renewability indicator of 0.27, they concluded that nearly three fourth of the work potential of algal biodiesel is used for its production and to restore the environment. This clearly shows that the production of algae is a critical stage which needs to be addressed in order to increase its exergy efficiency. Thus, the results from only one biodiesel production unit such as the transesterification unit alone cannot justify the thermodynamic feasibility of biodiesel production plants. A single unit may show very high exergy efficiency whilst a combination of all the processes may present a different results all together. Talens et al. [8] have also reported about 98.54% exergetically efficient production of biodiesel from used cooking oil. Their studied also focused on only transesterification unit because feedstock cultivation and oil extraction are not necessary when used cooking oil is used. The type of oil used also accounts for the final exergy efficiency of the whole production system.

Feedstock cultivation and oil extraction are reported to be energy intensive, and in any energy-intensive process, there is high destruction of exergy which tends to reduce the efficiency of the plant. It is in this respect that this study objectively assesses the feasibility of biodiesel production plants (from the feedstock cultivation to biodiesel purification) via exergy analysis so as to help locate possible improvement potentials within MME and JME production plants.

Irreversibility caused by entropy generation in industrial processes reduces the efficiencies of the processes. It is therefore important to design and build high performance engineering process equipment which are efficient not only in terms of the quantity of energy (the first law) but also the conservation of energy quality (second law) [7].

1.1. Thermodynamic analysis

The focus on environmental safety should be geared towards sustainable ways of transforming resources into useful products. Since most of the industrial processes are mainly energy conversion processes, sustainable development and efficient use of resources must be adopted to increase economic growth. Economic analyses as well as energy analysis have been criticized due to their inability to quantify the energy quality embedded in a resource as well as the degradation of energy in a process. According to the first law of thermodynamics, energy is conserved for all processes [9] hence cannot be degraded. Exergy analysis or second law analysis has been a better scientific tool that is used to promote sustainable energy development since the quantity of quality energy can be quantified and its consumption rate assessed. Exergy analysis therefore combines both the first and second laws of thermodynamics to detect thermodynamic imperfections in a system and help suggest improvement options.

Exergy is that part of energy that has the potential to be fully converted into mechanical work i.e. the most valuable form of energy or the content of energy that is drawn from a system when it is brought to thermal, mechanical or chemical equilibrium with its environment through reversible processes [10–12]. The second law of thermodynamics is used to describe the quality and quantity of energy utilized or degraded in a process. Thermodynamic efficiency assessment combines both the economic and environmental aspects of sustainability thus assigning the costs of obtaining their internal flows and products in a more comprehensive way [10,11]. Therefore, the efficient management of renewable energy resources should address the issues of resource availability, (exergy) consumption and utilization as well as the impacts on the environment.

In real processes, the conversion of resources to useful products results in the production of work, heat and materials. The final exergy contents of the products (including wastes) would differ from the initial exergy contents of the input resources; either the energy quality of the product is upgraded or degraded. Entropy generation ($S_{generation}$) leading to exergy destruction ($Ex_{destruction}$) in a system is the main cause of the change in the exergy contents of the products [10].

The applications of exergy analysis in design and development of sustainable processes would not only help in technology advancement towards resource saving and efficient technology, but would also provide valuable information for long-term planning of resource management and policy implementation [13].

2. Methodology

2.1. Process description and system boundary

Undocumented results and procedures from USM School of Engineering Environmental Research Laboratory work [14] as well as other experimental and literature values from [3,15–18] were used for the materials and energy balance calculations for MME plant. For JME production plant, results based on experimental and industrial production processes from [19–23] were used for the material and energy balance calculations.

The system boundaries for both cases (i.e. jatropha and microalgal biodiesel production processes) comprise feedstock cultivation, oil extraction, solid acid catalyzed transesterification, biodiesel purification and glycerin separation/methanol recovery which are summarized in Figs. 1 and 2 for MME and JME production plants respectively. The legends for both figures are given in Supplementary data.

Process chains such as the supply chain for fertilizer production, hexane, methanol, sulphated zirconia catalysts productions and the manufacture of machines and equipment are not included in the system boundary. The supply chain for the production of the seed algae (algal strains) used for culturing as well as the manufacture or *J. curcas* seed for cultivation are also not considered. This is because cumulative exergy consumption (CExC) values which take into consideration the chemical exergy for the initial production of all these resources (raw materials) are not used for this analysis but instead, only the chemical exergy values for the raw material are used.

Pre-treatment of microalgal oil before transesterification is not considered as part of the system boundary. Though microalgal oil may contain high content of free fatty acids (FFA), the acid catalyst (sulphated zirconia) used in this study is capable of esterifying the FFA to achieve high biodiesel yield hence no need for pretreatment of the oil [19].

All forms of wastes (e.g. microalgal biomass after solvent extraction) generated in the process are considered not treated or recycled. Most of the companies involved in algae cultivation, oil extraction processes and biodiesel production currently do not pretreat the cake or convert them to useful products due to lack of technology. Research and developments are currently in progress to address the use of microalgae and *J. curcas* biomass (cake) for conversion into sugars and other products. For this reason, various treatment processes on the cake are not considered as part of the system boundary in order to obtain a fair idea of the exergy analysis of current biodiesel production processes. The partial drying of *J. curcas* fruits under the sun onsite and manual harvesting of the fruits are part of the system boundary. Transportation of *J. curcas* fruits from farm to crusher and transportation within MME plant are part of the system boundary.

The direct energy utilization per hectare of farming land was calculated by using Eq. (1) for mechanized cropping system and normalized to 0.599 ha [24]:

$$ED = h \times AFU \times PEU \times RU \tag{1}$$

where, h = specific working hours per run (h/ha); ED = specific direct energy use (fuel) for field operation (MJ/ha); AFU = average fuel use per working hour (l/h); PEU = specific energy value per litre of fuel (MJ/l); RU = runs (number of application in the considered field operation)

The labour energy input (MJ/ha) at every stage in the production processes was estimated using Eq. (2) [24]:

$$\text{LABEN} = \frac{\text{LABOUR} \times \text{TIME}}{\text{AREA}} \times \text{LABENF} \tag{2}$$

where, LABEN = labour energy (MJ/ha); LABOUR = number of working labourers; TIME = operating time (h); AREA = operating area (ha); LABENF = labour energy factor (MJ/h).

Also for 1 ton biodiesel from microalgae, 2302 kg of *Chlorella* sp. strains were cultured in an organic medium (NPK fertilizer) to obtain the algae biomass using a photobioreactor. Methanol and hexane were used as solvents for microalgal and *J. curcas* oil extractions respectively at temperatures between 60 and 65 °C. The results were then normalized to 1 ton of biodiesel for both MME and JME production plants.

2.2. Simulation of biodiesel production processes in Aspen Plus software

Process simulation may not guarantee 100% correct results compared to real processes or plants but can provide opportunity to design and test the unit operations in the shortest possible time as well as justifying results that cannot be verified experimentally in

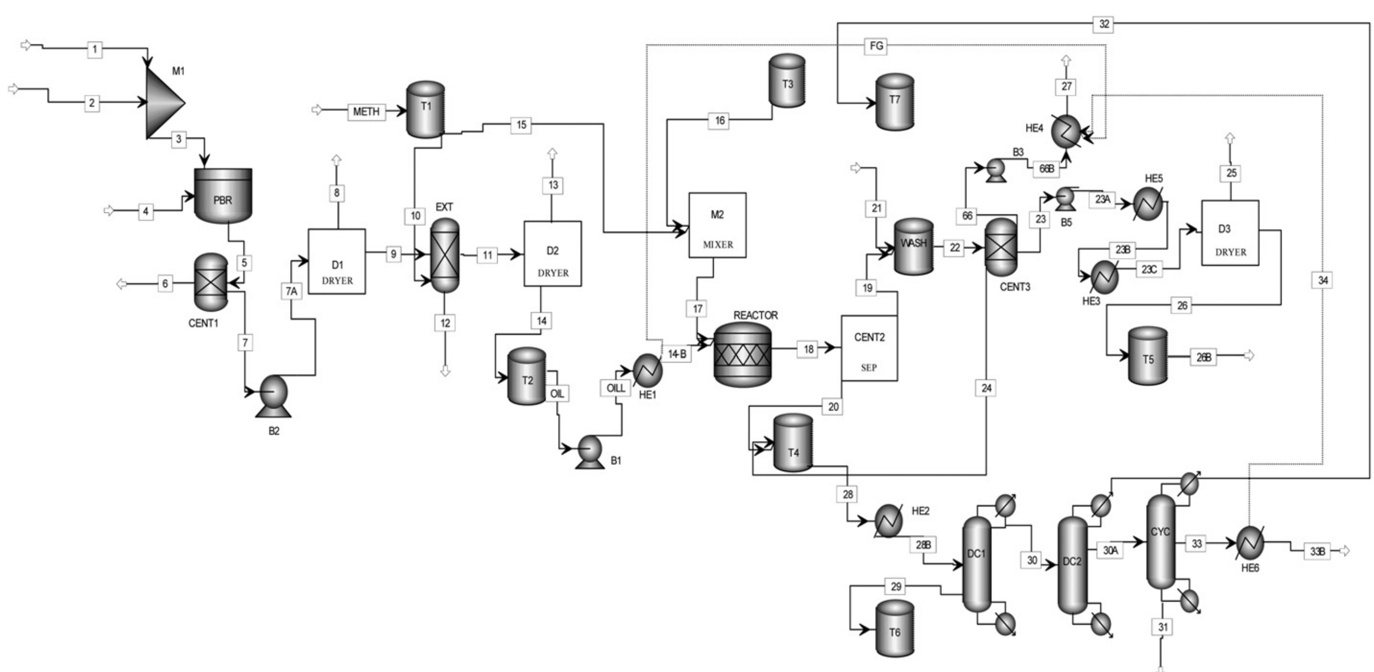

Fig. 1. Flow diagram of biodiesel production from *Chlorella sp*. Legend is shown in supplementary page.

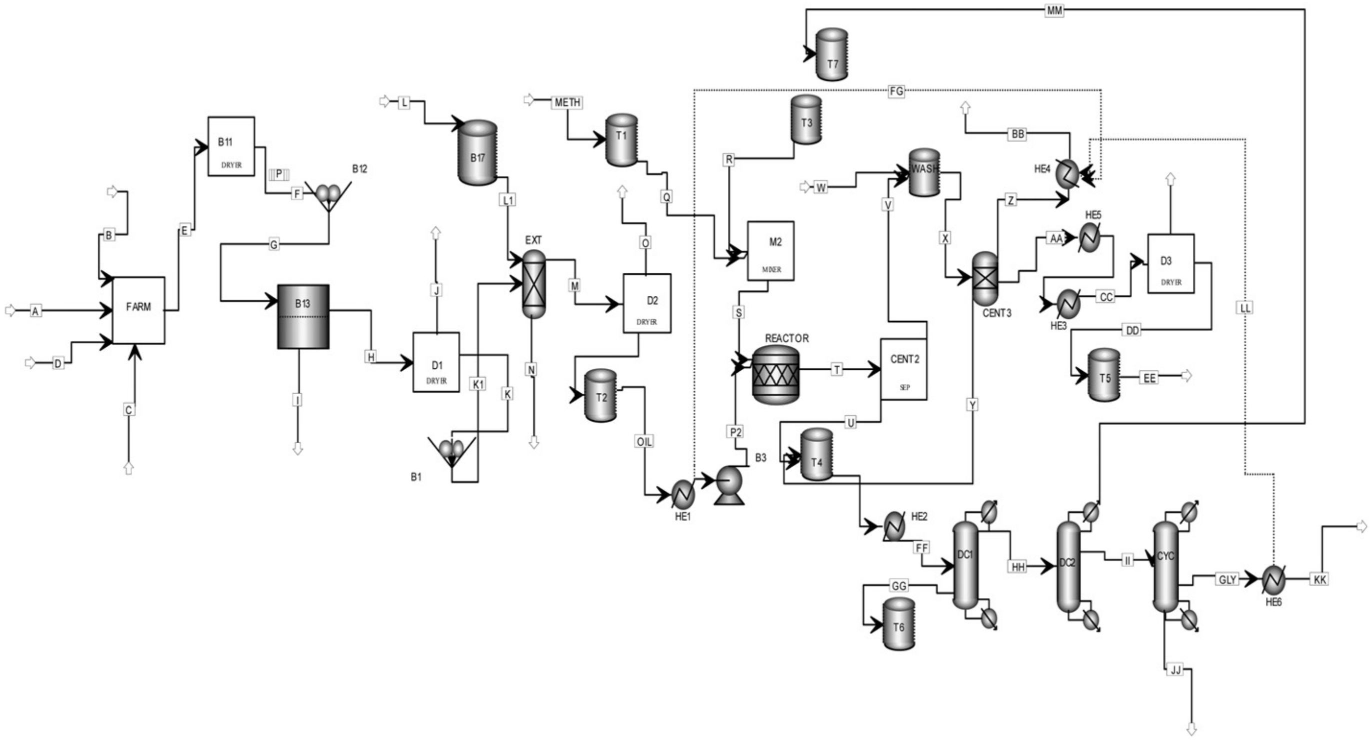

Fig. 2. Flow diagram of biodiesel production process from *Jatropha curcas* seeds (Legend is provided in the supplementary page).

laboratory or on pilot scale. For this study, due to the presence of vapour–liquid components such as methanol and glycerol, the Non-Random Two Liquid (NRTL) model was used to predict the activity coefficients of the components in the liquid phase [25]. NRTL model is developed to capture the local concentration gradient between the molecule of interest with the surrounding media. This scenario creates an interaction of energy difference among the involved molecules [26]. Process flows and conditions were chosen based on both experimental [19,27] and industrial data from literature [20,23,28,29].

Based on the data reported by Petkov and García [30] and Levine et al. [31], for *Chlorella* sp., three fatty acids with the highest compositions (triglycerides 16:0, 18:1 and 18:3) are chosen for the simulation. The algal oil, according to this work is assumed to largely contain the triglycerides C16:0 (palmitic acid), C18:1 (oleic acid) and C18:3 (Linolenic acid). Acid catalyzed transesterification using the solid acid catalyst sulphated zirconia (SO_4^{2-}/ZrO_2) was therefore used in this study. The optimum reaction temperature used was 150 °C at 1 bar. 96.7% of the triglycerides which enters the reactor were assumed to be transformed into biodiesel [19]. The methyl ester phase containing glycerides, methyl esters and methanol was fed into a water washer operating at 55 °C, to purify the biodiesel which was later separated and dried.

According to Edem [32], *J. curcas* oil is mainly composed of 44% oleic acid (C18:1), 34.3% linoleic acid (C18:2), 14.2% palmitic acid (C16:0), 7% stearic acid (C18:0) and the rest are other fatty acids. In this study, oleic acid, palmitic and linoleic acids were chosen to be the main fatty acids in *J. curcas* oil. A ten ideal stage with total condenser, kettle reboiler and a 2.5 reflux ratio were used to remove approximately 97% of the methanol in the biodiesel stream. Eight ideal stages with total condenser, kettle reboiler, and a 1.5 reflux ratio were used to separate the biodiesel from excess water. It has been reported by Gomez-Castro et al. [33] that column ideal stage between 9 and 15 is recommended for separation of water and methanol in biodiesel production.

2.3. Exergy calculations

In this work, steady-state flow processes originally at ambient conditions, P_0 (1atm) and T_0 (25 °C) were considered for the simulation. For streams comprising the physical mixing of solids or liquids at temperature T, chemical exergy, $Ex_{\mathrm{ch},i}$, is calculated using Eq. (3) [34–36]:

$$Ex_{\mathrm{ch},i} = \Delta G_{\mathrm{fo}} + \sum_i \nu_i Ex^0_{\mathrm{ch},i}. \tag{3}$$

where, ΔG_{fo} is the Gibbs free energy of formation; $Ex^0_{\mathrm{ch},i}$ is the standard chemical exergy of the ith component; ν_i = mole ratio of the ith component

The environmental states (surrounding's conditions), $T_0 = 25$ °C and $P_0 = 1$ atm are considered the same as the standard state, hence $Ex_{\mathrm{ch},i} = Ex^0_{\mathrm{ch},i}$. The exergy content (expressed as density) of microalgae was calculated from the expression proposed by Jorgensen [37] for the approximate calculation of exergy of organisms in an ecosystem, as stated in Eq. (4):

$$Ex = RT\sum\nolimits_{i=0}^{i=n_i} C_i In C_i/C_{io} \tag{4}$$

where, C_i = final concentration; C_{io} = initial concentration; R and T are the gas constant and temperature respectively

The contribution of exergy by detritus per litre of water can be obtained when g/l is used as the unit for the concentration. The chemical exergy of microalgae is therefore found to be 64.2 MJ/kg [37–39] based on energy contained in detritus i.e. 1 g detritus in average, has about 18.7 kJ exergy [37].

The physical exergy of each stream of matter were calculated based on the thermodynamic properties given by Aspen Plus after process simulation. The method and equation used by Szargut et al. [35] was used calculate the physical exergy of each stream.

3. Results and discussion

The chemical exergies of the main inputs and outputs for both cases are presented in Table 1. All the utilities used throughout the production processes were assumed to be fossil-based electricity, steam generated from fossil based firing and diesel from crude oil. The thermodynamic properties obtained after process simulation in Aspen Plus software are shown in Table 2.

The internal exergy destruction (which is unavoidable but can be minimized) was calculated by deducting the total exergy output (Ex_{out}) from the total exergy input (Ex_{in}) for every single unit operation with the help of the Gouy–Stodola theorem [40]. The external exergy destruction (which is avoidable) is equal to the sum of the exergy of all waste streams in the production process. Exergy efficiency, η, is the ratio of total exergy output to the total exergy input of the production process. The exergy improvement potential, $Ex_{improv\text{-}pot}$, is therefore defined mathematically by Eq. (5) [41]:

$$Ex_{improv-pot} = Ex_{dest-internal}(1-\eta) + Ex_{waste-to-environment} \quad (5)$$

where, $Ex_{dest\text{-}internal}$ is the internal exergy destruction (resulting from entropy generation); η is the exergy efficiency and $Ex_{waste\text{-}to\text{-}environment}$ is the external exergy destruction.

Table 1
Chemical exergy of major inputs and outputs into 1 ton of MME and JME production.

Substance	Stream number	Chemical formula	Mass kg	Standard Chem. exergy ($Ex^0_{ch,i}$) MJ/kg	Chemical exergy ($Ex_{ch,i}$) MJ
Inputs					
CULTIVATION					
Algae cultivation					
Chlorella vulgaris	4	$C_{24}H_{44}O_6$	2302.1	64.2[a]	147794.8
Water	1	$H_2O(l)$	11529.0	0.049	564.9
NPK fertilizer	2	N–P–K	63.6	18.57[b]	1181.1
Jatropha cultivation					
J. curcas treated seeds	C	$C_{56}H_{109}O_6$	3.74	17.73	66.3
Irrigation water	A	H_2O (l)	5970.0	0.049	292.6
NPK fertilizer	B	N–P–K	1626.3	18.57[b]	30200.4
Pesticide (chlorpyrifos)	D	$C_9H_{11}C_{13}NO_3PS$	87.0	19.13	1664.3
OIL EXTRACTION					
Algae oil extraction					
Methanol	10	CH_3OH	6965.4	22.44	156303.6
Algal biomass	9	$C_{24}H_{44}O_6$	2321.8	64.2[a]	149059.6
Jatropha oil extraction					
Hexane	L1	C_6H_{14}	2711.2	47.75[b]	129459.8
Ground Jatropha seeds	K1	$C_{56}H_{109}O_6$	4598.0	17.73	81522.5
TRANSESTERIFICATION					
Algal biodiesel process					
Sulphated zirconia	16	$Zr(SO_4)_2$	70.8	1.352	95.7
Algal oil	14	$C_{52}H_{96}O_6$	928.7	40.1	37240.9
Process Water	21	$H_2O(l)$	1246.4	0.049	61.1
Methanol	15	CH_3OH	328.5	22.44	7371.5
Jatropha biodiesel process					
Jatropha oil	P	$C_{54}H_{98}O_6$	1060.8	37.00	38719.2
Methanol	Q	CH_3OH	255.54	22.44	5734.4
Sulphated zirconia	R	$Zr(SO_4)_2$	113.1	1.352	152.9
Process Water	W	$H_2O(l)$	1424.5	0.049	69.8
Outputs					
Algal biodiesel	26	$C_{19}H_{34}O_2$	1000.0	39.98	39,980
Glycerol (MME)	33	$C_3H_8O_3$	93.1	22.30	2076.1
Jatropha fruits	E	$C_{56}H_{109}O_6$	7686.7	20.50	157577.4
Jatropha biodiesel	EE	$C_{19}H_{36}O_2$	1000.0	35.80	35,800
Glycerol (JME)	KK	$C_3H_8O_3$	60.8	22.30	1355.8

[a] Refs. [37–39].
[b] Ref. [5].

Table 2
Thermodynamic properties of major inputs and outputs of JME and MME production (for 1ton biodiesel) at $T_0 = 25$ °C and $P_0 = 1$ atm.

Substance	Mass kg	Enthalpy ΔH MJ/kg	Entropy ΔS MJ/kgK	Physical exergy ($Ex_{ph,i}$) MJ/kg	Physical exergy ($Ex_{ph,i}$) MJ
Inputs					
Chlorella sp.	2302.1	−2.885[a]	−6.58E-03[a]	0.923	2124.9
J. curcas treated seeds	3.74	−15.746[a]	−9.44E-02[a]	3.210	12.0
Algal oil	928.7	−2.340[a]	−3.15E-02[a]	7.057	6553.5
J. curcas oil	1060.8	−3.481[a]	−24.603[a]	6.911	7332.0
Outputs					
Algal biodiesel	1000	−14.751[a]	−6.074E-02[a]	3.360	3359.9
Jatropha biodiesel	1000	−7.328[a]	−13.478[a]	4.011	4011.0
Glycerol (algae)	93.1	−7.129[a]	−3.658E-01[a]	0.102E03	9489.5
Glycerol (jatropha)	60.8	−0.079[a]	−4.0117[a]	19.670	1196.0

Physical exergy values were calculated using entropy and enthalpy results from aspen plus.
[a] Values obtained from mathematical analysis with Aspen plus software [52].

3.1. Comparative exergy analysis

The exergy balance for the cultivation, oil extraction, transesterification and methanol recovery units for both MME and JME production plants are summarized in Figs. 3–6 respectively.

In the cultivation units, out of the total exergy destruction of 3464 MJ and 7547 MJ for MME and JME plants respectively, 29.3% and 53.2% are the exergy contents of wastes into the environment (external exergy destruction) respectively for 1 ton of biodiesel produced. JME cultivation unit produces more wastes with high exergy contents compared to MME cultivation unit. The main wastes generated in the MME cultivation unit are the algal cake and culture medium (after culturing). The high exergy content of algae render the content of any medium or stream within the MME plant exergetically higher and thus more dumping of these streams (without conversion into useful products) contributes to high external exergy destruction. For JME cultivation unit, the main wastes are the biomass (agricultural wastes) produced after harvesting the *J. curcas* fruits as well as the *J. curcas* fruit and seed husks. However, the main cause of exergy destruction in the both cultivation unit is entropy generation resulting from the turbulences arising from fluid motion and mass exchange especially in the centrifuge for MME cultivation. Also, turbulence could have generated specific mechanisms of irreversibilities because of both mean flow and fluctuating motion through the viscosity, the thermal diffusivity and the mass diffusion of the fluids interacting during the process [42]. Again, entropy generation resulting from heat transfer processes (especially dryers for JME cultivation unit) contributed to the internal exergy destruction in the JME cultivation unit. The dissipative effects of the light source (solar radiation for JME and light rays for MME production plants respectively) for cultivation in both cases also contributed to entropy generation hence exergy destruction in the cultivation units.

The total exergy efficiencies recorded for the cultivation units of MME and JME plants were 98.49% and 67.78% respectively. The total thermodynamic improvement potentials for microalgae and jatropha cultivation are 1051.9 MJ (30.37% of total exergy loss) and 5153 MJ (68.28% of total exergy destroyed) respectively. Jatropha cultivation unit has a higher thermodynamic improvement potential than that of microalgae hence needs more improvements in its processes.

In the oil extraction units as shown in Fig. 4, the total exergy destroyed in the MME and JME oil extraction units are 132,648 MJ

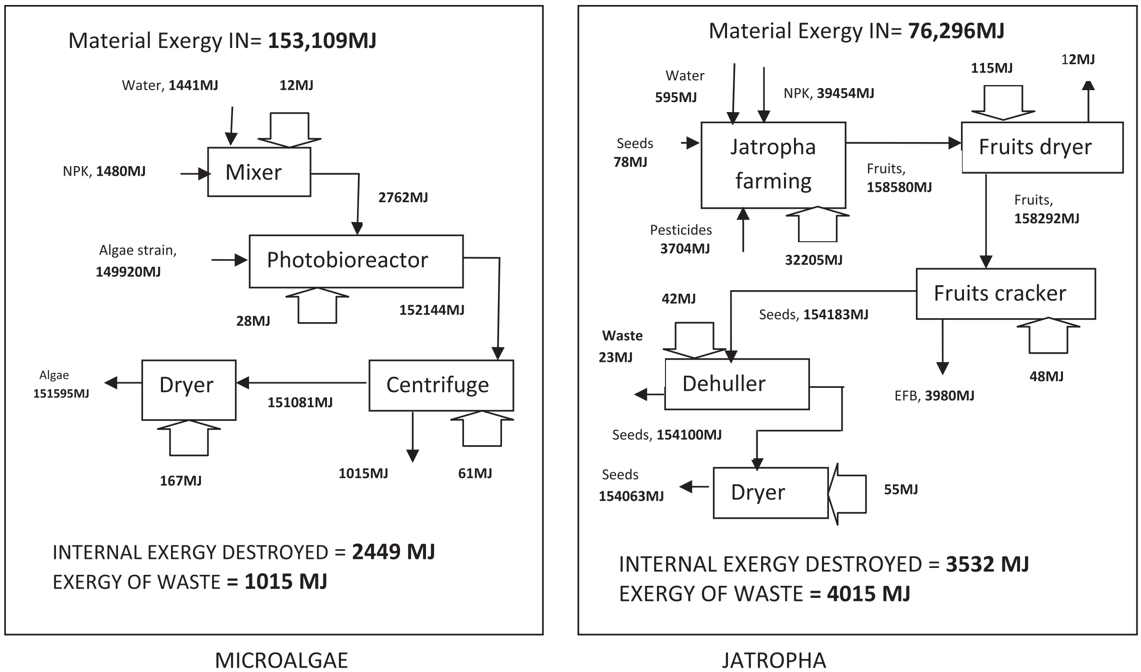

Fig. 3. Exergy balance of microalgae and jatropha cultivation.

and 115,161 MJ respectively for 1 ton biodiesel produced. 99.22% and 97.71% of the total destroyed exergy are the exergy contents of wastes into the environment (external exergy destruction which are avoidable) for MME and JME oil extraction units respectively. Only small percentages of the total exergy destruction are due to entropy generation which is unavoidable but minimizable. Out of the total exergy content of inputs that go into MME and JME oil extraction units, about 62% and 61% respectively are useful (i.e. available to do work).

The exergy efficiency of the extraction unit for microalgae (61.6%) is almost the same as that for jatropha (61.4%). These values are low due to poor performance of equipment, heavy utilization of fossil based utilities and less quality of inputs into the systems. The thermodynamic improvement potentials for microalgal and *J. curcas* oil extraction units are 131,737 MJ (99.31% of total exergy destroyed) and 113,546 MJ (98.59% of total exergy destroyed) respectively. These values are very high meaning both units need much attention in terms of improvement performances.

In the transesterification units of the MME and JME production plants, as detailed in Fig. 5, the total exergy destroyed are 2654 MJ and 1287 MJ respectively per ton of biodiesel. Microalgal oil transesterification unit recorded 52.45% exergy of waste out of the

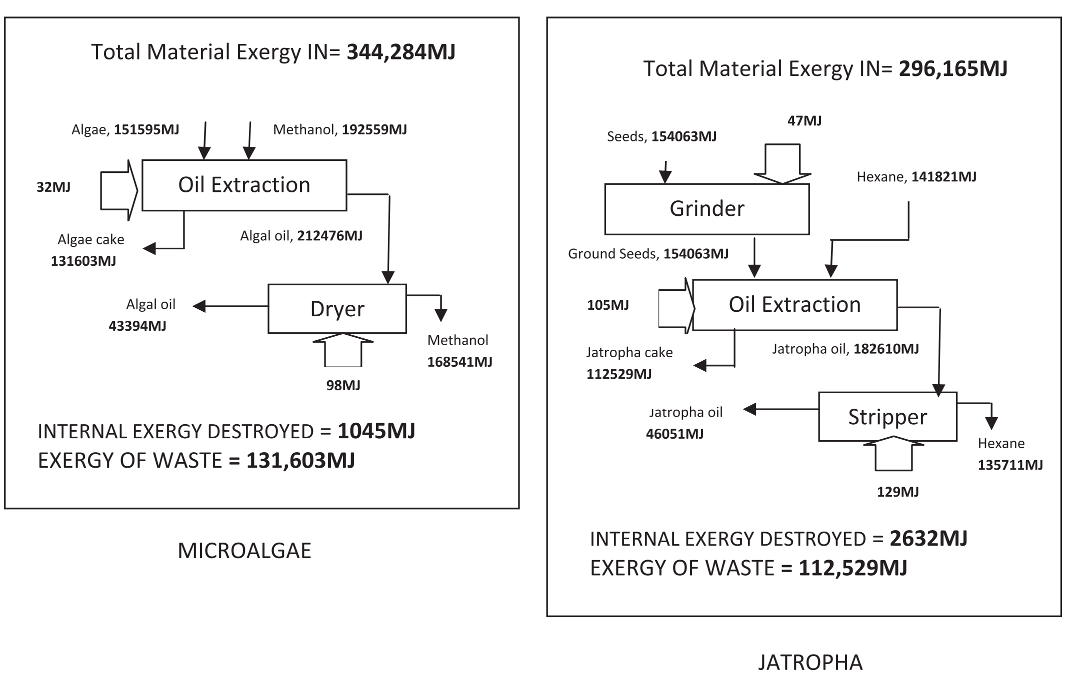

Fig. 4. Exergy balance of microalgae and *J. curcas* oil extraction processes.

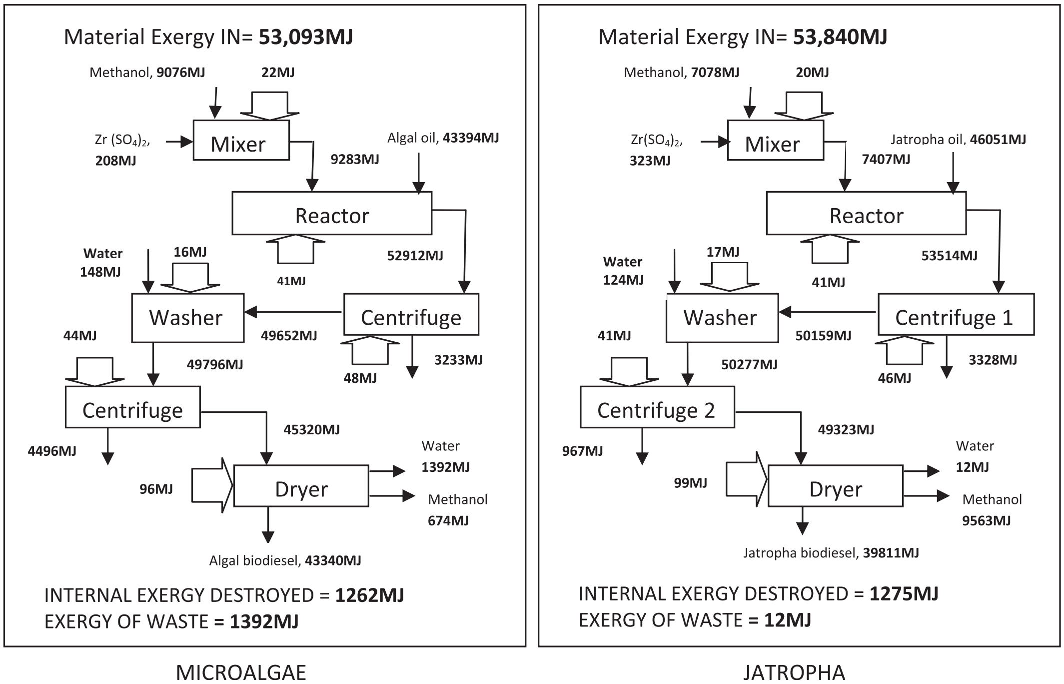

Fig. 5. Exergy balance of transesterification processes of microalgal and *J. curcas* oil into biodiesel.

total exergy destroyed, whilst jatropha had 0.93% exergy of waste out of the total exergy destroyed. The main wastes generated in both cases were water from the dryers which were not recovered. Wastes from microalgal oil transesterification section are so much due to the poor work done by the centrifuge which left a lot of water in the biodiesel phase. This water was evaporated as wastes into the environment. Exergy destruction caused by the centrifuge alone is about 84% of the total exergy loss for extraction system of MME production plant. Separation parameters e.g. retention time etc. were not favourable. If the waste water could be recovered or recycled, the exergy destructions could be reduced by over 80% to enhance effective processing.

Transesterification of *J. curcas* oil was more exergetically efficient (91.71%) than microalgal oil (82.89%) due to higher exergy destructions in the microalgal oil transesterification system. These values also represent the exergy content of input resources that were converted to useful products. The design parameters (heat transfer parameters, chemical reaction etc.) and performance of unit operation equipment can also account for these results. Extreme or very low operating conditions may result in inefficient processing hence either heat dissipation into the environment or low quality of products (in terms of exergy content) produced. The thermodynamic improvement potentials recorded for the microalgal oil and *J. curcas* oil transesterification units are 1607.9 MJ (60.59% of total exergy destroyed) and 117.7 MJ (9.15% of total exergy destroyed) respectively implying more room for improvements.

Methanol recovery units in the MME and JME production plants, as shown in Fig. 6, had waste exergies of 7009 MJ (81.79% out of the total exergy destruction of 8569 MJ) and 278 MJ (19.48% out of the total exergy destruction of 1427 MJ) respectively. The higher value for MME indicates a sharp enthalpy change occurring on the condenser side implying that the feed was introduced too high up in the column and should be moved down. If the catalyst recovered (untreated for reuse hence regarded as waste) are treated for further use, then the external exergy destructions become zero for

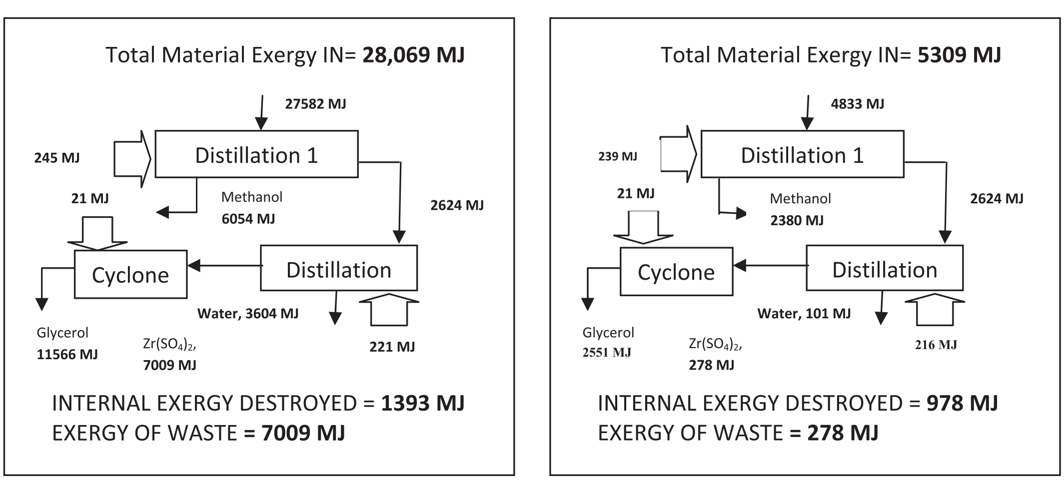

Fig. 6. Exergy balance of methanol recovery units of microalgae and jatropha biodiesel production processes.

both production plants. The internal exergy destructions in the methanol recovery units of both the MME and JME production plants are due to the high entropy generation (high irreversibilities) in the distillation columns. The types of fuels (fossil fuel) used in the units were not renewable thus environmentally unfriendly. Non-renewable energy resources emit gases upon combustion and contribute to the dissipative effects of energy resources into the production leading to exergy loss as wastes into the environment. Fossil fuel again has high exergy content (30 MJ/kg for coal and 46 MJ/kg for crude oil) [12,43] thus increasing the total exergy of input resources which further increases the external exergy destruction.

The results further show that methanol recovery unit for MME production plant is less exergetically effective (75.67%) than that of JME (95.15%). The thermodynamic improvement potentials were 7347.9 MJ (87.45% of total exergy destroyed) and 325.43 MJ (25.91% of the total exergy destroyed) respectively for the methanol recovery units of MME and JME production plants. Thus, the production processes employed in this work do not contribute to waste minimization and therefore needs further improvement or better options in converting the feedstock to biodiesel.

For the whole plants, the oil extraction units recorded the highest exergy losses of 132,648 MJ and 115,161 MJ for MME and JME production plants respectively. However, the exergy inputs into both extraction units are 344,284 MJ (to obtain 211,935 MJ of useful products) and 296,165 MJ (to obtain 181,762 MJ of useful products) for MME and JME production plants respectively. This means that for every ton of microalgal biodiesel produced, 38.5% of the input exergy into the oil extraction unit is destroyed. This is almost the same for *J. curcas* oil extraction (38.9% of the input exergy). The high exergy destruction is mainly due to the turbulence arising during the extraction processes. Turbulence could have generated specific mechanisms of irreversibilities because of both mean flow and fluctuating motion through the viscosity, the thermal diffusivity and the mass diffusion of the fluids interacting during the process [42]. On the other hand, the lowest recorded exergy destruction occurred in the transesterification units of both plants. Though these units can be improved further, they are considered exergetically efficient because their efficiency values are closer to 100% (i.e. over 82%). These results from the transesterification unit alone may indicate an exergetically sustainable production plants. However, if the cultivation of feedstock, oil extraction as well as the methanol recovery units are incorporated, the whole system becomes unsustainable exergetically. This is because the systems' efficiencies then become 44% and 56% (which are very far from 100%) respectively for MME and JME production plants.

Fig. 7 summarizes the exergy content distribution of inputs and outputs into the production of 1 ton biodiesel from microalgae and *J. curcas L.* In Fig. 7 for instance, out of 100% exergy inputs into JME cultivation, over 200% come out as exergy outputs. This is due to materials imbalance in the cultivation of biomass from small amount of *J. curcas* seeds which were used during the growing stage (small amount of seeds are used to obtain high quantity of fruits after three years of cultivation). The contribution of internal exergy destruction by each unit operation within MME and JME production plants are shown in Fig. 8 and Fig. 9. In the MME plant (see Fig. 8), the centrifuge for separating the algae biomass from the culture medium recorded the highest internal exergy destruction (15% of total internal exergy destruction). This means that the separation process encourage a lot of turbulence resulting in entropy generation. The dryer for algal oil drying also recorded the second highest internal exergy destruction (14% of the total internal exergy destruction) as a result of entropy generation within the dryer. The lowest recorded internal exergy destruction occurred in the methanol–catalyst mixer. For JME plant (see Fig. 9), the *J. curcas* fruits dryer, *J. curcas* oil dryer and the oil extractor–decanter recorded the highest internal exergy destruction (14% of the total internal exergy destruction). This means that entropy generation were high in the heat transfer equipment and the separation equipment thus the need for efficient performance of these operation units.

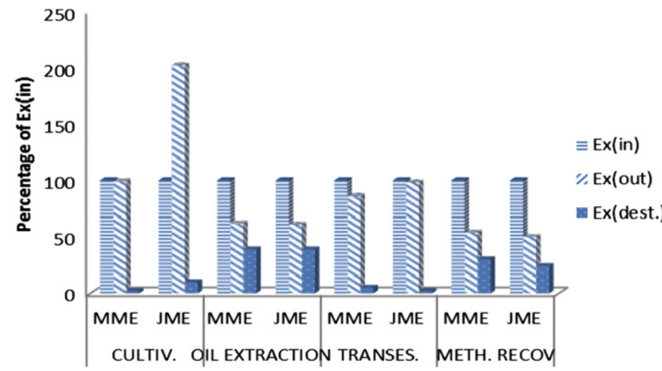

Fig. 7. Amount of exergy inputs converted to products in MME and JME production plants.

According to this study, MME and JME production plants are thermodynamically unsustainable. For sustainable production, the ratio of the work gain in the output resources to that of the input resources must be nearer to 1 (i.e. output to input ratio must be closer to 1) but this is contrary for MME (0.44) and JME (0.56) production plants. 4% and 7% of the total exergy destruction for MME and JME production plants respectively are internal exergy destruction due to irreversibilities which are unavoidable but can be minimized. Thus about 90% of exergy destruction can be avoided in MME and JME production plants which were not so for this studies (because most of the commercial and pilot scale biodiesel production from microalgae and jatropha follow the procedures outlined in this study) due to the wastes streams which are not treated or converted into useful products. Table 3 shows the summary of the contributions of internal exergy destruction by each unit operation within both MME and JME production plants. Table 4 summarizes the process conditions used for simulation in Aspen Plus.

Exergy analysis coupled with economics (thermo-economics and exergoeconomics) clearly relates the magnitude of exergy destruction to economic feasibility. An economic analysis

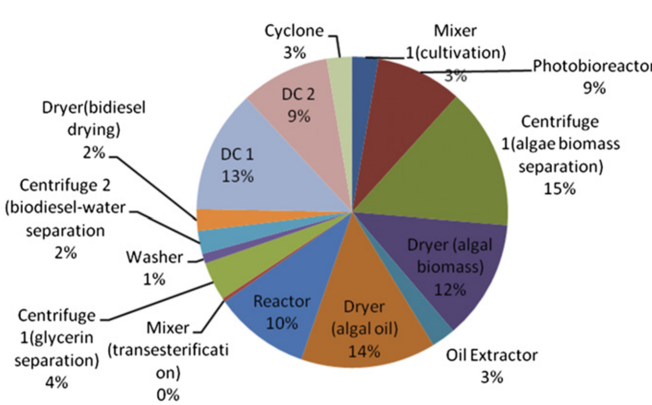

Fig. 8. Percentage of internal exergy destruction in the unit operations of MME production plant DC 1 – Glycerin-methanol separator DC 2 – Water-methanol separator.

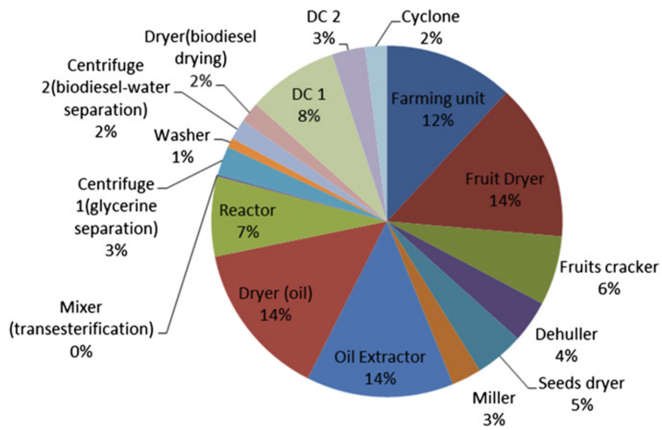

Fig. 9. Percentage of internal exergy destruction in the unit operations of JME production plant DC 1 – Glycerin-methanol separator DC 2 – Water-methanol separator.

performed on an MME production plant by Brian [17] shows that an economically viable algae-to-biodiesel commercialization would largely depend on government subsidies and the future price of crude oil as well as optimized biomass yields. The analysis shows that positive net present values with reasonable rates of return are only possible if moderately high yields of algal biodiesel and extremely high prices (>US$ 100 per barrel) of crude oil become are realized with substantial subsidies or tax breaks on renewable energy systems. This data indicates that, biodiesel production depends largely on subsidies and without these incentives, they become unsustainable.

Table 3
Contribution of exergy destructions by unit operations within both MME and JME production plants.

Stream name	MME production plant		JME production plant	
	Unit operation	% Total internal exergy destroyed	Unit operation	% Total internal exergy destroyed
Cultivation				
HIGHEST	CENT 1	37.0	D 1	35.0
LOWEST	M 1[a]	7.0	DHL	9.0
Oil extraction unit				
HIGHEST	D 2	85.0	D 3	47.0
LOWEST	EXT	15.0	ML 2	9.0
Transesterification unit				
HIGHEST	REACTOR	49.8	REACTOR	49.6
LOWEST	M 2	1.8	M 1[b]	1.1
Methanol recovery unit				
HIGHEST	DC 1[a]	51.8	DC 1[b]	62.1
LOWEST	CYC[a]	10.7	CYC[b]	14.9

CENT 1 – Centrifuge for algae biomass and culture medium separation.
M 1[a] – Culture medium mixer (MME plant).
D 2 – Algal oil dryer.
EXT – Solvent extractor-decanter.
REACTOR – Transesterification reactor.
M 2 – Catalyst mixer.
DC 1[a] – Glycerin-methanol separator (distillation column)-MME plant.
CYC[a] – Hydro-cyclone for glycerin-catalyst separation (MME plant).
D 1 – *J. curcas* fruit dryer.
DHL - *J. curcas* seeds dehuller.
D 3 - *J. curcas* oil dryer.
ML 2 - *J. curcas* seeds miller.
M 1[b] – Catalyst-methanol mixer (JME plant).
DC 1 – Glycerin-methanol separator (distillation column)-JME plant.
CYC[b] – Hydro-cyclone for glycerin-catalyst separation (JME plant).
[a] Represents MME plant.
[b] Represents JME plant.

Moreover, an economic analysis by Wiskerke [44] on jatropha cultivation indicates that the total production cost for 1 kg of seeds is US$ 0.10. His calculations also revealed a negative NPV of US$ 229/ha. Currently in Tanzania where jatropha is grown on commercial scale, a kilogramme of *J. curcas* seeds costs US$ 0.26 [45]. Economic analysis carried out by Marchetti et al. [46] on spent oil transesterification shows that 76–80% of the operating cost is associated with the cost of raw material. Thus, the cost of *J. curcas* oil (US$ 0.324) has a great impact on the profitability of the plant. A low cost raw material and the use of heterogeneous catalyst can be used to increase productivity and sustainability of the production plant.

3.2. Possible improvement options for sustainable performance of biodiesel production plants

In a system where the process involves heat transfer (e.g. heat exchangers, dryers, evaporators, distillation columns etc.), entropy generation becomes an important parameter to control and minimize. In a situation where streams have the same heat capacities, the driving force (e.g. temperature, pressure etc.) which happens to also be equal can be can be minimized (in order to minimize entropy generation leading to exergy destruction) by increasing the heat transfer area, or the overall heat transfer coefficient of the unit operation involved. This can further lead to a reduction in heat duty

Table 4
Steady-state (NRTL model) simulation of MME and JME production processes: Unit operation conditions.

Process unit	MME production process	JME production process
Cultivation		
Reactor model	RBatch reactor	Aspen Plus User models
Temperature (°C)	25	N/A
Pressure (atm.)	1	N/A
Residence/harvest time (days)	12	1095
Oil extraction		
Reactor model	Extract	Extract
Type of solvent	Methanol	Hexane
Triglyceride in oil	Oleic, linolenic	Oleic, linoleic
Temperature (°C)	55	55
Pressure (atm.)	1	1
Transesterification		
Reactor model	RStoic reactor	RStoic reactor
Ester type	Methyl oleate	Methyl oleate
Catalyst	$Zr(SO_4)_2$	$Zr(SO_4)_2$
Methanol: oil ratio (mol/mol)	9.88	9.88
Temperature (°C)	150	150
Pressure (atm)	1	1
Residence time (hours)	4	4
Conversion (%)	96.7	96.3
Biodiesel separation/purification		
Distillation subroutine	RadFrac	RadFrac
Number of ideal stages	10	10
Reflux ratio	2.5	2.5
Condenser/reboiler pressure (atm.)	0.395	0.395
% Methanol recovery	97	97
Glycerin separation/methanol recovery		
Reflux ratio	1.5	1.5
Number of ideal stages	8	8
Condenser/reboiler pressure (atm.)	1	1
Catalyst removal	Cyclone	Cyclone
Heat exchanger model	T & P change	T & P change
Pump model	Hydraulic	Hydraulic

Extract: Rigorous counter-current extraction of a liquid with a solvent.
Thermal and Phase (T & P) change heat exchanger models heaters, coolers and etc.
RStoic: Stoichiometric reactor based on known fraction conversion.
RadFrac: Rigorous 2 or 3 phase fractionation for modelling absorbers and strippers.

especially with distillation columns where the number of feed stages and reflux ratios are optimized (i.e. the column height can be increased or the feed stage can be increased in order to approach equilibrium at one or two points). According to Nguyen and Demirel [47] an appropriate feed placement removes the distortions on the column and may reduce the condenser or reboiler duty. Again, for drying equipment, the temperature difference between the air supply and the supply temperature of the product affects the exergy consumption in the drying process. According to Keey [48], if air recycle can be done effectively in continuous drying, the gain in thermal economy becomes worthwhile and performance of these systems can be improved effectively. Also, feed preheating or cooling can reduce thermal loss on the feed stage. Using heat sources available in the plant are desirable and side condensing and side reboiling provides the column with a cheaper cold or hot utility [47,49].

The production plants of MME and JME recorded overall thermodynamic improvement potentials of 69.43% and 50.48% of the total exergy destroyed respectively. This implies that over 50% of the various unit processes and operations within both plants need optimization to increase process efficiency. This can be achieved by minimizing the exergy losses due to irreversibilities and emissions (or wastes) into the environment. The exergetic efficiency can be further improved by process adjustments such as optimization of the free fatty acid (FFA) ratio in the oils to increase the purity and yield of the product [5]. In general, the exergy loss due to heat loss can also be minimized by reusing in-process heat thereby minimizing the energy supply.

Also, the methanol recovery unit of the MME production plant must be optimized i.e. reducing the reflux ratio to reduce heat duty. For the design and development of energy and exergy efficient production systems, turbulence and vorticity on entropy production in different processes as well as the influence of heat on the system and chemical composition of the inputs are vital for consideration. Also, work extraction devices such as the centrifuge should be properly designed to extract the maximum exergy contained in the product.

There is maximum exergy loss in the separation units of the plant when the temperature change is not constant (non-isothermal). This can be replaced by isothermal process equipment e.g. with the extractive decanter. To have a realistic size of equipment and make a given process take place in finite time, there is a greater need for a minimum driving force [50]. It is thus, always necessary to give allowances for the minimum potential difference while carrying out the analysis of a system with the aim of reducing the exergy loss.

The energy sources have serious effects on the efficiency of the system. Performing the mass and heat balances makes it possible to determine whether a particular heat source and/or sink present an appropriate option for the given duty. In the distillation columns, it is observed that the irreversibility increased with recirculation or increased reflux ratio and decreased number of ideal stages.

To increase the exergy efficiency and use energy in a more rational way, renewable energy resources like solar energy, which have low emissions into the environment may reduce the external exergy destruction. Fossil fuels and electricity from fossil fuel have high exergies. Electricity can be exploited with low exergy losses with high-coefficient of performance heat equipment and pumps. Use of fossil fuels for thermal purposes must be avoided.

Though the exergy content of the sun's energy is high, its exploitation with even low exergy efficiencies may produce a better impact (because it is a renewable energy source) compared to fossil fuel. Fossil fuel produces more emissions into the environment contributing to exergy inefficiencies but solar energy use shifts the production to more renewability or sustainability.

Thermally coupled reactive distillation process for biodiesel production has been shown to be feasible and recommendable [33]. This column uses vapour–liquid interconnections to achieve heat transfer by direct contact with the streams hence no need for double condensers and reboilers [33]. It has been shown that the Petlyuk column provides energy savings up to 50% as compared to conventional distillation trains because it does not present the remixing effect [51].

4. Conclusion

Exergy analyses of microalgal and jatropha biodiesel production processes are presented in this study. 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). The total entropy generations occurring in the unit operations of MME and JME production plants are 494 MJ/K and 419 MJ/K respectively. However, the process efficiencies for MME and JME production plants are 36% and 56% respectively which are very far from 100%.

The oil extraction units for both plants showed the highest exergy losses of 132,648 MJ and 115,161 MJ for MME and JME production plants respectively. However, the exergy inputs into both extraction units are 344,284 MJ (to obtain 211,935 MJ of useful products) and 296,165 MJ (to obtain 181,762 MJ of useful products) for MME and JME production plants respectively. The oil extraction unit of JME production plant also shows an exergy destruction of 39% of which only 2% is due to entropy generation, with 37% accounting for exergy of wastes and emissions.

However, 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.

In sum, energy is money and if so much useful portion of energy (exergy) is destroyed in producing biodiesel, then, there must be an exergetic saving means of reducing wastes in order to make the cost of biodiesel affordable and the existence of its production plants sustainable. This can be achieved by optimizing the processes (choosing optimum working operating conditions and efficient design of heat transfer equipment and reactors) whilst the government also supports with subsidies and incentives. One major way of improving the biodiesel production process is by the adoption of heat-integrated reactive distillation processes. The heat-integrated design proposed by Gomez-Castro et al. [33] is based on catalytic reactive distillation with sulphated zirconia as solid acid catalyst for fatty acids esterification which can help reduce the energy consumption by 45% [33].

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.applthermaleng.2011.12.010.

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