Thermodynamic assessment of algal biodiesel utilization

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ABSTRACT

In late 1990's some microalgae were found to be capable of producing lipids from carbon dioxide via photosynthesis with thirty times the efficiency of plants in terms of the amount of oil produced per unit area of the land allocated. This process raised hope in the fight against environmental problems caused by carbon dioxide accumulation in the atmosphere.

In the present paper, exergetic efficiency of the environment friendly algal biodiesel production process and renewability of the algae-biodiesel-carbon dioxide cycle are assessed. If any process is not feasible thermodynamically, it can never be used in the real world; however, thermodynamic feasibility does not imply the immediate use of the process either. If the limits offered in thermodynamic analysis cannot be attained immediately with the present technology, they may still be used to understand the area where new technology is needed. This paper points the direction for the development of new technology to decrease the carbon dioxide accumulation in the atmosphere.

The renewability indicator is found to be positive, showing that the algae-biodiesel-carbon dioxide cycle is indeed renewable. Any increase in the lipid content of the algae will improve the efficiency of the process. Genetic engineering techniques may be helpful to improve this efficiency drastically.

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1. Introduction

In 2002, the energy demand of the world was 3.8×10^{18} GJ and about 81% of it was derived from fossil fuels [1]. Carbon dioxide is produced in combustion processes and its concentration in the atmosphere is increasing since the beginning of the industrial revolution in 1850's [2]. Carbon dioxide accumulation in the atmosphere and its consequences are publically blamed for numerous environmental and climatic adverse observations. Any process, which helps to recycle the combustion products, may therefore help to fight against the life threatening developments associated with carbon dioxide accumulation in the atmosphere. High petroleum prices make the alternative energy sources economically more feasible than ever before. Therefore, harvesting energy from a carbon dioxide recycling process may be realistic enough to be commercialized.

In late 1990's some microalgae were found to be capable of producing fats from carbon dioxide via photosynthesis with 30 times of the efficiency of plants in terms of the amount of oil produced per unit area of the land allocated [3]. Algal biomass production is technically feasible, and biodiesel from algal oil can potentially completely replace fossil fuels [4]. This process raised hope in the fight against the environmental problems caused by carbon dioxide accumulation in the atmosphere [5].

This paper presents a thermodynamical analysis for the algae – biodiesel – carbon dioxide cycle. First law of thermodynamics phrases the conservation of energy. It states that energy can neither be created nor destroyed, but transferred due to mass, heat and work transfer. First law does not differentiate between the different modes of energy transfer. Second law of thermodynamics makes this differentiation by defining entropy, which is a measure for randomness and increases due to losses involved in processes. It provides insight on irreversibilities, helps to quantify the energy losses and proposes measures for minimization of the loss. Based on the second law, exergy (also called availability) is defined as the useful work potential. Exergy of a system is the maximum work that this system can produce if it is brought to thermal, mechanical and chemical equilibrium with its surroundings via reversible processes. In other words, exergy is the maximum energy content that can be extracted from a system without violating the laws of thermodynamics. In the last few decades, numerous studies are published on exergy (availability) analysis [6–10]. Especially in the assessment of renewable energy sources, where we need to weigh various processes and fuels with respect to their ability to produce useful work and to identify their impact on environment, exergy analysis provide a fair tool for comparison.

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Nomenclature

a	Constant kJ/K		η_{th}	Thermodynamic efficiency
b	Stream availability kJ/kmol		μ	Chemical potential kJ/kmol
B	Meissner equations constant		μ_{growth}	Specific microbial growth rate 1/s
C	Number of the members of a community		*Subscripts*	
c_p	Specific heat kJ/(kmol K)		0	Restricted dead state
e	Specific exergy kJ/kmol		ave	Average
g	Gibbs free energy kJ/kmol		b	Boiling
h	Enthalpy kJ/kmol		f	Formation
k	Specific heat ratio in a Diesel engine		gen	Generation
N	Number of moles kmol		i	Any species
P	Parachor		in	Inlet
Q	Heat kJ		m	Mixing
r	Compression ratio of a Diesel engine		out	Outlet
r_c	Cutoff ratio of a Diesel engine		p	Products
R_D	Molar refraction		Q	Heating
R_u	Universal gas constant = 8.314 J/(mol K) kJ/(kmol K)		r	Reactants
s	Entropy kJ/(kmol K)		W	Work
T	Temperature K			
v	Specific volume m^3/kg		*Superscripts*	
W	Work kJ		0	True dead state
x	Molar fraction		ch	Chemical
X	Exergy kJ		th	Thermomechanical
			vap	Vaporization

In the assessment of new energy sources sustainability, i.e. renewability, is an important concern. Sustainability depends on both the energy content of input materials and the process pathway [11]. A successful energy source has to be sustainable in terms of thermodynamical aspects, as well as social, economic and environmental aspects, which include -among other criteria- net carbon dioxide emission, competition with the food supply and waste management [12–15]. Some energy sources are found to be energetically, socially and economically renewable; although the exergy required to restore the environmental damages emerged during the production of the energy source is larger than the useful work produced by the energy source. A good example for this is bioethanol. Production of ethanol from corn gives a positive energy balance, emits no net carbon dioxide to the atmosphere and creates new work places. Hence it is considered as a sustainable energy source. However, the exergy analysis of the use of ethanol from corn as a biofuel shows that the process is not renewable, since exergy loss due to the consumption of non-renewable materials, resource processing and waste treatment is larger than the exergy produced. Exergy consumed during the process is nearly 5 times larger than the available work produced by ethanol [16,17].

In the following, renewability of the algae – biodiesel – carbon dioxide cycle is assessed from a thermodynamical point of view. Calculations presented for the three steps of the cycle: algal biomass production, biodiesel production and the consumption of biodiesel in a Diesel engine. The algal biodiesel cycle is found to be reversible. If the thermodynamic limits offered in this study cannot be attained in practice now, new technology may be developed to attain or approach these in the future. This paper points out the direction for the development of the new technology.

2. Methods

2.1. Renewability assessment

A renewable energy source should not destroy exergy. This means that the total work used to produce the energy source plus the total work used to restore environment to its initial state has to be smaller or equal to the work produced by this energy source. Fossil fuels, for example, are non-renewable, since the work required for the environment restoration is much larger than the produced work. During the production of biofuels however; non-renewable inputs are limited. Thus, these are closer to full renewability. In the following, the methodology to quantify renewability in terms of exergy is explained.

Szargut et al. [18], proposed the concept of cumulative exergy consumption (CExC), which is the sum of exergy of all resources consumed in all the steps of a production process. CExC represents the available work consumed to obtain a product. It involves the exergy cost of raw materials, transportation, work and heat transfer. Thus, it is a function of the pathway that the process follows. To apply this concept to renewable energy sources, Berthiaume et al. [16] extended Szargut's analysis by defining the cumulative net exergy consumption (CNEx) and the restoration work (W_r). Cumulative net exergy consumption is the difference between the cumulative exergy consumption and the exergy content of the main product (X_p):

$$CNEx = CExC - X_p \tag{1}$$

This equation can be illustrated with the following example: The chemical exergy of gasoline (X_p) is 35.6 MJ kg^{-1}. If the total amount of the exergy consumed (including the chemical exergy of raw materials, electricity and fuels used during the process) to produce gasoline in a petroleum refinery (CExC) is 42.4 MJ kg^{-1}, then CNEx is 6.8 MJ kg^{-1} [16]. In other words, 42.4 MJ of available energy is consumed to obtain a product, which has 35.6 MJ work potential.

The restoration work represents the net exergy cost to produce an energy source, without causing any environmental damage, like water and air pollution. It is defined as the sum of the net cumulative exergy consumptions during the production process and waste treatment:

$$W_r = CNEx_{production} + CNEx_{waste\ treatment} \tag{2}$$

For an energy source to be renewable the useful work gained by that source has to be larger than the restoration work. Accordingly, renewability indicator is defined as:

$$I_r = (W_p - W_r)/W_p \tag{3}$$

where W_p is the useful work obtained by the product. If the maximum work potential of the product is extracted via reversible processes, then W_p equals to X_p.

2.1.1. Cumulative net exergy consumption of the inputs

Cumulative net exergy consumption values of salts, fuels and electricity are taken from Szargut et al. [18]. The main raw material of the algal biodiesel production is ethanol. Recently, a number of papers are published on the energy balance of ethanol production [19–23]. Dewulf et al. [24] evaluated the exergy balance of three pathways to produce ethanol: from fossil resources, via agriculture (wheat) and fermentation and via hydrogen by use of solar energy captured by photovoltaic (PV) cells. Their analysis shows that the fossil resources based route is the most efficient, where 60.13 MJ of cumulative net exergy is required to produce 1 kg of ethanol. The pathway via agriculture and fermentation results in a cumulative net exergy requirement of 4247.6 MJ/kg. However, 4240 MJ of this comes from solar irradiation for the photosynthesis and only 7.6 MJ/kg comes from non-solar resources. PV-generated electricity and electrolysis of water to produce hydrogen for the synthesis of ethanol requires 338 MJ/kg of solar irradiation and 26.4 MJ/kg non-solar resources. This analysis shows that although fossil resources based production is more efficient than the PV-route and the bio-route (49 vs. 7 and 0.7% respectively), it has the largest share of non-renewable resources (0.98 vs. 8.9 and 0.2% respectively). In the following analysis the CNEx of ethanol is taken as 26.4 MJ/kg and the sensitivity of the results to the different production pathways are discussed in the "Results and discussion" section.

2.2. Thermodynamic analysis

Each process in the algae – biodiesel – carbon dioxide cycle is analyzed thermodynamically to determine the renewability indicator. The following equations represent the governing equations in integral form for a steady-flow open system.

Mass balance:

$$\sum (N)_{in} - \sum (N)_{out} = 0 \tag{4}$$

Energy balance:

$$\sum (Nh)_{in} - \sum (Nh)_{out} = Q - W \tag{5}$$

Entropy and exergy are not conserved quantities like mass and energy. Internal and external irreversibilities cause entropy generation and exergy destruction:

Entropy balance:

$$\sum (Ns)_{out} - \sum (Ns)_{in} - \sum_k \frac{Q_k}{T_k} = \Delta S_{gen} \tag{6}$$

Exergy balance:

$$\sum (Nb)_{in} - \sum (Nb)_{out} - \sum_k Q_k \left(1 - \frac{T_0}{T_k}\right) - W = X_{destroyed} \tag{7}$$

where k is the number of heat sources and b is the flow availability of a stream (neglecting the kinetic and potential energy contribution):

$$b = h - T_0 s - \sum x_i \mu_i^0 \tag{8}$$

A detailed explanation of the exergy analysis is given in the Appendix.

2.3. System boundary

The system involves algae production, algal oil separation, biodiesel production and the combustion in a Diesel engine. Major input into the system is sun light. Hydrosphere, lithosphere and atmosphere act as water and carbon reservoirs, and are included within the system boundaries. Nutrient rich water consumed during algae production and process water are fully recycled. Carbon dioxide consumed by algae to produce algal oil is released back to atmosphere during combustion in the Diesel engine. Hence there is no mass transfer through the system boundaries (Fig. 1).

Mass flow of each stream within the cycle is normalized so that the mass of the main product, i.e. biodiesel, is 1 ton. A zero-dimensional analysis is performed, where the dimensions of the flow field are not taken into account. Contents of each stream are considered as ideal homogenous mixtures. Furthermore, the temperature of the units is assumed spatially homogenous and equal to the boundary temperature. Pressure is taken as 1 atm throughout the biodiesel production process.

3. Algae and algal oil production process

Algal oil production process is described in Fig. 2. A glass covered pond was chosen to grow the algae in. Intensity of the sun light outside of the pond is reported to be 2000 µE/m²s [3]. A fraction of the sunlight will be reflected or absorbed by the glass and the algae at the upper layers of the pond. The depth of the growth medium will be adjusted to provide 200 µE/m²s of average light intensity within the growing region of the algae [3]. Sparged carbon dioxide provides sufficient mixing within the pond. Schimel et al. [25] estimated the carbon emission to the atmosphere in 1991 as 6.2 Giga ton/year, this number is predicted to be much higher now. The major anthopogenic sources of CO_2 generation are chemical processes like fossil fuel (coal, oil and natural gas) combustion or cement production [2], therefore providing carbon dioxide at the side of large scale producers like thermal power plants or cement factories is a feasible way for algal oil production.

Algae consist of two parts: the lipids and the rest of the cell. The so called "rest of the cell" has a similar elemental composition with a bacterial cell. Luria et al. [26] reported the
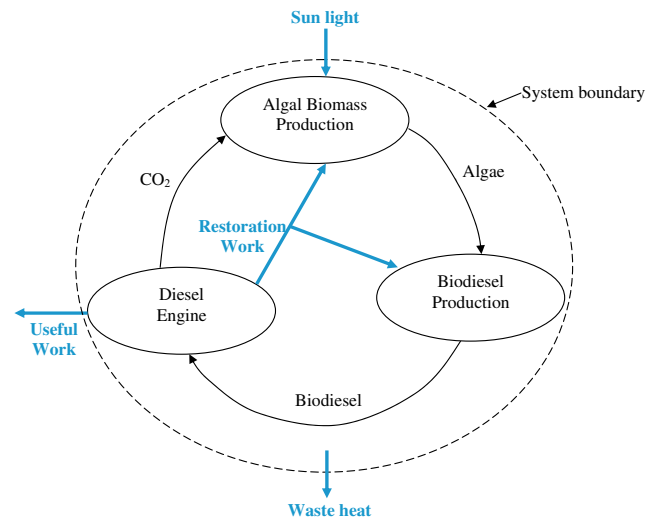

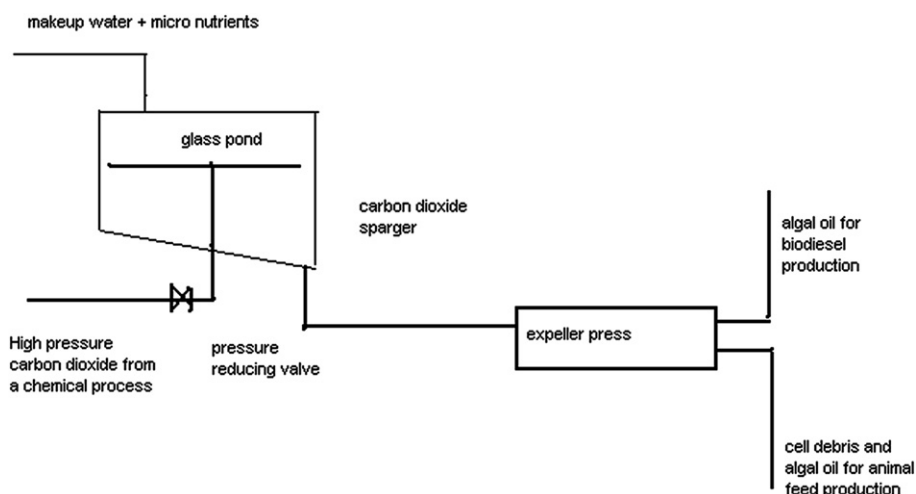
Fig. 1. Schematic representation of algal biodiesel cycle.

Fig. 2. Algal oil production process.

composition of the bacterial cell as 50% carbon, 20% oxygen, 14% nitrogen, 8% hydrogen, 3% phosphorus, 1% sulfur, 1% potassium, 1% sulfur, 0.5% calcium, 0.5% magnesium, 0.5% chlorine, 0.2% iron and about 0.3% others. Accordingly, the cell debris of the algae is described here with the following empirical formula: $C_{4.17}H_8O_{1.25}N_1P_{0.10}S_{0.03}K_{0.03}Na_{0.04}Ca_{0.01}Mg_{0.02}Cl_{0.01}Fe_{0.004}$. The following equation describes the synthesis of the organic parts of the cell debris with photosynthesis:

$$4.17CO_2 + 0.04NH_4^+ + 4H_2O \rightarrow C_{4.17}H_8O_{1.25}N_{0.04}$$
$$+ \text{Cellular Inorganics} \qquad (9)$$
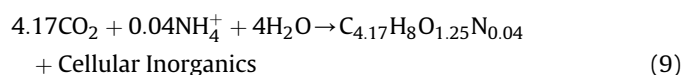
The cellular inorganic chemicals are provided by adding the following salts (per 100 kg of debris produced) into the pond: Make-up water 72 kg, $Ca(OH)_2$ 2 kg, KCl 6 kg, $MgSO_4$ 1 kg, NaH_2PO_4 4.7 kg, $FeCl_2$ 1 kg, NH_4Cl 16 kg.

Algal oil production process is suggested to achieve maximum energy savings. Solar energy is the major energy source and it is free. Carbon dioxide from a chemical process is compressed to increase its pressure and fed into the algal oil production facility described in Fig. 2. The energy requirement of the compressor is calculated as 226 kW. Algae grows in the pond, mature cells flocculate and settle in continuously. High pressure helps to improve the solubility of CO_2 in the pond as described by the Henry's law [27]. The high pressure above the pond also provides the driving force for the flow of the settled cells without consuming pump work. Energy requirement of an expeller press for 620–830 kg of oilseed processing was reported to be 22–30 kW [28].

4. Biodiesel production process

Thermodynamic analysis of the algal biodiesel production process is done considering the flowchart given in Fig. 3 [29]. In a conventional biodiesel production process, oils or fats go through transesterification reaction with an alcohol (methanol, ethanol, propanol or butanol) at 55–65 °C in the presence of a catalyst. The main reaction product (esters of the fatty acids) is marketed in a commercially and technically feasible way as biodiesel, whereas glycerol is obtained as a byproduct [30]. When the thermodynamic conditions are adequate, transesterification is a fast process. Freedman et al. [31] reported more than 98% conversion in 1 h for various vegetable oils at 60 °C. Mass transfer initially determines the rate of the reaction, where good mixing and high Reynolds numbers provide high reaction rates. In the later stages of the

reaction, temperature effects become dominant. Methanol reacts at room temperature with high reaction rate, but since it is a potent neurotoxicant and highly flammable, ethanol is preferred. The catalyst, i.e. sodium or potassium hydroxide or methoxide, affects the biodiesel yield and the saponification rate. Different versions of biodiesel production processes are described in the literature [4,29,30,32]. Vincente et al. [32] present a comparison of the yields and saponification rates while using different catalysts in biodiesel production from sunflower oil.

Algal oil mostly consists of triacylglycerol, with three fatty acid molecules attached to a glycerol backbone. Bayer [33] received a patent for a process where material with microbial, vegetable or animal origin was heated to 200–600 °C under the exclusion of air to produce solid, liquid and gaseous fuels. It was reported in the patent that carbohydrate, lipid, protein and humic acid containing materials gave higher energy. These results are not surprising, because combustion actually releases the energy stored within the bonds of the chemical species. Biomaterials, and especially lipids have bonds with very high energy, i.e., C≡C, C=O, C=C, O–H and C–H bonds have 828, 724, 607, 456 and 410 kJ/mol of bond energies, respectively [34]. Heat of combustion of the microbial oils is reported to be between 29,000 to 42,000 kJ/kg, whereas the heat of combustion of coal is 12,500 to 33,500 kJ/kg. These reported energies are actually released when the high energy bonds of the fuels are substituted with the lower-energy bonds of the combustion products like carbon dioxide (e.g. C–O bond has an energy level of 330 kJ/mol). Variation in individual combustion values is due to the variations in the starting material, reaction conditions, catalyst and amount of inorganic residues. The sulfur content of the algal oil (0.05–1% by weight) is also reported to be better than that of the highest quality petroleum (0.3–6% by weight) [33].

Mass, energy and exergy balances are performed for each unit operation in the plant separately, in order to determine the internal irreversibilities in each unit and identify the opportunities to decrease the lost work and to increase the second law efficiency.

In the following, details of the thermodynamic analysis are presented for each individual unit in the biodiesel production process.

4.1. Exergy balance around the mixer

In the first step of the biodiesel production process, catalyst (sodium ethanolate) is mixed with ethanol (Fig. 4). The amount of
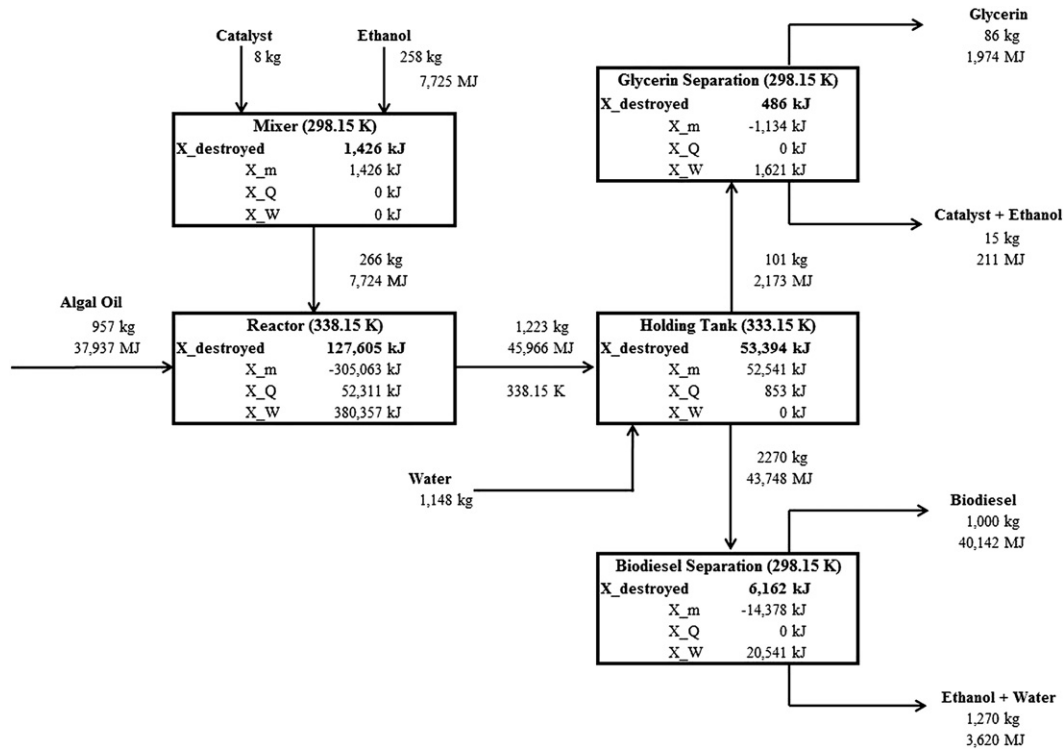
Fig. 3. Exergy flow diagram for the production of 1 ton biodiesel (this flow diagram was adapted from van Gerpen et al. [29] with some modifications for algal oil utilization).

the catalyst needed depends primarily on the volume of the oil. For 957 kg of algal oil, which is needed to produce 1 ton of biodiesel, 8 kg of catalyst is required. 100% excess ethanol, i.e. 258 kg, is used to increase the efficiency of the reaction and the yield. Mixing occurs adiabatically and isothermally at 25 °C. Outlet stream is an ideal solution, i.e. enthalpy of mixing is zero. Continuous stirring will accelerate the mixing process; however, here we neglect any work transfer. Energy balance around the mixer is:

$$\sum(Nh)_{in} = \sum(Nh)_{out} \tag{10}$$

Mixing is an irreversible process, and all the work potential is wasted. If mixing could be performed reversibly, e.g. through semi permeable membranes, some work could be produced. The

maximum amount of work that can be produced, nevertheless wasted, is equal to the difference between the exergy contents of the inlet and outlet streams.

$$X_{destroyed} = W_{max, \, out, \, mixing} = \sum(Nb)_{in} - \sum(Nb)_{out} \tag{11}$$

$$X_{destroyed} = 1426 \ kJ/ton \tag{12}$$

4.2. Exergy balance around the reactor

The dominant chemical reaction occurring in the reactor (Fig. 5) is:

$$C_{69}H_{98}O_6 + 6 \cdot C_2H_5OH \rightarrow 3 \cdot C_{24}H_{36}O_2 + C_3H_8O_3 + 3 \cdot C_2H_5OH$$
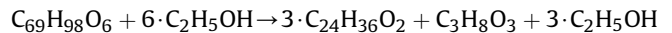
Besides this reaction hydrolysis, saponification and stepwise degradation of algal oil into diacylglycerol and monoacylglycerol also occurs. However, under the operating conditions trans-esterification dominates the kinetics. Hence, side products are neglected in the mass balance. Reaction occurs at 65 °C and with 100% excess alcohol. First and second laws of thermodynamics dictate the following equations for the reactor, given that the
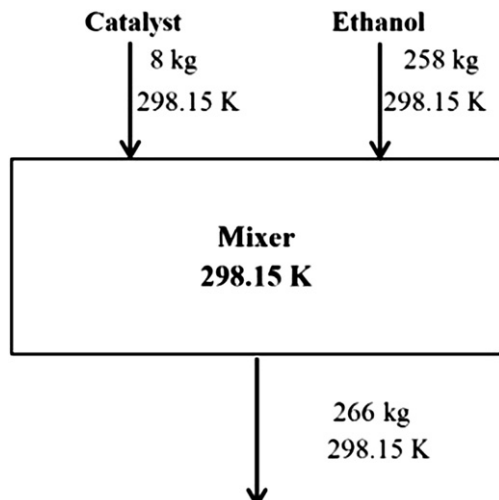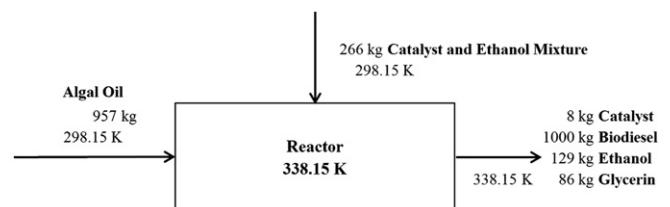

Fig. 4. Mass balance around the mixer.

Fig. 5. Mass balance around the reactor.

thermomechanical state of the inlet streams is equal to the restricted dead state, and therefore only the enthalpy of formation and the chemical exergy terms are non-zero at the inlet streams.

$$\sum \left(N_i h_{f,i}^0\right)_{in} - \sum \left(N_i \left(h_{f,i}^0 + c_{p,i}(T - T_0)\right)\right)_{out} = Q - W \qquad (13)$$

$$\sum \left(N_i \left[e_i^{ch} + \left(h_{f,i}^0 - T_0 \left[s_i^0 - R_u \ln x_i\right]\right)\right]\right)_{in} - \sum \left(N_i \left[e_i^{ch} + \left(h_{f,i}^0 \right.\right.\right.$$
$$\left.\left.\left. + c_{p,i}(T - T_0) - T_0 \left[s_i^0 + c_{p,i}\ln\frac{T}{T_0} - R_u \ln x_i\right]\right)\right]\right)_{out}$$
$$- Q\left(1 - \frac{T_0}{T}\right) - W = X_{destroyed} \qquad (14)$$

Enthalpy, chemical exergy and specific heat of each species are calculated based on the thermodynamic properties listed in Table 1. Consequently, the first two terms of both equations, i.e. the net enthalpy and exergy flow to the reactor are determined. In order to solve for the heat and work transfer terms, the energy and exergy balance equations are solved simultaneously. Chemical reactions involve irreversibilities, which arise due to fast reactions, mixing of the reactants and products, side reactions etc. The minimum work required to overcome these irreversibilities is computed as 266,250 kJ/ton of biodiesel. If the second law efficiency of this process is 70%, than the work input is 380 MJ, heat released is 442 MJ and the destroyed exergy is 128 MJ/ton of biodiesel.

4.3. Exergy balance around the holding tank

The outlet stream of the reactor enters into a holding tank (Fig. 6), where it is mixed with the washing water, cooled and separated into glycerin and biodiesel streams with the help of gravity. Glycerin and catalyst settle at the bottom of the holding tank due to their relatively high densities. Both biodiesel and glycerin phases contain alcohol. However, biodiesel contains a higher amount of alcohol since their densities are close to each other. Holding tank is at 60 °C. Since washing water is preheated to 55 °C, separation occurs nearly adiabatically. No net work input is required into the process, since gravity does the minimum work required for separation.

$$Q = \sum N_i \left(c_{p,i}(T_{in} - T_{out})\right) = -8123 \ \text{kJ/ton} \qquad (15)$$

Exergy is mainly destroyed due to the mass transfer:

$$\sum (N_i b_i)_{in} - \sum (N_i b_i)_{out} = 52541 \ \text{kJ/ton} \qquad (16)$$

Additionally, a small portion of exergy is destroyed due to heat transfer and the total exergy destroyed in the holding tank is 53,394 kJ/ton.

4.4. Exergy balance around the biodiesel separation tank

Biodiesel is purified by separating ethanol and water in the biodiesel separation tank (Fig. 7). During the separation, the inlet stream, which is at 60 °C is cooled to environmental temperature ($T_0 = 25$ °C). Since mixing is an irreversible process, a minimum
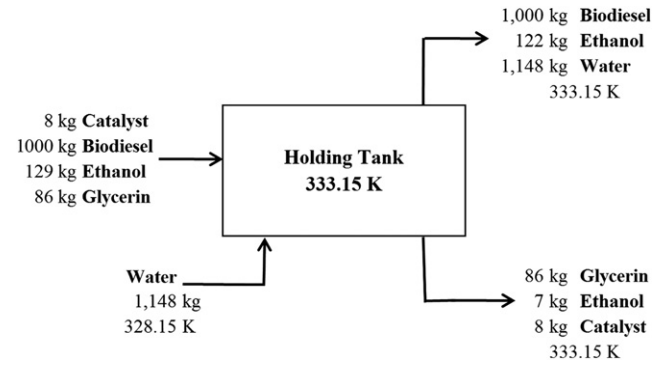

Fig. 6. Mass balance around the holding tank.

work input is required, which is equal to the net exergy flowing out of the system.

$$W_{min,\ separation,\ in} = \sum (N_i b_i)_{out} - \sum (N_i b_i)_{in} = 14378 \ \text{kJ/ton} \qquad (17)$$

If a separation efficiency of 70% is assumed, than the required work input becomes 20,541 kJ. Accordingly, a non-zero heat transfer term appears in the energy balance.

$$Q = \sum N_i \left(c_{p,i}(T_{in} - T_{out})\right) - W_{min,\ separation,\ in}$$
$$= -291207 \ \text{kJ/ton} \qquad (18)$$

Since heat transfer occurs through a system boundary, which is at the environmental temperature (25 °C), heat transfer does not destroy exergy. Destroyed exergy is the difference between the work input and the net exergy outflow, which is 6 MJ, if separation efficiency is 70%.

4.5. Exergy balance around the glycerin separation tank

Mass, energy and exergy balances around the glycerin separation tank are similar to the calculations performed for the biodiesel separation tank (Fig. 8). Outlet streams are at 25 °C. The minimum work of separation is calculated from the exergy balance as 1134 kJ. Heat release from the tank is 10,094 kJ. If the separation efficiency is 70%, than the exergy destroyed in this system is 486 kJ.

5. Work production

Biodiesel produced from algal oil is used as an energy source. It is assumed that useful work is produced via combustion in a Diesel engine. The first law efficiency of a Diesel engine cycle is a function of the compression ratio, cutoff ratio and specific heat ratio [35].

$$\eta_{th} = 1 - \frac{1}{r^{k-1}}\left(\frac{r_c^k - 1}{k(r_c - 1)}\right) \qquad (19)$$
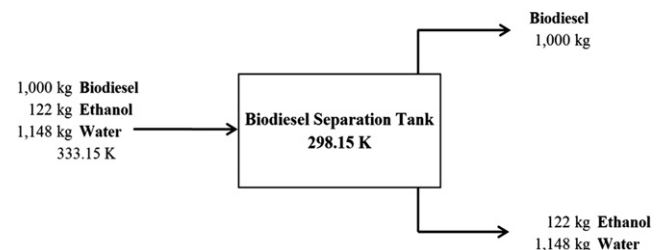
Table 1
Thermodynamic properties.

Chemical species	h_f^0 (kJ/mol)	s^0 (kJ/kmol K)	c_p (kJ/kmol K)	e^{ch} (kJ/kmol)
Biodiesel [$C_{24}H_{36}O_2$]	−429	833	940	14,299,365
Algal Oil [$C_{69}H_{98}O_6$]	−1056	2240	2725	40,541,751
Glycerin [$C_3H_8O_3$]	−670	206	220	2,113,793
Ethanol [C_2H_5OH]	−276	161	112	1,376,670

Fig. 7. Mass balance around the biodiesel separation tank.

Fig. 8. Mass balance around the glycerin separation tank.
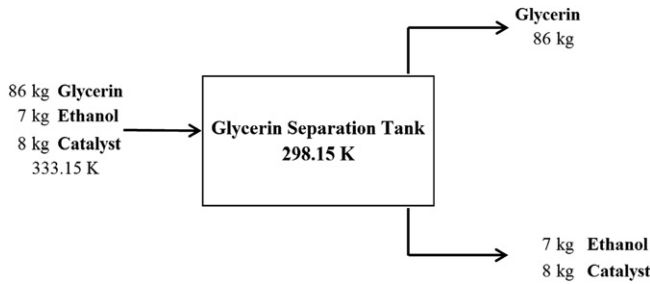
The exergy balance for the Diesel cycle is:

$$X_{destroyed} = T_0(s_{out} - s_{in}) - \phi\frac{\delta Q_{in}}{T_{in}} + \phi\frac{\delta Q_{out}}{T_{out}} \qquad (20)$$

Where, Q_{in} and Q_{out} are the inlet and outlet heat transfers, and T_{in} and T_{out} are the corresponding boundary temperatures. In a cyclic process the first term in the right hand side is zero, since thermodynamic properties at the inlet and outlet are the same. During the heat release, exhaust gas is ejected to the surroundings. In the following calculations, the boundary temperature is assumed to remain constant at the environmental temperature during the heat rejection process. Heat is added into the system due to the combustion of the biodiesel. Through the combustion process, system temperature increases. If heat is assumed as a linear function of the temperature, than δQ_{in} can be represented as:

$$\delta Q_{in}(T) = \int_{T-dT}^{T+dT} a\,dT \qquad (21)$$

The entropy increase due to the heat addition process, which occurs across a finite temperature difference, becomes:

$$\int_{T_2}^{T_3} \frac{\delta Q_{in}}{T_{in}} = 2a\ln\left(\frac{T_3}{T_2}\right) = 2a\ln(r_c) \qquad (22)$$

Finally, the destroyed exergy in the cycle can be represented as a function of the heat input, compression ratio, cutoff ratio and specific heat ratio.

$$X_{destroyed} = \left(\frac{Q_{out}}{T_{out}} - 2a\ln(r_c)\right)$$
$$= Q_{in}\frac{1}{kr^{k-1}(r_c-1)}\left(r_c^k - k\ln r_c - 1\right) \qquad (23)$$

In the operating conditions for a regular Diesel engine, values of the compression ratio, cutoff ratio and specific heat ratio can be approximated as: $r = 15$, $r_c = 5$ and $k = 1.4$. Thus, the first and second law analyses result in:

$$\begin{aligned} \eta_{th} &= 0.56 \\ X_{destroyed} &= 0.38 \cdot Q_{in} \end{aligned} \qquad (24)$$

6. Results and discussion

Net cumulative exergy of each input and the restoration work in each step are listed in Table 2. The total useful work produced by the algae-biodiesel-carbon dioxide cycle is about 12 MJ. The restoration work required to bring environment to its initial state is 9 MJ. Net work gained from the cycle is 3 MJ, and the renewability indicator is 0.27.

These results are specific to the algal oil production process described above. Technological choices alter the results drastically. For example, here the exergy consumed to produce 1 kJ of electricity is taken as 4.17 kJ, which is the value for fossil fuel based electricity generation [18]. If hydropower is used for electricity generation, the exergy cost reduces up to 0.006 kJ/kJ of electricity [16]. That would reduce the restoration work to 5980 MJ and the renewability indicator, I_r, would rise to 0.50. Another example is the CNEx of ethanol. If ethanol is produced from fossil resources, its CNEx raises to 60.13 MJ/kg, which leads to a non-renewable process with a renewability indicator of −0.09. Similarly, if the efficiency of Diesel engine can be improved in the future, produced work increases as well, which leads to higher renewability.

The analysis is performed for a simplified algae-biodiesel-carbon dioxide cycle. Hence it contains inaccuracies, which can be eliminated via detailed calculations. Nevertheless, the results indicate that the cycle is very renewable. Similar analyses performed for corn-ethanol-carbon dioxide cycles resulted in negative I_r values, thus indicating that the process is not renewable [16,17]. Since algae accumulate exergy more efficiently than plants, renewability indicator is higher.

Table 1 summarizes the thermodynamic properties. The data for biodiesel and algal oil are predicted based on the correlations mentioned in the appendix. Data for the rest of the compounds are taken from the literature. In this model the group increments are best accurate to 0.5 kJ/mol for h_f^0, 0.05 J/(mol K) for s^0 and c_p. Chemical exergy predictions may involve an inaccuracy of about 1%. Main results of the first and second law analyses are summarized in Fig. 3 and Table 3. In the flow diagram, the effect of the three different exergy transfer mechanisms (due to mass X_m, heat X_Q and work transfer X_W) is shown explicitly.

The total exergy loss in the biodiesel production process is 0.19 GJ per ton of biodiesel. The major source for the exergy destruction is the reactor. Due to the uncontrolled and fast chemical reactions occurring in the reactor irreversibilities arise. The second largest exergy destruction source is the holding tank, where the biodiesel and glycerin are separated. The operating temperature of the holding tank is set as 60 °C and the process is nearly adiabatic, since washing water is preheated to 55 °C. Here, exergy is mainly destroyed due to the change in the composition of the inlet and outlet streams. Variations in the inlet water temperature, operating temperature and the compositions of the outlet streams may decrease the total exergy loss in this process and hence, increase the second law efficiency of the unit. The mixer and the separation units make a small contribution to the total exergy loss. In a separation process, the minimum work input required is equal to the exergy destroyed due to mass transfer. In the calculations, a second law efficiency of 70% is assumed for each separation process. Depending on the design of the separation units, the second law efficiency and the resulting exergy destruction may vary. In this analysis, calculations are performed for a simplified theoretical plant. Only the main processes, which are the dominant sources of exergy destruction, are considered. Auxiliary utilities such as pumps, pipelines, heat exchangers are not taken into account. Furthermore, in an actual plant there will be deviations from the ideal operation conditions, which will cause incomplete reactions, side products, incomplete separation, heat losses, etc. The total exergy destruction is expected to be larger in an actual plant due to the auxiliary utilities and the deviation from the best operating condition. For example, Talens et al. [10] have calculated a total exergy loss of 0.49 GJ/ton for an actual production plant, which converts used cooking oil to biodiesel.

Table 2
Exergy consumed by non-renewable resources to produce 1000 kg of biodiesel from microalgae.

To produce 1000 kg of biodiesel						
Input	kg	W(kJ)	Source	CNEx (kJ/kJ) or (kJ/kg)		W_R (kJ)
Algae production						508,498
Ca(OH)$_2$	7.4			1,395	kJ/kg	10,317
KCl	22.2			190	kJ/kg	4,215
MgSO$_4$	3.7			271	kJ/kg	1,004
NaH$_2$PO$_4$	17.4			351	kJ/kg	6,096
FeCl$_2$	3.7			1,259	kJ/kg	4,659
NH$_4$Cl	59.2			6,056	kJ/kg	358,394
Compressor work		25,685	Electricity	4.17	kJ/kJ	107,107
Water recycling		4,006	Electricity	4.17	kJ/kJ	16,706
Algal oil production						711,402
Press work		170,600	Electricity	4.17	kJ/kJ	711,402
Transportation						1,731,022
Transportation	32.5		Diesel fuel	53,200	kJ/kg	1,731,022
Biodiesel production						5,851,942
Ethanol	129			26,400	kJ/kg	3,405,600
Estimated lost work; i,e, Exergy loss		402,519	Electricity	4.17	kJ/kJ	1,678,503
Recycling for water		153,258	Electricity	4.17	kJ/kJ	639,087
Recycling for ethanol		30,527	Electricity	4.17	kJ/kJ	127,297
Recycling for catalyst		349	Electricity	4.17	kJ/kJ	1,454
Total ecological cost for biodiesel						8,802,864
Work produced by this product in a Diesel Engine						12,042,584
Chemical exergy	1000			40,141	kJ/kg	12,042,584
Irreversibility indicator: I_r						0.27

The major exergy inputs to the process are algal oil and ethanol (Table 4). In the process, exergy content of the reactants is upgraded by converting these into biodiesel and glycerin. A total exergy increase of 0.29 GJ/ton of biodiesel is achieved in the outlet streams. The exergy content of ethanol is decreased by 3.9 GJ/ton of biodiesel, since it leaves the process in form of liquid solutions.

To be able to use a fuel in Diesel engines it has to inherit certain characteristics concerning its viscosity, density, flash point, solidifying point etc. Xu et al. [36] gave a comparison of biodiesel produced from microalga "Chlorella protothecoids" with conventional diesel fuel and ASTM biodiesel standards. As energy source, the most important property is the heating value. In the case of hydrocarbons, the chemical availability is closely related to the heating value. The chemical exergy of the proposed biodiesel is compared with those of the other fuels in Table 5. Algal biodiesel has ca. 8.8 GJ/ton higher chemical exergy than that of the biodiesel from cooking oil, but ca. 7 GJ/ton less exergy than common diesel fuel and gasoline.

In a Diesel Engine, combustion of the fuel is usually the major source of the exergy destruction. Exergy destruction via combustion is in general the most obscure and difficult cause of irreversibilities. Irreversibilities in the combustion rise with the number of atoms in the molecule (i.e. lighter molecules have less irreversibilities when they burn) and decrease with the oxygen content, due to better mixing with the reactants [6]. Studies show that fuels with higher average chain lengths cause lower NO$_x$ emissions [37,38]. If biodiesel from algae is compared with octane, it is seen that biodiesel is heavier and contains oxygen. So, better mixing properties and more irreversibility during combustion are expected. Since these are competing mechanisms, experimental investigation is necessary to be able to compare the overall exergy destruction during the combustion of both fuels. On the other hand, since biodiesel has longer molecules, NO$_x$ formation is expected to be lower.

Exergy of the algal biodiesel (exergy available for consumption in the Diesel engine) is 40 GJ/ton, whereas the total exergy loss in the algal biodiesel production process is 0.19 GJ/ton, implying that exergy available for consumption in the engine is almost 213 times of what is consumed in the production process. This simple calculation implies that the efficiency of this process is very high.

An important issue in the assessment of a new energy source is its economic value. Production of the conventional diesel costs about 0.35 USD/L, whereas biodiesel costs 0.5 USD/L [36]. It is feasible to use the cheapest resource first. Hence, fossil fuels are still attractive in economical point of view. However, the stockpile of the fossil fuels is used up thousands of times faster than it was built up, and the trend is not sustainable [9]. Furthermore, the environmental consequences and the increase in carbon dioxide levels related to the fuel combustion force us to use renewable, biodegradable and non-toxic alternatives. In the last decade, numerous

Table 3
Exergy destruction in each unit operation.

Exergy destroyed in		
Mixer	1426 kJ	0.75%
Reactor	127,605 kJ	67.49%
Holding tank	53,394 kJ	28.24%
Biodiesel separation	6,162 kJ	3.26%
Glycerin separation	486 kJ	0.26%
Total exergy destroyed	189,074 kJ	

Table 4
Exergy content of each component (normalized for 1 ton of biodiesel production).

Exergy input	
Algal Oil	37.9 GJ
Ethanol	7.7 GJ
Exergy output	
Biodiesel	40.1 GJ
Glycerin	2.0 GJ
Ethanol	3.8 GJ

Table 5
The chemical exergy of the proposed biodiesel and those of the comparable fuels.

Fuel	Chemical exergy (GJ/ton)
Algal biodiesel	40.1
Biodiesel from cooking oil [18]	31.3
Common diesel fuel	47.2
Gasoline	46.9

Table 7
Exergy content of algal oil per mass of algae.

Lipid content of algae (dry matter basis)	Total chemical exergy of algal oil per 1 kg of algae
10%	4,035 kJ
20%	8,070 kJ
40%	16,141 kJ
80%	32,281 kJ

researches are conducted on the production of biodiesel. Most of these are focused on biodiesel production from vegetable oil [10,11,39,40]. There are two major drawbacks, if vegetable oil is selected as the raw material. Firstly, even if the process is sustainable according to social, economical and environmental aspects, its renewability according to exergy analysis is questionable. Secondly, a competition with the food industry becomes inevitable. Allocation of large fertile areas for biofuel production is not feasible. A promising alternative is to use algal oil.

Algae make use of sunlight for photosynthesis and convert carbon dioxide, which has low exergy content, into algal oil (Fig. 2). During photosynthesis, solar exergy is used to upgrade the exergy level of the input materials. Vegetation on earth uses nearly 3% of the solar exergy, the rest (ca. 97%) is dissipated. Sun is a nearly infinite source of exergy. Hence, using some part of this exergy, which would otherwise be destroyed via dissipation, increases the overall second law efficiency of the process.

The second major input of the photosynthesis is carbon dioxide. Since this process removes one of the most problematic pollutants from the atmosphere, it may actually offer a new balance for the highly distorted carbon cycle. One of the first human population growth models were suggested by English political economist and demographer Thomas Malthus between 1798 and 1826 in his six times edited treatise "*An Essay on the Principle of Population*" by assuming an unrestricted population growth rate (dC/dt) in proportion with the number of the members of the community (C). Malthus knew the fact that at some stage population growth would precede expansion of the population's resources like food, but this was not incorporated into the model. An improvement for the Malthusian model was suggested a few decades later by Verlhurst, Pearl and Reed by including an inhibition term ($1 - C/C_{max}$), to formulate the *logistic model* of population growth [41]:

$$\frac{dC}{dt} = \mu_{growth} C \left(1 - \frac{C}{C_{max}}\right) \quad (25)$$

where parameter μ_{growth} may be regarded as frequency of giving birth to new members, C_{max} (carrying capacity) is the maximum attainable population provided that the resources supporting the population remain unchanged. The term ($1 - C/C_{max}$) introduces the influence of the saturation of the medium into the mathematical model, in other words as C approaches to C_{max} population feels the adverse effects of over-crowding and the growth slows down. This term also includes the influence of the pollutant products or by-products released to the environment by the population. Since C_{max} is the maximum attainable population in the medium, when C equals C_{max}, population cannot sustain positive growth anymore. The growth of the human population on earth is described by the *logistic model* [42]. Logistic equation is also widely used in the microbial systems [43,44]. Wang et al. [45] reported that after the initial rapid growth a batch culture of microorganisms may enter into the idiophase, where the microorganisms start feeling the inhibitory affects of approaching the carrying capacity of the growth medium. Depletion of the nutrient, metabolic end-product accumulation, difficulty of oxygen supply and over-heating of the medium due to accumulation of metabolic heat are among the adverse affects of over-crowding in the microbial populations. Increase of the global temperature and depletion of the nutrients may also be among the reasons for observing the logistic behavior of human population on earth. The recently proposed algal biodiesel cycle appears to be critical from this point of view. Carbon dioxide, which is released to the atmosphere as a result of combustion processes, is upgraded by microalgae via photosynthesis to synthesize lipids (Fig. 1). The algal biodiesel cycle prevents net carbon dioxide release in the atmosphere. Accordingly, this cycle results in a new balance for carbon dioxide concentration, for global temperature increase, and subsequently for human population increase.

It is worth to mention the effects of the algae type and its lipid content on the efficiency of the algal biodiesel cycle. Algae consist of nucleic acid, proteins, carbohydrates and lipids in varying proportions. Lipids are extracted from the harvested algae and converted into algal oil. Algal oil contains unsaturated fatty acids, like arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid and linoleic acid. The chemical exergy of lipids containing these fatty acids are listed in Table 6. Proportional to the molecular size of a fatty acid, its chemical exergy increases. Lipid content of algae varies in a large range. For instance, the lipid content of *Scenedesmus quadricauda* is only 1.9% of its dry weight, whereas *Scenedesmus dimorphus* can have a lipid content of up to 40%. It is possible to genetically modify algae to increase their lipid content. In order to demonstrate the increase in the total chemical exergy of algal oil with respect to algae's lipid content, the total chemical exergy per 1 kg of algae is calculated as a function of lipid content. Results are summarized in Table 7. The linear relationship between the lipid content and the total exergy shows that, if the lipid content of algae could be doubled by genetic modifications, the amount of algal oil required to produce the same amount of work would be halved.

7. Conclusion

The algae – biodiesel – carbon dioxide cycle provides a positive amount of useful work. The renewability indicator is found to be 0.27. This means that nearly three fourth of the work potential of algal biodiesel is used for its production and to restore the environment. Thus, the net available work gain from this process is about one fourth of work produced by the algal biodiesel. The renewability indicator can be increased, if electricity from renewable sources (eg. hydropower) is used, or the lipid content of the algae is enhanced. Genetic engineering techniques may be helpful to improve this efficiency drastically.

Table 6
Exergy content of lipids found in different algae species.

Lipids with 3 branches of	Molecular formula of the fatty acid	Molecular weight of the lipid (kg/kmol)	e^{ch} (kJ/kg)
Linoleic acid	$C_{18}H_{32}O_2$	879	39,930
Arachidonic acid	$C_{20}H_{32}O_2$	921	40,150
Docasahexaenoic acid	$C_{22}H_{32}O_2$	1,023	40,352

Appendix A. Exergy analysis

The exergy content of a stream may change because of a change in its thermodynamic state (temperature, pressure, composition) and chemical structure (due to chemical reactions). Accordingly, the flow exergy of a medium is the sum of its thermomechanical and chemical exergy:

$$e = e^{th} + e^{ch} \tag{26}$$

Maximum useful work can be obtained from a system as it interacts with its surroundings through reversible processes and reaches the thermal, mechanical and chemical equilibrium. The exergy of a system that is in equilibrium with its environment is zero. The state of the environment is defined as the dead state. Thermomechanical equilibrium is reached at the "restricted" dead state, which is usually chosen as $T_0 = 298.15$ K and $P_0 = 1$ atm. Chemical equilibrium is achieved at the "true" dead state, when all the components in the system is oxidized or reduced in a reversible way, so that the only components that remain in the system are the components in the environment. In the true dead state the composition of the main components are taken as 20.35% O_2, 0.03% CO_2, 75.67% N_2 and 3.03% H_2O [46,47].

The thermomechanical exergy content of a stream is the difference between the flow availability of the stream and that of the same stream at its restricted dead state:

$$e^{th} = b^{th} - b_0^{th} = (h - h_0) - T_0(s - s_0) \tag{27}$$

Here h and s are defined as:

$$h(T, v, N) = h_f^0 + \int dh \tag{28}$$

$$s(T, v, N) = s^0 + \int ds \tag{29}$$

Where h_f^0 and s^0 are the enthalpy of formation and absolute entropy, respectively. In the absence of any chemical reaction, the chemical composition of the inlet and outlet streams remains the same. Therefore, the terms involving the absolute values of enthalpy and entropy drop out of the balance equations. Only terms representing the change due to the thermodynamic state (ds and dh) remain in the governing equations:

$$dh = \left(\frac{dh}{dT}\right)_{v,N} dT + \left(\frac{dh}{dv}\right)_{T,N} dv + \sum \left(\frac{dh}{dN_i}\right)_{T,v,N_j} dN_i \tag{30}$$

$$ds = \left(\frac{ds}{dT}\right)_{v,N} dT + \left(\frac{ds}{dv}\right)_{N,T} dv + \sum \left(\frac{ds}{dN_i}\right)_{v,T,N_j} dN_i \tag{31}$$

In the case of a liquid mixture, second terms on the left hand side of these equations are negligible, because of the incompressibility ($dv = 0$). Furthermore, $\left(\frac{dh}{dT}\right)_{v,N} = c_p$ and $\left(\frac{ds}{dN_i}\right)_{v,T,N_j} = \frac{\mu_i}{T}$.

For an ideal liquid solution, the enthalpy of mixing becomes zero and the chemical potential, μ_i, can be represented as a function of the molar fraction, x_i. Accordingly, equations (8) and (9) assume the following forms:

$$h = \sum_i x_i \left(h_{f,i}^0 + c_{p,i} \Delta T \right) \tag{32}$$

$$s = \sum_i x_i \left(s_i^0 + c_{p,i} \ln \frac{T}{T_0} - R_u \ln x_i \right) \tag{33}$$

For a large number of substances thermodynamic properties are listed in reference books [48,49]. During the calculations, data from reliable databanks are used whenever possible. However, thermodynamic properties for algal oil and biodiesel are not listed in the open literature. Therefore, approximate values are calculated based on group additivity estimates [48] and Kopp's rule [50]. The group additivity estimates provide an approximation for the enthalpy of formation and the absolute entropy of a chemical structure based on the bond energies. Since this estimate provides values for the gas phase, the effect of phase change is taken into account separately.

$$h_{f,i}^0 = h_{f,gas,i}^0 - \Delta H_i^{vap} \tag{34}$$

$$s_i^0 = s_{gas,i}^0 - \frac{\Delta H_i^{vap}}{T} \tag{35}$$

In the calculations, Trouton's rule, which provides a good approximation for most liquids, is employed [28].

$$\frac{\Delta H_i^{vap}}{T} = 88 \frac{kJ}{kmolK} \tag{36}$$

Meissner's equation is used to determine the boiling temperature:

$$T_b = \frac{637(R_D)^{1,47} + B}{(P)} \tag{37}$$

The molar refraction R_D, parachor P and the constant B are taken from the corresponding tables [49]. Kopp's rule is employed in order to predict the heat capacities, which is approximated as the sum of individual atomic heat capacities [50].

Chemical exergy content of a stream is defined as the maximum useful work that can be produced via a reversible, complete, stoichiometric combustion of that stream.

$$e^{ch} = g_f(T_0, P_0) - \left(\sum (x\mu)_p - \sum (x\mu)_r \right) \tag{38}$$

Here, the index p denotes the products (i.e. CO_2, H_2O etc.), and r the reactants (e.g. biodiesel). Chemical exergy content of a substance can be calculated based on the known chemical exergy values of the products at the true dead state. For liquid hydrocarbon fuels of the type C_zH_y, chemical exergy can be predicted with the following equation [46]:

$$e^{ch} = LHV \left(1.04224 + 0.011925 \frac{y}{z} - \frac{0.042}{z} \right) \tag{39}$$

where LHV abbreviates the lower heating value.

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