Life cycle assessment of pyrolysis process of *Desmodesmus* sp.

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Abstract: This paper described a comprehensive assessment of the pyrolysis process of 1 kg *Desmodesmus* sp. cultivated in BG11 medium at the optimum temperature by using life cycle assessment method. This assessment took 1 kg of *Desmodesmus* sp. as a functional unit, and chose energy efficiency analysis and potential environmental impact as assessment indices. The results showed that the energy conversion efficiency index of the pyrolysis process was above 1, which meant the pyrolysis process was beneficial. The primary impact of the pyrolysis process on the environment was eutrophication; which followed by photochemical ozone synthesis and acidification; and global warming impact was the last. The overall environmental impact during the whole life cycle was 1 347.63 mPE_{T2000}.

Keywords: life cycle assessment (LCA), microalgae, pyrolysis, energy conversion efficiency, environmental impact
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1 Introduction

Microalgae enjoy such advantages as high photosynthesis efficiency, a short growth cycle, high oil content, and that they can be produced at a large scale and high density without requiring farm land[1]. In addition, microalgae can grow on organic matters and inorganic salts present in fresh water, sea water and sewages; in this way, they can help to solve such environmental problems as eutrophication of water bodies[2]. Therefore, as an important source of biofuel, microalgae may be one of the potential resources which are most likely to replace fossil fuels in the future.

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At present, the conversion of microalgae into renewable energy by pyrolysis has been getting more and more attentions from experts both in China and abroad. A variety of energy products, including the pyrolysis gas (CO_2, H_2, CO and CH_4), bio-oil (mainly constituted by oxy-organics) and biochar, can be obtained after the microalgae biomass pyrolysis[3]. However, it is largely unknown how much energy the pyrolysis process will consume; how about the energy conversion efficiency; and what about the impacts of the whole process on environment. Therefore, it is necessary to conduct a systematic study about energy consumption of the pyrolysis process and pollutants release in each link.

Life cycle assessment (LCA) is a kind of environmental management method used to understand how a certain type of product or service goes "from cradle to grave"[4]; its objective is to assess the impact of energy use and materials and waste release on the environment, and to seek for opportunities to improve the environment and understand how to make good use of these opportunities[5]. This assessment runs through the whole life cycle of a product, a process or an activity: namely, extraction and processing of raw materials;

manufacturing, transportation and sale of products; use, reuse and maintenance of products; recycling and final disposal of wastes[6].

The analysis steps of LCA mainly include objective and scope definition, inventory analysis, impact assessment, result interpretation and assessment improvement, as shown in Figure 1[7,8]. Taking the pyrolysis process of 1 kg *Desmodesmus* sp. as the target sample, this study conducted a comprehensive assessment of energy consumption and environmental impact of the pyrolysis process of *Desmodesmus* sp.

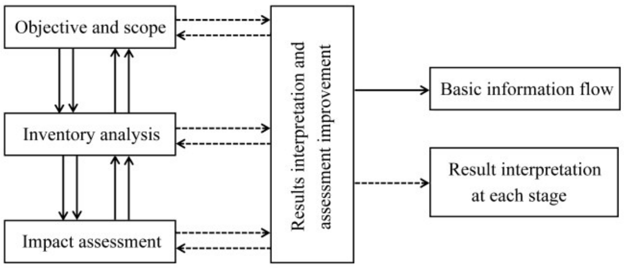

Figure 1 Phases of life cycle assessment defined by ISO14040

2 Materials and methods

2.1 Algae strain and culture condition

Algae strain was a wild-type *Desmodesmus*sp. EJ 8-10, which was isolated from fresh water. It was preserved in BG11 medium and listed in Table 1. Algae were inoculated at 10% (v/v) in 250 mL Erlenmeyer flasks containing 100 mL liquid medium. The culture conditions were as follows: illumination intensity (6000±100) lux; temperature(25±1)°C; illumination duration 14 h : 10 h (light : dark). The BG11 medium and Erlenmeyer flasks were sterilized at 121°C for 20 min.

Table 1 Chemical composition of BG11 media

No.	Chemicals	Concentration/g·L^{-1}
1	$NaNO_3$	1.5
2	K_2HPO_4	3×10^{-2}
3	$MgSO_4\cdot7H_2O$	7.5×10^{-2}
4	$CaCl_2\cdot2H_2O$	36×10^{-2}
5	Citric Acid combined with Ferric	6×10^{-3}
6	Ammonium Citrate	6×10^{-3}
7	EDTA	1×10^{-3}
8	Na_2CO_3	6×10^{-3}
9	H_3BO_3 $MnCl_2\cdot4H_2O$ $ZnSO_4\cdot7H_2O$ $NaMoO_4\cdot5H_2O$ $CuSO_4\cdot5H_2O$ $Co(NO_2)_2\cdot6H_2O$	2.86×10^{-3} 1.81×10^{-3} 2.22×10^{-4} 3.9×10^{-4} 7.9×10^{-5} 4.94×10^{-4}

EJ 8-10 was preserved in BG11 medium for 14 d and the culturing condition was described as 2.1. After 14 d cultivation, algae cells were harvested by centrifugation at 10 000 r/min for 10 min and dried by a vacuum freeze dryer (Savant Instruments Inc., USA), then stored at 4°C before being analyzed, which was named as BG11/8-10.

2.2 Research objective

The objective of current study was to evaluate the pyrolysis process of BG11/8-10 via LCA. Based on previous studies, the optimal pyrolysis temperature of BG11/8-10 was 700°C. With1 kg of EJ 8-10 as a functional unit, a comprehensive assessment of the BG11/8-10 pyrolysis process at the optimum temperature was investigated by using LCA method, including energy efficiency and environmental impact potential analysis.

2.3 System's boundary

The life cycle system boundary of the BG11/8-10 pyrolysis process mainly defined 3 unit sections, including the cultivation section, harvest section, and pyrolysis section (Figure 2).

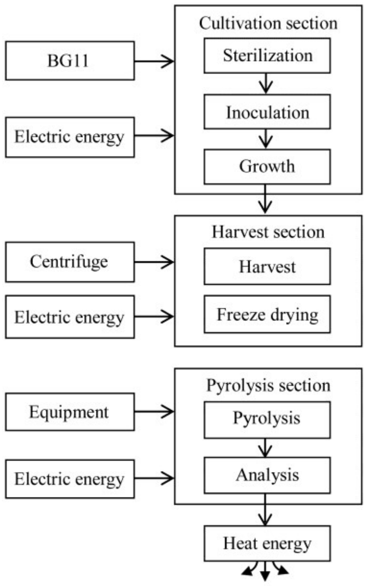

Figure 2 System boundary of BG11/8-10 pyrolysis process

In this study, the following hypotheses and simplifications are:

(i) This study focuses on analysis of the 3 unit sections of cultivation, harvest and pyrolysis. The depreciation and losses within centrifuges and pyrolyzers were ignored;

(ii) The environmental impact of the microalgae growing process was ignored;

(iii) Pollutants produced in all sections of the system were directly released into the environment without post-treatment and reuse;

(iv) Since the ambient temperature coincided with the required growth temperature of microalgae, the energy consumption of the temperature control devices was ignored.

3 Results and discussion

3.1 Environmental impact assessment

Based on the basic principles and framework of LCA defined in ISO 14040[9], the whole process was divided into four steps: definition of objective and scope; inventory analysis; impact assessment; and results interpretation.

3.1.1 Inventory analysis

3.1.1.1 Cultivation section of BG11/8-10

In this study, laboratory cultivation of BG11/8-10 mainly consisted of three processes: medium sterilization (20 min at 121°C); inoculation on a super-clean work bench; and cultivation for 14 d on a culture shelf. As shown in Table 2, the main energy consumption included power consumption of the autoclave, power consumption of the super-clean work bench, and power consumption of the illumination on the culture shelf.

Table 2 Inventory analysis of BG11/8-10 cultivation process

Energy consumption	Electricity	kW·h	242.7
	Needed energy	MJ	1946.5
Gaseous pollutants	CO_2	g	176175.9
	CO	g	55.8
	CH_4	g	436.9
	NO_x	g	271.8
	SO_2	g	276.7
	PM_{10}	g	17
	VOC	g	9.7

The cultivation section of BG11/8-10 mainly consisted of the following processes: sterilization of the BG11 medium (20 min at 121°C); inoculation on a super-clean work bench; and 14 d cultivation on a culture shelf. This test used 5 L Erlenmeyer flasks (with the effective capacity of 3 L), and 0.612 g/L of biomass was obtained after 14 d cultivation. Due to limited capacity of the autoclave, only 8L of BG11 medium can be treated each batch; therefore, to obtain 1 kg of BG11/8-10 required 204 batches of sterilization, which consumed 210.8 kW·h electricity. With limited operating space on the super-clean work bench, a maximum of ten 5 L Erlenmeyer flasks can be inoculated every batch; with an inoculation duration of 10 min, to obtain 1 kg BG11/8-10 required 55 batches of inoculation, which meant a total inoculation duration of 550 min, and electricity consumption of 3.7 kW·h. The cultivation period lasted 14 d, a total of 4 illumination sources of 36 W for plants were used; and the light and dark period was 14 h:10 h, which would consume 28.2 kW·h of electricity.

3.1.1.2 Harvest section of BG11/8-10

Centrifugation method was used to harvest BG11/8-10. Before centrifugation, the 5 L Erlenmeyer flasks were settled down for over 24 h, so as to achieve a clear boundary between solid and liquid parts; the large amount of culture fluid at the upper-supernatant was suck out with a rubber tube, until the fluid level decreased to 1 L. Pollution to the environment caused by the culture fluid at the upper- supernatant was not taken into consideration in this process. This method was simple and no energy consumed, which reduced the workload of subsequent centrifugation. The EJ 8-10 suspension obtained by centrifugation was lyophilized into algae powder, which shall be used as the raw material for subsequent pyrolysis.

In the harvest section of BG11/8-10, due to limited capacity of the centrifuge, only 1.5 L can be centrifuged every batch. With a centrifugation duration of 10 min, and a rotation rate of 6 000 r/min, to obtain 1 kg of BG11/8-10 requires 1090 batches of centrifugation, which would consume 1 199 kW·h of electricity (Table 3). In the lyophilizing process, the vacuum freeze dryer worked for 48 h, and to obtain 1 kg of BG11/8-10 would consume 91.2 kW·h of electricity.

Table 3 Inventory analysis of BG11/8-10 harvest process

Energy consumption	Electricity	kW·h	1290.2
	Needed energy	MJ	10347.4
Gaseous pollutants	CO_2	g	877758.3
	CO	g	278.1
	CH_4	g	2322.4
	NO_x	g	1445
	SO_2	g	1470.8
	PM_{10}	g	90.3
	VOC	g	51.6

3.1.1.3 Pyrolysis section of BG11/8-10

The pyrolysis section of BG11/8-10 consisted of pyrolysis in the pyrolyzer, and online analysis of pyrolysis products. BG11/8-10 was pyrolyzed at the optimal temperature (700°C). Py-GC/MS was adopted for real-time analysis of pyrolysis products; and the results were compared with NIST 2011 spectra library (Version 2.0, National Institute of Science and Technology, USA) to determine the constituents and relative compounds of the pyrolysis products. Based on the properties of the Py-GC/MS instrument, the following assumptions were made:

(i) Since pyrolysis of BG11/8-10 in the pyrolyzer took the form of instant pyrolysis, the energy consumption was neglected.

(ii) Transmission of energy inside the pyrolyzer was neglected.

(iii) Since the pyrolysis duration was minimal compared to the service life of pyrolyzer, the maintenance cost of device was neglected.

(iv) Real-time analysis of the pyrolysis products only considered power consumption in the whole process of programmed heating, separation and mass spectral online detection after the pyrolysis products being injected into GC/MS and all other energy consumptions were neglected. Based on previous conclusions, the programmed heating lasted for 50 min, which meant the pyrolysis products analysis would consume 2.2 kW·h of electricity.

In the pyrolysis section of BG11/8-10 at 700°C, it took 15 min for furnace temperature to rise from the ambient temperature (25.6°C) to the optimal temperature (700°C), which meant the pyrolysis of 1 kg BG11/8-10 would consume 1000 kW·h of electricity (Table 4).

Table 4 Inventory analysis of BG11/8-10 pyrolysis process

Energy consumption	Electricity	kW·h	1002.2
	Needed energy	MJ	8037.6
Gaseous pollutants	CO_2	g	727497
	CO	g	230.5
	CH_4	g	1804
	NO_x	g	1122.5
	SO_2	g	1142.5
	PM_{10}	g	70.2
	VOC	g	40.1

3.2 Impact assessment

3.2.1 Energy efficiency analysis

Energy consumption in the life cycle of BG11/8-10 pyrolysis process equals to the sum of energy consumption at each section. Table 5 listed energy consumption in the entire life cycle of BG11/8-10. It showed that energy consumption in the whole life cycle was 20 331.5 MJ, in which, the energy consumption of harvest section was the highest, accounting for up to 50.89%. The pyrolysis section ranked at the second; and energy consumption in the cultivation section was the lowest. The relationship of three sections in terms of their energy consumption was: harvest section >pyrolysis section > cultivation section.

$$\eta = q_{\text{pyrolysis products}} / LCA_{\text{energy}} \tag{1}$$

where, η is energy conversion efficiency; $q_{\text{pyrolysisproducts}}$ is the high heating value (HHV) of the pyrolysis products, MJ/kg; LCA_{energy} is energy consumption in the life cycle, MJ/kg.

Table 5 Life cycle energy consumption of BG11/8-10. pyrolysis process

Stage	Energy consumption/MJ	Percentage/%
Cultivation	1946.5	9.57
Harvest	10347.4	50.89
Pyrolysis	8037.6	39.53
Sum	20331.5	99.99

The HHV of the pyrolysis products of BG11/8-10 was calculated according to Equation (2) and Equation (3)[10]:

$$HHV\,(\text{OLS}) = 1.87C^2-144C-2082H+63.8C\cdot H+129N+20147 \tag{2}$$

$$HHV\,(\text{PLS}) = 5.22C^2-319C-1674H+38.6C\cdot H+133N+21028 \tag{3}$$

where, C, H and N represent the content of the elements of carbon, hydrogen and nitrogen in the sample, respectively. Equation (2) and Equation (3) are obtained respectively by applying the ordinary least square method (OLS) and the partial least square method (PLS) on the regression analysis of the samples' HHV. Based on recommendations by Friedl et al.[11], the mean value of HHV was calculated using Equation (4).

$$HHV\ (\text{MJ/kg}) = \frac{HHV(\text{OLS}) + HHV(\text{PLS})}{2} = (3.55C^2-232C-2230H+51.2C\cdot H+131N+20600)\times 10^{-3} \tag{4}$$

In order to facilitate data calculations, following assumptions were made for the process:

(i) Summarization and comparison were conducted for those pyrolysis products with larger peak areas and more stable detection results; and those pyrolysis products with a matching degree of over 80% were studied.

(ii) In order to calculate the HHV of the pyrolysis products and to determine the relative content of each constituent of the pyrolysis products, the peak area normalization method should be employed; the chemical formula of each pyrolysis product was determined based on their CAS No.; then the quantity of atoms of each element in the chemical formula was multiplied by the relative content of each constituent to get a new chemical formula; finally, all pyrolysis products were combined together, and fitted into a new empirical formula, namely, $C_xH_yO_zN_iS_m$, based on the principle of adding up the quantity of atoms of the same element.

(iii) A new empirical formula, $C_xH_yO_zN_iS_m$ was proposed.

Based on previous conclusions, the products of BG11/8-10 pyrolysis at 700°C (matching degree over 80%) were fitted into a new chemical formula ($C_{567.71}H_{881.22}O_{7.08}N_{8.94}S_0$). Then, the HHV of $C_{567.71}H_{881.22}O_{7.08}N_{8.94}S_0$ was calculated as 23 655.45 MJ/kg based on Equation (4). The ratio between the amount of the generated energy and that of the consumed energy was calculated to be 1.16>1 based on Equation (1), which means that the pyrolysis process of BG11/8-10 was beneficial.

The energy conversion efficiency (η) of BG11/8-10 pyrolysis process was >1, which meant that the process was beneficial.

3.2.2 Environmental impact load

3.2.2.1 Calculation of environmental impact potential

A potential environmental impact of product refers to the total impacts of all releases to the environment (including resource consumption) in the whole product system, which can be described by the Equation (5):

$$EP(j) = \sum EP(j)_i = \sum[Q(j)_i \cdot EP(j)_i] \qquad (5)$$

where, $EP(j)$ is the contribution of the study system to the type of potential environmental impact i; $EP(j)_i$ is the contribution of the substance i released to the type of potential environmental impact j; Q_i is the release amount of the substance i; $EP(j)_i$ is the equivalent factor of the released substance i for the type of potential environmental impact j[6,12].

This study analyzed the following types of environmental impacts: global warming, acidification, photochemical ozone synthesis, and eutrophication[6,13-15].

3.2.2.2 Contribution potential of global warming

Table 6 revealed that the contribution potential of global warning of the whole life cycle of BG11/8-10 was 2 648.688 kg of CO_{2eq}.; CO_2 emission was the main impact factor; NO_x emission came at the second; and emission of CH_4 and CO came at last.

Table 6 Global warming potentials of BG11/8-10 pyrolysis process

Global warming substance	Effect equivalent factor	Quantity /kg	Sum/kg $CO_{2eq.}$	Proportion/%
CO_2	1	1781.4	1781.4	64.57
CH_4	21	4.56	95.76	3.47
NO_x	310	2.84	880.4	31.91
CO	2	0.564	1.128	0.041

3.2.2.3 Contribution potential of acidification

Table 7 showed the contribution potential of acidification of BG11/8-10 pyrolysis process. The contribution to acidification of SO_2 was greater than that of NO_x.

Table 7 Acidification potentials of BG11/8-10 pyrolysis process

Acidification substance	Effect equivalent factor	Quantity /kg	Sum/kg SO_2 eq.	Proportion/%
SO_2	1	2.89	2.89	59.25
NO_x	0.7	2.84	1.988	40.75

3.2.2.4 Contribution potential of photochemical ozone synthesis

As shown in Table 8, the contribution of the BG11/8-10 pyrolysis process to photochemical ozone synthesis was a result of emission of the gases of volatile organic compound (VOC), CO and CH_4. The greatest contribution came from CO; and VOC was slightly larger than CH_4.

Table 8 Photochemical ozone synthesis potentials of BG11/8-10 pyrolysis process

Photochemical ozone synthesis substance	Effect equivalent factor	Quantity/kg	Sum/kg $CO_{2\,eq.}$	Proportion/%
VOC	0.6	0.1014	0.06084	23.22
CO	0.3	0.564	0.1692	64.58
CH_4	0.007	4.56	0.03192	12.18

3.2.2.5 Contribution potential of eutrophication

The contribution potential of eutrophication of the BG11/8-10 pyrolysis process was listed in Table 9. The contribution of eutrophication came completely from emission of NO_x.

Table 9 Eutrophication potentials of BG11/8-10 pyrolysis process

Name	Eutrophication	Quantity /kg	Effect equivalent factor	Sum /kg $PO_{4eq.}$	Proportion /%
BG11/8-10	NO_x	2.84	0.13	0.3692	100

3.2.3 Normalization of the environmental impact potential

Although the types of environmental impact and the equivalent factors have been determined, it is still unable to assess the results of inventory analysis, which requires normalization of the environmental impact potential. The normalization process is mainly about establishing a basis for normalization, and providing a criterion for comparing relative magnitude of each type of impact. The data normalization formula used for inventory analysis is according to Equation (6)[12]:

$$NP(j) = P(j) \times \frac{1}{T \cdot R(j)} \tag{6}$$

where, T is product service period; $R(j)$ is the reference basis of year i; $P(j)$ is various environmental impact potential or resource consumption. In the system, all depreciation and loss of apparatus were neglected. Therefore, in this study, T was 1 invariable[12]. Thus, the normalization formula for data of inventory analysis can be simplified as Equation (7):

$$NP(j) = P(j) \times \frac{1}{R(j)} \tag{7}$$

Data normalization must be conducted by using data of the same period. In this study, the year of 2000 was chosen as the reference year. Based on Equation (7), the normalized values of environmental impact potentials were calculated and listed in Table 10[17]. Normalized environmental impact potentials took normal person equivalent (PE) as the unit, namely, average environmental impact potential per person per year[18].

In the four types of assessed environmental impacts (Table 10), the BG11/8-10 pyrolysis process had the greatest impact on global warming, after normalization, this impact accounted for 57.64% of its overall impact; its impact on acidification came as the second, accounted for 27.89%; and then followed with the impact on eutrophication and photochemical ozone synthesis, accounted for 13.4% and 1.08%, respectively.

Table 10 Normalized environmental impact potentials of BG11/8-10 pyrolysis process

Impact category	Quantity	Normalization reference value	Normalized potential	Proportion /%
Global warming	2758.688 kg $CO_{2\,eq}$/kg	6869 kg CO_2	401.61 mPE	57.64
Acidification	4.878 kg SO_{2eq}/kg	52.26 kg SO_2	93.34 mPE	13.40
Eutrophication	0.3692 kg $PO_{4\,eq.}$/kg	1.9 kg PO_4	194.32 mPE	27.89
Photochemical ozone synthesis	0.262 kg $C_2H_{4\,eq.}$/kg	34.72 kg C_2H_4	7.55 mPE	1.08

3.2.4 Weighted assessment and environmental impact load

The data obtained by normalization can only indicate the relative magnitude of potential environmental impacts. That a same value of impact potential is obtained by normalization of different types of environmental impact potentials doesn't mean that their potential impact on the environment is equally serious. Therefore, it is necessary to analyze composition of the various environmental impact indices, so as to obtain a composite index of environmental impact, and to provide a comparable assessment result: namely, to assign different weights to different environmental impact types is needed. A ranking of different types of environmental impacts was generated so as invariably to distinguish the magnitude of their harm to the environment.

$$WP(j) = WF(j) \times NP(j) = WF(j) \cdot \frac{1}{T \cdot R(j)} P(j) \tag{8}$$

where, $WF(j)$ is the weight factor of the type of environmental impact j; $NP(j)$ is the normalized impact potential[6].

There are three types of commonly used weight determination method[17]- deliberation by a panel of experts; the distance-to-target method: the target values used in this method usually are environmental policy reference, and specified values of environmental criteria; environmental cost assessment method, which determines weight based on monetized criteria. The current study chose the distance-to-target method, as shown in Equation (9), to determine the weight factor.

$$WF(j) = \frac{ER(j)_{90}}{ER(j)_{T2000}} \tag{9}$$

where, $ER(j)_{90}$ is the sum total of global or regional environmental impact potentials in 1990; $ER(j)_{T2000}$ is the sum of global or regional environmental impact potentials in 2000[12].

The environmental impact potentials obtained after weighted reflect their relative importance, and are comparable. The relative magnitude of various environmental impact potentials also can be obtained by comparison. Therefore, a comparable single index, named as environmental impact load (EIL), is obtained by conducting compositional analysis of various environmental impact potentials; and the index reflects the magnitude of the system's impact on the environment in the entire life cycle. The equation is listed as Equation (10).

$$\begin{aligned}\mathrm{EIL} &= \sum WP(j) = \frac{ER(j)_{90}}{ER(j)_{\mathrm{T2000}}} \times \frac{EP(j)}{ER(j)_{90}} \\ &= \sum\left[\frac{\Sigma Q(j)_i \times EF(j)_i}{ER(j)_{\mathrm{T2000}}}\right]\end{aligned} \tag{10}$$

where, $WP(j)$ is the type of weighted environmental impact; Q_i is the release amount of substance i; $EF(j)_i$ is the equivalent factor for the potential environmental impact j of the released substance i; $ER(j)_{\mathrm{T2000}}$ is the basis of environmental impact potential in 2000.

The environmental impact potentials of BG11/8-10 were weighted: namely, the results obtained after normalization was multiplied by corresponding weighting factor, and then the results were added up to get an overall environmental impact load, as shown in Table 11[19-20]. After weighted, the overall environmental impact load in the life cycle of the pyrolysis process of 1 kg BG11/8-10 was calculated to be 1 347.63 $\mathrm{mPE_{T2000}}$. The primary impact on the environment was eutrophication, accounting for 57.68% in the overall impact; what came next were photochemical ozone synthesis and acidification, accounting for 22.19% and 17.45%, respectively; and the global warming impact came at the last, which only accounted for 2.68%.

Table 11 BG11/8-10 weighted value of environmental impact potentials

Impact category	Normalization value /$\mathrm{mPE_{T2000}}$	Weight factor	Weighted value /$\mathrm{mPE_{T2000}}$	Proportion /%
Global warming	401.61	0.09	36.15	2.68
Acidification	93.34	2.52	235.22	17.45
Eutrophication	194.32	4	777.28	57.68
Photochemical ozone synthesis	7.55	39.6	298.98	22.19

4 Conclusions

Taking the pyrolysis process of 1 kg of BG11/8-10 as a research subject, this study came to the following conclusions after conducting analysis by inventory analysis and establishing a life cycle impact assessment model:

(i) The amount of energy consumed in the pyrolysis process of 1 kg BG11/8-10 was 1 002.2 kW·h of electricity. It was found that the energy consumption of microalgae harvest section > pyrolysis section > cultivation section. It indicated that the harvest section accounted for a large part in the energy consumption of the microalgae's whole pyrolysis process.

(ii) The energy conversion efficiency (η) of the whole pyrolysis process of 1 kg BG11/8-10 (namely, the ratio between the potential energy contained in the pyrolysis product and the energy consumed in the whole process) was >1, which meant this process was beneficial.

(iii) The whole life cycle environmental impact of the pyrolysis process of 1 kg BG11/8-10 was 1 347.63 $\mathrm{mPE_{T2000}}$. The primary environmental impact was eutrophication (accounting for 57.68%), photochemical ozone synthesis (22.19%),and acidification (17.45%) and global warming (2.68%).

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