Bioenergy co-products derived from microalgae biomass via thermochemical conversion – life cycle energy balances and CO_2 emissions

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ABSTRACT

An investigation of the potential to efficiently convert lipid-depleted residual microalgae biomass using thermochemical (gasification at 850 °C, pyrolysis at 550 °C, and torrefaction at 300 °C) processes to produce bioenergy derivatives was made. Energy indicators are established to account for the amount of energy inputs that have to be supplied to the system in order to gain 1 MJ of bio-energy output. The paper seeks to address the difference between net energy input-output balances based on a life cycle approach, from "cradle-to-bioenergy co-products", vs. thermochemical processes alone. The experimental results showed the lowest results of Net Energy Balances (NEB) to be 0.57 MJ/MJ bio-oil via pyrolysis, and highest, 6.48 MJ/MJ for gas derived via torrefaction. With the complete life cycle process chain factored in, the energy balances of NEB_{LCA} increased to 1.67 MJ/MJ (bio-oil) and 7.01 MJ/MJ (gas). Energy efficiencies and the life cycle CO_2 emissions were also calculated.

Keywords

Microalgae-to-bioenergy, thermochemical process, life cycle energy input-output, energy efficiency

List of Abbreviations

EBR	Energy Balance Ratio (EBR)
EE_{LCA}	Life cycle energy efficiency
ER%	Energy recovery percentage
FER	Fossil Energy Ratio
LCA	Life cycle assessment
LD	Lipid-depleted
NEB	Net Energy Balance
NEB_{LCA}	Life Cycle Net Energy Balance
NER	Net Energy Ratio
TC	Thermochemical

1 Introduction

1.1 Microalgae-to-bioenergy

In order for biofuels to be seen as a sustainable alternative to replace fossil fuels, they should provide a net energy gain and be produced in large quantities without any additional environmental burdens. Compared to land-cultivated crop biomass (corn, sugarcane, palm oil, etc), microalgae biomass offers the main advantages of: i) having high photosynthetic efficiencies (Peng et al., 2001; Schenk et al., 2008), ii) being able to be cultivated in water media with varying conditions to give high lipid contents (Rodolfi et al., 2009), and most importantly iii) does not create competition for land and food crops (Clarens et al., 2010; Khoo et al., 2011; Soratana and Landis, 2011). Additionally, if biofuel production were to be introduced at large-scale or national levels, social concerns such as safeguarding global food supply and security has to be accounted for. In addressing this area of concern, microalgae offers the benefit of utilizing non-edible biomass resources (Ahmad et al. 2011).

By coupling the photosynthetic efficiency of these fast growing marine biomass with bio-energy production systems, microalgae is seen as a sustainable pathway to obtain renewable energy

resources for the near future (Greenwell et al., 2009; Scott et al., 2010). However, an investigation to determine the energy efficiencies of the microalgae-to-biofuels pathways from a systems perspective is called for. For this purpose, several authors has carried out life cycle energy and CO_2 balances of biofuel production chains to investigate the environmental performance and feasibility of the bio-energy pathways (Clarens et al., 2010; Jorquera et al., 2010; Khoo et al., 2011).

1.2 Thermochemical conversion

The conversion of microalgae biomass to biofuels and value added products are globally gaining significant prominence and there has been an increased focus on this research area over the last few years. However, despite strong interest among the science and research community, there is to our knowledge no large-scale industrial or commercial plant producing high volumes of biofuels from microalgae. Most studies on deriving value-added products from microalgae have been restricted to experimental and modeling approaches (e.g., Bridgwater, 2003; Aresta et al. 2005; Tock et al., 2010; Grierson et al., 2011). Bioenergy from microalgae can be derived by several conversion methods. Thermochemical (TC) processes can be employed to produce char, oil and gas; and transesterification process converts algal lipids to biodiesel. Development of efficient processes in microalgae conversion to bioenergy are still in the initial phases of research and yet to be fully realized. Three of the thermochemical (TC) methods explored for biomass-to-biofuel conversion processes introduced here are: pyrolysis, gasification and torrefaction.

Pyrolysis is the chemical decomposition of biogenic carbon substances by heating – usually in the absence of oxygen, at high heating rates (ca. 50 – 1000 °C/min). The constituents of biomass pyrolysis when rapidly cooled or quenched will form a liquid product that is usually termed as pyrolytic liquid or bio-oil. Bio-oil has a water content ranging from 15 – 30wt%. The water comes from the original moisture within the feedstock and also from dehydration reactions during pyrolysis (Bridgwater, 2003; Demirbas, 2006; Mohan et al., 2006; Wang et al., 2013).

Unlike pyrolysis, gasification can take place under inert or reduced oxygen atmosphere. It can convert biomass into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture i.e.

syngas is itself a fuel. Gasification has the advantage of producing a product (syngas) that is consistent regardless of the source of biomass used as feedstock. This makes gasification especially useful for dealing with urban waste and other wastes that routinely consist of mixed biomass (Demirbas, 2006; Mohan et al., 2006).

Torrefaction is a thermochemical treatment of biomass at lower temperatures compared with pyrolysis and gasification at less than 300 °C. In this process the biomass partly decomposes giving off various types of volatiles and some non condensable gasses. The remaining torrefied biomass (solid) has approximately 30% more energy content per unit of mass and is usually pelleted to allow for higher densification (620-650 kg/m^3) than regular biomass (820-850 kg/m^3). Pellets are homogeneous, hydrophobic, free of biological activity and produce less smoke upon incineration. Torrefied pellets also contain substantially more energy per unit of volume due to a higher energy (18-20 GJ/m^3 versus 10-11GJ/m^3) content (Friedl et al., 2005; Mohan et al., 2006; Kleinert and Barth, 2008).

The main products of biomass pyrolysis can be broadly described as char (solids), condensable organics (liquids), non-condensable organics (gas) and ash (inorganic metals/minerals). The relative fractions of the various solids, liquids and gaseous products are highly dependent on the reactor's operating conditions especially temperature, pressure, heating rates and residence times. Various thermochemical conversions based on pyrolysis have been developed and three of the more common processes are summarised in Table 1.

Table 1. Summary of common thermochemical techniques that have been applied to biomass

There are limited reports on the energy products derived from the TC process of microalgae or marine biomass. Among the few recent experimental investigations is the use of hydrothermal liquefaction for generating energy products from microalgae (Barreiro et al., 2013). Other research work relating to TC methods carried out in the past decade are: slow pyrolysis of microalgae *Tetraselmis chui* at a maximum temperature of 500 °C (Grierson et al., 2011); thermal conversion of microalgae remnants in a fluidized bed reactor (Wang et al., 2013); the

effect of varying temperature during the pyrolysis of *Chlorella protothecoides* (Demirbas, 2006); batch pyrolysis and thermogravimetric analysis of *Chlorella spp.* and *Nannochloropsis* (Rizzo et al., 2013); fast pyrolysis of *C. protothecoides* and *M. aeruginosa* (Miao et al., 2004), and experimental studies of marine biomass (Campanella et al., 2012; Muradov et al., 2010). These are summarized in Table 2.

Table 2. Experimental studies on co-products derived from microalgae

None of the work (in table 2) described energy balances or efficiencies in detail. These two important factors will be introduced in later sections as important indicators to determine the feasibility of the TC process as well as life cycle process chain.

2. Materials and methods

2.1 Experimental procedure

In a previous research work, attempts were made to convert lipid derived from microalgae (*Nannochloropsis sp.*) into biodiesel (Khoo et al., 2011). This current work expands upon our earlier research by obtaining value-added bioenergy products from microalgae. Further studies were made to convert lipid depleted (LD) dry biomass to produce three bioenergy co-products – char, bio-oil and gas – under three different thermochemical (TC) processes.

The details of the cultivation of *Nannochloropsis sp.* in an integrated photobioreactor (PBR) raceway can be found in Khoo et al. (2011). In this new investigation, lipid-depleted (LD) microalgal biomass will serve as the raw material for downstream investigation of TC processes.

A fixed-bed reactor was selected for this study. The experimental setup used to study the thermochemical conversion of microalgae is shown in Fig. 1. It consists of a 1.5 inch diameter stainless steel tubular reactor with a sample holder (capacity ca. 15cm^3) placed inside a horizontal furnace (Carbolite). The furnace is capable of heating the reactor up to 1200 °C and at a rate of 20 to 30 °C/min.

Figure 1. Fixed-bed pyrolysis experimental set-up

Sweep and/or reacting gas can be provided via the two gas flow controllers which enabled variations in gas compositions and reactor residence times. For the current work, a nitrogen flow rate of 650 ml/min was used and this translated to a residence time of ca. 2 seconds. A thermocouple was also placed inside the fixed-bed reactor in contact with the pyrolysing cellulose to ensure consistent reaction temperatures.

The incoming gas was preheated prior to contact with the pyrolysing sample. The volatile tars and gasses then leave the reaction zone and were allowed to cool immediately via the cooling coil (ca. 0 - 4 °C). The condensed volatiles were then collected within the liquid sampler and subsequently analysed using an Elemental Analyser (EuroEA3000) for C, H and N content. Any entrained volatile tars were then trapped in Liquid traps 1 and 2 and the mass collected within them was carefully measured for mass balance calculations. The cleaned gas stream then passed through the gas sampler where sealed, evacuated vials collect ca. 5 ml of gas for GC-TCD (Agilent: 7890A GC) analysis of the non-condensable gas composition and yields. The residual char was also removed from the reactor and carefully collected for analysis using the Elemental Analyser. Based on the C, H, and N results of the bio-oil and char, the higher heating values (HHV) were calculated based on the empirical relationship given by Friedl et al. (2005).

2.2 LCA of TC process

Within the various areas of research efforts that focus on marine biomass-to-fuels, only a few studies have applied LCA to investigate the energy balances or net energy value (i.e., typically calculated as accumulated energy requirements deducted by the energy value of products), as well as, the CO_2 emissions associated with each stage of the life cycle (Clarens et al., 2010; Jorquera et al., 2010; Stephenson et al., 2010). In order to determine if bio-energy products provide a sustainable alternative to conventional fuels, a throughout accounting of the direct and indirect inputs and outputs of the production chain should be assessed. The life cycle information relating to the cultivation of *Nannochloropsis sp.* in an integrated photobioreactor (PBR) raceway, harvesting, and dewatering processes, can be found in Khoo et al. (2011).

In this paper, the LCA of thermochemical conversion of LD biomass into char, bio-oil and gas are carried out to calculate the energy balances and associated CO_2 emissions for the co-products of bio-oil, gas and char derived from *lipid-depleted (LD) dry microalgae*. These co-products are generated from three experimental TC methods:

i. Gasification at T = 850 °C
ii. Pyrolysis at T = 550 °C
iii. Torrefaction at T = 300 °C

2.2.1 LCA goal and scope

The goal and scope is to compare the energy balances of three bioenergy co-product derived from lipid-depleted microalgae. The experimental conversion processes applied are gasification, pyrolysis and torrefaction. The comparisons are made according to the functional unit of 1 MJ of each co-product of char, bio-oil and gas. The "end use" stage of LCA is not included but will be further discussed in an "integrated bio-biorefinery model".

2.2.2 System Boundary

The system boundary is from "cradle-to-bioenergy co-products". Transportation stages are not included in the LCA system since the experimental set up for the biomass cultivation facility and the TC processes are both located within the same research institute in Singapore.

2.2.3 Inventory data

The energy inputs for microalgae cultivation is displayed in Table 3. Process information and material inputs (e.g., nutrients) for the raceway and photobioreactor have been already been reported in Khoo et al. (2010). This LCA study is based on a lab-scale experimental set-up and will not include emissions from technology. The HHV value of LD *nannochloropsis sp.* is calculated to be 15.18 MJ/kg = $E_{(BIO)}$.

Table 3. Energy requirements in life cycle stages of biomass production

In LCA, allocation methods will directly affect the outcome of the study. In this investigation, mass allocation method is used because of the observed close relation between the physical property and the value of the co-products. From the previous assessment, the authors reported that 1 kg dry biomass contains 25% lipid. Using mass allocation, this implies that 1 kg of lipid depleted (LD) feed can be produced from 1.33 kg dry biomass.

A simple mass balance shows that:

1.33 kg Dry biomass → 1 kg LD biomass → x% bio-oil + y% char + z% gas;

where (x + y + z)% = 100%

Figure 2. LCA system consisting of microalgae production stage, lipid extraction, and thermochemical conversion

3. Theory/Calculation

3.1 Life cycle energy and CO_2 calculations

Energy balances involve accounting for the amount of energy supplied to each process stage and the value of energy contained in the biofuels produced from the system. Within the system boundary (Fig. 2), the main energy values are designated as:

E_1: Energy required for biomass cultivation, harvesting and dewatering to produce dry biomass (in MJ/kg dry biomass)

E_2: Energy required for LD biomass production (MJ/kg)

$E_{(TC)i,j,k}$: Energy required for TC process *i*, *j* or *k*

Where *i* = gasification; *j* = pyrolysis; and *k* = torrefaction

$E_{(BIO)}$ Energy content of LD biomass (HHV in terms of MJ/kg feedstock)

E_{oil} Total MJ of co-product (oil) derived from TC process *i, j or k according to wt%*

E_{char} Total MJ of co-product (char) derived from TC process *i, j or k according to wt%*

E_{gas} Total MJ of co-product (gas) derived from TC process *i, j or k according to wt%*

The energy requirement (E_2) for the process of lipid extraction is estimated at 114 MJ per kg lipid depleted dry biomass (Khoo et al., 2011). We attempt to differentiate the net energy balances for the entire life cycle and TC process alone. Therefore, two definitions are coined: *Net Energy Balance (NEB)* and *life cycle Net Energy Balance (NEB_{LCA}).*

By applying mass allocation in LCA, the Net Energy Balance (NEB) per co-product is defined as the:

NEB = % fraction of co-product x [energy input for TC process/total energy output in MJ of co-product]

$$= [(wt\%)_{oil/char/gas}] * \frac{M_{LD} * [E_{BIO} + E_{(TC)i,j,k}]}{[E_{oil}, E_{char}, E_{gas}]_{i,j,k}} \quad \text{Eqn (1)}$$

Where

M_{LD} = mass of lipid-depleted feed input = 1 kg

And life cycle Net Energy Balance (NEB_{LCA}), from "cradle-to-bioenergy co-products" is defined as follows:

NEB_{LCA} = % fraction of co-product x [total life cycle energy input/total energy output in MJ of co-product]

$$= \frac{[(wt\%)_{oil/char/gas}] * M_{LD} * [E_1 + E_2 + E_3]}{[E_{oil}, E_{char}, E_{gas}]_{i,j,k}} \quad \text{Eqn (2)}$$

Where $E_3 = E_{(BIO)} + E_{(TC)i,j,k}$

The estimated energy input required by the TC processes, rated at typical values of 90% conversion efficiency with 80% thermal efficiency, is estimated from literature to be: $E_{(TC)i}$ = 8.26 MJ/kg; $E_{(TC)j}$ = 6.25 MJ/kg; and $E_{(TC)k}$ = 2.11 MJ/kg for 1 kg input microalgae biomass (Aresta et al., 2005; Xu et al., 2011; van der Stelt et al., 2011). The corresponding life cycle energy efficiency (EE_{LCA}) is rated as: $EE_{LCA} = [NEB_{LCA}]^{-1} \times 100\%$

Finally, total life cycle CO_2 per MJ co-product is:

Total life cycle CO_2 = $[(wt\%)_{oil/char/gas}] * M_{LD} * [-C_{BIO}] + C_{E1} + C_{E2} + C_{E(TC)i,j,k,}$ Eqn (3)

Where

C_{BIO}: CO_2 sequestered during biomass growth

And $C_{E1;}$ C_{E2}; C_{ETC}: CO_2 emitted due to E_1; E_2; $E_{(TC)i,j,k,}$ respectively

4. Results and discussions

The energy requirements (E_1 total) for biomass cultivation, harvesting and dewatering, and associated CO_2 emissions are displayed as Figs 3a and 3b. Both results are allocated to the amount of 1 MJ dry LD biomass generated.

Fig 3a. Life cycle energy (E_1) results allocated to produce 1 MJ dry biomass produced

Fig 3b. Associated CO_2 results allocated to produce 1 MJ dry biomass

The TC experimental results for each co-product (char, bio-oil, gas) are shown in **Table 4.** The HHV value of LD dry biomass, $E_{(BIO)}$ = 15.18 MJ/kg.

Table 4 Results of percentage weight (wt.%) of co-products derived from 1 kg LD dry biomass input under three TC conditions

Among the three co-products generated from the TC processes, a large percentage turned out to be char – 58.18 wt.% from gasification, 70.62 wt.% from pyrolysis and 74.82 wt.% from torrefaction. The largest and least amounts of gas produced was from gasification at 850 °C, which was 28.08 wt.% and 6.74 wt.% respectively. From the TC experimental results, the HHV of gas derived displayed values as low as 2.67 MJ/kg (from torrefaction) to as high as 38.3 MJ/kg (from gasification). As for char, a low HHV value of 17.0 MJ/kg (on average) was obtained for all three TC process. Comparatively, the HHV values of gas and char from other experimental studies are reported to be around 3 MJ/kg and 25 MJ/kg (average) respectively (Grierson et al., 2011; Wang et al., 2013). These differences may be due to different microalgae

species (e.g., *Chlorella spp., Tetraselmis chui, Lemna minor*) used along with different experimental methods (table 2).

All three TC processes resulted in bio-oil yields of nearly the same fractions – 13.74 wt.% (gasification), 15.37 wt.% (pyrolysis), and 18.44 wt.% (torrefaction). The bio-oils derived from the experiments display HHV values of 15.5, 34.1, and 37.3 MJ/kg (table 4). With the exception of the low HHV value of 15.5 MJ/kg (from torrefaction), the energy contents of the co-product agree well with other studies. The literature compiled in table 2 reports microalgal derived bio-oils having HHV values in the range of typically 28 – 39.7 MJ/kg (Miao et al., 2004; Demirbas, 2006; Grierson et al., 2011). Other sources also verified that the HHV of algal oils fall in the range of 33 – 39 MJ/kg (Shirvani et al., 2011). An exceptionally high HHV of 57 MJ/kg bio-oil derived from *Chlorella vulgaris* was reported by Wang et al. (2013).

The results of NEB are displayed in Fig 4a.

Fig 4a. Results of NEB

The results of net energy balances (Eqn 1) seem most favorable results obtained from pyrolysis and gasification for producing bio-oil (0.57 and 0.69 MJ/MJ respectively) and gas (0.56 and 0.71 MJ/MJ respectively); and least preferred for the generation of gas from torrefaction (6.48 MJ/MJ).

In view that any bioenergy pathways should offer more sustainable alternatives than conventional fuels, the importance of energy balance cannot be ignored. Several other energy indicators have been developed. Among them, Xu et al. (2011) proposed an overall energy balance coined Fossil Energy Ratio (FER) as:

$$FER = \frac{HHV_{biofuel} * [\text{ GJ products }]}{E_{input} * [\text{ GJ fossil energy input}]}$$

The authors reported values of FER of 1.50 and 1.37 for two scenarios for the pyrolysis of microalgae *C. vulgaris* to biofuels. Synonymous to Eqn 1, $(FER)^{-1}$ is 0.67 and 0.73, which are

comparable to the TC results of this study for bio-oils generated from pyrolysis/gasification. Duan and Savage (2011) carried out hydrothermal liquefaction of microalgae species *Nannochloropsis sp.* to produce bio-oil under the influence different types of catalysts. The authors analyzed the bio-product energy balance (E_{oil}/E_{algae}) as "chemical energy (HHV) in the bio-oil product relative to those quantities in the microalgal feedstock…" (p. 60). The results of E_{oil}/E_{algae} ranged from 0.74 – 1.19 MJ/MJ. These values translate to energy input-per-output of 0.84 to 1.35 MJ/MJ. No other work has been found on the energy balances or ratios for the co-products of both char and gas derived from microalgae via thermochemical conversion alone.

Khoo et al. (2011) claimed that one of the main challenges faced in microalgal derived biofuel is the high amount of energy use, especially during lipid extraction. In the previous work, lipids are utilized to produce the bulk of the biodiesel, whereas in this study the lipid-depleted biomass is thermochemically converted to bio-oil, char and gas. A comparison of biodiesel from the same species of microalgal (*Nannochloropsis sp.*) is also shown in the next energy balance result, displayed as Fig. 4b. When the complete life cycle process chain of microalgae-to-biofuel is factored in, the energy ratios NEB_{LCA} (Eqn 2), increases according to: i) the proportions of the wt.% of each co-product; ii) energy demands of E_1 (microalgae production), and iii) E_2 (lipid extraction and separation).

Fig 4b. Results of NEB_{LCA} for char, bio-oil and gas from LD microalgae biomass (and comparison with biodiesel from lipid microalgae)

In another LCA study of biofuels, Shirvani et al. (2011) conducted a life cycle energy balance of algal-derived biodiesel. The authors introduced Energy Balance Ratio (EBR) as:

$$EBR = \frac{\text{Total fossil energy input (MJ)}}{\text{Total energy output (MJ)}}$$

The reported EBR is 3.22 MJ/MJ, from microalgae-to-biodiesel. Comparatively, Khoo et al. (2011) reported a higher value of 4.44 MJ input per MJ biodiesel. Slade and Bauen (2013, p. 2), on the other hand, defined Net Energy Ratio (NER) as the "sum of the energy used for cultivation, harvesting and drying, divided by the energy content of the dry biomass", to

investigate the life cycle net energy balances of a few microalgae-to-biomass production systems. Out of 11 comparisons, the NER of six cases resulted below 1.0, and the rest of the results had a range between about 1.2 MJ/MJ to as high as 6 MJ/MJ. However, these results are limited to the energy content of dry biomass, and did not include biomass conversion to any form of bio-energy products.

Razon and Tan (2011) claimed that the high energy input required for microalgae production and oil extraction will practically result in more energy consumed than produced. In their analysis, bio-diesel and bio-gas was derived from *Nannochloropsis.* They reported a range of 8.3 to 11.1 MJ per MJ biogas from *Nannochloropsis.* Soratana and Landis (2011) conducted LCA comparisons of different microalgae systems to project various environmental impacts. However, energy balances of algae-to-bioenergy products were not reported.

To date there has been no other investigations found reporting a life cycle production chain energy ratio pertaining to co-products based on mass allocation of wt.% of each bio-oil, gas or char yields.

Following Eqn (2), the EE_{LCA} of gasification is 16.8% for char, 56.4% for oil and 34.1% for gas; and for pyrolysis, 14.6% (char), 55.9% (oil) and 59.9% (gas). Compared to the first two TC processes, torrefaction does not boast good life cycle energy efficient results: 14.4% (char), 38.9% (oil) and 14.3% (gas). The results are compiled in Table 5.

Table 5. Results of life cycle energy efficiency of the whole system (EE_{LCA})

In an attempt to evaluate the energy efficiency of algal-to-energy processes, Biller and Ross (2011) calculated the energy recovery percentage (ER%) using the following equation:

$$ER\% = \frac{\text{HHV of bio-crude} * \text{mass of bio-crude}}{\text{HHV of feed} * \text{mass of feed}} \times 100\%$$

The ER% results range from 41% to 66% for bio-crudes derived from *Nannochloropsis sp*., and 19.3% to 50.7% from *Spirulina*. However, these energy efficiency results did not factor in the

life cycle of microalgae production, nor the energy required during the conversion of algal biomass to biofuels.

Both results (NEB and NEB_{LCA}) are comparable to near-similar types of research efforts reporting various energy indicators (i.e., FER, EBR, NER) of biomass-to-bioenergy systems (Xu et al., 2011; Shirvani et al., 2011; Slade and Baun, 2013). A summary of the energy indicators are displayed in Table 6.

Table 6. Summary of energy indicators

A graphical comparison of some selected energy ratios are presented in Fig. 5. The bioenergy derivatives from microalgae are compared against conventional diesel as a benchmark, which has a life cycle energy input-to-output ratio of 1.2 MJ/MJ (NREL, 1998).

Fig 5. Comparisons of NEB_{LCA} with energy input-to-output ratios from selected sources

One of the reasons for the unusually low energy balances reported by Duan and Savage (2011) is that a full chain LCA is not considered, nor the energy requirements for hydrothermal liquefaction. Another two optimistic results displayed by Xu et al. (2011) may be due to the high thermal efficiency of pyrolysis which is rated as 95%. Except for these four sets of results, the energy efficiencies of the microalgal production chain for the rest are displayed. A measure of 83.3% energy efficiency can be used as a practical benchmark for any bioenergy pathways.

The life cycle CO_2 results allocated to char, bio-oil and gas from LD microalgae biomass is displayed in Fig. 6.

Fig 6. Life cycle CO_2 results of char, bio-oil and gas from LD microalgae biomass (comparison with biodiesel from microalgae)

Microalgae is reported to be one of the most efficient plants when it comes to converting sunlight and CO_2 into biomass. Therefore, by coupling the photosynthetic efficiency of microalgae with

biomass-to-bioenergy production, a sustainable pathway to renewable energy sources is expected (Greenwell et al., 2009; Scott et al., 2010). However, as displayed in Fig. 6, the CO_2 emissions from energy demands of the production chain outweigh the benefit of CO_2 amounts absorbed during microalgae cultivation.

4.1 Key issues for sustainable bioenergy production

The quest to obtain bioenergy and other bio-based products from renewable resources are a growing need to reduce the dependence on depleting fossil fuels. Biofuels from microalgae have attracted global research interest since they offer the benefit of utilizing non-edible biomass and does not compete with land used for growing food crops. However, in order for microalgae-derived biofuels to be seen as sustainable scheme, they should provide a net energy gain and be produced in large quantities without any additional environmental burdens. Many challenges still need to be overcome before microalgae-derived biofuels become commercially viable and environmentally sustainable.

Apart from the need for cost-effective microalgae production facilities with high efficiencies, downstream processing remains a major issue in microalgal-to-bioenergy pathways. Thermochemical methods such as pyrolysis seem to be a growing area of research and development where high conversion rates have been reported (e.g., Demirbas, 2006; Miao et al., 2008; Muradov et al., 2010). Some of the other key development areas highlighted are (Kirrolia et al., 2013):

- cost-effective and high productivity rate of microalgae feedstock, including efficient drying and extraction methods
- advancement of TC processes that are thermally efficient
- advancement of methods that offer high conversion rates of biomass to value-added products
- use of bio-energy residues (char) as an additional source of power
- an introduction of integrated bio-refineries to broaden microalgae co-product ranges that are commercially beneficial, such as nutraceuticals
- genetic engineering of algal strains that exhibit high growth and productivity rates

A conceptual bio-refinery model is illustrated in **Figure 7.** In order to make the LCA investigation more complete, future work is recommended to further explore the "end uses" of bioenergy or various other co-products derived from microalgae resources.

Figure 7. Proposed integrated biorefinery model

5 Conclusions

In this case study, the net energy balances for the entire life cycle and TC process alone were differentiated by *NEB and* NEB_{LCA}. The TC results showed the range of NEB for gasification to be 1.34 (char), 0.69 (bio-oil), and 0.71 (gas); for pyrolysis: 1.26 (char), 0.57 (bio-oil) and 0.56 (gas); and finally for torrefaction to be 1.04 (char), 1.12 (bio-oil), and 6.48 (gas). When the entire life cycle process chain is factored in, the energy balance, $NEB_{LCA,}$ increases according to both the proportions of the wt.% of each co-product and energy demands of E_1 (production) and E_2 (extraction and separation).

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Bioenergy co-products derived from microalgae biomass via thermochemical conversion – life cycle energy balances and CO_2 emissions

Khoo, H.H.; Koh C.Y.; Shaik, S.; Sharratt, P.N.

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Table 1. Summary of common thermochemical techniques that have been applied to biomass

Process	**Conditions**	**Products**
Torrefaction	Temperature: 200-300 °C Pressure: 1 bar Heating rates: <50 °C/min Inert atmosphere	Primarily solid (yield: 80% dry basis)
Pyrolysis (e.g. fast-, flash-, ultra-, vacuum-pyrolysis)	Temperature: 500-800 °C Pressure: 1< to 10 bars Heating rates: up to 10,000 °C/min Inert atmosphere	Primarily liquids (75%) [acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans]
Gasification	Temperature: 700-1000 °C Pressure: 1< to 10 bars Heating rates: up to 10,000 °C/min Inert atmosphere	Primarily gases (85%) [CO, CO_2, H_2 and CH_4]

Table 2. Experimental studies on co-products derived from microalgae

Species	Method/operating parameters	Co-product yields	Co-product properties	Reference
Tetraselmis chui	2.4g of microalgae sample was heated in a fixed bed infrared pyrolysis oven for a maximum temperature of 500 °C.	24-43wt.% pyrolytic oil and 34 – 63 wt.% char	pyrolytic oil (28 MJ/kg) and char (14.5 MJ/kg)	Grierson et al. (2011)
Chlorella vulgaris	C. vulgaris was cultivated in an indoor 3800 L closed tubular photobioreactor. Lipids were removed from the dried algae sample. Next fast pyrolysis of algae remnants in a fluidized bed reactor was carried out at 500 °C.	53 wt.% bio-oil; 31 wt% biochar; 10 wt.% gas	bio-oil (57.4 MJ/kg; C:N:H = 52.3: 60.3:66.8); biochar (36.8 MJ/kg; C:N:H = 42.5: 29.6:17.4); gas (2.69 MJ/kg; C = 7.34, H = 4.36).	Wang et al. (2013)
Chlorella protothecoides	Slow pyrolysis conversion of *Chlorella protothecoides* to obtain optimum bio-oil yield. Maximum yield obtained at 502 °C.	Max. yield of of 55.3 wt.% of bio-oil	bio-oil (39.7 MJ/kg)	Demirbas (2006)
Chlorella spp.	Batch pyrolysis of microalgae sample at 450 °C. Next, non-isothermal thermogravimetric analysis (TGA) in nitrogen (N) atmosphere at T up to 800 C was carried out. Solid residues produced at both 300 °C and 800 °C from TGA were also analysed.	Yield of 29 wt.% char; 34 wt.% liquid; 37 wt.% gas	Not reported	Rizzo et al. (2013)
Chllorella protothecoides and *Microcystis aeruginosa*	Fast pyrolysis of both microalgae samples were performed in a fluid bed reactor up to T = 500 °C. Gas chromatograph analyses was carried out. Results showed that bio-oils from microalgae were comparable to diesel fuel.	Bio-oil yields from *C. protothecoides* and *M. aeruginosa* were 17.5 wt.% and 23.7 wt.% respectively.	Bio-oil heating value = 30 MJ/kg (from *C. protothecoides*) and 29 MJ/kg (from *M. aeruginosa*)	Miao et al. (2004)
Lemna minor	Slow pyrolysis of marine biomass at T = 500 °C with Argon (AR) as inert gas. Yields of co-products (gas, oil, char) were determined as a function of T and Ar flow rate.	38wt.% pyrolytic oil and 44 wt.% char	Not reported	Muradov et al. (2010)
Lemna minor	Thermolysis experiments of marine microalgae (14.9 MJ/kg) carried out in a fixed-bed reactor. Co-products distribution and yield were identified with experimental parameters.	Yield of 10.7 wt.% of bioleum; 24.9 wt.% of aquous phase; 45.0 wt.% char; 19.44 wt.% gas	Bioleum (0.13 MJ/kg); aquous phase (0.13 MJ/kg); char (0.31 MJ/kg); gas (0.42 MJ/kg)	Campanella et al. (2012)

Table 3. Energy requirements in life cycle stages of biomass production (E_1)

Process	MJ/kg dry biomass output	Process	MJ/kg dry biomass output
PBR (and CO_2 pump)	3.21 (and 0.146)	Harvesting	0.0167
Raceway	1.152	Dewaterwing	0.36

Table 4. Experimental results of percentage weight (wt.%) of co-products derived from 1 kg LD dry biomass input under three TC conditions

TC Process	Char	Bio-oil	Gas
		Co-Product weight fraction (wt%)	
Gasification (T @ 850 C)	58.18%	13.74%	28.08%
		HHV of co-product in MJ/kg	
	17.5	34.1	32.9
		Co-Product weight fraction (wt%)	
Pyrolysis (T @ 550 C)	70.62%	15.37%	14.01%
		HHV of co-product in MJ/kg	
	17.0	37.3	38.3
		Co-Product weight fraction (wt%)	
Torrefaction (T @ 300 C)	74.82%	18.44%	6.74%
		HHV of co-product in MJ/kg	
	16.6	15.5	2.67

Table 5. Results of life cycle energy efficiency of the whole system (EE_{LCA})

TC Process	Energy efficiency		
	Char	***Bio-oil***	***Gas***
Gasification (T @ 850 C)	16.8%	56.4%	34.1%
Pyrolysis (T @ 550 C)	14.6%	55.9%	59.9%
Torrefaction (T @ 300 C)	14.4%	38.9%	14.3%

Table 6. Summary of energy indicators

Energy indicator	Description	Result/Value	Reference
NEB	Net Energy Balance [Eqn(1)] $\frac{[(wt\%)_{oil/char/gas}]*M_{LD}*[E_{BIO} + E_{(TC)i,j,k}]}{[E_{oil}, E_{char}, E_{gas}]_{i,j,k}}$	Most favorable results obtained from pyrolysis and gasification for producing bio-oil (0.57 and 0.69 MJ/MJ respectively) and gas (0.56 and 0.71 MJ/MJ respectively). Least favored case is the torrefaction of microalgae-to-gas (6.48 MJ/MJ)	This study
NEB_{LCA}	Life Cycle Net Energy Balance [Eqn (2)] $\frac{[(wt\%)_{oil/char/gas}]*M_{LD}*[E_1 + E_2 + E_3]}{[E_{oil}, E_{char}, E_{gas}]_{i,j,k}}$	Most favoured results also from pyrolysis and gasification: about 1.78 MJ/MJ bio-oil) and 1.67 – 2.93 MJ/MJ gas.	
EE_{LCA}	Life cycle energy efficiency $[NEB_{LCA}]^{-1}$ x 100%	14 – 16 %	
E_{oil}/E_{algae}	Defined as chemical energy in bio-oil product relative to microalgae	0.74-1.19 MJ/MJ	Duan and Savage (2011)
EBR	Energy Balance Ratio $\frac{\text{Total fossil energy input (MJ)}}{\text{Total energy output (MJ)}}$	3.22 MJ/MJ for microalgae-to-biodiesel	Shirvani et al. (2011)
FER	Fossil Energy Ratio $\frac{HHV_{biofuel} * [\text{GJ products}]}{E_{input} * [\text{GJ fossil energy input}]}$	1.50 and 1.37 MJ/MJ for pyrolysis of microalgae C. vulgaris to biofuels.	Xu et al. (2011)
NER	Net Energy Ratio. Defined as sum of energy used for cultivation, harvesting and drying; divided by energy content of dry biomass	11 cases investigated, where six resulted < 1 MJ/MJ; the rest 1.2 – 6 MJ/MJ.	Slade and Bauen (2013)
† ER%	Energy Recovery Percentage $\frac{\text{HHV bio-crude*mass of bio-crude}}{\text{HHV of feed * mass of feed}}$ x100%	41% - 66% for *Nannochloropsis sp.*; 19.3% - 50.7% from *Spirulina.*	Biller and Ross (2011)

† ER% does not factor in the life cycle of microalgae production, nor the energy required during the conversion of algal biomass to biofuels.

Bioenergy co-products derived from microalgae biomass via thermochemical conversion – life cycle energy balances and CO_2 emissions

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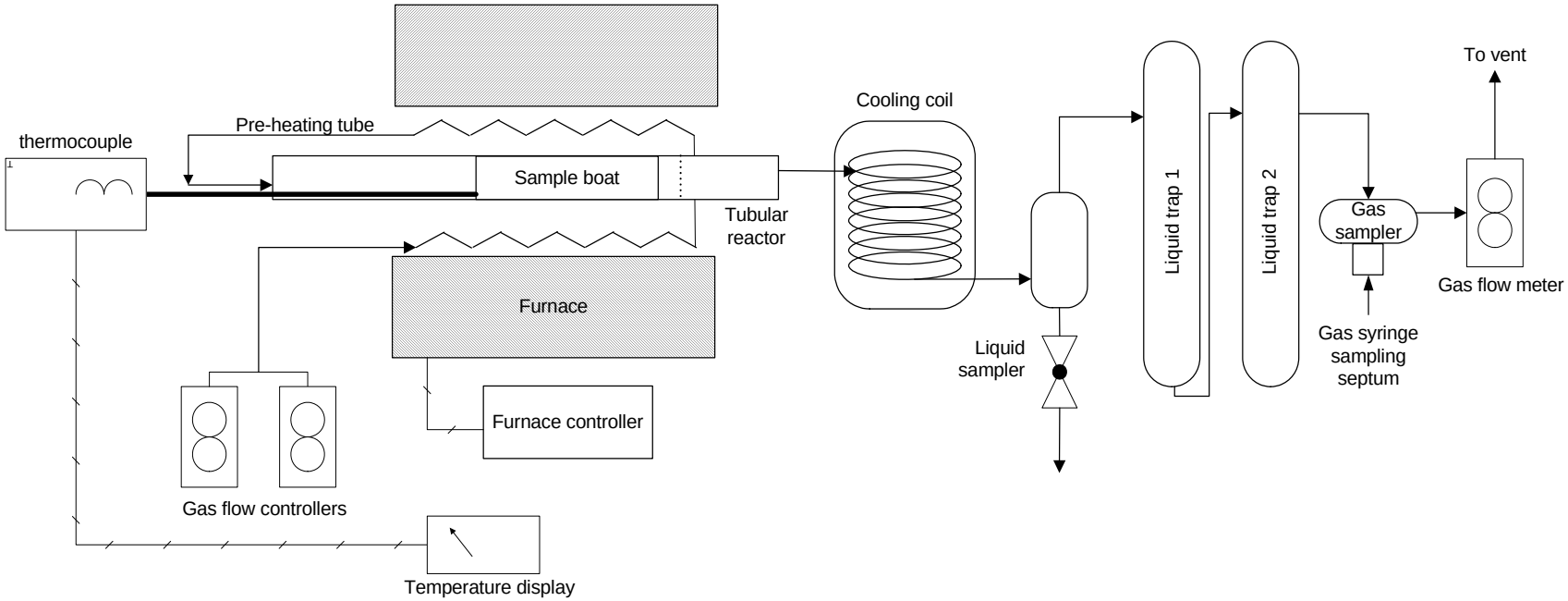


Figure 1. Fixed-bed pyrolysis experimental set-up

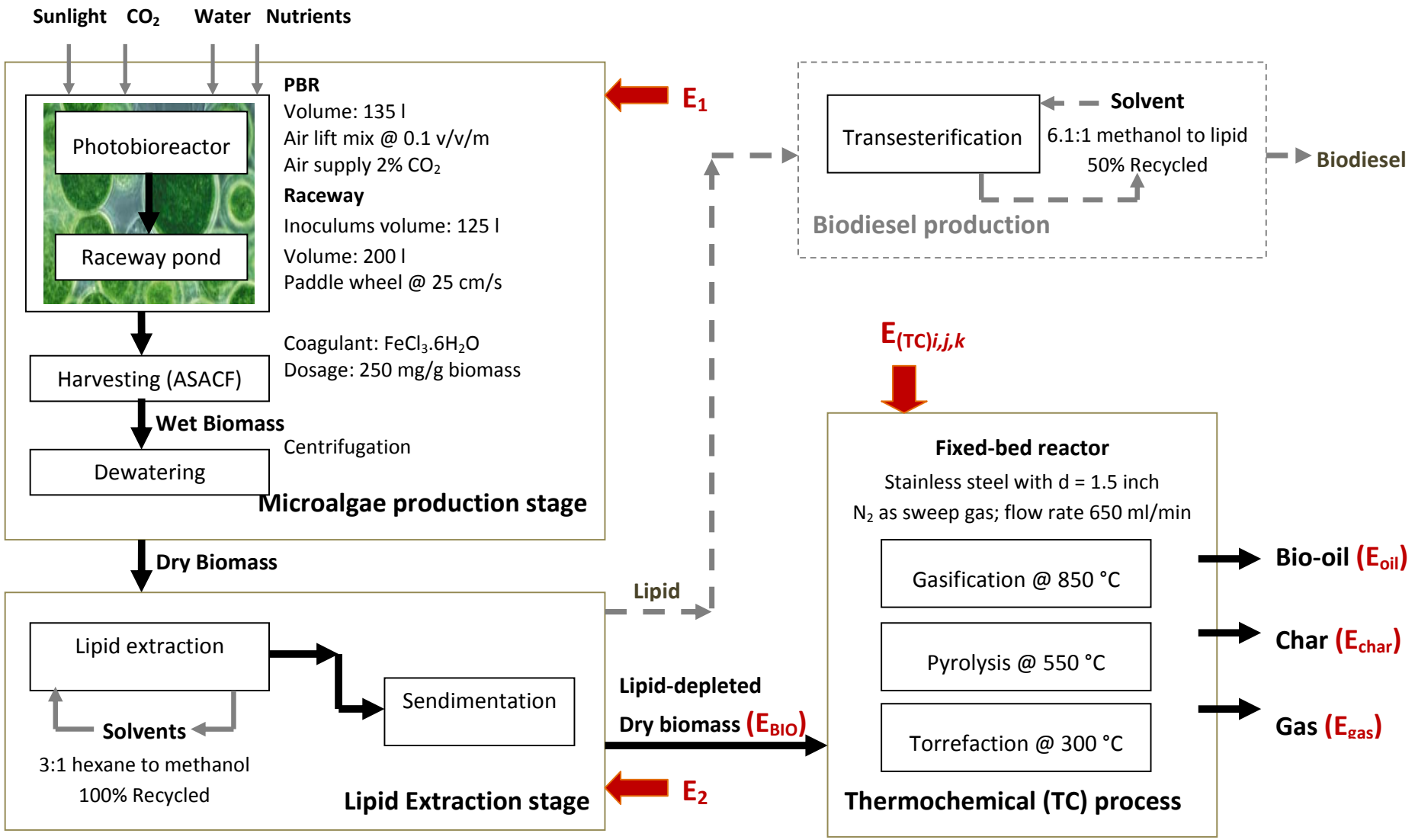
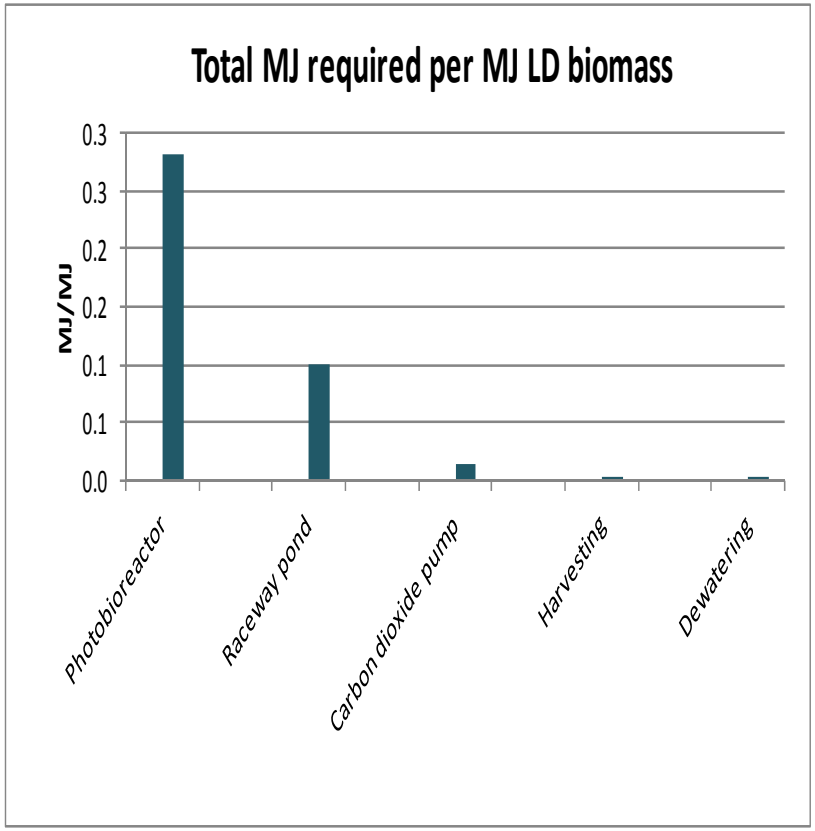


Figure 2. LCA system consisting of microalgae production stage, lipid extraction, and thermochemical conversion. Main material flows illustrated as bold arrows.



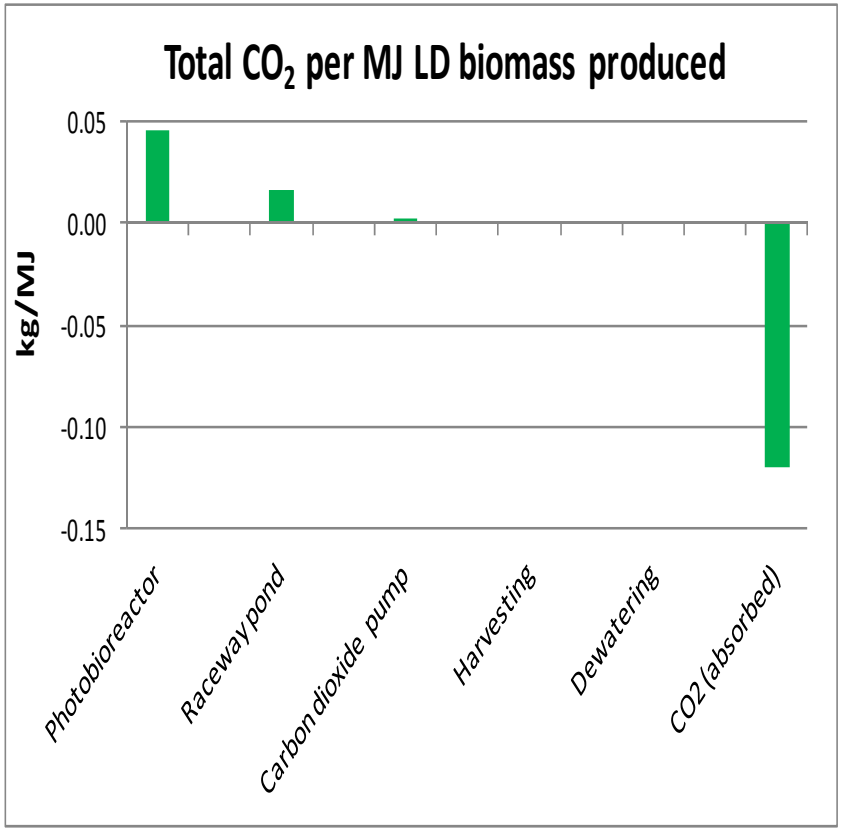


Figure 3a. Life cycle energy (E_1) results allocated to produce 1 MJ dry biomass

Figure 3b. Associated CO_2 results allocated to produce 1 MJ dry biomass

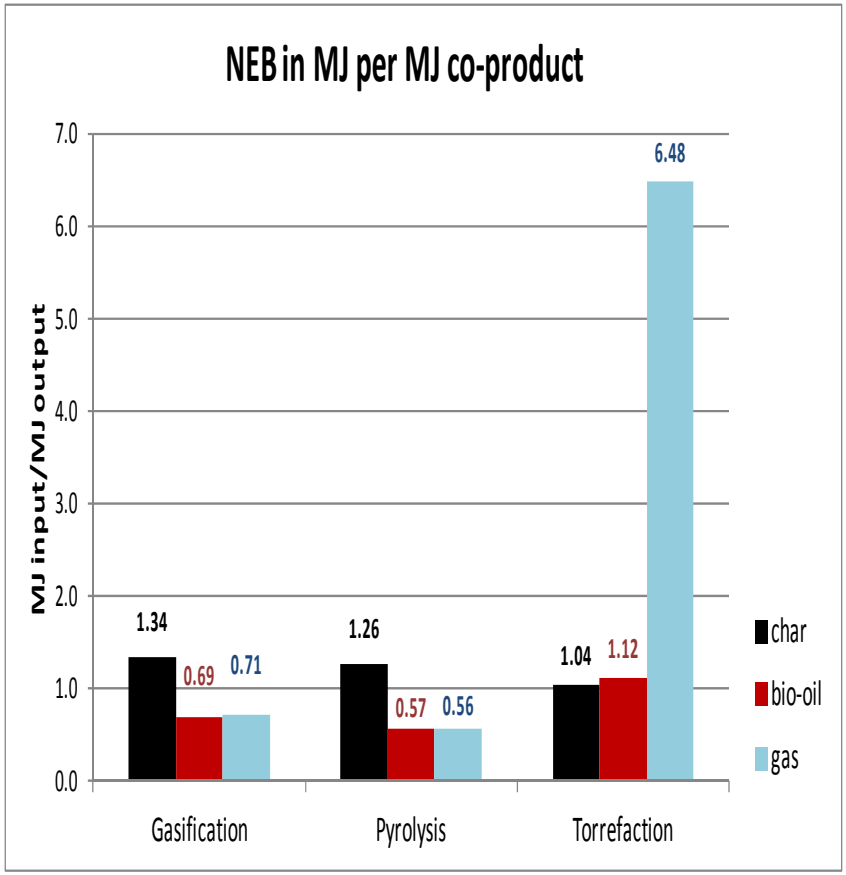


Figure 4a. Results of NEB

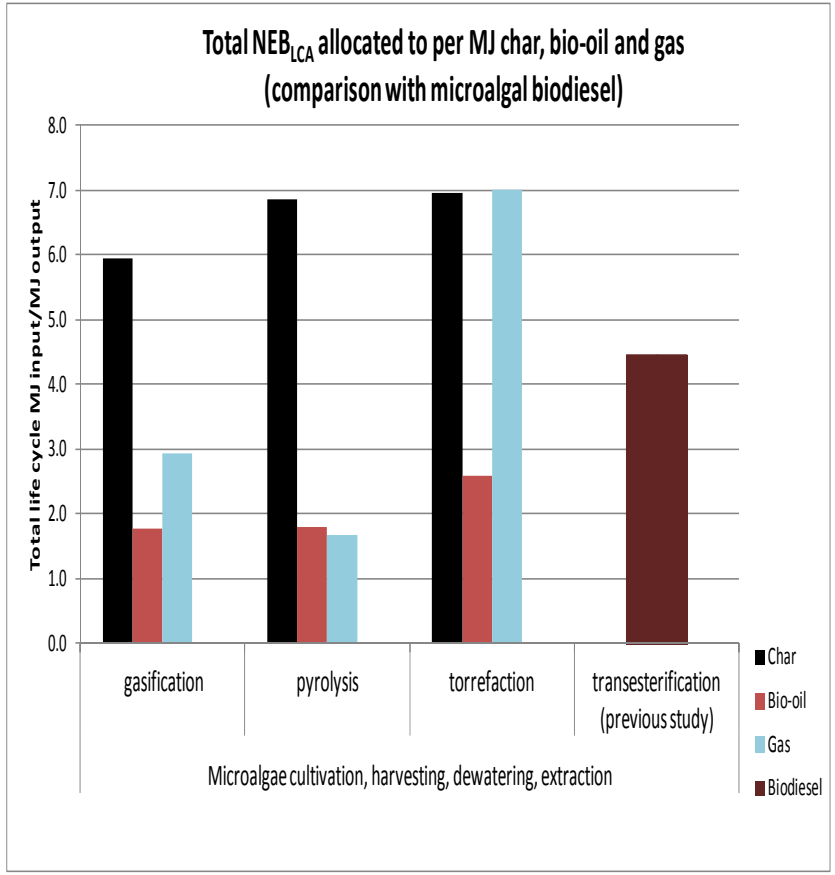


Figure 4b. Results of NEB_{LCA} for char, bio-oil and gas from LD microalgae biomass (and comparison with biodiesel from lipid microalgae)

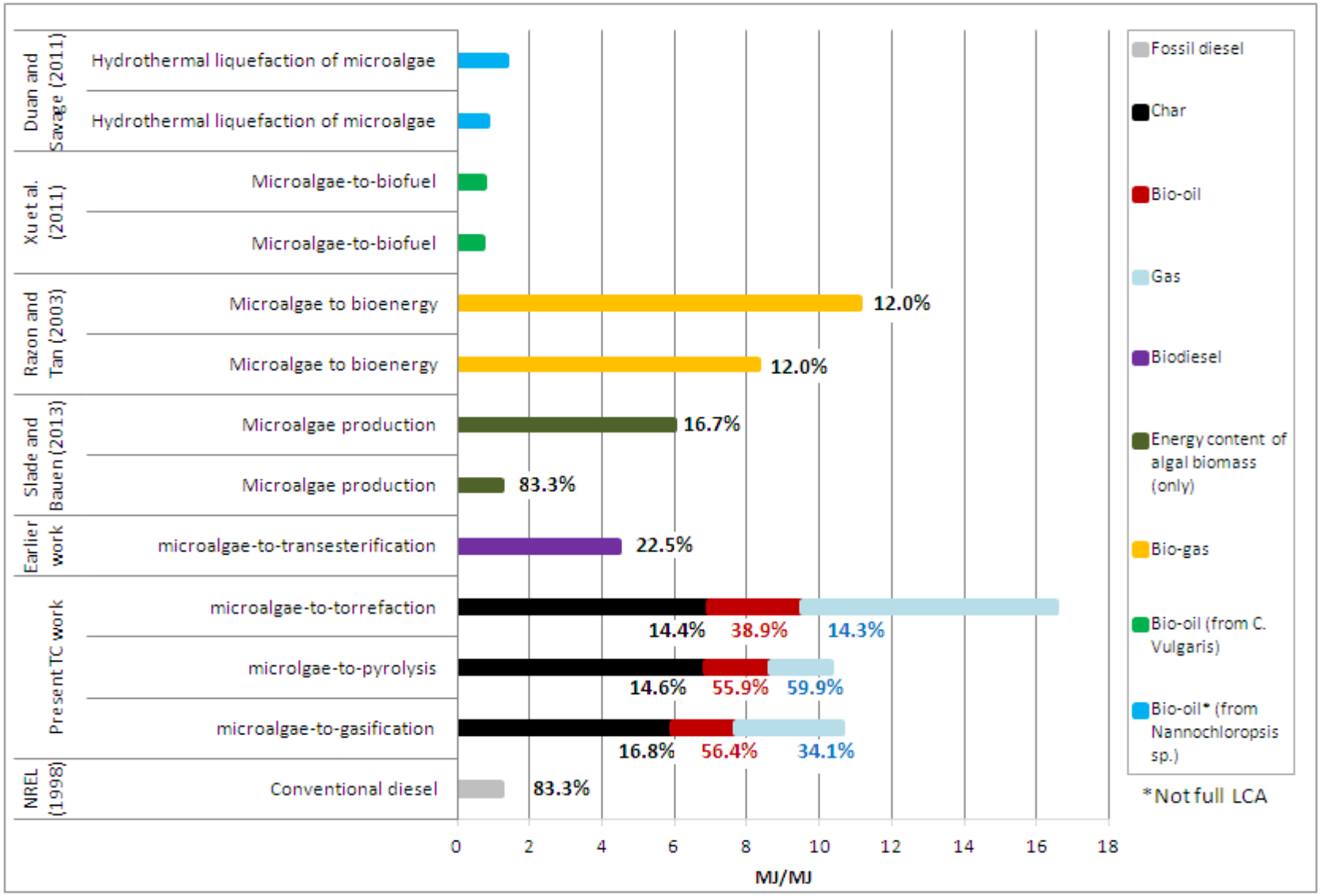


Figure 5. Comparisons of $NE_{IO\text{-}LCA}$ with energy input-to-output ratios from selected sources

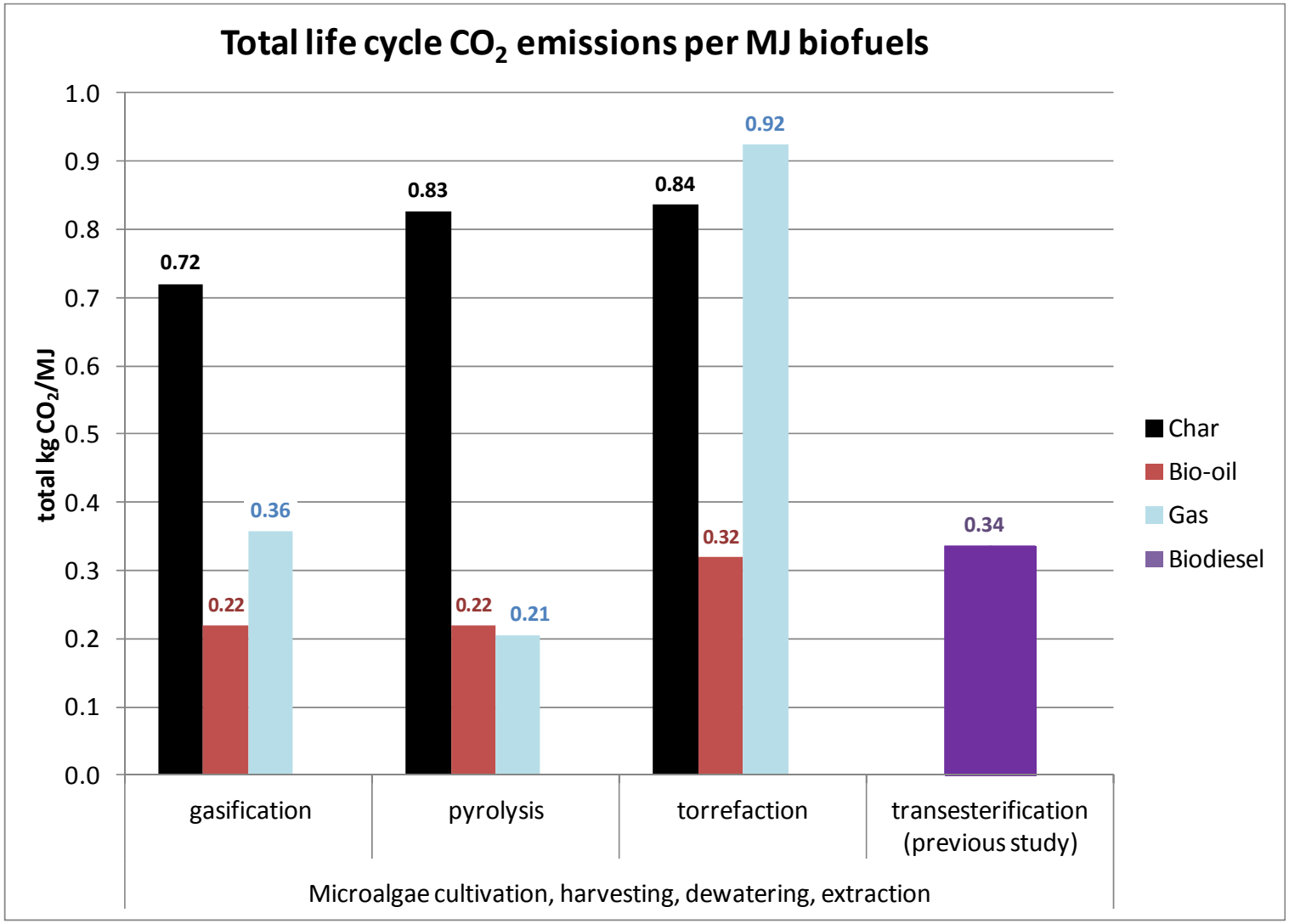


Figure 6. Life cycle CO_2 results of char, bio-oil and gas from LD microalgae biomass

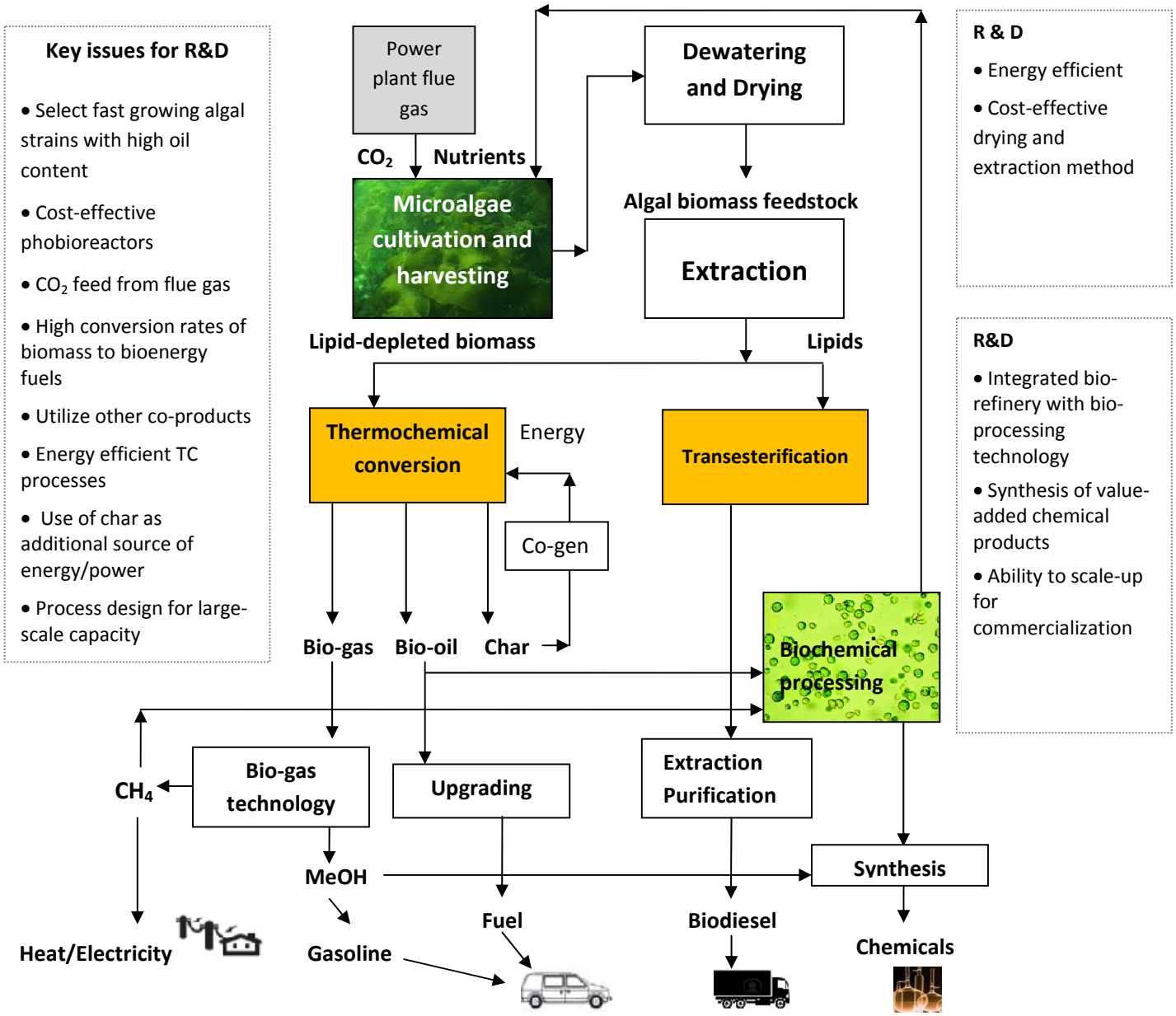


Figure 7. Proposed integrated biorefinery model