Integrated biorefineries: CO_2 utilization for maximum biomass conversion

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Biomass-derived fuels can contribute to energy sustainability through diversifying energy supply and mitigating carbon emissions. However, the biomass chemistry p`oses an important challenge, i.e., the effective hydrogen to carbon ratio is significantly lower for biomass compared to petroleum, and biomass conversion technologies produce a large amount of carbon dioxide by-product. Therefore, CO_2 capture and utilization will be an indispensable element of future biorefineries. The present research explores the economic feasibility and environmental performance of utilizing CO_2 from biomass pyrolysis for biodiesel production via microalgae. The results suggest that it is possible to increase biomass to fuel conversion from 55% to 73%. In addition, if subsidies and fuel taxes are included in the economic analysis, the extra produced fuel can compensate the cost of CO_2 utilization, and is competitive with petroleum-derived fuels. Finally, the proposed integrated refinery shows promise as CO_2 in the flue gas is reduced from 45% of total input carbon to 6% with another 19% in biomass residue waste streams.

Key words: Energy sustainability, Integrated Biorefineries, Biomass Pyrolysis, Microalgae Cultivation, CO_2 Utilization, Technoeconomic Assessment, Life Cycle Analysis.

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1. Introduction

Motivated by scarcity of energy resources, and the pollutions associated with fossil fuels, significant research is devoted to exploring alternative renewable resources in addition to carbon capture and utilization [1]. Among other options, biomass-derived fuels can play an important role in diversifying energy supply and enhancing its security. In addition, from a 'well-to-wheel' life cycle perspective, greenhouse gas (GHG) emissions occurred in production and use of biomass-derived fuels can be partially offset by the biogenic carbon sequestered in the biomass [2]. While the conventional biofuels (*e.g.*, bioethanol) are produced from agricultural crops, with the disadvantage of competition with human food supply chains, recent research has widely focused on producing advanced biofuels [3] from lignocellulosic biomass [4], algae [5,6] and various wastes [7-10].

The conversion pathways include pyrolysis, hydrothermal liquefaction and gasification [11], among which pyrolysis is widely recognized as the cheapest route toward renewable liquid fuels [12-14]. Despite the economic incentives, our knowledge of the pyrolysis pathway is still relatively limited. For example, Mettler *et al.*, [15] identified ten research challenges for biofuel production through biomass pyrolysis, with emphasize on understanding the reaction mechanism. Nevertheless, research into biomass pyrolysis is multi-disciplinary and multi-dimensional. The diverse array of these research activities include advanced analytical chemistry methods for bio-oil characterization [16-18], developing kinetic models for the pyrolysis reactions [19], computational fluid dynamic studies [20], design of new reactors [21], developing new heating methods such as microwave assisted pyrolysis [22-23], optimizing the bio-oil yield [24], developing various bio-oil upgrading methods [25], process intensification [26], techno-economic analysis [27, 28] and environmental assessment [29], in addition to enterprise-wide and supply chain optimization [30-32]. A recent review of the research into biomass fast pyrolysis is provided by Meier *et al.*, [33].

Nevertheless, biofuel commercialization poses an important challenge; the ratio of hydrogen atoms available for combustion to carbon atoms, (H-2×O)/C, of biomass is significantly smaller than fossil fuels. For example, the effective hydrogen to carbon ratio for hybrid poplar ($C_{4.1916} H_{6.0322} O_{2.5828}$) is as low as 0.207 [35]. By comparison the same value for Octane (a representative component of

Gasoline) is 2.25. As a result, in order to convert biomass to liquid fuels, compatible with current energy infrastructure, all the oxygen atoms and a large portion of carbon atoms should be removed as carbon dioxide which deteriorates economic competitiveness of the biomass conversion processes. Therefore, CO_2 utilization is crucial for profitability of future biorefineries.

Several important integration schemes have been proposed by various researchers; an important strategy is to design for hybrid feedstock processes [36]. Examples of hybrid feedstock processes are co-processing coal and biomass [37, 38], and co-processing biomass and natural gas [39]. The important features of hybrid feedstock processes include improving the carbon conversion by adjusting the feedstock ratio and flexibility against fluctuations in the energy market. Similarly, integrating bioprocesses to existing petroleum infrastructures has gained researchers' interests [40, 41]. In parallel, other researchers [42, 43] proposed cogeneration of fuels and chemicals. While producing biofuel requires a high degree of deoxygenation, the application of biomass for producing chemicals may potentially skip costly oxidative processes and provide viable pathways toward production of alcohols, carboxylic acids, and esters [44, 45]. While these integrated biorefineries benefit from economies of scale and diversity of bioresources, they also face a challenge with respect to imbalanced product markets. This is because the chemical market is only approximately 5% of the fuel market.

In addition to the above-mentioned biorefineries with their advantages and limitations, a new class of integrated biorefineries should be proposed, based on carbon dioxide capture and utilization. The options for carbon capture vary from solvent-based technologies such as Absorption/desorption using Monoethanolamine (MEA) [46, 47], to underdeveloped methods such as oxyfuel combustion [48], membrane separation [49, 50], nanomaterial sorbents [51] and chemical looping [52, 53]. In parallel, intensive research is devoted to CO_2 utilization for producing fuel and products [54], and among them microalgae cultivation has gained significant research interest [55, 56]. The diverse array of the algae research activities includes microalgae strain selection and lipid yield enhancement, [57-58] microalgae cultivation and dewatering [59], oil-extraction and different upgrading methods [60-67], in addition to anaerobic digestion of the lipid extracted algae [68], nutrient recovery [69] and biosorption of metals using algae biomass [70]. For a comprehensive review of microalgae technologies, the interested reader may refer to [71-73].

With the aim of enhancing the overall biofuel yields and improving the environmental impacts, the present research proposes an integrated biorefinery comprising of biomass pyrolysis, in addition to solvent-based carbon capture and utilization through microalgae cultivation. The process integration is based on the synergies between the processing steps of these processes, as shown in Fig. 1, and discussed later. It is also notable that the abovementioned combination (pyrolysis/solvent-based carbon capture/microalgae cultivation) is not unique. Other combinations of biomass conversion technologies (pyrolysis, gasification, torrefaction, fermentation, etc.) where considerable amount of high concentration CO_2 is available and can be exploited by a carbon capture technology (solvent-based, adsorption, membrane, chemical looping, etc.) and utilized for biofuel (algae cultivation) or biochemical (e.g., urea) production can potentially fall into the proposed class of integrated biorefineries. Here the rationale behind process integration is synergies between the involved sub-processes in terms of sharing processing steps (e.g., hydrogenation for upgrading, anaerobic digestion for waste treatment and biogas production) and the cost-efficiency of carbon capture and utilization. With the present demonstrating case study, we aim at encouraging future research into process integration and CO_2 utilization among biorefineries.

While the proposed notion of integrated biorefineries featuring CO_2 utilization will benefit from the advancements in all the above-mentioned research directions, the present research will apply the already established base-lines (discussed later) from literature in order underpin the economic and environmental implications of the proposed integration scheme. In the subsequent sections in order to identify the incentives for process integration, firstly, the process description of each sub-process is discussed. Then, the Method Section reports the approaches that were employed for process modelling, economic evaluation and life-cycle analysis. Later, the results of the studies are presented and discussed. The paper concludes with discussion of research achievements and identifying the key research frontiers.

2. Process description

The following text describes the pyrolysis, carbon capture and microalgae processes as they operate stand alone. This introduction initiates a proposal for integration of these processes based on synergies between them.

2.1. Biomass fast pyrolysis and bio-oil upgrading

This process consists of a high-temperature, low-residence time pyrolysis reactor, followed by fast quenching in order to supress undesired secondary reactions which otherwise would decrease the yield of the condensable product in favour of light gases and char. The pyrolysis condensates form a brownish mixture with some undesirable properties. It has a higher oxygen content and a lower energy content compared to petroleum-derived fuels. It is also highly acidic and is immiscible with petroleum-based fuels. Therefore, it is necessary to upgrade the pyrolysis oil by hydrogenation and cracking heavy residues in order to improve the hydrogen content and convert oxygenates.

Bio-oil upgrading consists of several subsections. In the first section, the crude bio-oil is stabilized through hydro-deoxygenation reactions. Then, the stabilized effluents undergo a sequence of separation processes where the water, light dissolved gases and the de-oxygenated fraction with similar properties to diesel and gasoline are separated from the heavy fraction. The final stage of the upgrading process involves hydro-cracking of the heavy fraction and separation of the products.

2.2. Carbon capture and storage (CCS)

In order to separate the carbon dioxide from the flue gases, it is firstly cooled and cleaned of any particulate in a water-wash tower and then fed to an absorption column. In this column, carbon dioxide is chemisorbed into a solvent (*e.g.*, Monoethanolamine-MEA). The cleaned flue gas is washed with water in the upper section of the absorption column in order to minimize the solvent loss. The rich solvent, loaded with the absorbed carbon dioxide, is sent to the desorption column where the carbon dioxide is stripped and separated as the overhead product. The lean solvent is recycled and reused in the first column. The absorption process is exothermic and the desorption process is endothermic. Therefore, the lean solvent needs to be cooled and the temperature of the rich solvent should be increased, providing a heat integration opportunity between these two process streams.

2.3. *Producing biofuel using autotrophic microalgae*

This process converts the carbon dioxide to biodiesel. The first section consists of photobioreactors (PBRs) or open ponds (OPs) where carbon dioxide is converted to microalgae using solar energy and nutrients. Then, the microalgae concentration in the reaction effluent is increased using mechanical methods such as settling, flocculation, and centrifugation. Microalgae consist of lipids, carbohydrates and protein, from which only lipids can be converted to biodiesel. In the next stage, the microalgae cells are disrupted by pressurized homogenization and then the lipids are extracted using a butanol solvent. The effluent mixture, *i.e.*, the extracted lipids and solvent, is then sent to a distillation column for recovery and recycling of the solvent. The crude oil from the bottom of the distillation column is then sent to a hydrogenation reactor where the oxygenated compounds (triglycerides) are converted to biodiesel and a small fraction of naphtha. The residues of solvent extraction comprising of remaining lipids, carbohydrates and protein are sent to the anaerobic digestion section where they are partially converted to methane, carbon dioxide (biogas) and cell-mass (bacteria). The produced biogas is exploited in a combined heat and power cycle (CHP) in order to produce electricity and steams. The water from microalgae concentration and also lipids extraction stages, containing the demineralized nutrients, is recycled back to the algae cultivation section.

2.4. *Incentives for process integration*

There are various synergies and integration opportunities among the above-mentioned technologies:

- The carbon conversion efficiency of the stand-alone pyrolysis is relatively low, which should be attributed to the biomass chemistry and the large amount of carbon dioxide produced during pyrolysis and upgrading. By converting the emitted carbon dioxide to microalgae biodiesel, integration can improve the overall carbon yield significantly, *i.e.,* more carbon is fixed in the products.
- The pyrolysis and microalgae processes both need hydrogen to upgrade the intermediate crude oils. In addition, the upgraded effluents need distillation in order to produce the end-use products. This synergy suggests that their integration can benefit from economies of scale.
- Carbon dioxide is produced during the pyrolysis and upgrading processes. In addition, CO2 is

produced during production and combustion of biogas in the anaerobic digestion section. The costs of collecting, capturing and recycling of the carbon dioxide are minimal for the proposed integrated refinery because during the day the flue gas can be directly injected to the microalgae bioreactors, and the costs of carbon capture, compression and storage are only incurred during the night, and there is no need for CO_2 transportation.

Based on these synergies, the present research proposes an integrated biorefinery that is shown in Figs. 2a and 2b and comprised of Section 100: biomass pyrolysis, Section 200 upgrading, Section 300: product separation, Section 400: CO2 capture, Section 500: hydrocracking, Section 600: Hydrogen Production, Section 700: microalgae cultivation, and Section 800: anaerobic Digestion (AD). The applied method for integrating these sections is explained in Section 3.2. The flow diagrams of these sub-processes, their process descriptions and the applied modelling assumptions are reported in Electronic Supplementary Material (ESM).

3. Methods

The following sections report the research methodology. The features of interests include the choice of modelling baselines, seamless integration of the process sections, the assumptions regarding the economic evaluations, and the applied method for the environmental impact assessments.

3.1. Choice of modelling baselines

In order to develop reliable baselines for economic and environmental analysis, three established studies were selected from literature and used as the starting points for the process modelling. The pyrolysis model was based on a study by US Department of Energy (DOE), conducted by Jones, *et al.* [74]. The microalgae model was based on studies by Davis, *et al.* [75] at National Renewable Energy Laboratory (NREL) and Frank, *et al.* [76] at Argonne National Laboratory (ANL). In addition, Process Systems Enterprise has published an example [77] of a rate-based model of the CO_2 capture process by MEA, which is validated based on experimental data [78]. This model was used as the starting point and was adapted to the process conditions. The process throughput was 2000 ton per day of biomass based on the DOE study. Accordingly, the algae process was scaled up to match this throughput. On this basis, the required land and water for the new scaled process is 4.24 larger than the NREL process for the Open Pond scenario and 6.29 times larger for the Photobioreactor scenario. These measures ensured that the modelling assumptions of those studies hold and the proposed biorefinery can be constructed in practice.

3.2. Seamless process integration

Figs. 2a and 2b show the day and night operations. As mentioned earlier, the process throughput was similar to Jones *et al*.,' study [74], *i.e.,* 2000 ton per day (tpd) hybrid poplar fed to the Pyrolysis Section 100 The Upgrading (200), Separation (300), Hydrocracking (500), Hydrogen Production (500), and Anaerobic Digestion (AD) sections operate 24 hours per day and their capacity is based on the pyrolysis section. However, since microalgae cultivation (Section 700) requires solar energy, it can only operate during daylight (assumed 12 hours per day on average). Therefore, for seamless process integration, the microalgae section (unit 700) should be sized at two times larger than the other processes. In addition, the carbon capture process operates only in the night-time. The produced CO_2 is captured, compressed and stored for the next day's operation. The CO_2 stored during the night is later consumed during the day. In addition, during the day operation, the flue gas is directly injected to the microalgae reactors (OP or PBR) in order to minimize the separation costs. Similarly, half of the produced lipids and lipid extracted microalgae are stored in the storage tanks during the day and fed to the corresponding processes during the next night. All the intermediate storage tanks were sized at five times the overall process capacity in order to ensure that malfunctioning of a section would not interrupt the overall production for at least ten days. It was assumed that any produced steam is fed to the site steam headers and can be used in other parts. In addition, it was assumed that any extra electricity or steam produced can be exported and sold at the battery limit, at constant prices.

3.3. Economic evaluation

3.3.1. Cost estimation

It is assumed that this is the nth plant. This eliminates additional costs associated with pioneer plants by assuming other plants using the same technology are currently in operation. It is also assumed that 100% of the required investment is supplied from equity. The Total Capital Investment (TCI) is determined from to Total Purchased Equipment Cost (TPEC) and Total Installed Cost (TIC). The costs of process equipment are evaluated based on the developed process models. In the present study, the costs of conventional unit operations (*e.g.*, distillation columns, pumps, and vessels) were calculated using the Aspen Process Economic Analyzer™. However, the costs of the nonconventional unit operations (*e.g.*, catalytic reactors, pressure swing absorber) were calculated based on the following relation and with reference to the economic data from literature [74-77]:

$$\text{New cost} = \text{Base cost} * \left(\frac{\text{New size}}{\text{Base size}}\right)^{f_{scale}} \qquad (1)$$

A list of detailed equipment cost can be found in ESM. Once the TIC was determined, the indirect costs including engineering (32% of TPEC), construction (34%), project contingency (37%), legal and contractors' fees (23%) were added to yield the TCI. Land cost is $3000 per acre [75] for the algae cultivation section and 6% of the TPEC for the other sections. The variable operating costs including raw materials, utilities, and waste landfill charges are summarized in Table 1. The fixed operating costs including labour and maintenance and overheads as 95% of labour cost were scaled up based on Philipp, *et al.*'s study [84]. Maintenance and insurance were estimated to be 4% of the TCI.

3.3.2. Discounted cash flow method

Once the total capital investment and operating costs were determined, the minimum fuel selling price (MFSP) was calculated using a discounted cash flow analysis. The MFSP refers to the gasoline and diesel blendstock price at which the net present value of the project is zero at a set discounted rate of 10%. While two products are produced, (gasoline and diesel), they were combined and referred to as a 'biofuel product' for simplicity. The economic parameters used in the discounted cash flow calculation were adapted from [74]. The lifetime of plant is 20 years with 2.5 years as construction period and 6 months as start-up time. The income tax rate is 35% and the capital depreciation period is 7 years (MACRS method). The MFSP is reported as 2012 USD for cost distribution analysis and as 2007 USD for comparing with DOE's [74] and NREL's [75] recent studies.

3.3.3. Pump prices

In addition to comparison with the abovementioned baselines, this study also evaluated the economic competitiveness of the produced biofuel with the equivalent petroleum-derived fuels. The selected criteria was the biofuel price at pump, which was determined by including the production cost (MFSP), the fuel distribution cost (0.14 $/gallon [85]), sales tax (4% as general tax in the US [86]), fuel excise tax (0.244 \$/gallon [87]) and subsidies (1.0 \$/gallon [88]). The pump price of biofuel was then compared with the petroleum-derived diesel retail price (\$ 3.97/gallon in 2012) and gasoline retail price (3.68 \$/gallon in 2012) [89].

3.4. Life Cycle Analysis for GHG emissions calculation

The Life cycle analysis (LCA) approach was applied to count GHG emissions for gasoline and diesel through their 'well-to-wheel' life cycles. The functional unit is defined as '1km travelled by a light-duty passenger vehicle'. The GHG emissions results are also reported for 1MJ of fuels produced to facilitate comparison with other LCAs. The machinery in hybrid poplar cultivation and the infrastructure in biofuel production were not included in the system boundary. The analysis of greenhouse gas emissions also included the waste streams from the pyrolysis and hydrotreating sections as listed in Table B.1. of [74]. The life cycle impacts of the biofuel production processes were allocated between gasoline and diesel on an energy-content basis (68.1% is allocated to diesel and 31.9 % is allocated to gasoline in PBR scenario whilst 64.4% is allocated to diesel and 35.6% is allocated to gasoline in OP scenario). The inventory data for poplar production were adopted from Gasol, *et al*.'s study (2009) and summarized in Table 2.

The mass balance including chemical utilisation and energy demand were obtained from an ASPEN Plus™ process simulation. The GHG emission factors for inputs in poplar cultivation, biofuel production processes and fuel storage as well as distribution were taken from the Ecoinvent database v2.2 (Table 3) [91]. Due to the lack of GHG emission factor for CoMo catalyst in hydrotreating and hydrocracking sections, data for zeolite was used as the surrogate [84]. Emission factors for production and use of diesel as well as field emission factors of fertilizers were from IPCC, [92]. Assumptions about transportation are listed in Table 4. With regard to the utilisation of fuel in a passenger vehicle, 0.070 kg gasoline and 0.059 kg diesel are required to travel 1 km [93]. The GHG emissions occurr in vehicle operation when the passenger car travels 1 km, are 0.226 kg CO_2 eq. for gasoline and 0.190 kg CO_2 eq. for diesel [76]. The greenhouse gas emissions analysis also included the waste streams from the pyrolysis and hydrotreating sections [74]. The GHG emissions were derived from Ecoinvent database cooperated in Simparo™ software and were included in the LCA study.

4. RESULTS

4.1. Mass and carbon balance

Figs. 3a-c show the results for the carbon yield distributions; these are based on 2000 ton per day (tpd) biomass feedstock. These results suggest that while the carbon conversion from biomass to biofuel products is limited to 55% in the pyrolysis stand-alone scenario, CO_2 utilization via the microalgae process increases the yield up to 72.9% and 67.6% for PBR and OP scenarios, respectively. Another important feature of interest is that while in the pyrolysis standalone scenario, 45% of the carbon is emitted to the environment, in the integrated scenario this measure is reduced to 6% and 19.3% for PBR and OP scenarios, respectively. In other words, for the integrated scenarios, more carbon is fixed in the products and most of the waste co-products are in the form of biomass residues and can be used as fertilizer or be landfilled.

4.2. Economic assessment

In order to compare the results of the present study with those in liteature [74, 75], the MFSP is recalculated backward to 2007 USD and represented in Fig. 4. The lowest benchmark is the result of Jones, *et al.*'s study [74] that reported the MFSP for gasoline and diesel blendstock to be 2.04 $/gallon for standalone pyrolysis scenario. The highest MFSP for diesel is found in Davis, *et al.*'s study [75] where diesel is produced by algae from CO_2 purchased from a nearby refinery using a photobioreactor system. They reported 20.53 $/gallon and 9.84 $/gallon (2007 USD) for the PBR and OP scenarios, respectively. The MFSPs in the present study are 6.64 $/gallon and 3.53 $/gallon (2007 USD) for the PBR and OP scenarios, respectively. The integrated biorefinery features a significantly better economic performance than the stand-alone algae-derived diesel plant. Please note that these results do not include the fuel tax and biofuel subsidies and are based on year 2007.

The cost breakdown for the PBR and OP scenarios are shown in Figs. 5a and b, respectively. The resulting MFSP for diesel and gasoline blendstock are 7.33 $/gallon and 3.80 $/gallon (2012 USD), for PBR and OP scenarios respectively. In addition, in order to identify the key cost contributors, the detailed lists of equipment costs are reported in Tables S1 and S2 in the ESM. In both scenarios microalga cultivation, and hydrogen production are more costly than others. However, in the PBR scenario, the main capital cost contributor by far is photobioreactors which consist 68.1% of the total capital costs. For comparison this value is 8.9% for the open ponds. The contributions of each process section to the minimum fuel selling price (MFSP) are shown in Fig.s 6a and b. The microalgae cultivation Section 700, accounts for up to 67% of the MFSP in the PBR scenario. In this scenario, Hydrogen Production Section 600 is responsible for 12.5% of MFSP. By comparison, Sections 700 and 600 are responsible for 27.4% and 27.9% of MFSP in the OP scenario, respectively. In the PBR scenario the important raw material costs include: 43% hydrogen production, 24% pyrolysis and 24% algae nutrients and extracting solvent. Those values for the OP scenario are 45%, 25%, 21%, respectively. The algae cultivation and lipid extraction Section 700 accounts for 54% of the total electricity consumption in the PBR scenario. This large amount is needed for flocculation, centrifuge, homogenization and pumping the recycled water. This measure is even larger for the OP scenario (61%) due to more dilute effluents. The net electricity production of the combined heat and power cycle in Section 800 only addresses 3% and 5% of the PBR and OP scenarios, respectively. The reason is the high total electricity demand and low partial pressure of methane (67% on volumetric basis) in the biogas. While expansion of the stored CO_2 during the day offsets the required electricity demand for the CCS Section 400, the exergy loss results in the net loss of the available work and this section is a net consumer of electricity, *i.e.,* 15% for the PBR scenario and 11% for the OP scenario. Another comparison (Fig. 7) can be made between the produced biodiesel and conventional fossil-derived diesel in terms of *pump price* which also includes the tax credits. In this case, the pump price of the biofuel (65% biodiesel and 35% biogasoline) in the OP scenario is 3.35 \$/gallon which is cheaper than the petroleum-derived diesel (3.97 \$/gallon in 2012) and gasoline (3.68 \$/gallon in 2012) retail prices [89].

4.3. Environmental impacts

Figs. 8a and b illustrate the overall net GHG emissions of diesel and gasoline and their contribution analysis. The ‘above-the-line’ scores are environmental burdens, whilst the ‘below-the-line’ ones are biogenic carbon sequestered in biomass feedstock and GHG credits from surplus steam in Pyrolysis (Section 100), Upgrading (Section 200) and Hydrocracking (Section 500). As shown in Figs. 8a and 8b, the biggest score from the *vehicle operation* is the emissions from fuel combustion and the second biggest is the flue gas exhaust from CCS, (Section 400). They are partially offset by biomass carbon sequestration, because carbon in the biofuel is biogenetic carbon that was originally sequestered in biomass feedstock. The emissions from algae cultivation and anaerobic digestion are mainly from the production of nutrients and electricity. For PBR scenario, the emissions from biomass production and harvesting are small and only account for 12.9% for diesel and 16.5% for gasoline, respectively. Similar measures for the OP scenario are 9.7% and 9.6% respectively for diesel and gasoline. Overall, the net 'well-to-wheel' GHG emissions are 0.05 kg CO_2 eq./km for diesel and 0.02 CO_2 eq./km for gasoline for the PBR scenario whilst the net GHG emissions for the OP scenario are 0.07 kg CO_2 eq./km for diesel and 0.04 kg CO_2 eq./km for gasoline. These results are compared with 'well-to-wheel' GHG emissions for diesel and gasoline reported by Hsu, [93] for stand-alone biomass pyrolysis process and that for refinery gasoline in Fig. 9a. The implication is that for the OP scenario, the GHG emissions for diesel and gasoline are reduced by 50% and 70% respectively compared to equivalent measures corresponding to the biomass pyrolysis stand-alone. In addition, the GHG emissions factor for gasoline in the present study is around 15% of that for refinery gasoline. The PBR scenario delivers higher GHG emissions reductions (65% for diesel and 84% for gasoline) compared to the biomass pyrolysis stand-alone and results in a GHG emission factor for gasoline which is 7% of that for refinery gasoline. Similarly, Fig. 9b shows the 'Well-to-Gate' (from biomass cultivation to fuels production) GHG emissions for diesel and gasoline in the present study compared to those in Hsu's study [93] for biomass-derived diesel and Frank, *et al.*'s study [76] for algae-derived diesel using OP system. It is found that GHG emissions factors for diesel in our PBR scenario are 65% and 64% smaller than those in Hsu, [93] and Frank, *et al.*'s [76] studies, respectively. In the OP scenario, these numbers are 51% and 49% respectively. The overall observation is that the integrated process can deliver significantly better GHG results than the stand-alone poplar pyrolysis plant and the stand-alone algae diesel plant. Moreover, the GHG emissions reduction of the biodiesel produced from the proposed integrated biorefinery can fulfil the threshold of 50% for biomass-based biodiesel regulated by Renewable Fuel Standards [92].

5. Discussions and conclusion

The inherent chemistry of biomass poses an important challenge toward producing liquid fuels *i.e.,* a large amount of biomass carbon should be removed as carbon dioxide in order to adjust the effective hydrogen to carbon ratio to a level compatible with the current energy infrastructure. Therefore, CO_2 utilization is essential for sustainability of future biorefineries. The present study explored the techno-economic and life-cycle assessment of an important instance of future integrated biorefineries, in which the carbon dioxide produced during biomass pyrolysis and upgrading is utilized for microalgae cultivation. Such process integration is motivated by the inherent synergies through bio-oil upgrading and refining, and minimization of the costs associated with CO_2 capture and hydrogen production. The proposed biorefinery has profound environmental impacts, because firstly, based on the same amount of biomass, it produces significantly higher amount of fuel. The implication is less deforestation and environmental protection. Secondly, the amount of emitted CO_2 is substantially reduced from 45% of initial carbon to only 6%. The implication is that the contribution of the produced fuel to decarbonisation of the transportation infrastructure is almost an order of magnitude higher than the equivalent standalone pyrolysis process. Finally, the extra produced fuel can compensate the cost of CO_2 utilization, and is still competitive with respect to petroleum-derived fuel. Furthermore, there are plenty of opportunities to improve the economic and environmental performance of the proposed integrated scheme. With respect to carbon conversion, it was shown that the GHG emissions can be suppressed to as low as 6%. However, still a large amount (19%) of carbon is converted to fertilizer (biomass residues). This is because the lipid content of microalgae is as low as 25% and only less than half of the microalgae is anaerobically digestible. Therefore, improving the lipid yield and the anaerobic digestion efficiency has the potential to enhance the overall biomass conversion. Furthermore, there is an important trade-off between the costs of bioreactor and carbon emission, and commercializing more efficient and economic bioreactors is highly desirable. The integrated biorefinery may also benefit from new upgrading methods that can co-process the bio-oil and extracted lipids. All these in addition to cheaper methods for carbon capture will benefit commercialization of the proposed integrated biorefineries.

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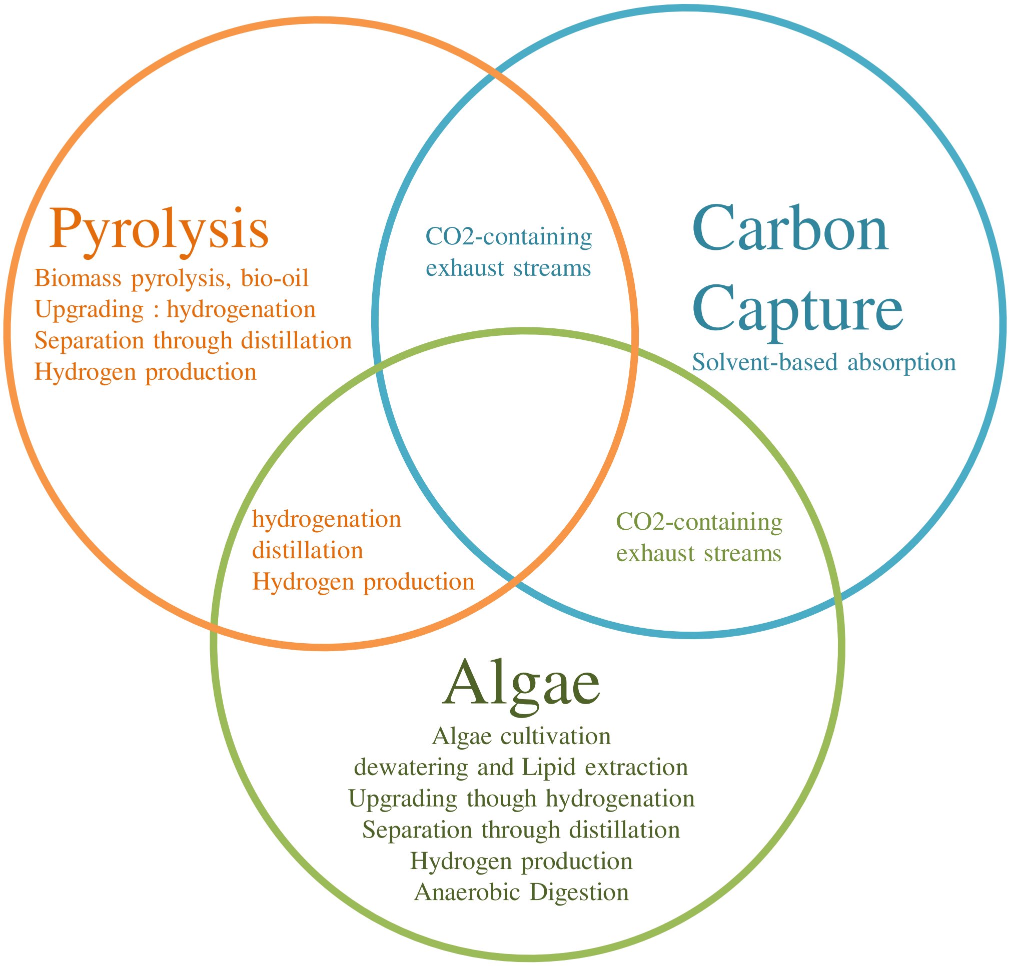
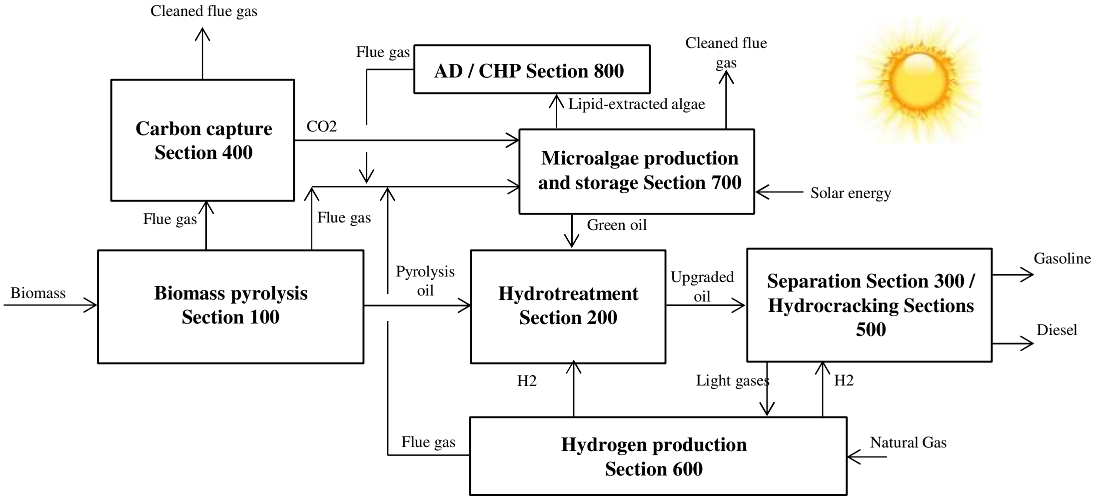
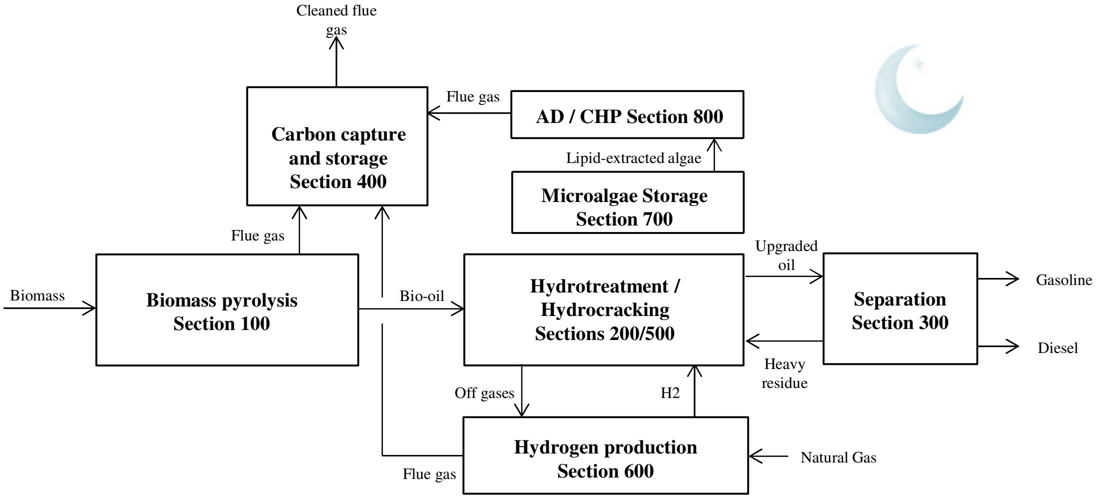


Fig. 1. Integrated refineries based on biomass pyrolysis and featuring CO_2 utilization through microalgae production

Process Block diagram (a): Day



Process Block diagram (b): Night



Figs. 2a, and b. The integrated biorefinery: day and night operational procedures.

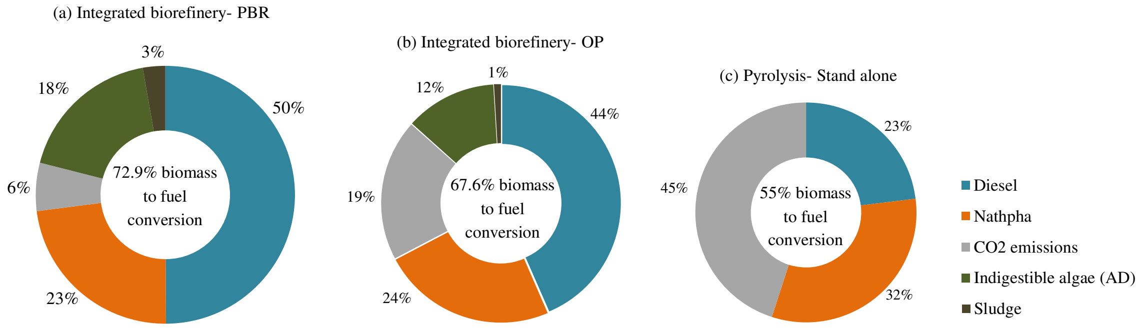


Fig. 3. Carbon yield distributions for (a and b): the present study (c): Jones *et al.*, [74]

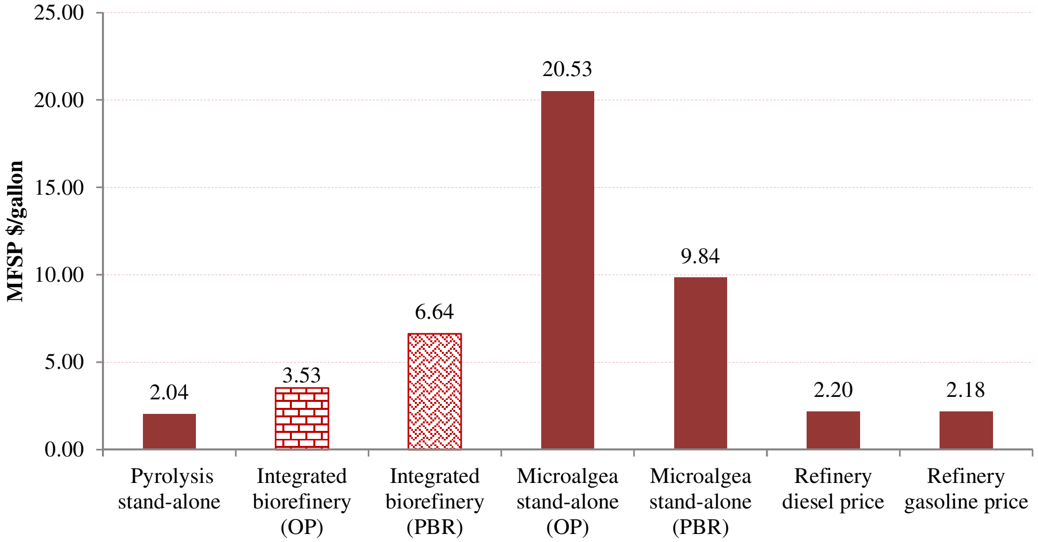


Fig. 4. Fuel cost in various studies compared with refinery diesel and gasoline prices at 2007. The Pyrolysis stand-alone scenario is the benchmark from Jones *et al*., [74]. The Microalgae PBR and OP scenarios are the benchmarks from Davis *et al*., [75].

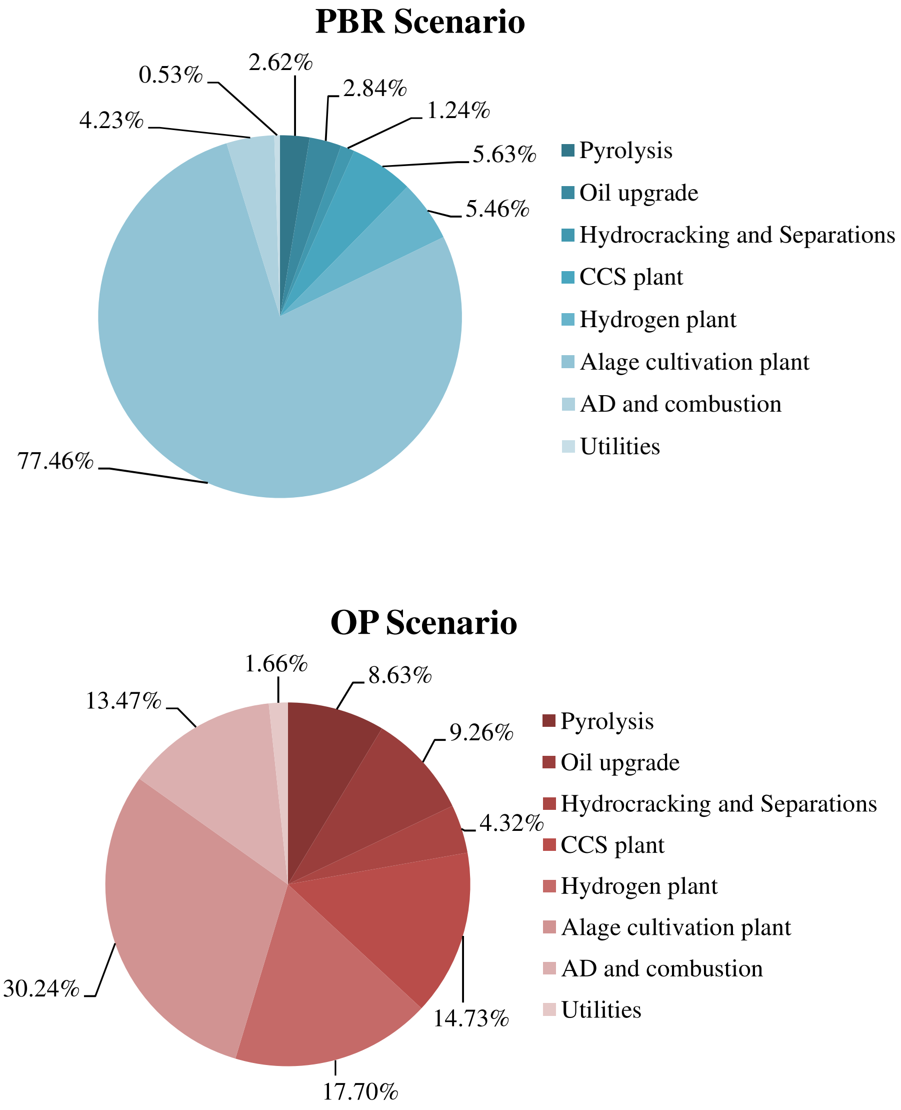


Fig. 5. The cost breakdown of MFSPs for gasoline and diesel blendstock: (a). photobioreactor scenario (b) open pond scenario.

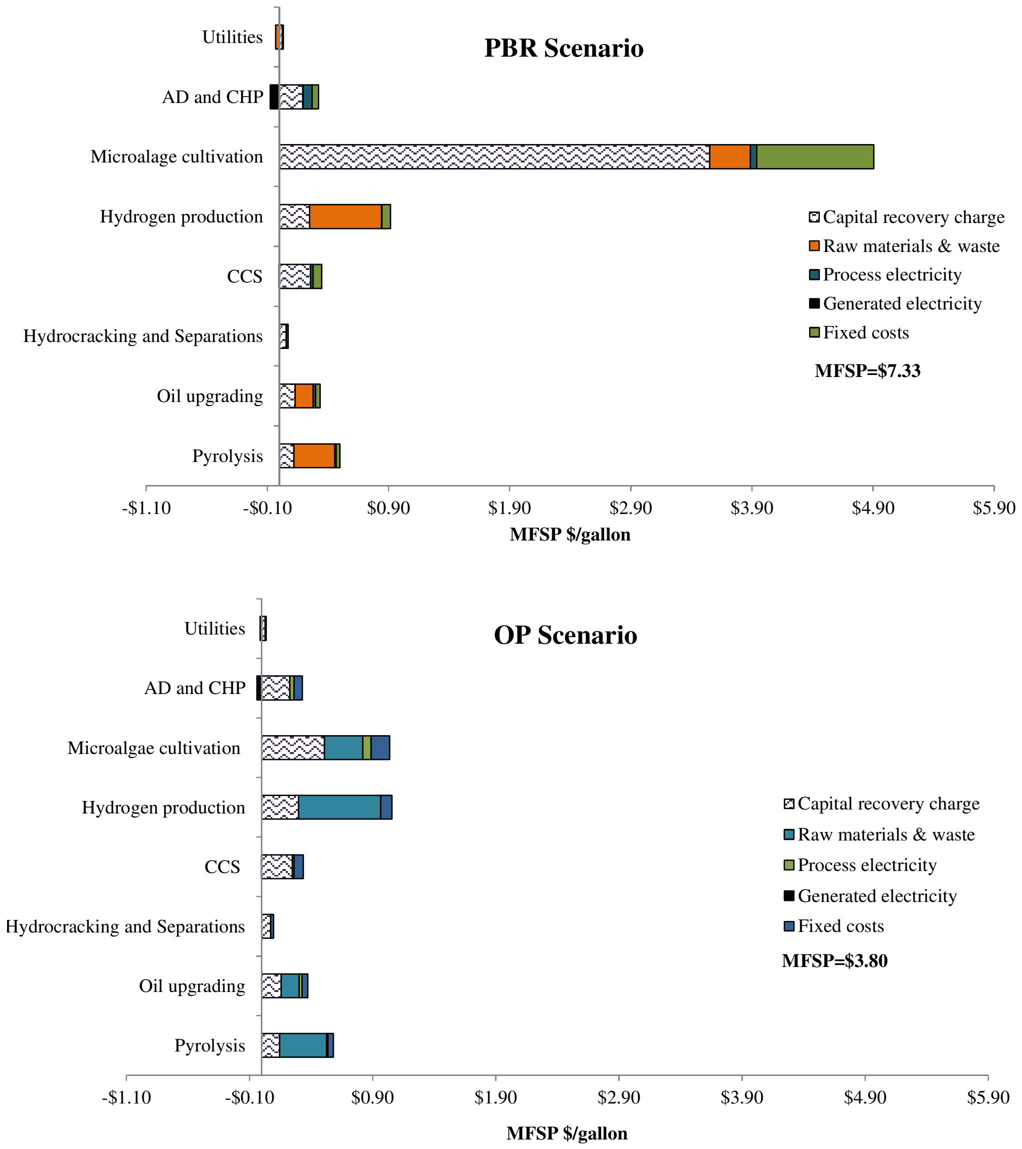


Fig. 6. The cost breakdown of MFSPs for gasoline and diesel blendstock for each section of the integrated bio refinery: (a) photobioreactor scenario (b) open pond scenario (2012-USD).

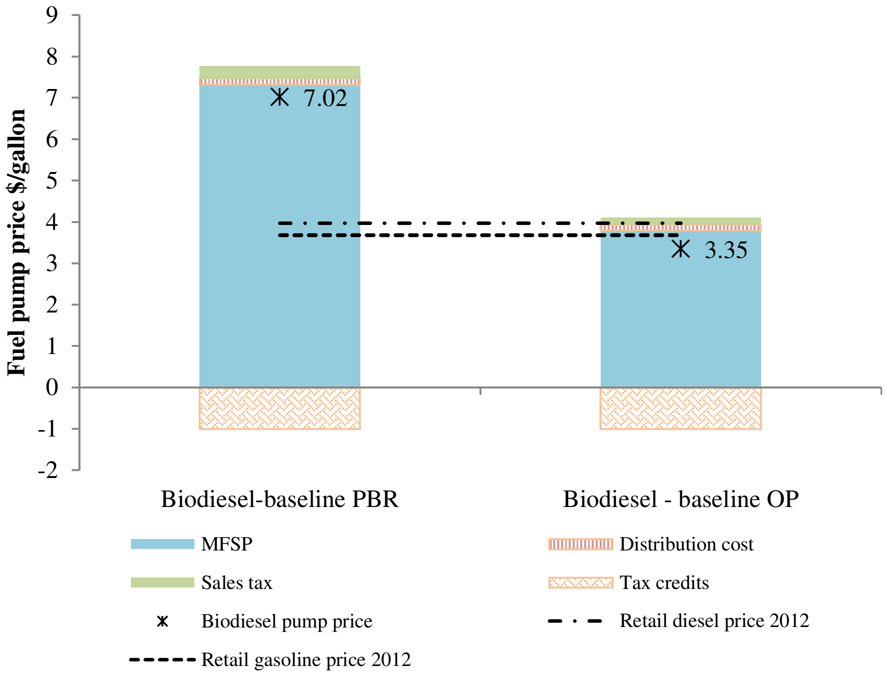
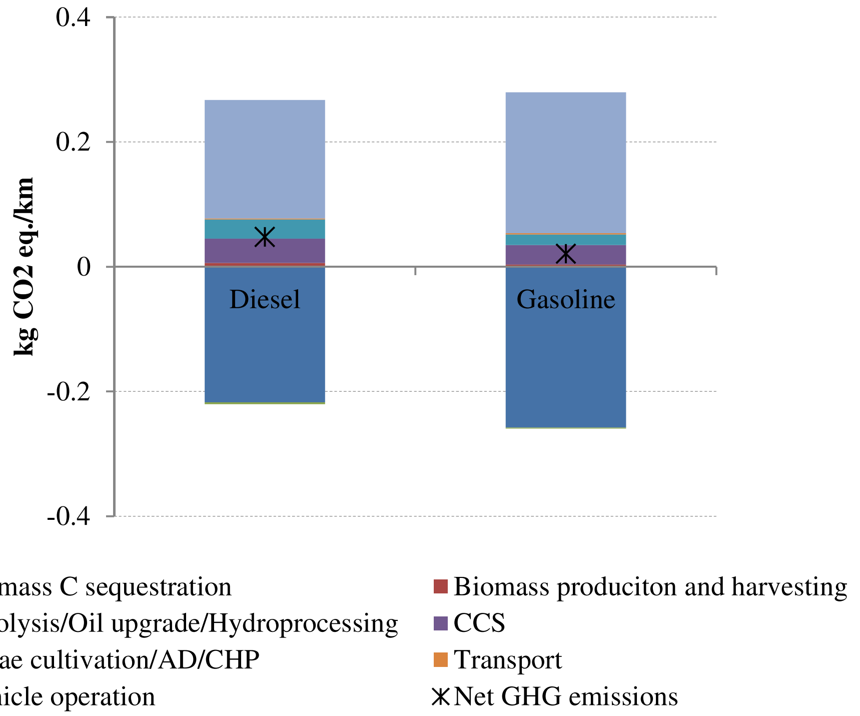
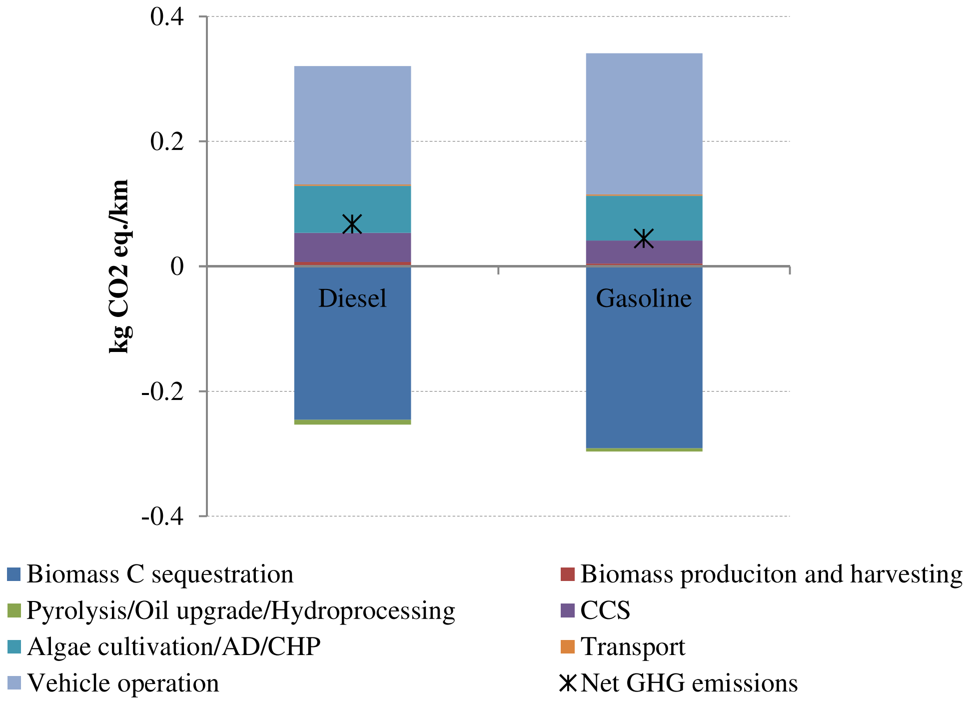


Fig. 7. Comparison of pump price of the biodiesel from PBR and OP scenarios, with the conventional diesel retail price (dashed line) and gasoline retail price (dotted line).

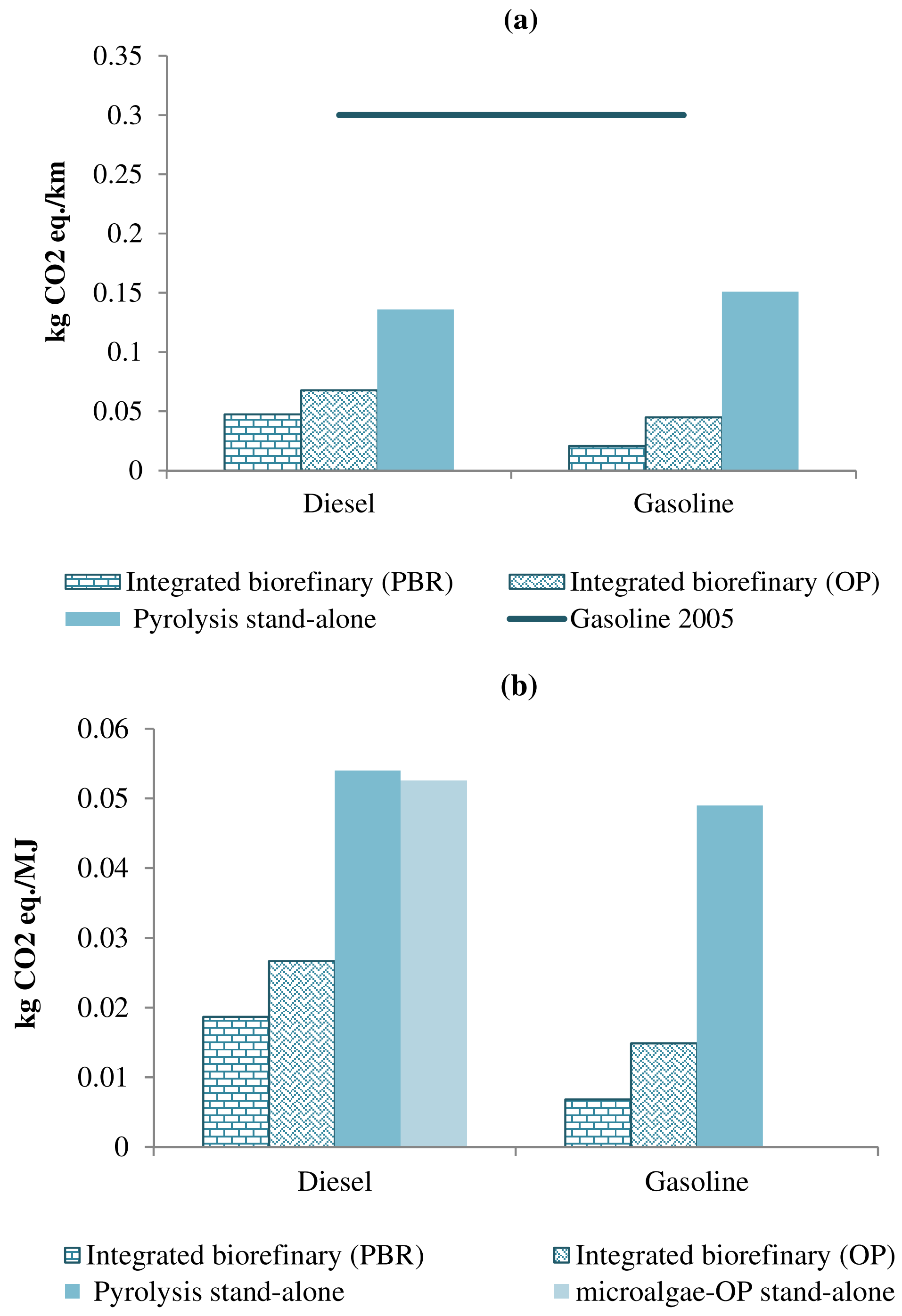
(a) PBR Scenario



(b) OP Scenario



Figs. 8. GHG emissions of diesel and gasoline (Unit '1km travelled by a light-duty passenger vehicle')



Figs. 9. Comparison with other studies: (a) 'Well-to-Wheel' Unit '1km travelled by a light-duty passenger vehicle'); (b) 'Well-to-Gate' Unit: '1MJ of fuel')

Nomenclature

AD	anaerobic Digestion
ANL	Argonne National Laboratory
CCS	Carbon capture and storage
DOE	Department of Energy
F_{scale}	The exponent used for scaling equipment costs
GHG	greenhouse gas
LCA	Life cycle analysis
MACRS	Modified Accelerated Cost Recovery System
MEA	Monoethanolamine
MFSP	minimum fuel selling price
NREL	National Renewable Energy Laboratory
OP	open ponds
PBR	photobioreactor
TCI	Total Capital Investment
TIC	Total Installed Cost
tpd	ton per day
TPEC	Total Purchased Equipment Cost

Table 1. Summary of variable operating costs

Materials/Chemicals/ Utilities	Cost	Reference
Hybrid poplar	50.07 $/short ton	[74]
Natural gas	3.89 $/1000 scf	[81]
Hydrotreating catalyst	15.5 $/lb	[74]
Hydrocracking catalyst	15.5 $/lb	[74]
Hydrogen plant catalyst	15.5 $/lb	[74]
CCS solvent (MEA)	1.25 $/kg	[79]
DAP (algae cultivation nutrient)	0.44 $/lb	[75]
Ammonia (algae cultivation nutrient)	0.41$/lb	[75]
Butanol (algae extraction solvent)	0.94 $/lb	[75]
Fresh water	0.05 $/1000 gal	[75]
Disposal of ash	18.00 $/short ton	[74]
Waste water treatment	0.11 $/m^3	[80]
Electricity	37.02 $/MWh	[82]
Steam	0.003 $/kg	[83]
Fire heater	4.5 $/mmBtu	[83]
Cooling water	4.43×10^{-6} $/kg	[83]

Table 2. Summary of inventory data for poplar cultivation [90]

Outputs (over 16 years)	
Poplar	216 o.d.t/ha
Inputs (over 16 years)	
Fertilizer (9N/18P/27K)	1800 kg/ha
Ammonium nitrate (33.5% N)	750 kg/ha
Stools	10000 stools/ha
Glyphosate (herbicide)	4 l/ha
Metil-pirimidos (insecticide)	1.5 l/ha
Propineb 70% (insecticide)	1 l/ha
Machinery	23.31 h/ha
Diesel consumption	345.4 l/ha

Table 3. Summary of GHG emissions factors (EF)

	Production GHG EF in poplar cultivation, kg CO_2 eq./kg material	**Use GHG EF in poplar cultivation, kg CO_2 eq./kg material**		**GHG EF in biofuel production, kg CO_2 eq./kg material**
Diesel [a]	0.43	2.98	Natural gas	0.011 [c]
N fertilizer	9.12	0.011 [b]	Zeolite	2.90
P fertilizer	2.68	-	MEA	3.39
K fertilizer	0.8	-	DAP	2.76
Ammonia Nitrate	8.47	-	Ammonia	2.08
Glyphosate	10.2	-	Butanol	3.98
Insecticide unspecific	16.3	-	Electricity	0.48 [d]
			Steam	0.23
			Fire heater	0.07 [c]
			Ash to landfill	0.61
			Wastewater treatment	0.38 [e]

Note: [a] kg CO_2 eq./L; [b] Field emissions as N_2O are calculated based on IPCC method and reported as kg CO_2 eq./kg o.d.t poplar biomass; [c] kg CO_2 eq./MJ; [d] kg CO_2 eq./KWh; [e] kg CO_2 eq./m^3

Table 4. Assumptions about transportation

Materials	Mode	Distance
Fertilizers, insecticides, herbicide from wholesalers to farm	Diesel lorry 28 ton	500 km
Poplar chips from farm to bio-oil plant	Diesel lorry 16 ton	25 km
Chemicals from wholesalers to bio-oil plant	Diesel lorry 16 ton	50 km
Solid waste from bio-oil plant to landfill	Diesel lorry 16 ton	20 km

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Fresh water	0.05 \$/1000 gal	[75]
Disposal of ash	18.00 \$/short ton	[74]
Waste water treatment	0.11 $\$/m^3$	[80]
Electricity	37.02 \$/MWh	[82]
Steam	0.003 \$/kg	[83]
Fire heater	4.5 \$/mmBtu	[83]
Cooling water	4.43×10^{-6} \$/kg	[83]

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Metil-pirimidos (insecticide)	1.5 l/ha
Propineb 70% (insecticide)	1 l/ha
Machinery	23.31 h/ha
Diesel consumption	345.4 l/ha

Table 3. Summary of GHG emissions factors (EF)

	Production GHG EF in poplar cultivation, kg CO_2 eq./kg material	Use GHG EF in poplar cultivation, kg CO_2 eq./kg material		GHG EF in fuel production, kg CO_2 eq./kg material
Diesel [a]	0.43	2.98	Natural gas	0.011 [c]
N fertilizer	9.12	0.011 [b]	Zeolite	2.90
P fertilizer	2.68	-	MEA	3.39
K fertilizer	0.8	-	DAP	2.76
Ammonia Nitrate	8.47	-	Ammonia	2.08
Glyphosate	10.2	-	Butanol	3.98
Insecticide unspecific	16.3	-	Electricity	0.48 [d]
			Steam	0.23
			Fire heater	0.07 [c]
			Ash to landfill	0.61
			Wastewater treatment	0.38 [e]

Note: [a] kg CO_2 eq./L; [b] Field emissions as N_2O are calculated based on IPCC method and reported as kg CO_2 eq./kg o.d.t poplar biomass; [c] kg CO_2 eq./MJ; [d] kg CO_2 eq./KWh; [e] kg CO_2 eq./m^3

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Solid waste from bio-oil plant to landfill	Diesel lorry 16 ton	20 km