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# Comparing Energy Efficiency for Emerging Fuel Production Technologies: 3rd Generation Biodiesel vs Methanol from Solar Power

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In the last decade, microalgae cultivation has become an attractive solution for biomass valorisation. From an industrial standpoint, one important aspect is the combination of the mixotrophic growth of microalgae with the biosynthesis of fatty acids, which represents a sustainable feedstock for the biodiesel chain. Nevertheless, the actual energy-effectiveness of the whole process is doubtful as the indispensable biomass recovery and drying steps are energy-intensive. To discuss this issue, this work presents a comparison between a 3rd generation biodiesel production plant and a methanol synthesis facility, powered by photovoltaic (PV) electricity from sunlight. The objective is to evaluate the energy efficiency of the two production processes (by means of KPIs) given the same solar incidence area. The two process designs assume the best available technologies for the operations involved, in terms of reaction conversions and separation performances to maximise the yield in the final product.

## 1. Introduction

Transitioning from petrol-based fuels towards renewable energy sources is the biggest challenge humanity has been facing for the last two decades and from whose result life's sustainability on Earth will depend for the next years. The need for such a profound change in the present energy generation processes comes from two main concerning issues: on one hand, the increasing depletion of fossil fuels in the accessible sinks due to anthropic exploitation; on the other one, the increase of airborne $CO_2$ concentration up to 400 ppm, the main responsible for the average temperature increase driving this dramatic climatic change (Olah et al., 2018). Scientific advancement is boosting the plants' conversion towards more sustainable facilities, using renewable energy sources, the recovery of waste streams and flues, together with the application of energy integrations, process intensification strategies and the introduction of novel possible feedstocks for energy and chemicals production. Studies where the energy efficiency is proven, enable novel technologies to start their establishment process, opening them the way to scale-up strategies, process optimisation, detail design and final implementation. Thus, it appears essential to accompany state-of-the-art processes and innovative strategies for producing common chemicals, combustibles and energy with proper energetic analysis, helping the scientific community to visualize and discuss the possible convenience and the limits of the presented alternatives. In this framework, the scope of the present work is to compare the energy efficiency of two frontier processes producing two "fuel-grade" combustibles: 3rd generation biodiesel produced by microalgae vs. methanol synthetized from carbon dioxide via catalytic hydrogenation. 3rd generation biodiesel is made of fatty acid methyl esters (FAMEs) obtained from the lipids extracted from microorganisms or microscopic vegetal species. The advantages of exploiting microalgae as feedstock are multiple: they make fruitful solar energy and $CO_2$ fixation through photosynthesis is a Carbon Capture and Utilisation strategy (CCU); moreover microalgae do not compete with food production for land use and their potential for integration with waste water treatments was extensively proven with good results (De Sousa, Da Hora, Sales, & Perelo, 2014); finally microalgae are the best solution until present for phytoremediation of waters contaminated with heavy metals

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(Suresh Kumar, Dahms, Won, Lee, & Shin, 2015). Dealing with lipids biosynthesis, *Nannochloropsis oculata* is a microalgal species endowed with both high growth rate and high lipid accumulation rate when cultivated in mixotrophic conditions; moreover it was recognised as one of the best options for industrial scale cultivations for biodiesel production according to the properties of the biodiesel synthetized from its lipids (Islam et al., 2013). Differently from dedicated crops cultivations, limited area is needed for microalgae to grow given their huge areal productivity, especially when the configuration consists of photobioreactors (oil yield per unit area can be even 30 times higher than crops' one) (Demirbas & Fatih Demirbas, 2011).
The actual scale for 3$^{rd}$ generation biodiesel production process is at the pilot level considering scale-up troubles for photobioreactors because of light exposition, $CO_2$ dispersion, optimal agitation, nutrients choice and concentration, medium's composition and salinity (Ma, Chen, Yang, Liu, & Chen, 2016). In addition, the process is not sustainable from the energetic point of view, the bottleneck step being the oil recovery from the algal cells: Chisti et al. highlighted that the main energetic requests lie in the concentration and drying steps of the diluted biomass when traditional technologies are applied (centrifugation, microfiltration, drying, cell-disruption, etc.) (Chisti, 2013). Methanol was selected for the comparison with biodiesel since it has been receiving great interest in the last decades, especially because of the successful "Methanol Economy" concept by the Nobel Prize Olah (Olah et al., 2018): the simplest alcohol is, in fact, a favourable energy-carrier and its sustainable production route from $CO_2$ and $H_{2,}$ hydrolytically obtained from solar power, represents a possible solution embracing both exploitation of Renewable Sources and CCU strategies. The routes for $CO_2$ hydrogenation at present are electrochemical reduction and thermochemical catalysis, with the first one being more promising but still at low stage of development, mainly because of the low selectivity and conversion of the reactions involved (Al-Saydeh & Zaidi, 2018). Both in electrochemical reduction and thermochemical catalysis, hydrogen production and stocking still present some energetic, technical and safety issues, anyway catalytic hydrogenation was successfully brought to industrial production: Carbon Recycling International® in Iceland owns a plant with 50,000 t/y of methanol productivity (CRI, 2019).
In this work, the common base of process design was the solar power obtainable from the identical solar panel area: the solar duty was only addressed to satisfy the energy requirements of the core operation of each process, namely the microalgae cultivation in the photobioreactors and the catalytic hydrogenation reactor. In the biodiesel production plant, the technologies were selected according among the ones in the literature in order to maximise the energy gain, that is, the ones with milder energy duties required and, at the same time, with higher efficiency improving the product yields and recoveries after separation.

## 2. Process schemes description

### 2.1 Third Generation Biodiesel from microalgae

The plant can be divided into two main sections: microalgae growth and the downstream, which consists of biomass harvesting, dehydration, reactive wet extraction lipid extraction, biodiesel purification operations. Photobioreactors (PBRs) are chosen for microalgae cultivation as they assure the complete control over culture parameters and minimize the land use given the vertical configuration and the quite high L/D ratio, favoring maximum biomass concentration (Kroumov, 2015). A module of PBRs (Figure 1) consists of parallel reactors for photosynthetic growth in series with an equal number of heterotrophic PBRs. Light is conveyed via light collectors that concentrate the solar power coming from the panels. $CO_2$ is supplied as 1.8 times the weight of the final dry biomass and is sent at the bottom disperser of the PBRs to assure a gas partial pressure of at least 0.2 kPa even at the top of the equipment (Posten & Rosello-Sastre, 2012). Nutrients are added to the heterotrophic reactors according to the specific consumption rate by *Nannochloropsis oc.* during respiration and specific stress factors, especially nitrogen starvation, are applied to the culture to promote triacyclglycerols' biosynthesis (Ma et al., 2016). Water removal for biomass harvesting is performed in two steps: microfiltration suits the purpose given microalgae average diameter of 30 μm and increases biomass concentration from 1g/L to 150 g/L with a unitary recovery efficiency. This dewatering step requires 6,000 kJ per $m^3$ processed for both liquid pumping and membrane cleaning; given the operative pressures across the membrane we assume that retentate's recycle is auto-sustained by the pump (Gerardo et al., 2014). The thickening step is performed with rotating drums dryers from which 90% of evaporated water is recycled back; 65 wt% biomass concentration in medium is reached in order to enter the following step of reactive wet extraction (RWE). RWE avoids the common use of homogenizers or microwave cell destruction: as observable in (Dvoretsky et al., 2019), pre-extraction treatments enhance solvent performance as much energy is input. The selected RWE employs 15 L of solvent and 1.5 L of sulfuric acid per kg of wet biomass, with the solvent being a mixture 2:1 of chloroform and methanol. This one-pot operation has a biodiesel yield of 91 % over triglycerides' content and is run at 95 °C, so that the reactor needs to be controlled in temperature (Im, Lee, Park, Yang, & Lee, 2014). Finally, the oleic phase obtained from separation is sent to a washing column with 84 % refining yield; the utility stream is distilled water at 50 °C amounting for three-times the oil mass. The exiting stream respects the specifications previa contacting the product stream with heated $Na_2SO_4$ and finally filtrating for particles removal, as demonstrated by (Karaosmanoğlu, Ciğizoğlu, Tüter, & Ertekin, 1996).

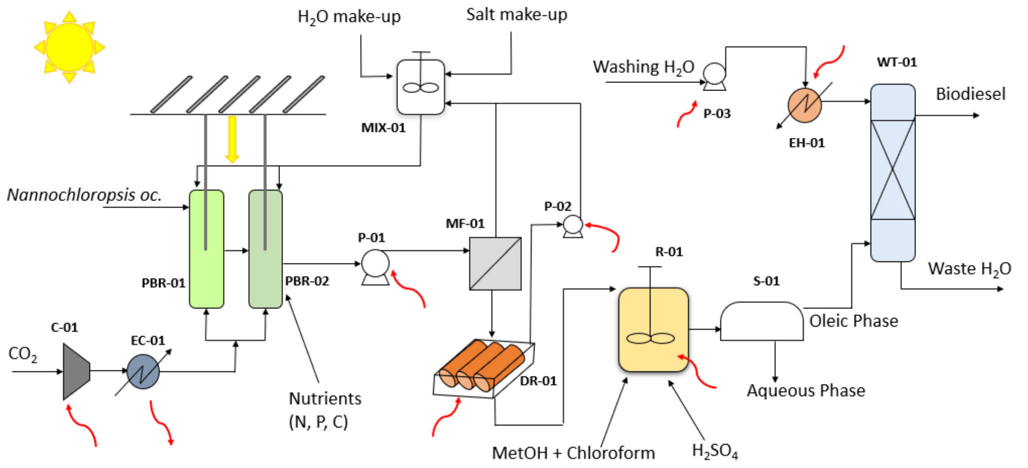


*Figure 1. Process Flow Diagram of the production module of 3rd generation biodiesel from microalgae.*

### 2.2 Methanol from $CO_2$ via catalytic hydrogenation

The scheme chosen for the methanol production on industrial scale is the one reported in Figure 2 (Matzen et al., 2015) in which the catalytic hydrogenation of $CO_2$ to methanol is run in a low-pressure isothermal packed reactor operating at T = 235 °C and P = 50 bar. The catalyst used is $Cu/ZnO/Al_2O_3$ and the optimized $H_2/CO_2$ ratio at the reactor inlet is 2.8, thus achieving a $CO_2$ pass conversion of 47 % with a methanol selectivity higher than 99.7 %. In the upstream section of the plant $H_2$ and $CO_2$ are pressurized up to 50 bar (from the initial conditions of T = 25 °C, P = 33 bar and T = -25 °C, P = 16 bar, respectively) and mixed. After a two-step pre-heating to gain the reactor temperature, they are converted according to the linearly independent reactions in Eq(1) and Eq(2) that produce methanol, water and carbon monoxide.

$$CO_2 + 3H_2 = CH_2OH + H_2O \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

In the downstream section, the process stream is cooled to ambient temperature in two steps, the first of which exchanging thermal power with the first heater for energy recovery (Matzen et al., 2015). Since the cooled stream is biphasic, the vapor phase, mainly composed of unconverted $H_2$ and $CO_2$, is recycled back to the reactor, whereas the liquid phase is expanded to ambient pressure to remove residual gases and then distilled in order to recover methanol from water.

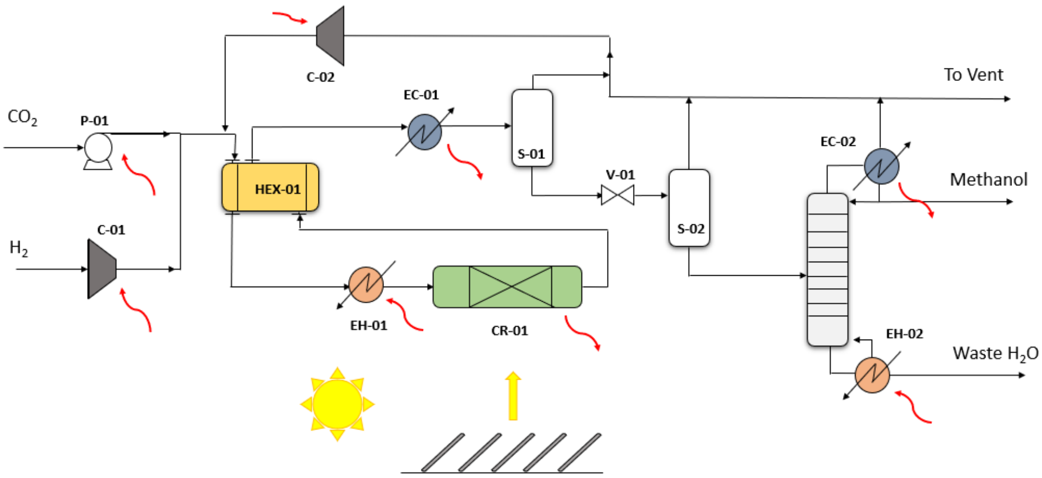


*Figure 2. Process scheme for the methanol plant (according to Matzen et al., 2015).*

## 3. Methodology

The design of operations was aimed to reach the specifications of "fuel-grade" combustibles, according the guidelines of the EN1421:2012 Regulation for biodiesel and by pursuing a component purity of 99.7 % for methanol. The first approach applied aimed to saturate the energy duty needed at the core operation of each process: this was possible by setting a base of calculation, that was the irradiation area (with the figure of 350 $m^2$) which is known to be capable to produce 33 t/y of dried biomass, given the productivity of some industrial facilities in Southern Italy that operate with the microalgae *Nannochloropsis oculata* (ENI, 2019). For this species, a biomass productivity of 1/(g·L) was assumed as in the work of Ma et al.; in agreement with Islam et al., the lipid content on the dry weight was selected as 41 %, an intermediate value in the range given by other authors.

### 3.1 Mass and energy balances

For the 3rd generation biodiesel plant productivity was already linked to surface area irradiated with no process sizing occurrence (ENI, 2019). According to biomass productivity, *Nannochloropsis oculata*'s typical lipid content and downstream technologies selected in paragraph 2.1, the mass balances were solved in each node knowing the operation performances with respect to the entering streams' variables.
Thermal energy requirements for each operation $i$ ($D_i$ in the following) were also determined knowing the specific thermal and electrical powers; the latter ones, obtained for pumps and compressors, were converted into thermal duties assuming electricity was produced by a Combined Gas Turbine Cycle (CCTG) whose efficiency was conservatively taken as 0.55 (Liu & Karimi, 2018). The sum of the accessory energy duties (without accounting for solar power) gave the evaluation of the needed total energy duty ($TED$) as in Eq(3).

$$TED = \sum_i D_i \qquad (3)$$

Starting from the same irradiation area and considering the same geographical location, the power output of solar panels installed ($SP$) was estimated considering the average annual solar radiation, through the utilization of the database "Solar source data" (NREL, 2019) and according to Eq(4). The "two-axis tracking" array and the "premium" module were chosen to maximize the solar exposition of the panels.

$$SP = A \cdot Irr \cdot \varepsilon \qquad (4)$$

where $A$ is the surface available to irradiation [$m^2$] and $\varepsilon$ is the panel efficiency, assumed equal to 20 % (Meehan, 2019). Considering the selected methanol plant, the knowledge of $SP$ guides the re-scale of this operation, known its specific power duty $\widehat{D}_{React}$ [kW/$kg_{MetOH}$] as per Eq(5). Similarly to the biodiesel case, all the thermal power requirements $D_i$ [kW] were defined according to the new methanol capacity and to their specific values $\widehat{D}_{i,MetOH}$ [kW/($kg_{MetOH}$)] on methanol output stream, as shown in Eq(6).

$$\dot{m}_{MetOH} = \widehat{D}_{React} \cdot SP \qquad (5)$$

$$D_i = \dot{m}_{MetOH} \cdot \widehat{D}_{i,MetOH} \qquad (6)$$

### 3.2 Calculation of energy efficiency indicators

Efficiency indicators are introduced to assess the energetic convenience of the chosen configurations: the Total Energy Ratio ($TER$) in Eq(7) is the "overall" indicator considering the chemical energy kept in the synthetized fuel against all power types provided within the plant boundaries, from the first transformation up to the products at "fuel-grade" standards. In order to account for the mechanical power obtained from biodiesel and methanol combustions (in compression and spark-ignition engines respectively) their typical brake thermal efficiencies($\eta_{engine}$) were inserted in the modified parameter $TER_{use}$, which is reported in Eq(8).

$$TER = \frac{\dot{m}_{fuel}\, LHV}{SP + TED} \qquad (7)$$

$$TER_{use} = \frac{\dot{m}_{fuel}\, LHV\, \eta_{engine}}{SP + TED} \qquad (8)$$

where $\dot{m}_{fuel}$ is the mass flow of the fuel produced by each plant [kg/h] and $LHV$ is the Lower Heating Value expressed in [W/kg] (Qi, Chen, Geng, & Bian, 2010). The peak value for the brake thermal efficiency of CI-engines using neat biodiesel (BD-100) variates between 25 and 35 % in literature, so that an average value of 30 % is assumed, as from the results of (Murillo, Míguez, Porteiro, Granada, & Morán, 2007). For methanol combustion, the peak $\eta_{engine}$ of a M100-SI engine is 42 % according to the experimental studies made by the U.S. EPA's National Vehicle and Fuel Emissions Laboratory (Brusstar & Bakenhus, 2013). The convenience of solar power integration supporting the process core operation is evaluated using the Net Energy Ratio indicators $NER$ and $NER_{use}$ in Eq(9) and Eq(10), derived from the total energy ratios but considering only the actual power and thermal utilities to supply.

$$NER = \frac{\dot{m}_{fuel}\, LHV}{TED} \tag{9}$$

$$NER_{use} = \frac{\dot{m}_{fuel}\, LHV\, \eta_{engine}}{TED} \tag{10}$$

## 4. Results and discussion

In *Figure 3*, the normalized Operation Duties $D_i$ are reported for each scheme, along with the power fraction produced from solar panels and received by the sun-light based operations. Normalization was made with respect to the overall energy input ($TED$+$SP$) in order to highlight the more energy-demanding operations.

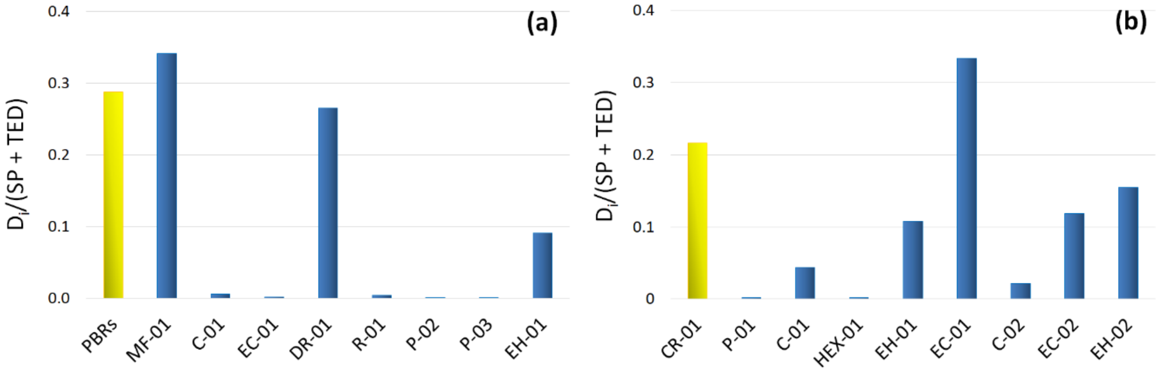


*Figure 3. $D_i$ referred to the overall energy input: the biodiesel plant case (a) and the methanol plant case (b).*

In biodiesel production process from microalgae, biomass harvesting performed with microfiltration and drying (MF-01 and DR-01) is responsible for 85 % of all $TED$, as many groups delineated (Khoo, Dasan, Lam, & Lee, 2019). In the methanol plant energy requirements are more distributed among equipment. The integrated $SP$ in the PBRs and in the catalytic reactor (CR-01) cover the 29 % and 22 % of all energy duties for biodiesel and methanol plants, respectively. By grouping the normalized $D_i$ into upstream and downstream, it follows that the downstream section is always more energy-demanding than the upstream, with methanol plant's upstream surpassing biodiesel's one (37 % and 30 %, respectively). From Table 1, methanol productivity is more than ten times higher than biodiesel's one and specific accessory duties for biodiesel and methanol are worth about 104 and 14 MJ/kg of product, respectively. Coherently with these figures, the processes' scale-down basing the whole energy supply on the same $SP$ showed similar fuels productivities (0.37 $kg_{BD}$/h and 3.08 $kg_{MetOH}$/h).

*Table 1. Main results from the process design starting from the same solar power input using KPIs indexes.*

| Plant | $\dot{m}_{fuel}$ in [kg/h] | $TED$ in [MJ/h] | $TER$ | $NER$ | $TER_{use}$ | $NER_{use}$ |
|---|---|---|---|---|---|---|
| **Biodiesel** | 1.29 | 134.7 | 0.25 | 0.36 | 0.08 | 0.11 |
| **Methanol** | 14.3 | 197.7 | 1.13 | 1.44 | 0.47 | 0.60 |

The figures depict photosynthesis as the less efficient reaction in terms of synthesis capacity, but it should be noticed that in $CO_2$ catalytic hydrogenation the duty supplied to CR-01 is just meant to keep the reactor temperature constant and not to activate the reaction. The Energy Ratios indexes show a clear superiority of the $CO_2$ catalytic hydrogenation process as regards the energy efficiency, with a $NER$ standing out with the value of 1.4 for the case of solar power integration; however, after the correction made with the brake thermal efficiencies, the indexes are all sensibly reduced without reversing the ranking of processes.

## 5. Conclusions

In this work, a comparison between two innovative processes for biodiesel vs. methanol production was carried out. It was assumed that both the core operations (i.e. the reactors) were powered by a PV system characterised by a surface of 350 $m^2$ located in Southern Italy. Energetic evaluations were performed to assess the efficiency, fuel productivity, thermal and electric duty of each process and to compare them by means of ad hoc KPIs..

Considering the overall process, the methanol production via catalytic hydrogenation of carbon dioxide neatly wins the comparison, mainly because the energy duties associated to upstream and downstream operations are reduced with respect to biodiesel production from algae. Still, focusing on the rectors (operations powered by solar energy), the best performance is shown by the biodiesel production process, since the algae cultivation section is completely self-sustained by the solar irradiation.

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