

Review

# Life Cycle Based GHG Emissions from Algae Based Bioenergy with a Special Emphasis on Climate Change Indicators and Their Uses in Dynamic LCA: A Review

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**Abstract:** Life cycle-based analysis is a key to understand these biofuels' climate benefits. This manuscript provides a state-of-the-art review of current biofuel production, primarily through algae-based routes. Standalone biofuel production has an unfavorable environmental and energy footprint. Therefore, industrial symbiosis is required to reduce the environmental impacts of biofuel. The availability of waste heat, CO<sub>2</sub>, renewable energy, and colocation of other industries, especially renewable energy and dairy firms, have been demonstrated beneficial for producing biofuel through the algal route. Dynamic life cycle assessment (DLCA) issues were discussed in detail. DLCA is one of the highlighted areas of the Life Cycle Assessment (LCA) paradigm that can improve the applicability of climate change indicators used in the LCA. Various climate change indicators, global warming potential (GWP), global temperature change (GTP), and climate tipping point (CTP) were discussed in detail. Special emphasis was given to waste-based bioenergy production and its LCA as this route provided the lowest GHG emissions compared to the other bioenergy production pathways (e.g., from energy crops, using lignocellulosic biomass, etc.). The use of LCA results and modification of life cycle inventory (e.g., modification in the form of the regional energy mix, dynamic Life Cycle Inventory (LCI), etc.) was another highlight of this study. Such modifications need to be incorporated if one wants to improve the applicability of LCA results for net zero target analysis.

**Keywords:** climate change indicators; net zero target; dynamic LCA; industrial symbiosis



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## 1. Introduction

Researchers have a consensus that energy consumption generates a significant fraction of greenhouse gas (GHG) emissions, as most of the energy is derived from fossil fuels [1,2]. Furthermore, some crude oil-derived products also show high embodied GHG emissions [3]. One needs to use low-carbon embodied products to develop a low-intensity carbon-based economy. Nevertheless, alternative processes to manufacture low-carbon products are still under development. Bio-based products, such as biofuel, bioplastics, etc., have low embodied carbon [4].

Similarly, shifting our energy mix from fossil fuel-dominated systems to a renewable energy-intensive energy mix reduces the carbon intensity of the products. In the USA, the transportation sector is the highest GHG emitter contributing to 30% of the total GHG emissions, corresponding to 2000 MMT CO<sub>2</sub> in 2019 [5]. Hence, there is considerable scope for decreasing the GHG emissions from the transportation sector by introducing biofuel. Biofuel produced from virgin materials mainly dedicated energy crops and other

biomasses, has considerable GHG emissions. If one considers the land use change, the resultant GHG emissions are higher than those of fossil fuels [6]. The Intergovernmental Panel on Climate Change (IPCC) has advocated for biofuel as one of the main contributors to their GHG emissions reduction strategies. However, bioenergy produced from oil seeds and lignocellulosic biomass has considerable GHG emissions [7].

Introducing waste biomass or waste nutrients for biomass production provides low-cost biofuel with lower life cycle GHG emissions than biofuel produced from biomass that is generated using virgin nutrients or dedicated energy crops [8,9]. Hiloidhari et al. [10] reported that 14% of the renewable energy produced in India was derived from biomass. They also reported that energy produced from animal manure has a lower GHG footprint than coal-based power. Biogas produced from biomass and manure can be used as a clean fuel for cooking. Biogas as a cooking fuel provides access to clean fuel to a large part of the rural population, who are otherwise forced to use biomass and dry cow dung as fuel for cooking [11]. Mittal et al. [12] estimated that in India, around 12.7 EJ/year of energy could be produced from biomass. These biomass feedstocks are mostly crop residue or animal manure, which are used to produce biogas through anaerobic digestion. However, several other routes can produce different types of biofuels and provide an opportunity to reduce fossil-derived energy demand and GHG emissions. Biofuel from algae is one of the most attractive ones, considering the GHG emissions and biofuel production per acre of land [13].

Life cycle assessment has been extensively used to estimate the various environmental impacts generated from biofuel production from different biomass feedstock such as dedicated energy crops [14,15], forest and agriculture residues [7], or microalgae [16]. Some studies also provided excellent reviews on the life cycle assessment of biofuels, specifically bioethanol, biodiesel, biomethane, (Fischer-Tropsch) FT-diesel [14,17], ethanol from sugarcane, biodiesel from soybean and palm oil [18], second generation ethanol [19], algal biodiesel [20,21], and algal biorefineries [22]. Levasseur et al. [23] and Collet et al. [24] provided excellent recommendations for applying LCA to biofuel. These studies highlighted various issues with published literature on LCA. Some of these studies tried to harmonize the results obtained from LCA [25,26]. Harmonization efforts were required as the differences in the results are due to methodological differences, especially in the system boundaries, allocation issues, and type of LCA approach used to conduct the study [19,22,27]. Some studies also highlighted the various issues associated with several approaches in an LCA, i.e., consequential vs. attributional methodology [28]. Conventional LCA approaches do not consider the temporal variation in the life cycle inventory (LCI). The incorporation of temporal LCI would affect the LCA results. Therefore, this study was developed to understand the various causes which generated temporal dynamics in the LCA results.

This manuscript was developed to identify the reasons behind the dynamic nature of life cycle impacts in bioenergy research. How these dynamic issues can affect the results and the different models used for estimating dynamic life cycle impact are also discussed in detail. For this purpose, various climate change indicators used to describe the results of dynamic LCA are discussed in detail. Later, a detailed recommendation was delineated, which helped to better estimate the GHG emissions from futuristic technology and thus helped to achieve the net zero target for GHG emissions. Algae-based biofuel has been one of the most promising biofuels in recent years. Some recent publications on the LCA of algal biofuel introduced dynamic issues in LCA and are discussed in detail in this manuscript.

## **2. Current State of Knowledge on Life Cycle GHG Emissions from Biofuel from Algae Cultivated Using Waste Nutrients**

Exploring the sustainability issues associated with algal biofuel started in 2009 when Lardon et al. [29] first published their research on life cycle-based analysis of algal biofuel. They first recognized that algal biofuel production was not energetically favorable if biomass had to be dried for algal biofuel production. Later, several researchers tried

to reduce the energy burden associated with algal biofuel production by extracting oil from wet algal biomass [30,31]. Some researchers used residual biomass left after oil extraction for further energy production through anaerobic digestion [32,33]. Others estimated the impacts when the microalgal biomass was converted to biofuels through pyrolysis or supercritical gasification [34]. Residual biomass management is also critical if a considerable portion of our energy demand has to be produced from the biomass-based route. For example, if 50% of the US petroleum demand was supplied by algal biodiesel, almost  $8 \times 10^8$  tons of residual biomass would be produced annually. The amount of residual biomass would be almost 1000 times higher than that of dry solids generated from the US wastewater treatment system [35]. Residual biomass left after oil extraction also contains most of the nutrients sequestered in the algal biomass.

Therefore, recovering nutrients from the residual biomass reduces our dependency on virgin nutrients. In that context, anaerobic digestion can solubilize the nutrients present in the algal biomass and produce energy as biogas. A few studies have shown that further processing of residual algal biomass through anaerobic digestion can reduce the energy demand and greenhouse gas emissions of algal biofuel production [32,33]. Yuan et al. [36] reported that integrating anaerobic digestion with algal biofuel production could reduce the nitrogen and phosphorus demand by 66% and 90%, respectively. Another option for using residual biomass was as a protein-rich animal feed [37]. However, some researchers also used or advocated for a thermochemical route to produce biofuel from residual microalgae biomass [34] or sewage sludge [38]. Hydrothermal liquefaction, however, can recover part of the nutrients bound to the biomass. Nutrients recovered through hydrothermal liquefaction can be in organic and inorganic forms and hinder algal strains' growth [39,40].

A few experimental studies demonstrated successful uses of waste nutrients from animal [41], dairy [42] or municipal [43] waste, and biomass hydrolysate [44] for algal biomass production. Some wastewater-based algal biofuel production showed a high algae growth rate with low to medium lipid accumulation [45]. Chowdhury et al. [33] showed that energy burden and GHG emissions from algal biofuel were not dependent on the lipid content of the algae if anaerobic digestion was used for residual algal biomass processing. Hence, even though waste nutrient-based algal biomass has low lipid content, energetically favorable and environmentally benign biofuel can be produced if appropriate biomass processing can be integrated into the biofuel production process chain. Anaerobic digestion and pyrolysis used for residual biomass processing also reduced the energy demand and greenhouse gas emissions from biofuel production compared to stand-alone biofuel production facilities [33,34]. The introduction of waste biomass and waste nutrients-based biofuel production further reduced the produced biofuel's greenhouse gas emissions and energy demand [38,46]. Therefore, waste nutrients-based biofuel production not only reduces our dependency on virgin nutrients but also reduces the environmental and energy burden compared to biofuel produced using virgin nutrients.

Anaerobic digestion [33], enzymatic hydrolysis [47], thermochemical conversion [34], including gasification followed by the Fischer-Tropsch process, and combinations of anaerobic digestion, biodiesel production, enzymatic hydrolysis, pyrolysis and up-gradation of bio-oil to synthetic diesel and gasoline [48–50] have been employed for the residual biomass processing. However, the extent of biomass processing through the earlier processes affected the biofuel production and environmental impacts of the produced biofuel [49]. Increasing the extent of biomass processing increased the bioenergy production by at most 38% compared to algae-based biofuel production, followed by anaerobic digestion of residual biomass. However, the production of extra energy through various processes, i.e., pyrolysis, enzymatic hydrolysis, etc., increased energy consumption compared to energy production. Chowdhury and Franchetti [48] observed that such additional energy production consumed 1.5 GJ of energy to produce 1 GJ of bioenergy. In this regard, it is worth mentioning that stand-alone biodiesel production from algae was not energetically favorable as per the current practice. However, increasing biomass production, and using waste heat for drying, wet extraction, etc., are some measures one should incorporate

to produce energetically favorable biodiesel even from stand-alone biodiesel production facilities [51]. Hence, collocating the algal biofuel production facility with the waste heat source and other waste materials utilized for algae production and downstream processing would benefit the overall energy balance. A detail about the industrial symbiosis for algal biofuel production is given below.

### 2.1. Industrial Symbiosis

Some sustainability studies on algal biofuel also suggest that algal biomass-based biofuel production can only be sustainable if the location provides plenty of CO<sub>2</sub> without cost [24]. In that context, algal biofuel plants close to the thermal power plants and cement production plants provide a steady flow of CO<sub>2</sub> for algal growth [52]. However, the requirement of waste nutrients, a steady flow of CO<sub>2</sub>, and plenty of water would reduce the possibility of using most of the waste nutrients for algal biofuel production and eliminate the potential to develop algal biofuel as a key player in the alternative energy sector [52]. Somers and Quinn [53] reported that CO<sub>2</sub> transport within a 100 km range was the only economically viable option for producing algal biofuel. Hence, around 360 million gallons of biofuel could be produced yearly using waste CO<sub>2</sub> in the USA. According to these researchers, CO<sub>2</sub> is the limiting nutrient for producing economically viable biofuel. However, such estimate is based on a stand-alone biofuel production process. Ou et al. [54] reported that high-purity CO<sub>2</sub> sources are most attractive for algal growth. Other diluted CO<sub>2</sub> sources, for example, flue gases from thermal power plants and other facilities, would affect the algal productivity. Ou and his co-workers [54] observed that the Midwest region of the USA is the most suitable for algae production if one considers the availability of high-purity CO<sub>2</sub>.

On the other hand, Chowdhury and Franchetti [48] showed that using waste nutrients produced in the USA in the form of dairy waste could produce around  $3.14 \times 10^9$  GJ bioenergy per year, which corresponds to 2.5 billion gallons of biofuel. The study used perpetual recycling of nutrients, which increased the nutrient content by more than double within three years. The study also proposed futuristic scenarios. Such a study provides a first-hand estimate of the potential of dairy waste for biofuel production. Such a facility would be built close to large dairy farms. Wang et al. [55] reported that various types of waste biomass from various sources, including animal waste, could produce 110–170 PJ of energy in British Columbia, Canada, per year. However, such energy can only be economically viable if it is used for district heating and to produce ethanol. Tua et al. [56] observed that integrating algae-based municipal wastewater treatment and biogas production from sludge reduced the GWP of the whole municipal wastewater treatment facility.

Passell et al. [57] and Kohlheb et al. [58] also investigated the industrial symbiosis in biofuel production. Passell et al. [57] observed that due to low biomass production in a pilot-scale algae-based biodiesel production facility, the net energy ratio and GHG emissions from the produced biofuel were higher than those from conventional diesel and soy biodiesel. Their pilot-scale algae production facility was collocated with a thermal power plant and downstream algal biomass processing facilities. Hence, even though industrial symbiosis reduces the overall energy demand of algal biofuel, there is a requirement to increase biomass production capacity per unit area cultivated to increase the attractiveness of produced biofuel. Kohlheb et al. [58], on the other hand, observed that treating municipal wastewater using algae required less electricity as compared to the conventional activated sludge process. Hence, integrating wastewater treatment with algal biofuel production may provide energetically favorable biofuel. The studies conducted by Passell et al. [57] and Kohlheb et al. [58] were based on studies on pilot-scale facility. Hence, researchers used data taken from real-life scenarios. Several studies, including our previous research, developed scenarios integrating various processes that could provide extensive biomass utilization from algal biofuel production facilities. Such studies also used laboratory-based data for various processes used in the simulation and showed that integration of such processes could produce energetically favorable bioenergy. Mu et al. [59] also

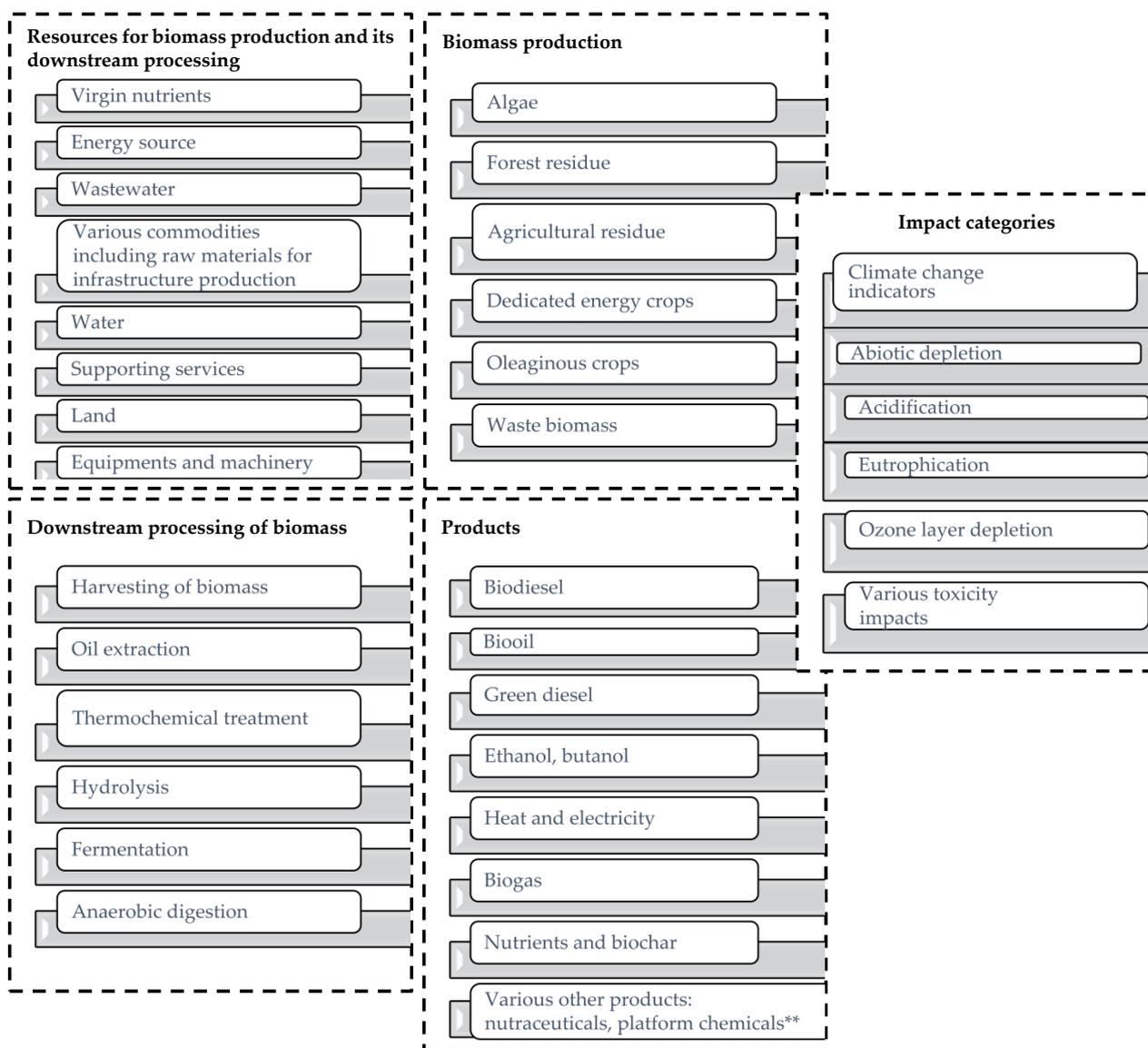
reported that waste nutrients-based algal biomass production followed by wet extraction of lipids and residue combustion had lower energy demand and GHG emissions than petroleum. Chowdhury et al. [51] observed that stand-alone biodiesel production could only be energetically favorable if waste heat were available from other industrial sources. Recently, several studies highlighted the uses of marginal land and renewable energy for biofuel production [60–62]. Especially, sunlight integration with algal biofuel production is the key to high algal biomass growth, followed by uses of excess sunlight as heat for drying and algal biofuel production. Verma et al. [60] reported that sunlight intensity is favorable for producing low-cost algal biomass in various parts of India and Nigeria. In contrast, such a facility could not be economical in the UK. This study also advocated using the heat energy produced from excess sunlight that can be integrated with other processes in a biorefinery. Besides solar energy integration, solar light/shedding also provides necessary heating and cooling of the algal reactors. Morales et al. [63] concluded that algal ponds partially covered by photovoltaic panels provided optimum GHG emissions reduction benefits. Sunlight also increased the temperature of the culture media. Hence, controlling the culture temperature by cooling or heating would also increase the GHG emissions from algal biomass production [64].

## *2.2. Life Cycle Assessment-Based Methodology and Scenario Adopted for Algal Biofuel Production*

Life cycle assessment methods are taken from [65] and [66] guidelines. To develop an LCA study, one needs to define a system boundary (goal and scope definition) and scenario. The estimated impacts are also different depending on the scenario and system boundary. Detail about the changes of impact due to differences in system boundary is given by Tu et al. [26] and Valente et al. [20]. A schematic of bioenergy production taking into consideration various processes and its LCA found in literature is shown in Figure 1.

Most LCA studies on biofuel production divided the processes incorporated into the system boundary into background and foreground processes. Later, the joint research commission (JRC) of the European Union (EU) advocated for dividing the system boundary further into 1, 2, 3, and 4th-degree processes depending on their relationship with the foreground processes [67]. Such division can make an LCA more streamlined, and the impact of the results can be determined precisely. For example, current GHG emissions accounting from LCA studies could not be divided into various scopes of GHG emissions as advocated by various organizations that provided recommendations for GHG emissions accounting. From the current LCA practices, if one wants, one can divide the GHG emissions into scope one and scope two categories. For example, GHG emissions from energy utilization for foreground processes were included in the scope two categories. However, scope three emissions could not be estimated from the current LCA practices. In this regard, the recommendation put forth by JRC, EU can help the practitioners disseminate the LCA results to a greater audience. Some studies on LCA of biofuel did not provide the type of energy they used for their study (primary vs. final energy), which hindered the comparison of results with other studies.

LCA of algal biofuel contains two types of scenarios, i.e., (i) scenarios built from pilot scale study. Hence, data used in those studies are realistic or obtained from processes that have already reached maturity. Hence, there is little chance of changing the process data due to changes in the Technology Readiness Level (TRL), (ii) scenarios that are built on taking futuristic and hypothetical cases. Futuristic and hypothetical scenarios are developed from data obtained from laboratory-scale studies or taking data from commercial-scale processes, which may or may not be part of the whole scenario in its industrial-scale production. Hence, results obtained from such scenarios are designed by LCA practitioners. However, such studies provide us with the environmental profiles of the biorefinery that would be built in the future.



**Figure 1.** A nutshell of bioenergy production from biomass and its LCA taking into account various processes found in the literature. Resources for biomass production includes in background process Biomass production is a part of foreground process. Downstream processing of biomass is a foreground process, The Figure includes a partial list of products. \*\* An exhaustive list of products can be found in Wery et al. [68]. Various impact categories and their indicators are incorporated to interpret the results. Attributional vs. consequential modeling issues were addressed by changing the LCI generated from foreground and background processes. Allocation issues arise from multifunctional process where several products are produced.

The first few studies on the LCA of biofuel envisaged that the uses of virgin nutrients had little scope to make biofuel an environmentally benign product [69]. Hence, using waste nutrients for biofuel production was an environmentally attractive process [45,49]. Recently, Kohlheb et al. [58] conducted an LCA study for algae-based wastewater treatment and compared their results with conventional wastewater treatment. They reported their results for various impact categories such as global warming potential ( $146.27 \times 10^{-3} \text{ kg CO}_2/\text{m}^3$  wastewater treated or  $19 \text{ g CO}_2/\text{kg}$  of algal biomass produced) and energy consumption ( $0.032 \text{ kWh/kg}$  algae produced). The estimated GHG emissions were comparable with those from the waste nutrient-based algal biofuel production [30,49].

Besides developing scenarios, the LCA of biofuel or biomass-based energy production requires reference scenarios for comparison with the biofuel scenario. The proposed product is replacing these reference scenarios or flows. Sometimes, an LCA can have more than one reference scenario or flow. Depending on the reference flow, the study's outcome can be different [56,70]. In most biofuel production studies, GHG emissions from fossil fuels (replaced products) were taken as the reference flow. A direct comparison of the GHG emissions between two products (biofuel vs. fossil fuel) can estimate the reduction in GHG emissions due to biofuel deployment. However, the reference flow can sometimes be very complex, especially for forest-based bioenergy. Depending on the reference flow, it was observed that produced biofuel had very high GHG emissions as compared to business-as-usual practices or when forest biomass was used in building construction [70,71]. In the LCA studies on algae-based biofuel production, uses of reference flow are rare. The use of waste nutrients for algae-based biofuel production and associated LCA studies need a reference flow to understand the role of waste nutrients and sludge diversion from the agricultural field.

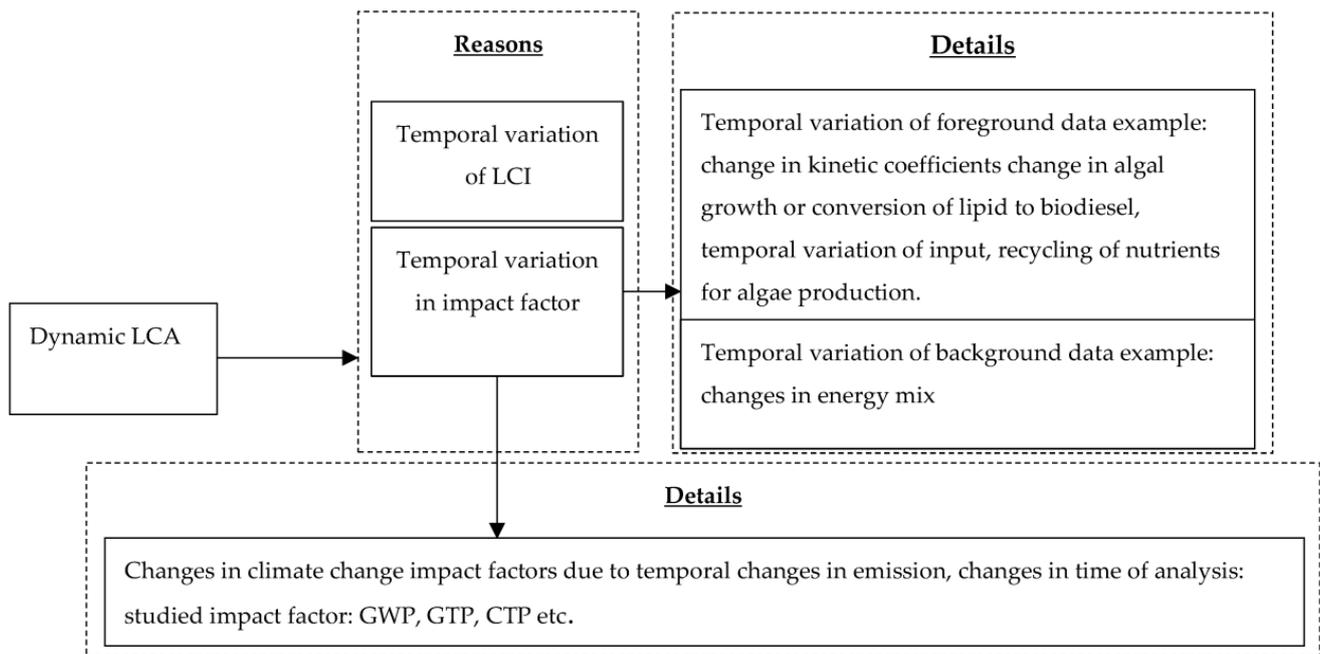
Depending on the scenario, the LCA can be mono or multifunctional. Multifunctional processes produce more than one product, or these processes provide several functions, e.g., waste treatment and nutrient recovery. Multifunctional processes introduce difficulties in an LCA to incorporate those multi-functionalities in a hardly found appropriate functional unit. It is most desirable to divide the process by which multiple products are produced. Upstream of these processes, the cumulative environmental burden is divided among the various products using mass, cost, or energy value. However, most of the time, this approach could not be undertaken in biomass-based biofuel research. Hence, the environmental burden associated with the whole scenario is divided among the various products as per the products' mass, cost, or energy value. It is advisable to use cost-based allocation of burden. However, for emerging products, there is no market price for such products. Hence, mass or energy-based allocation methods are preferred.

Depending on the allocation procedure, the life cycle impacts would also differ [72]. Besides allocation, the system expansion approach has also been used to tackle the multifunctionality problem in LCA. In this case, the produced product would replace the conventional products, and the environmental burdens of the replaced product were subtracted from the whole life cycle burden of the scenario. However, in attributional LCA, generally, the system expansion approach has been avoided. If one incorporates the system expansion approach in attributional LCA, nationwide average data of the replaced products should be taken for subtraction. In consequential LCA, marginal data or the environmental burden of the replaced product on a local scale can be used. Depending on the allocation vs. system expansion approach, the life cycle impacts of a product can differ [73,74].

Several national policy documents advocated for a particular method of allocation or substitution procedures. For example, the European Union recommended an energy-based allocation procedure, whereas the US government stipulated a substitution-based approach [24]. Several review papers highlighted various issues and associated problems with allocation. Readers may consult those manuscripts to understand better allocation issues and associated changes that may occur in life cycle impacts [19,20,26,57,74,75].

### 3. Dynamic Issues in LCA

Most of the LCA studies are static, which means that life cycle impacts are constant with respect to time. However, in several cases, static nature could not simulate several realistic scenarios. For example, recycling nutrients and variable input of raw materials for biofuel production develop a life cycle inventory variable with time [48,76,77]. Temporal dynamics in algal biofuel production could also be developed due to the (i) growth or reaction kinetics of algal biomass production, (ii) biofuel production from transesterification, or (iii) biochemical or thermochemical conversion of algal biomass (Figure 2).



**Figure 2.** Various reasons behind the dynamic issues in the LCA. GWP: global warming potential (mass of CO<sub>2</sub> equivalent), GTP: (global temperature change/°K), CTP: climate tipping points. Details about these indicators and their references are given in the main text.

Most studies on the dynamic LCA of biofuel production simulated the dynamic issues using temporal patterns of climate change indicators used in an LCA. Levasseur et al. [78] were the first to introduce such a dynamic issue in ethanol production from corn. Later, Shimako et al. [79] extended the use of dynamic LCA related to algal biofuel. Several mathematical models can simulate the temporal changes of radiative forcing from greenhouse gases. These models found their usefulness in estimating the climate benefits of forest-based bioenergy production. Details about these models and their uses are given in various scientific literature focused on bioenergy from biomass [17,80,81] or even more complicated systems such as the combination of hydroelectric-wind-biomass-geothermal-solar systems or biomass combined heat and power and microbial fuel cell systems [82]. The dynamic nature of the GWP was developed using the Bern climate model, whereas GWP and absolute global warming potential (AGWP) were estimated using Equations (1) and (2). For simulating dynamic GWP, an algebraic equation was used (Equation (3)). The various coefficients of the algebraic equation were given in Cherubini et al. [17] and Levasseur et al. [78]. Equation (3) has three to six exponential functions, which are used to simulate various sinks of CO<sub>2</sub>. Later, several versions of the Bern model were developed, which used seven exponential functions for simulating various sinks of CO<sub>2</sub> [83].

$$\text{GWP}_i = \frac{\int_0^t r_i C_t dt}{\int_0^t r_r C_t dt} \quad (1)$$

$$\text{AGWP}_i = \int_0^t r_i C_t dt \quad (2)$$

where  $r_i$  is the radiative efficiency of gas  $i$  and  $r_r$  is the radiative efficiency of a reference gas. In all the cases, the reference gas was CO<sub>2</sub>.  $C_t$  is a set of decay function of GHG emissions (here for CO<sub>2</sub>) used to find the concentration of a GHG after a time  $t$  (Equation (3)).

$$C_t = a_0 + \sum_{i=1}^{i=3,6} a_i e^{-t/T_i} \quad (3)$$

Values of parameters ( $a_0, a_i, T_i$ ) are given in Table 1.

**Table 1.** Values of various parameters used for calculating decay of CO<sub>2</sub> in atmosphere. These values are derived from Bern climate model (3 and 6 parameters). Values of parameters in underlined italics were taken from Lan and Yao [81]. Values of parameters given in bold were taken from Lepasseeur et al. [78] and Cherubini et al. [84].

BERN model	$a_0 = 0.217$ $a_0 = 0.2173$	$a_1 = 0.259$ $a_1 = 0.2240$ $T_1 = 172.9$ years $T_1 = 394.4$ years	$a_2 = 0.338$ $a_2 = 0.2824$ $T_2 = 18.51$ years $T_2 = 36.54$ years	$a_3 = 0.186$ $a_3 = 0.2763$ $T_3 = 1.186$ years $T_3 = 4.304$ years				[78,81,84]
BERN SCM 1.0 model	$a_0 = 0.013691$	$a_1 = 0.27022$ $T_1 = 0.07027$	$a_2 = 0.45937$ $T_2 = 0.57621$	$a_3 = 0.094671$ $T_3 = 2.6900$	$a_4 = 0.10292$ $T_4 = 13.617$	$a_5 = 0.0392835$ $T_5 = 86.797$	$a_6 = 0.012986$ $T_6 = 337.30$	[83]

For dynamic GWP (GWP<sub>dynamic</sub>) estimation, the integral of the numerator has a different time frame depending on the time of the release of CO<sub>2</sub> into the atmosphere (Equation (1)).  $C_t$  is the concentration of CO<sub>2</sub> in the atmosphere after releasing of CO<sub>2</sub> from biomass. A detailed description of the derivation of such concentration can be found in the literature [17,81,85,86]. Time-dependent release of a mass of CO<sub>2</sub> can also be used as a multiplier of  $C_t$  instead of ambient concentration of CO<sub>2</sub> for GWP calculation (Equations (4)–(6)).

Dynamic global warming due to time dependent release of GHG into the atmosphere (DCF) is given by Equation (4).

$$DCF = \sum_{i=1}^n DCF_i = \sum_{i=1}^n \int_{k-1}^k r_p C_t dt \quad (4)$$

where  $DCF_i$  ( $i = 1, n$  are the number of GHG emissions for same or different GHGs) is the dynamic absolute GWP for a puff emission of a GHG emission  $p$  at a time  $k-1$ ,  $k$  is the time for which the GWP needs to be calculated.  $r_p$  is the radiative efficiency of a GHG emission  $p$ . For CO<sub>2</sub>  $r_p$  is given by Equation (5) [81,82].

$$r_p = \frac{\alpha}{C} \quad (5)$$

where  $\alpha = 5.35 \text{ W/m}^2$  and  $C$  is the atmospheric concentration of CO<sub>2</sub> for a particular time, or the average concentration over the time frame for which the Equation (3) needs to be evaluated. Equation (3) can be used to find the concentration or mass of GHG emissions remaining after a particular time frame.

Hence,

$$GWP_{\text{dynamic}} = \frac{\sum_{i=1}^n DCF_i}{\int_0^k r_p C_t dt} \quad (6)$$

There are several other estimation approaches for GWP also available in the literature. A thorough description of such methodologies can be obtained from relevant references [78,80,85–87].

The two models mentioned earlier (Table 1) and others given in the literature provide different atmospheric CO<sub>2</sub> concentrations from a pulse input of CO<sub>2</sub> [81,84,85]. Hence, associated dynamic GWP factors could also differ depending on the models used. IPCC [88] used the first model (Bern model) in Table 1 for GWP estimation. Various climate models were tested to check their sensitivity against emissions or temperature changes. These climate models have been shown to provide comparable results when they were used to simulate the atmospheric CO<sub>2</sub> concentration after a pulse input of 100 Gt C. These models showed temperature sensitivity (temperature change) no less than 1.5 °C [83]. Incorporating such inherent discrepancy in GWP calculation, dynamic LCA of forest bioenergy showed various exciting features because of the long sequestration time of CO<sub>2</sub> due to the growth of plants in the forest. Cherubini and his group tried to capture the dynamic nature of GWP from forest bioenergy in their various papers. They have used plant growth and CO<sub>2</sub>

decay models in the atmosphere to capture the CO<sub>2</sub> sequestration in various compartments, i.e., biosphere, ocean, land, etc. [15,17,84]. Later, a French group led by Dr. Pierre Collet reported that the analysis time frame, and way of analysis, affected the results obtained from the dynamic LCA of forest bioenergy [89]. Levasseur et al. [90] also observed that the way of analysis affected the outcome of the study. Collet and his group, to some extent, followed the models developed by Cherubini and his team [17,84,85,91]. However, they mentioned that instead of keeping the dying trees for decay by natural processes, using mature trees for bioenergy production provided climate benefits. They estimated that depending on the analysis procedure, the GWP from forest bioenergy provided lower or higher GWP (Approx ± 75%) as compared to GWP produced from the static LCA approach (GHG emissions from burning biofuel are carbon neutral). Collet and his group argued that dynamic issues in forest bioenergy are very prominent because of the long duration of CO<sub>2</sub> sequestration. They developed such dynamic models taking into account time-dependent uptake and release of CO<sub>2</sub> to and from biomass. They also coupled a partial equilibrium model and time-dependent GWP indicators for calculating the dynamic nature of the GHG emissions from forest bioenergy [89,91,92]. The team argued that the dynamic nature of the forest bioenergy is aroused because of the prolonged growth period of the forest biomass. Change in surface temperature does not follow the changes in radiative forcing. Surface temperature change is a more end-point-oriented impact than GWP. The global temperature change potential (GTP) was developed to simulate the global temperature change profile because of the release of GHGs. Change in surface temperature, deltaT<sub>p</sub>, was simulated using Equation (7).

$$\text{deltaT}_p = \sum_{i=1}^2 \frac{C_i}{d_i} e^{-t/d_i} \quad (7)$$

where C<sub>1</sub> = 0.631; C<sub>2</sub> = 0.429; d<sub>1</sub> = 8.4; and d<sub>2</sub> = 409.5 (d<sub>1</sub> and d<sub>2</sub> are in years)

$$\text{AGTP}_i = \int_0^t r_i C_t \text{deltaT}_p dt \quad (8)$$

Absolute global temperature change (AGTP) and global temperature (GTP) can be estimated using Equations (8) and (9), respectively

$$\text{GTP}_i = \frac{\int_0^t r_i C_t \text{deltaT}_p dt}{\int_0^t r_{\text{CO}_2} C_{\text{tco}_2} \text{deltaT}_p dt} \quad (9)$$

The climate tipping point (CTP) was developed to understand the effect of GHG emissions on a particular climate target developed by IPCC as a representative concentration pathway (RCP) [93]. Hence, in CTP calculation, the ambient concentration of GHGs in CO<sub>2</sub> equivalent was also considered [94,95]. CTP formulation has two cardinal times: (i) time of emission of GHG (t<sub>e</sub>); (ii) target time or the time at which the tipping point needs to be estimated (T) [Equation (10)–(12)]. CTP is the ratio of two factors (i) capacity and (ii) impact factor.

$$\text{Capacity} = \int_{t_e}^T (C(T) - C(t)) dt \quad (10)$$

where C(T) and C(t) are the target atmospheric GHG concentration in CO<sub>2</sub> equivalent (ppm) at target time T and t, respectively. The time step for the integral was taken as 1 year, and average atmospheric concentration of GHG for 1 year was used for calculation of C(t).

$$\text{Impact} = \frac{\text{AGWP}}{A_{\text{CO}_2, \text{ppm}}} \quad (11)$$

where  $A_{\text{CO}_2, \text{ppm}}$  is the specific radiative forcing of  $\text{CO}_2$  for 1 ppm with a background concentration of 378 ppm. AGWP can be estimated using Equation (2).

$$\text{CTP} = \frac{\text{impact}}{\text{capacity}} \quad (12)$$

Characterization factor for CTP, Equation (12), was estimated for unit mass of GHG emissions. Hence, for 'm' kg of GHG emissions, resultant CTP would be  $m \times \text{CTP}$ .

CTP and GTP were primarily used in LCA for forest bioenergy production. Changes in the earth's surface temperature lag behind the radiative forcing. Hence, the GTP also lags behind the GWP. Guest and Strømman [95] observed that harvested wood used in various products increased the storage of biogenic carbon and thus could affect climate change. Depending on the forest management scenario and the fraction of wood used in wood products, net cooling of surface temperature could be achieved in 100 years. However, depending on the time horizon and forest biomass management, net warming of climate was observed when one considered GWP as an indicator, whereas net cooling was observed if GTP was used as an indicator. This study, therefore, elaborated on the importance of indicators to understand the impact on the climate of GHG emissions from a product. In the calculation procedure of GTP or GWP, the ambient concentration of GHG was not taken into consideration. However, IPCC advocated for various targets for GHG reduction. To accommodate year-wise targets and variable GHG concentration, CTP was developed. If one compares the two indicators, it can be observed that the effect of time of emission is different in these two indicators. In GTP, the effect of GHG emissions was higher as time passed, whereas, for CTP, the impact was higher, if GHG was emitted close to the target time. Hence, these two indicators provide different implications, which cannot be compared to each other. The developers of this indicator [93] also advocated that CTP be used with other climate change indicators in an LCA.

These dynamic issues in an LCA can be estimated using various software used for mathematical calculation, including MS Excel. Later, a matrix-based method was used to estimate the dynamic GWP for bioenergy. The mathematical structure was the same as the input-output analysis, where a technical coefficient matrix was developed to find a relationship between input of resources vs. product or reference flow (in input-output analysis, flow is a transaction in \$ between two industries) [96,97].

Bioenergy produced from short-rotation biomass, for example, algae, could also have dynamic nature. This dynamic nature, however, was not developed from biomass growth and biofuel burning. The dynamic nature of the LCA was developed because of the slow release of greenhouse gases from land application of residual biomass or biochar produced as a by-product of bioenergy production (biodiesel, biogas, bio-oil, etc.). The temporal release of greenhouse gases can be coupled with temporal climate change indicators (GWP, GTP, etc.) to fully capture the dynamic nature of indicators from algae-based bioenergy production. Such issues, especially the time-dependent release of greenhouse gases, can be modeled using biogeochemical models such as Roth C, Denitrification–Decomposition (DNDC), or in-house models developed to simulate the GHG emission [98–100]. Incorporating biogeochemical and plant growth models can simulate the coupling of N and P with the carbon cycle. However, these biogeochemical models do not have an ocean component. Some of these models are being used for regional biogeochemical modeling (i.e., DNDC). GHG emissions estimation for a short duration using the DNDC model taking inherent biogeochemical processes provided a better estimate of GHG emissions. Ignoring the ocean component for short-duration simulation does not incorporate considerable error as the ocean works as a very slow sink for GHGs. Guo et al. [99] used the DNDC model to derive the  $\text{N}_2\text{O}$  emission from wheat production. Later,  $\text{N}_2\text{O}$  emission was fed into the LCA model used to develop biopolymer production. The model can be used to develop temporal GHG emissions from crop rotation and the application of residual biomass on agricultural land. Collet and his group developed such a dynamic model using temporal emission of greenhouse gases from land application of residual biomass, crop residue, or

organic amendments [92]. They have simulated the temporal release of CO<sub>2</sub> using a set of differential equations. Instead of using IPCC guidelines for residual carbon remaining after a stipulated time frame, they collected kinetic coefficients of biomass degradation in different soil and moisture conditions. They used the kinetic models of biomass mineralization for temporal CO<sub>2</sub> emissions simulation. They found that incorporating temporal CO<sub>2</sub> release and associated dynamic GWP estimation provided climate benefits compared to the static LCA approach [89].

Types of energy technologies, especially fossil-based energy vs. renewable energy, particularly solar energy, showed strikingly different results in the dynamic vs. static approach in LCA. When operational CO<sub>2</sub> was high (fossil energy), the dynamic and static LCA provided comparable results in a longer time frame, i.e., 100 years. On the other hand, GWP for renewable energy (solar PV, geothermal, wind, etc.) showed higher values in short and long-time frames (35–100 years) in a dynamic approach as compared to a static approach. These contrasting results occur because of different residence times of GHG gases [81].

Current GHG emissions accounting procedures and GWP calculation methods provided by the IPCC did not consider the dynamic GWP calculation [101]. However, dynamic issues provided higher or lower GWP than the static approach. The lower GWP obtained from a dynamic approach can be beneficial for implementing net zero goals announced by most countries. The current LCA practice can be refined to simulate the more accurate GWP required to achieve the net zero target and will be discussed in detail in the next section.

#### 4. Application of LCA Approach for Net Zero Target Achievement

Bioenergy will play a vital role in climate mitigation and achieving the net zero emissions target. Estimated global bioenergy potential is ranged 40–300 EJ/year with a potential of carbon sequestration. Implementing bioenergy with carbon capture and storage will play a vital role in achieving stringent and ambitious representative concentration pathways (RCP) to limit the average global temperature rise to 1.5 °C. Some bioenergy can have carbon sequestration potential as high as 3–10 Gt C/year [7]. However, these estimates are based on 1st and 2nd generation biofuel and do not include microalgal feedstock and waste-based bioenergy, except forest residues.

Currently, the USA emits around 6.5 Gt CO<sub>2</sub> and 3.5 Gt GHG annually from energy consumption (electricity and transportation) [102]. In the USA, as per the current record of the United States Department of Agriculture (USDA), around 6 million tons of N and 1 million tons of P were produced as dairy manure [48]. Besides this nutrient source, pig-gery and poultry facilities also produce considerable waste nutrients. Poor management of these wastes generates a large amount of GHG emissions. Only dairy manure produces 5.8 Mt of CO<sub>2</sub> annually [103]. Due to the poor management of manure, a large amount of nutrients in the form of nitrogen and phosphorus are lost. Dairy manure can be processed further to produce bioenergy. Hence, dairy manure management and its uses can significantly impact the net zero emission target set by the US government. As mentioned, dairy waste can produce  $3.14 \times 10^9$  GJ energy per year, which can satiate almost 10% of the US transportation energy demand [48]. Even if the energy production from the dairy waste stream can satiate only a minor fraction of the transportation energy demand, a high GHG emissions reduction is possible. An estimated 0.17 Gt CO<sub>2</sub> emissions reduction is possible by using biofuel in the transportation sector. The GHG emissions reduction estimate has been carried out using a life cycle approach and assuming the GHG emissions from diesel as 85 kg CO<sub>2</sub>/GJ of energy [14]. However, the reduction can be higher if the replaced energy was coal-based energy [104].

The current process-based LCA approach could only incorporate some sectors or processes involved directly or indirectly in producing a product. Hence, the LCA approach provides an approximate GHG emission from a product or process. Therefore, such an estimate could only be used with caution for net zero target setting. LCA, developed from the input-output model, i.e., Economic Input-Output Life Cycle Assessment (EIO-LCA)

developed by Carnegie Mellon University ([www.eiolca.net](http://www.eiolca.net)) [105], can be an excellent tool for GHG accounting from a product at a national level. However, the data in this model are old, and because of aggregation issues, the model could not be used to simulate the GHG emissions at the product level. For example, the model aggregates all the emissions from the steel sector into two or three products. Hence, if one tried to simulate the GHG emissions from steel used in car production, it would not be possible from this model. In addition, due to the non-availability of the model in the public domain, data curation and modification could not be carried out.

Hybrid models can be developed using input-output and process-based models to have quick and effective LCA models. The process-based LCA model can easily incorporate future changes in emissions from the manufacturing of various products, especially energy systems. GHG emissions from bioenergy production, especially algae-based bioenergy, were driven by GHG emissions from fossil energy in the biofuel supply chain. Currently, the energy industry has been going through a time-consuming decarbonizing process. Such changes in the energy industry will provide an energy mix that has lower GHG emissions as compared to the present energy mix. Hence, the GHG intensity of bioenergy will be reduced with the gradual decarbonization of the energy industry. Therefore, temporal changes in the GHG intensity of the bioenergy should be modeled so that such temporal GHG emissions can be integrated with the net zero goal or with the RCP scenario developed by IPCC. Yang and Chen [86] used such changing LCI for energy systems to model the GHG emissions of biofuel produced from crop residue. Uses of dynamic LCI for energy mix will not suffice to develop an accurate GWP from the proposed technology. The existing attributional approach used the average energy mix of a country in the life cycle inventory. This energy inventory could not catch the variation in GHG emissions from different regional energy mixes [106]. Hence, the uses of energy mixes of a grid from which electricity was derived should be used in the LCI. Distinguishing between electricity and heat energy helps estimate better GHG emissions from the LCA of a product. Besides the regional energy mix, the operational characteristics of power plant operation (running in peak load vs. base load) need to be integrated with emissions calculation. It was reported that CO<sub>2</sub> emissions increased by several folds if a coal-fired power plant was run in base load vs. peak load [107]. Hence, for better accounting of GHG emissions, the duration of running a thermal power plant in various cycles need to be well documented or incorporated during emission factor calculation.

GHG emissions reduction in bioenergy systems was estimated in the form of GHG reduction in the supply chain and by using carbon capture and storage technologies. However, residual biomass originating from biofuel production can provide carbon sequestration. The incorporation of dynamic GWP calculation provides a better estimate of GWP than static GWP. Depending on the type of biomass, the dynamic GWP can be higher or lower than the static GWP [71,78,89,92]. IPCC advised that 10–20% of the applied carbon would be taken as sequestered carbon after 100 years [108]. Most countries have announced that they will achieve a net zero target 2050–2070. Hence, carbon sequestration potential from residual biomass in a short time frame relevant to the net zero emission target is much higher than 100 years time frame.

Various biogeochemical or in-house models can be used to simulate the temporal GHG emissions from the residual biomass. Some of these models used either a complex set of coupled differential equations in which carbon nitrogen and phosphorus dynamics and plant growth are solved together or only CO<sub>2</sub> released in the atmosphere is simulated [109–111]. Among these models, a mathematical model for simulating the soil organic carbon dynamics was well documented for Daisy, developed by a group of researchers from Technical University of Denmark [112]. Daisy [112,113] and DNDC [114,115] was used extensively by the researchers for simulating the (i) GHG emission, (ii) effects of crop rotation, (iii) fertilizer, (iv) residual biomass application on the soil organic carbon dynamics. A set of differential equations with various kinetic parameters were used to simulate the soil organic carbon content. Some of

these models were trained with experimental studies carried out for a long duration. These long-duration experimental studies have been carried out in some parts of Europe [116–118].

It is also not possible to find long-term experimental data for soil organic matter depending on the soil type, moisture content, and other parameters, which can affect the soil organic matter degradation and accumulation. These problems were discussed in several publications [92,98]. Albers et al. [92] collected various kinetic parameters of soil organic matter degradation for different soil types and moisture content in France. They have used the above-mentioned data (kinetic coefficients) for simulating the CO<sub>2</sub> emission from soil application of residual biomass. Hence, depending on the training of the kinetic parameters with experimental data, the temporal pattern of CO<sub>2</sub> mass released is different and residual carbon remaining in the soil would also be different after a specific time frame. Therefore, the reliability of the residual carbon and temporal CO<sub>2</sub> profile would be the primary concern for developing GHG sequestration potential from residual biomass after a short duration relevant to the time frame of the net zero targets. Developing a robust methodology for climate change indicator calculation (GWP, GTP, etc.) provides a way to reach the net zero target with less cost. Most developed countries announced their net zero targets and the associated cost. Such exorbitant cost is a major obstacle to achieve the target. For low- and medium-income countries, such exorbitant costs would not be possible to spend. Hence, biomass-based biofuel production and residual biomass management provide a cheap way to sequester carbon in the near future. Reduction in GHG emission due to temporal changes of soil organic carbon and storage of carbon in biochar was not taken as the storage carbon in IPCC and other policy documents [95,119]. Most of the technologies advocated by IPCC are also in their infancy, and the costs of such technologies (hydrogen fuel, carbon storage, sequestration, CO<sub>2</sub> sequestration from air) are exorbitant. Hence, the approach presented here provided a new avenue to achieve the target. Several researchers advocated that biofuel and incorporating dynamic issues in the GWP calculation for a shorter time frame can buy time to develop other proof of concept or low TRL high-cost technologies to the economically viable commercial state [119].

## 5. Conclusions

Dynamic issues have been extensively studied in the literature, especially in forest bioenergy. However, its application for microalgae bioenergy production, mainly when the residue produced from biofuel is applied on the land, should be studied in detail. Regional inventory for background data and temporal changes in LCI are some amendments one should implement to acquire a better estimate of GHG emissions, which can be applied for net zero target setting. IPCC advocated for mitigating the GHG emissions from transportation sector by incorporating 1st and 2nd generation biofuel. However, waste-based bioenergy especially dairy waste has one of the key ingredients for biofuel production. Depending on the production route and location, such waste can produce  $3 \times 10^9$  GJ of bioenergy. Produced energy has low GHG emissions. However, for providing a better estimate of GHG emissions and for estimating associated climate change indicators, a dynamic approach should be considered. Especially the time-dependent release of GHG from applied residual biomass provided a better estimate of the climate impact of biofuel. Using biogeochemical models for estimating GHG release from residual biomass provides a better simulation of GHG emissions and helps to estimate a better climate change indicator as compared to static approach.

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