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Life Cycle Assessment of Wheat Straw Pyrolysis with Volatile Fractions Chemical Looping Combustion

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Abstract: Among the approaches to facilitating negative CO_2 emissions is biochar production. Biochar is generated in the pyrolysis of certain biomasses. In the pyrolysis process, carbon in the biomass is turned into a solid, porous, carbon-rich, and stable material that can be captured from the soil after a period of from a few decades to several centuries. In addition to this long-term carbon sequestration role, biochar is also beneficial for soil performance as it helps to restore soil fertility and improves the retention and diffusion of water and nutrients. This work presents a Life Cycle Assessment of different pyrolysis approaches for biochar production. Biomass pyrolysis is performed in a fixed-bed reactor, which operates at a mild temperature (550 °C). Biochar is obtained as solid product of the pyrolysis, but there are also liquid (bio-oil) and gaseous products (syngas). The pyrolysis gas is partly used to fulfil the energy demand of the pyrolysis process, which is highly endothermic. In the conventional approach, CO_2 is produced during the combustion of syngas and emitted to the atmosphere. Another approach to facilitate CO_2 capture and thus obtain more negative CO_2 emissions in the pyrolysis process is burning syngas and bio-oil in a Chemical Looping Combustion unit. Life Cycle Assessment was performed of these approaches toward biomass pyrolysis to evaluate their environmental impact. The Chemical Looping Combustion approach significantly reduced the values of 7 of the 16 environmental impact indicators studied, along with the Global Warming Potential among them, it slightly increased the value of one indicator related to the use of fossil resources, and it maintained the values of the remaining 8 indicators. Environmental impact reduction occurs due to the avoidance of CO_2 and NO_x emissions with Chemical Looping Combustion. The CO_2 balances of the different pyrolysis approaches with Chemical Looping Combustion configurations were compared with a base case, which constituted the direct combustion of wheat straw to obtain thermal energy. Direct biomass combustion for the production of 17.1 MJ of thermal energy had CO_2 positive emissions of 0.165 kg. If the gaseous fraction was burned by Chemical Looping Combustion, CO_2 was captured and the emissions became increasingly negative, until a value of −3.30 kg/17.1 MJ was generated. If bio-oil was also burned by this technology, the negative trend of CO_2 emissions continued, until they reached a value of −3.66 kg.

Keywords: biomass pyrolysis; Chemical Looping Combustion; Life Cycle Assessment; environmental impacts; carbon footprint

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1. Introduction

To reach zero net CO_2 emissions and limit global warming to 1.5 °C following the Paris Agreement [1], it is necessary to remove and permanently store CO_2 from the atmosphere. Thus, carbon dioxide removal technologies are needed. In 2018, the International Panel on Climate Change officially listed biochar as a negative emissions technology, signaling that it may hold the key to solving some of our most pressing environmental challenges [2]. Biochar can be converted into one of the safest, fastest, and most efficient technologies to remove large amounts of CO_2 from the atmosphere. This is achieved since during its production, the C from the CO_2 that plants have removed from the atmosphere through photosynthesis is fixed in a very stable way in biochar, thus preventing it from being released again into the atmosphere due to the action of microorganisms decomposing.

There are many works in the literature on the properties of biochar that enable it to enhance the CO_2 uptake, including physical, chemical, and physicochemical treatments. According to the latest findings, a balance between the textural (specific surface area and micropore volume) and surface chemical attributes (basicity, mineral content, various functional groups, non-polarity, and hydrophobicity) should be reached to produce biochar with a high CO_2 uptake capacity, strong selectivity towards CO_2 over other gases, and stable performance through multiple cycles of CO_2 adsorption–desorption [3]. Another aspect to be considered for biochar to be a key factor in the world of sustainability is its scalability.

One of the ways to obtain biochar is by subjecting biomass residues to a high-temperature process in the absence of or a low content of oxygen (pyrolysis) [4]. The biochar obtained presents a high content of very stable organic carbon and high porosity. These properties make biochar a highly versatile material, which may be used not only for CO_2 capture but also in areas as diverse as agriculture, gardening and landscaping, livestock farming, water purification, soil recovery and decontamination, and construction [5].

Together with biochar, the other products obtained after biomass pyrolysis are water, oil, tar, and gases like hydrogen, methane, carbon dioxide, and carbon monoxide. The amounts and properties of these products in different phases depend upon the pyrolysis conditions and the characteristics of the input biomass. Especially interesting is the bio-oil obtained, which is a highly complex mixture of many oxygenated hydrocarbons. Once upgraded, it could be used as fuel to replace fossil fuels, with the advantage of its renewability and low NO_x and SO_x emissions [6]. The pyrolysis gases are useful in heat and power generation, either for the pyrolysis process itself or other processes, including conversion into new fuels.

When pyrolysis gases are burned for energy generation, CO_2 may be emitted. These CO_2 emissions could be considered as neutral since they are generated from biomass, which is a neutral fuel. If the combustion of pyrolysis gases leads to CO_2 capture, the biochar production process will have even greater potential to achieve negative CO_2 emissions. In order to capture this CO_2, the combustion of pyrolysis gases may be achieved using Chemical Looping Combustion technology (CLC). This is based on a simple principle, i.e., the oxygen required for combustion is supplied by a solid oxygen carrier circulating between two interconnected reactors, which first transfer the oxygen to the fuel (fuel reactor) and subsequently perform reoxidation (air reactor) [7]. Commonly, fluidized beds have proposed for fuel and air reactors, although a fixed bed has also been tested as an option. CLC avoids direct contact between the fuel and air [8], thus facilitating the generation of a concentrated CO_2 stream, which is easy to capture (see Figure 1).

The development of an adequate oxygen carrier holds vital importance for the development of this technology. Over the last 20 years, different oxygen carriers have been developed and tested in continuous CLC units [9], mostly based on nickel, copper, manganese, and iron oxides or combinations of them [10]. Not only should the reactivity and selectivity of the oxygen carriers be considered but also their mechanical properties. Furthermore, since the oxygen carrier is one of the main costs of using CLC technology, attrition during operations should be considered for scale-up of the materials [11].

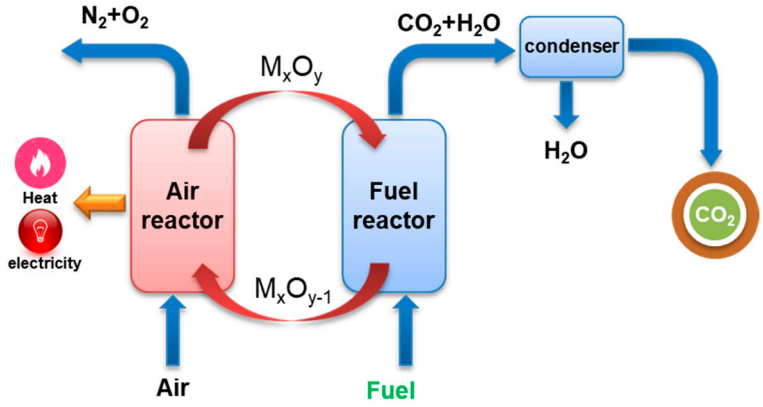

Figure 1. Scheme for the Chemical Looping Combustion process.

Chemical Looping Combustion has previously been coupled with biomass pyrolysis for syngas or hydrogen production, but there are some disadvantages to direct biomass chemical looping pyrolysis, like looping material deactivation, a high solid recirculation rate, and the requirement for separation of looping materials and biomass ash [12–14]. For these reasons, CLC has been used to burn the volatile fractions [15] or the biochar fraction [16] in biomass pyrolysis for hydrogen or syngas production. In this study, CLC was coupled with volatile fractions with the aim of covering pyrolysis reactor thermal energy requirements, with the surplus thermal energy considered a credit.

In recent years, Life Cycle Assessment (LCA) has been the most commonly used scientific tool to quantify the environmental impacts of processes and products [17,18]. LCA has been extensively applied to biomass pyrolysis [19–22] with the aim of quantifying its environmental impacts, and there are several reviews in the literature that draw together the key conclusions and recommendations for LCA's application in biomass pyrolysis. Yu et al. [23] concluded that pine biomass is the best in terms of Global Warming Potential, but there is a lack of LCA studies to have considered its further environmental impacts. The same authors also proposed that LCA studies should delve deeper into bio-oil upgrading, and that same the functional unit should be used for different LCA comparisons. Gahane et al. [24] likewise emphasized the need include bio-oil upgrading in LCA studies. They also remarked that LCA studies should include biochar impact reduction given its soil applications, like soil amendment, water holding capacity, soil structure, and soil organic carbon. Finally, the authors suggested that LCA of different types of biomass feedstocks should be performed. Ubando et al. [25] concluded in their review that it is very difficult to compare LCA studies because of the different functional units, study limits, and environmental impacts used. Patel et al. [26], meanwhile, concluded in their review that the development of a standardized approach is needed for a meaningful biomass pyrolysis LCA comparison, and they proposed that different categories from Climate Change should be used.

We did not find any studies in the literature regarding LCA applied to biomass pyrolysis coupled with CLC, only one study on standard biomass pyrolysis coupled with CLC [27] for a bio-oil fraction to achieve hydrogen production. In this study, authors demonstrate that this technology reduces carbon footprint compared with conventional hydrogen production technologies.

The objective of the present work was to evaluate the environmental impacts of different approaches to biochar production with the combustion of pyrolysis gases and bio-oil for energy production. In the conventional approach, the pyrolysis gas is partly used to fulfil the energy demand of the pyrolysis process, which is highly endothermic. In the CLC approach, syngas and bio-oil are burned in a CLC system. LCA was performed in order to compare the environmental impacts of the different configurations. As has been established, there is a lack of scientific literature about LCA applied to CLC coupled with biomass pyrolysis, making it challenging to evaluate its possible environmental impact and

better performance. This work was aimed at filling this research gap, which we approached by following scientific literature recommendations for biomass pyrolysis LCA; with our novel findings, we contribute to Chemical Looping Combustion development.

2. Methods

The LCA was carried out following the standards specified in ISO 14040 [28] and ISO 14044 [29]. This study followed the four main LCA steps, which are 1—goal and scope definition, 2—Life Cycle inventory analysis (LCI), 3—Life Cycle impact assessment (LCIA), and 4—interpretation. This LCA was based on the material and energy flows required by the three systems studied. This section details the definition of scope, inventory analysis, and impact assessment for those systems.

2.1. Definition of the Scope

ISO 14044 [29] stipulates that as a first step, the LCA goal, functional unit to be used, limits of the study, environmental impact indicators (EIIs) to be used, and data sources have to be described. The LCA presented in this paper followed the recommendations by the European Platform on Life Cycle Assessment [30]. The scope of this study included all the process steps outlined in Figure 2. The LCA limits included impacts associated with wheat grain cultivation to obtain straw, oxygen carriers' manufacture, oxygen carriers' manufacture and end of life, and emissions related to volatiles' combustion. Biochar was considered as having negative CO_2 emissions, and the surplus thermal energy obtained in volatiles' combustion after heating the pyrolysis reactor was considered negative and produced by natural gas combustion. For the LCA simulation, Sphera® LCA for Experts version 10.7 software was used, together with the databases associated with this software. Regarding time and geographical references, processes located in Spain were taken into consideration. Otherwise, data from the European Union or Germany were considered.

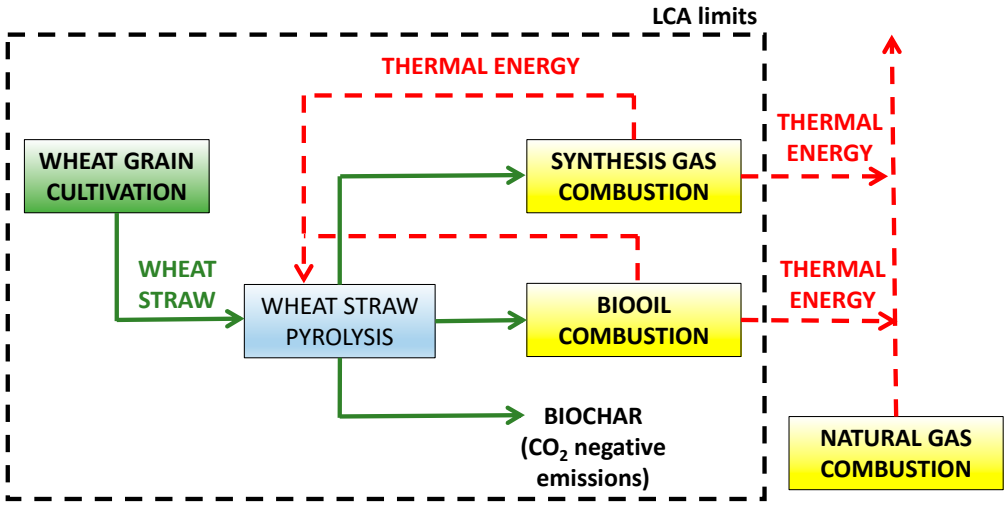

Figure 2. Limits and processes studied in the LCA.

2.1.1. Functional Unit and Base Case

The functional unit of this study was the pyrolysis of 1 kg of wheat straw to obtain 0.62 kg of syngas, 0.06 kg of bio-oil, and 0.32 kg of biochar [31]. Comparative LCAs were conducted with reference to Case I in Figure 3A using this functional unit. In the three cases studied, 1 kg of wheat straw was pyrolyzed on a rotary kiln at 550 °C to obtain the same fractions of products. The calculation data in terms of straw pyrolysis energy requirements were 0.55 MJ/kg to pyrolyze dry wheat straw [32] and 0.77 MJ/kg for a 7.5% wheat straw water content. The composition of exhaust gases of pyrolysis was as follows: H_2, 13%v, CO, 34%v, CO_2, 24%v, and CH_4, 29%v [31].

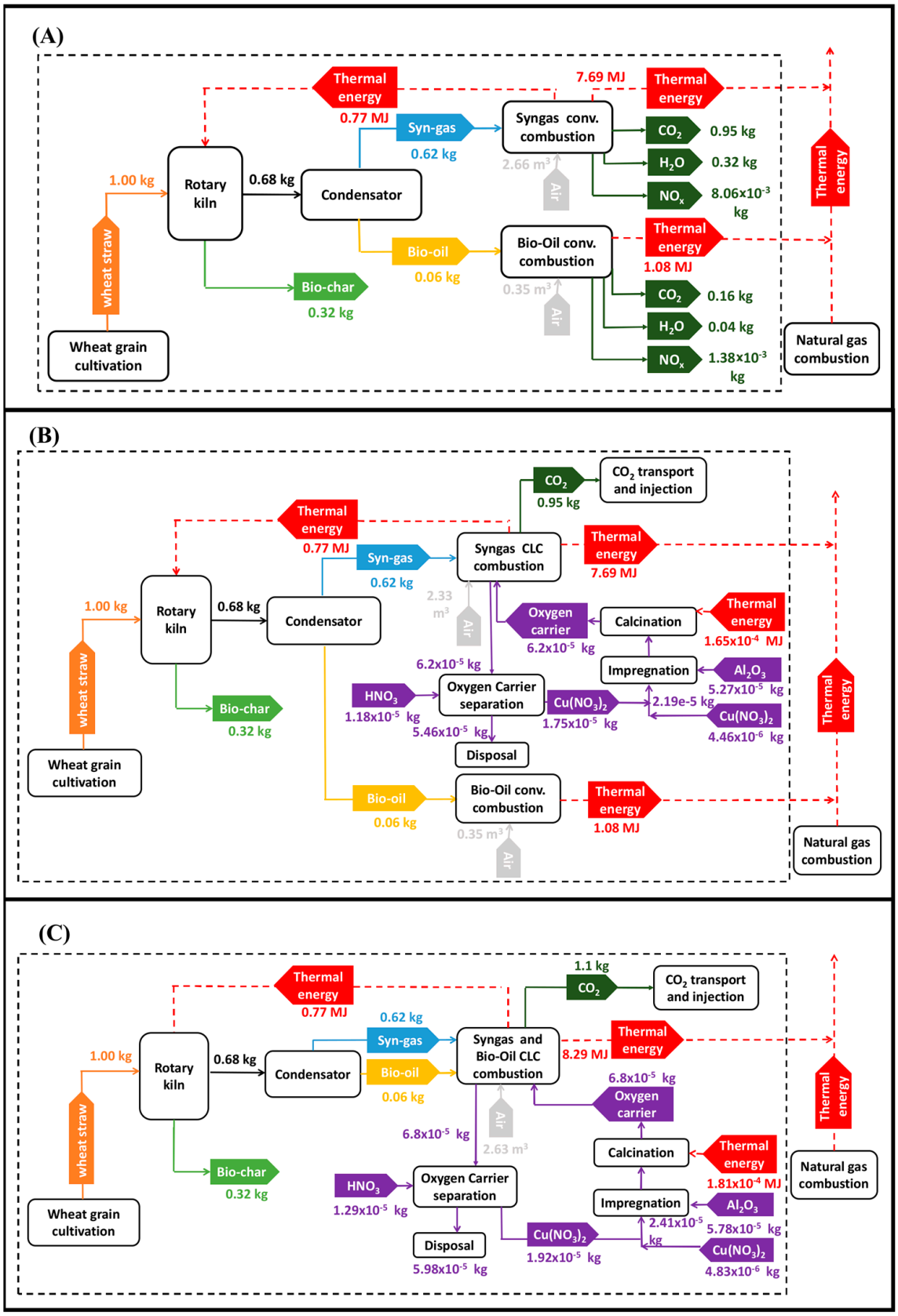

Figure 3. Life Cycle boundaries and inventories for 1 kg wheat straw pyrolysis with (**A**) conventional syngas and bio-oil combustion; (**B**) syngas CLC combustion and conventional bio-oil combustion; (**C**) syngas and bio-oil (volatiles) CLC combustion.

(i) Case I—Conventional gas fraction combustion

In the first case, 1 kg of wet wheat straw is pyrolyzed, with the gas fraction burned by conventional combustion to supply the heat necessary for pyrolysis (Figure 3A). When considering the Syngas LHV and the efficiency of conventional combustion as 95%, a combustion heat of 0.62 kg will release 8.46 MJ of thermal energy. If 0.77 MJ is used to heat the pyrolysis reactor, 7.69 MJ of thermal energy will leave the LCA limits. The environmental impacts of the production of this thermal energy by natural gas combustion are subtracted in the LCA. When considering stoichiometric combustion, the syngas burner exit gas composition is 0.95 kg CO_2, 0.32 kg H_2O, and 8.06 $\times$ 10^{-3} kg NO_x (3/350 kg NO_x/kg CO_2). The air necessary for conventional combustion is 30% in excess of that for stoichiometric combustion [33]. For conventional bio-oil combustion, $C_{10}H_{12}O_2$ is taken as the average bio-oil composition and its LHV is 19.0 MJ/kg [34]. As in the case of syngas, 95% is considered efficient combustion, the air requirement is 30% in excess, CO_2 and H_2O are the stoichiometric combustion exit gases, and NO_x is calculated with the ratio 3/350 kg NO_x/kg CO_2.

(ii) Case II—Gas fraction CLC combustion and conventional bio-oil combustion

In this case, the wheat straw pyrolysis gas fraction is burned on a CLC reactor instead of a conventional combustion reactor (Case I). For the CLC combustion, the efficiency is reduced to 90% [35], and, therefore, the heat released is now 8.03 MJ (Figure 3B). CLC combustion releases CO_2 in a pure stream that is transported and injected into an underground deposit (0.95 kg) and avoids NO_x emissions. For an oxygen carrier based on copper oxygen (Cu15, 15%w CuO over Al_2O_3), it is necessary that there is 0.025 kg per MWh of syngas burned [36], so 6.2 $\times$ 10^{-5} kg of Cu15 was necessary in this study for gas fraction CLC combustion. The oxygen carrier is synthesized through the impregnation of copper nitrate over Al_2O_3 and then calcined at 500 °C. Part of the Cu15 elutriated in CLC reactors is recovered with a new impregnation with copper nitrate and the other part is sent to the landfill as inert waste. Detailed descriptions of the oxygen carrier's manufacture, its recovery, and the final treatment can be found in a previous work [37]. To calculate the necessary air, it is considered that 0.5% in excess of that for stoichiometric combustion is suitable [36].

(iii) Case III—Gas fraction and bio-oil CLC combustion

In this third case, the gas fraction and the bio-oil (volatiles in Figure 3C) produced by wheat straw pyrolysis are combusted by CLC. The combustion efficiency is 90% and the heat released is now 8.49 MJ. We consider 0.68 kg of synthesis gas for a Cu15 mass calculation. The air necessary for CLC combustion is 0.5% in excess of that for stoichiometric combustion. The CO_2 captured after combustion is the sum of the amounts released during the combustion of the synthesis gas fraction and bio-oil, as calculated in the previous sections.

2.1.2. Impact Categories

Sphera® LCA for experts version 10.7 enabled the calculation of 16 environmental impact indicators (EIIs), following the recommendations by the European Commission Joint Research Center [30]. These EIIs with their abbreviations and units are presented in Table 1, ordered according to their recommendation level.

Table 1. Environmental impact indicators [38].

Environmental Impact Indicator	Abbreviation	Unit
Climate Change	GWP	kg CO_2 eq.
Ozone depletion	ODP	kg CFC-11 eq.
Respiratory inorganics	RI	Disease incidences

Table 1. *Cont.*

Environmental Impact Indicator	Abbreviation	Unit
Ionizing radiation—human health	IR	kBq U235 eq.
Photochemical ozone formation—human health	POF	kg NMVOC eq.
Acidification—terrestrial and freshwater	AC	Mole of H^+ eq.
Eutrophication—terrestrial	EUT	Mole of N eq.
Eutrophication—freshwater	EUF	kg P eq.
Eutrophication—marine	EUM	kg N eq.
Cancerous human health effects	HTC	CTUh
Non-cancerous human health effects	HTNC	CTUh
Ecotoxicity—freshwater	ECFW	CTUe
Land use	LU	Pt
Water scarcity	WU	m^3 world equiv.
Resource use—mineral and metals	RDM	kg Sb eq.
Resource use—energy carrier	RU	MJ

2.2. Life Cycle Inventory

ISO 14040 [28] stipulates that inventory analysis involves data collection and calculation procedures to quantify relevant inputs and outputs of a product system. Here, we considered that 1.66 kg of wet wheat straw is produced [39] for 1 kg of wheat grain, and the ECOINVENT database was used for the simulation of wheat cultivation. The potassium chloride and phosphorous oxide used in wheat cultivation were also simulated with the ECOINVENT database. Meanwhile, the ammonium nitrate and pentachlorophenol used in wheat cultivation were simulated using stoichiometry. Alumina manufacture was modeled with data from the last LCA profile of European Aluminium [40]. With Sphera® LCA for Experts version 10.7 software, we simulated the diesel mix, electricity mix, electricity from wind power, hydropower and photovoltaic, thermal energy from natural gas, sulfuric acid, Na_2CO_3, oxygen, ammonia, chlorine, phenol, inert landfill matter, copper mix, tap water, bauxite, quicklime, and sodium hydroxide. The CO_2 captured during wheat growing was considered neutral, with only CO_2 released during cultivation and harvesting by machinery considered to be emitted. An oxygen carrier manufacture inventory is detailed in [37], and a CO_2 transport and injection simulation is described in [8] and considered as negative emissions. The carbon content in biochar is 70% [31], and the CO_2 captured from biochar is considered as negative emissions. Finally, the thermal energies released from synthetic gas and bio-oil combustion were considered as avoided by natural gas combustion, and their production of environmental impacts was subtracted in the LCA.

3. Results

This section presents the outcomes of steps 3—Life Cycle impact assessment (LCIA) and 4—interpretation of the LCA. ISO 14040 [27] describes the third LCA step as the impact assessment phase, aimed at evaluating the significance of potential environmental impacts using the LCI results, and the forth step as the phase in which the findings from the inventory analysis and the impact are interpreted. Figure 4 shows the total EII values for the three cases multiplied by different factors, allowing us to show 16 EIIs in the same graph. As can be seen, Case II reduces the environmental impacts from Case I for seven environmental indicators (GWP, ODP, RI, POF, AC, EUT, and EUM). On the other hand, Case II slightly increases the value of the RU indicator, and it maintains the values of the remaining eight indicators (IR, EUF, HTC, HTNC, ECFW, LU, RDM, and WU). In Case III, it can be seen that the same seven indicators as Case II decrease with respect to Case I (GWP, ODP, RI, POF, AC, EUT, and EUM), but to a greater extent than in Case II. Case III

slightly increases the value of the RU indicator and maintains the values of the remaining eight indicators (IR, EUF, HTC, HTNC, ECFW, LU, RDM, and WU).

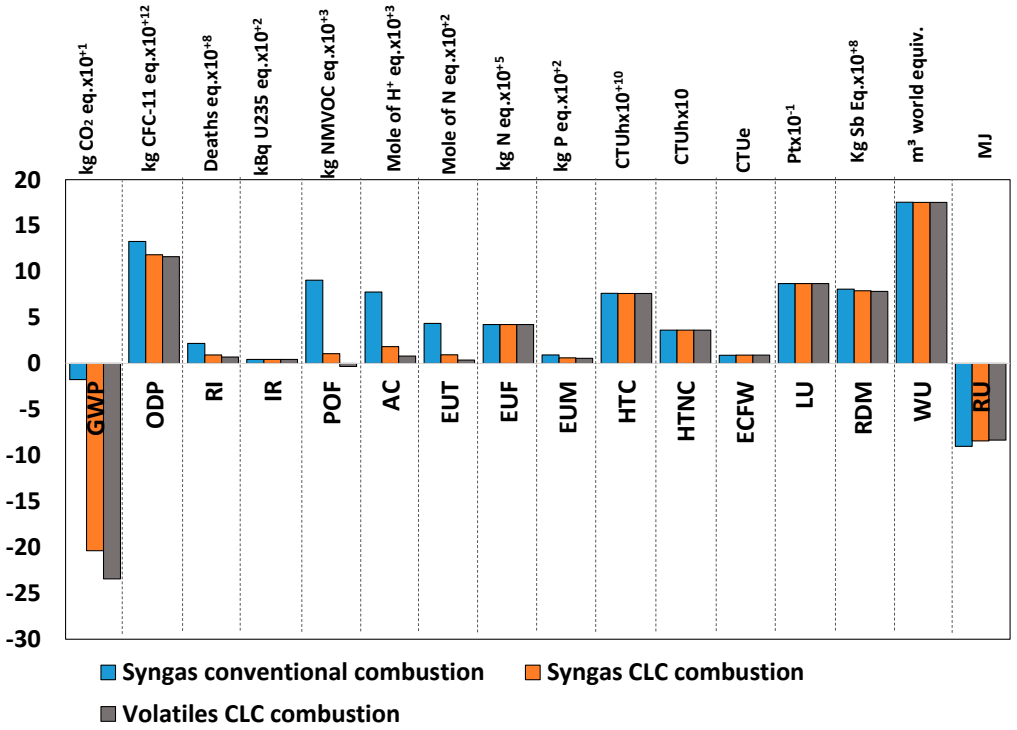

Figure 4. Environmental impact indicator values multiplied by different factors for the three cases studied: Case I (blue), Case II (orange), and Case III (grey).

When looking into the values of the EIIs of the three cases, along with the contributions of each process to the total values, it is possible to find reasons for the differences in Figure 3. This is what is represented in Figure 5, with the contributions of the different processes to the total values for Cases I, II, and III (Figures 5A, 5B and 5C, respectively). The numerical values for each case are shown in Tables S1–S3 of the Supplementary Material.

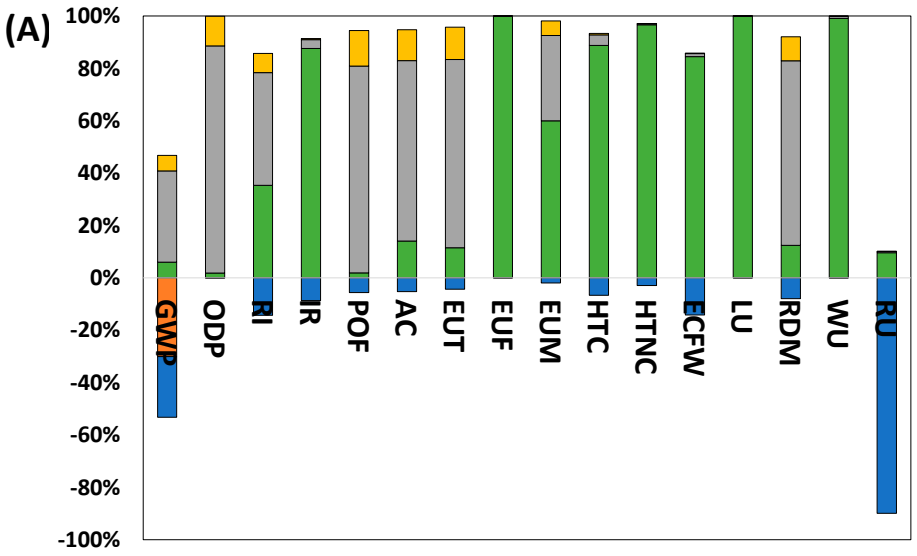

Figure 5. *Cont.*

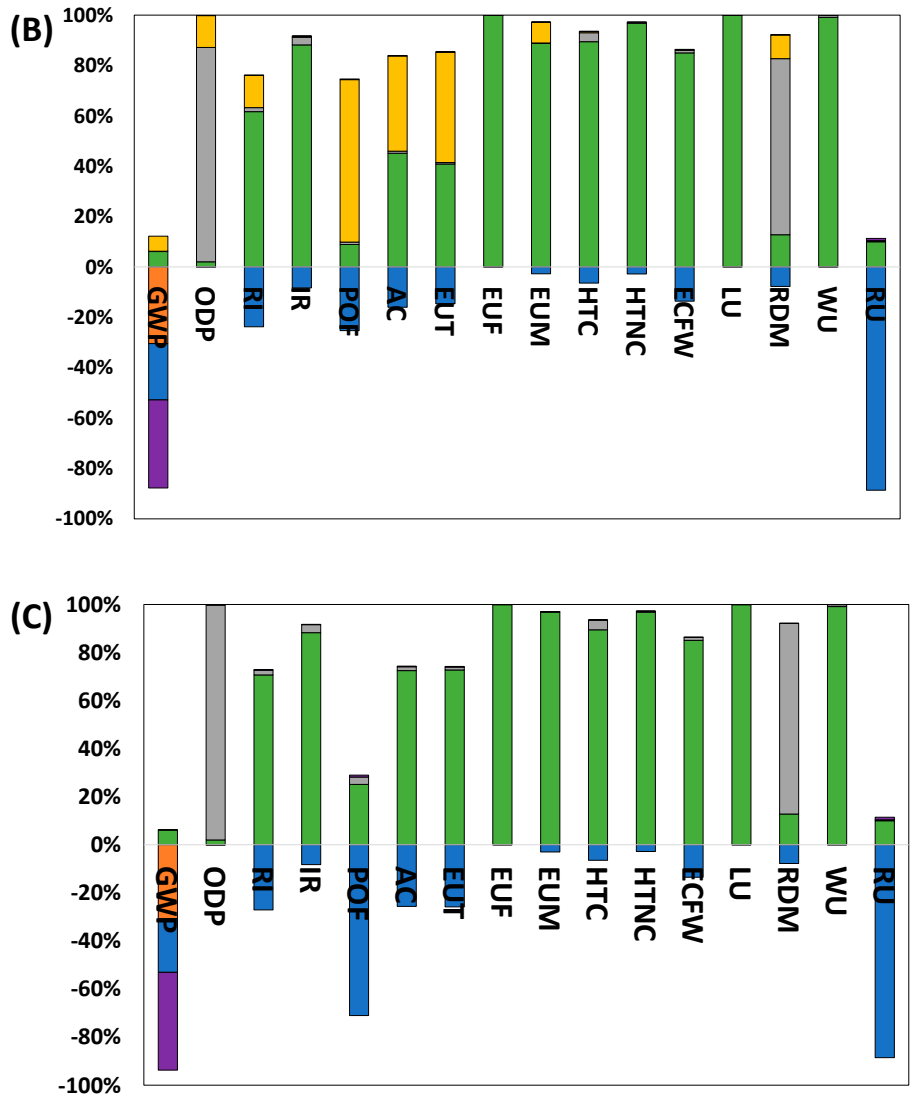

Figure 5. Contributions of the different processes to the EIIs total values for Case I (**A**), Case II (**B**), and Case III (**C**): CH_4 thermal energy equivalence (blue), conventional bio-oil combustion (Cases I and II, gold), CO_2 transport and injection (Cases II and II, purple), CO_2 biochar sequestration (orange), wheat straw production (green), conventional syngas combustion (Case I, grey), syngas CLC combustion (Case II, grey), syngas and bio-oil CLC combustion (Case III, grey).

The GWP value is reduced for Cases II and III due to the transport and injection of CO_2 after the combustion in CLC. Since, in Case III, both syngas and the bio-oil are burned by CLC, the reduction in the GWP value is greater. Regarding the indicators RI, POF, AC, EUT, and EUM, the reduction is due to the fact that NO_x is not emitted in the CLC processes, and since, in Case III, less NO_x is emitted than in Case II, the EII reductions are greater. Finally, the RU indicator value increment for Cases II and III with respect to Case I is determined entirely by the fact that the amount of natural gas saved in the thermal energy emitted in the combustion of syngas or bio-oil is less pronounced in Cases II and III. The reason of this variation is the efficiency of the combustion process for CLC (which is considered 90% for conventional combustion) is 95%.

It can be concluded in the view of these results that the combustion of the gaseous fraction in wheat straw pyrolysis decreases most of the EIIs due to CO_2 and NO_x emissions avoided; this decrease is more pronounced when both the gaseous and liquid fractions (volatile fractions) are burned by CLC. In the next section, the GWP reduction is presented in detail when compared with the direct combustion of wheat straw.

Study of the CO_2 Avoided

The CO_2 balances of the three different configurations studied in this work are compared with a base case, which is the direct combustion of wheat straw to obtain thermal energy. With conventional fuels derived from fossils, the term CO_2 avoided is frequently used to compare plants with and without carbon capture. In this context, CO_2 avoided is the emissions per kWh of a plant with CO_2 capture compared to the emissions of a baseline plant that does not capture CO_2 [41]. However, this comparison is not useful for energy plants with biomass as fuel because, in this case, combustion emissions should be considered neutral and doing otherwise could lead the incorrect conclusions to be drawn. That is why, in this section, the three cases studied are compared in terms of the CO_2 balance instead of CO_2 avoided.

Table 2 shows the CO_2 fluxes for the generation of 17.1 MJ of energy for the four energy plants studied. The energy generated during the direct combustion of 1 kg of wheat straw is 17.1 MJ, considering its LHV as 18.0 MJ/kg [42], carbon content as 52.85%w, and efficiency of combustion as 95%.

Table 2. CO_2 emissions captured and avoided for the generation of 17.1 MJ of thermal energy by wheat straw combustion (biomass combustion) and pyrolysis with conventional gas fraction and bio-oil combustion (Case I), gas fraction CLC combustion and conventional bio-oil combustion (Case II), and volatile fractions CLC combustion (Case III).

	Biomass Combustion	**Case I**	**Case II**	**Case III**
Biomass amount (kg)	1.00	1.95	2.05	2.06
CO_2 emissions (kg)				
Production	0.165	0.322	0.338	0.340
Combustion	1.938	2.178	0.332	0.000
CO_2 captured (kg)				
Biochar	0.00	1.605	1.685	1.696
CLC	0.000	0.000	1.956	2.302
Total emitted (kg)	2.103	2.501	0.670	0.340
Total captured (kg)	0.000	1.605	3.641	3.998
Balance (kg CO_2)	2.103	0.896	−2.971	−3.657
Net balance (kg CO_2)	0.165	−1.283	−3.303	−3.657

Cases I, II, and III need more biomass (1.95, 2.05, and 2.06 kg) to generate 17.1 MJ of thermal energy than direct biomass combustion (1 kg) because the energy released in these configurations is the result of syngas and bio-oil pyrolysis fractions burning after heating the rotary kiln (thermal energy fluxes that leave the LCA limits in Figure 3A–C). CO_2 emissions during production comprise the CO_2 released in wheat grain cultivation and from harvesting machinery using fossil fuels. However, it can be assumed that this CO_2 will be neutral in the close future as this machinery will be powered by electricity. The CO_2 absorbed by a wheat plant through photosynthesis is considered neutral, as it is the CO_2 emitted in biomass combustion. CO_2 is captured in two ways—biochar (Cases I, II, and III) and after CLC combustion (Cases II and II)—and considered as negative emissions. The total emitted and total captured (Table 2) are the sums of the CO_2 emitted and captured and are represented in Figure 6A for the base case and the three cases studied in this work. A classic comparison with fossil fuels between different cases with CO_2 capture systems and a base case without capture systems may use the term CO_2 avoided, calculated by subtracting the total CO_2 emissions in Cases I, II, and III and the base case. However, this calculation, as has already been said, may lead to incorrect conclusions when biomass is used as fuel. Instead, Figure 6B represents the CO_2 emitted and captured but considering the CO_2 emissions in combustion as neutral and the CO_2 captured in biochar and CLC as negative. It can be seen that the biomass combustion emissions are only due to wheat grain cultivation. The CO_2 captured in biochar is subtracted from the CO_2 emissions during cultivation (Case I). Then, the CO_2 captured after CLC combustion is subtracted from CO_2

fluxes (Cases II and III). Finally, if the CO_2 with positive and negative signs are summed, the CO_2 net balances are calculated (Table 2), as are presented in Figure 6C. In this figure, it is possible to see that direct biomass combustion for the production of 17.1 MJ of thermal energy has positive CO_2 emissions of 0.165 kg, while these emissions have a negative value if wheat straw is pyrolyzed instead of directly burned and if the gas and liquid fractions are burned by CLC to obtain thermal energy. If gas and bio-oil fractions are conventionally combusted, the CO_2 emissions are negative with a value of −1.283 kg. If the gaseous fraction is burned by CLC, the CO_2 is captured and emissions become increasingly negative until a value of −3.30 kg/17.1 MJ is generated. If bio-oil is also burned by CLC, the negative trend of CO_2 emissions continues until reaching a value of −3.66 kg.

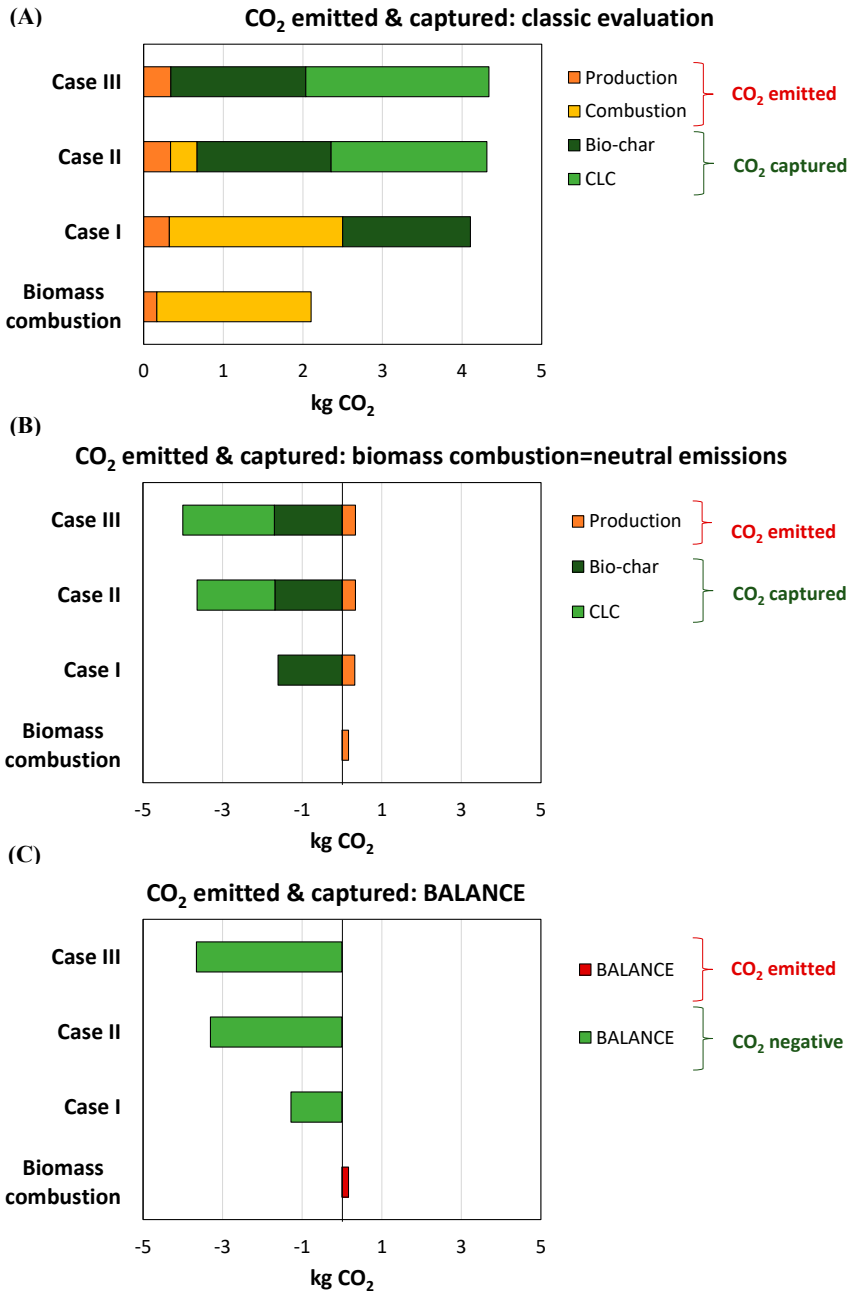

Figure 6. CO_2 balances for the generation of 17.1 MJ of thermal energy by wheat straw combustion and pyrolysis with conventional gas fraction and bio-oil combustion (Case I), gas fraction CLC combustion and conventional bio-oil combustion (Case II), and volatile fractions CLC combustion (Case III).

4. Conclusions

Biochar is a negative emissions technology and one of the most efficient technologies for removing large amounts of CO_2 from the atmosphere. One of the ways to obtain biochar is by subjecting biomass residues to a high-temperature process in the absence of or a low content of oxygen (pyrolysis). When pyrolysis gases are burned for energy generation, CO_2 may be emitted and can be considered neutral. If these CO_2 emissions are captured, the biochar production process has a greater potential to achieve negative CO_2 emissions. In this work, the gas fraction and bio-oil produced by wheat straw pyrolysis were combusted by Chemical Looping Combustion, and the CO_2 emitted was stored underground and considered negative emissions. LCA comparison was performed to confirm the environmental benefits of this technology when compared with direct combustion of the gas fraction and bio-oil. CLC combustion reduced 7 of the 16 EIIs studied, mainly due to CO_2 and NO_x emissions avoided, slightly increased the value of 1 indicator related to the use of fossil resources, and maintained the values of the remaining 8 indicators. Finally, the CO_2 balance was assessed to compare energy production via direct biomass combustion and pyrolysis with the conventional and CLC gas and bio-oil fraction combustion methods. Direct biomass combustion for the production of 17.1 MJ of thermal energy had positive CO_2 emissions of 0.165 kg. If the gas and bio-oil fractions were conventionally combusted, the CO_2 emissions were negative, with a value of −1.283 kg. If the gaseous fraction was burned by Chemical Looping Combustion, the CO_2 was captured and emissions became increasingly negative until a value of −3.30 kg/17.1 MJ was generated. If bio-oil was also burned by this technology, the negative trend of CO_2 emissions continued until reaching the value of −3.66 kg. It can be concluded from this study that biomass pyrolysis coupled with CLC for the combustion of the volatile fractions is the optimal technology to adopt because it achieved high levels of GWP reduction per kg of biomass. However, it has to be highlighted that more comprehensive research is needed into all the environmental, technological, and economic aspects associated with this technology, to achieve a better understanding of how it can be utilized as an effective energy technology to reduce our carbon footprint. At the same time, because there is no single solution to the CO_2 capture problem, and because each solution depends on the context of the emissions, before making any decision, it is important to compare biomass pyrolysis's performance and costs with other negative-emissions technologies such as direct atmospheric CO_2 capture (DAC) or pre-combustion and post-combustion technologies.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su16104013/s1. Table S1: Numerical values of the EIIs for the processes of Case I. Table S2: Numerical values of the EIIs for the processes of Case II. Table S3: Numerical values of the EIIs for the processes of Case III.

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References

1. ONU United Nations Framework Convention for Climate Change. The Paris Agreement. Available online: http://unfccc.int/paris_agreement/items/9485.php (accessed on 2 April 2024).

2. Shukla, P.; Skea, J.; Reisinger, A.; Slade, R.; Fradera, R.; Pathak, M.; Al Khourdajie, A.; Belkacemi, M.; van Diemen, R.; Hasija, A.; et al. IPCC, 2022: Summary for Policymakers. In *Climate Change 2022: Mitigation of Climate Change*; Cambridge University Press: Cambridge, UK, 2022.
3. Shafawi, A.N.; Mohamed, A.R.; Lahijani, P.; Mohammadi, M. Recent Advances in Developing Engineered Biochar for CO_2 Capture: An Insight into the Biochar Modification Approaches. *J. Environ. Chem. Eng.* **2021**, *9*, 106869. [CrossRef]
4. Tripathi, M.; Sahu, J.N.; Ganesan, P. Effect of Process Parameters on Production of Biochar from Biomass Waste through Pyrolysis: A Review. *Renew. Sustain. Energy Rev.* **2016**, *55*, 467–481. [CrossRef]
5. Li, Y.; Xing, B.; Ding, Y.; Han, X.; Wang, S. A Critical Review of the Production and Advanced Utilization of Biochar via Selective Pyrolysis of Lignocellulosic Biomass. *Bioresour. Technol.* **2020**, *312*, 123614. [CrossRef]
6. Oasmaa, A.; Czernik, S. Fuel Oil Quality of Biomass Pyrolysis Oils—State of the Art for the End Users. *Energy Fuels* **1999**, *13*, 914–921. [CrossRef]
7. Czakiert, T.; Krzywanski, J.; Zylka, A.; Nowak, W. Chemical Looping Combustion: A Brief Overview. *Energies* **2022**, *15*, 1563. [CrossRef]
8. Mattisson, T.; Keller, M.; Linderholm, C.; Moldenhauer, P.; Rydén, M.; Leion, H.; Lyngfelt, A. Chemical-Looping Technologies Using Circulating Fluidized Bed Systems: Status of Development. *Fuel Process. Technol.* **2018**, *172*, 1–12. [CrossRef]
9. Lyngfelt, A. Chemical Looping Combustion: Status and Development Challenges. *Energy Fuels* **2020**, *34*, 9077–9093. [CrossRef]
10. Daneshmand-Jahromi, S.; Hashem Sedghkerdar, M.; Mahinpey, N. A Review of Chemical Looping Combustion Technology: Fundamentals, and Development of Natural, Industrial Waste, and Synthetics Oxygen Carriers. *Fuel.* **2023**, *341*, 127626. [CrossRef]
11. Lyngfelt, A.; Leckner, B. A 1000 MW_{th} Boiler for Chemical-Looping Combustion of Solid Fuels—Discussion of Design and Costs. *Appl. Energy* **2015**, *157*, 475–487. [CrossRef]
12. Li, F.; Zeng, L.; Fan, L.-S. Biomass Direct Chemical Looping Process: Process Simulation. *Fuel* **2010**, *89*, 3773–3784. [CrossRef]
13. Kevat, M.D.; Banerjee, T. Intensification Insights from Chemical Looping Combustion Using Coal–Biomass Mixtures with Fe-Based Oxygen Carrier. *Processes* **2022**, *10*, 1242. [CrossRef]
14. Zhao, X.; Zhou, H.; Sikarwar, V.S.; Zhao, M.; Park, A.-H.A.; Fennell, P.S.; Shen, L.; Fan, L.-S. Biomass-Based Chemical Looping Technologies: The Good, the Bad and the Future. *Energy Environ. Sci.* **2017**, *10*, 1885–1910. [CrossRef]
15. Zhou, X.; Jin, H.; Li, N.; Ma, X.; Ma, Z.; Lu, P.; Yao, X.; Chen, S. New Process Combining Fe-Based Chemical Looping and Biomass Pyrolysis for Cogeneration of Hydrogen, Biochar, Bio-Oil and Electricity with In-Suit CO_2 Separation. *Molecules* **2023**, *28*, 2793. [CrossRef]
16. Situmorang, Y.A.; Zhao, Z.; An, P.; Yu, T.; Rizkiana, J.; Abudula, A.; Guan, G. A Novel System of Biomass-Based Hydrogen Production by Combining Steam Bio-Oil Reforming and Chemical Looping Process. *Appl. Energy* **2020**, *268*, 115122. [CrossRef]
17. Navajas, A.; Uriarte, L.; Gandía, L. Application of Eco-Design and Life Cycle Assessment Standards for Environmental Impact Reduction of an Industrial Product. *Sustainability* **2017**, *9*, 1724. [CrossRef]
18. Navajas, A.; Echarri, I.; Gandía, L.M.; Pozuelo, J.; Cascarosa, E. Life Cycle Assessment in Higher Education: Design and Implementation of a Teaching Sequence Activity. *Sustainability* **2024**, *16*, 1614. [CrossRef]
19. Azam, M.U.; Vete, A.; Afzal, W. Process Simulation and Life Cycle Assessment of Waste Plastics: A Comparison of Pyrolysis and Hydrocracking. *Molecules* **2022**, *27*, 8084. [CrossRef]
20. Handaya; Marimin; Indrawan, D.; Susanto, H. A Comparative Life Cycle Assessment of Palm Kernel Shell in Ceramic Tile Production: Managerial Implications for Renewable Energy Usage. *Sustainability* **2022**, *14*, 10100. [CrossRef]
21. Peters, J.F.; Iribarren, D.; Dufour, J. Biomass Pyrolysis for Biochar or Energy Applications? A Life Cycle Assessment. *Environ. Sci. Technol.* **2015**, *49*, 5195–5202. [CrossRef]
22. Roy, P.; Dias, G. Prospects for Pyrolysis Technologies in the Bioenergy Sector: A Review. *Renew. Sustain. Energy Rev.* **2017**, *77*, 59–69. [CrossRef]
23. Yu, Z.; Ma, H.; Liu, X.; Wang, M.; Wang, J. Review in Life Cycle Assessment of Biomass Conversion through Pyrolysis-Issues and Recommendations. *Green Chem. Eng.* **2022**, *3*, 304–312. [CrossRef]
24. Gahane, D.; Biswal, D.; Mandavgane, S.A. Life Cycle Assessment of Biomass Pyrolysis. *Bioenergy Res.* **2022**, *15*, 1387–1406. [CrossRef]
25. Ubando, A.T.; Rivera, D.R.T.; Chen, W.-H.; Culaba, A.B. A Comprehensive Review of Life Cycle Assessment (LCA) of Microalgal and Lignocellulosic Bioenergy Products from Thermochemical Processes. *Bioresour. Technol.* **2019**, *291*, 121837. [CrossRef]
26. Patel, M.; Zhang, X.; Kumar, A. Techno-Economic and Life Cycle Assessment on Lignocellulosic Biomass Thermochemical Conversion Technologies: A Review. *Renew. Sustain. Energy Rev.* **2016**, *53*, 1486–1499. [CrossRef]
27. Heng, L.; Xiao, R.; Zhang, H. Life Cycle Assessment of Hydrogen Production via Iron-Based Chemical-Looping Process Using Non-Aqueous Phase Bio-Oil as Fuel. *Int. J. Greenh. Gas Control* **2018**, *76*, 78–84. [CrossRef]
28. *ISO 14040:2006*; Environmental Management-Life Cycle Assessment-Principles and Framework. International Organization for Standarization: Geneva, Switzerland, 2006.
29. *ISO 14044*; Environmental Management. Life Cycle Assessment. Requirements and Guidelines. International Organization for Standardization: Geneva, Switzerland, 2007; Volume 3, p. 16.
30. EC-JRC Recommendations Based on Existing Environmental Impact Assessment Models and Factors for Life Cycle Assessment in European Context. ILCD Handbook. Available online: http://publications.jrc.ec.europa.eu/repository/bitstream/JRC61049/jrc61049_ilcd%20handbook%20final.pdf (accessed on 3 March 2024).

31. Kern, S. Niedertemperatur Drehrohrpyrolyse als Vorschaltprozess für die Co-Verbrennung von Unkonventionellen Brennstoffen in Thermischen Anlagen. Ph.D. Thesis, Technischen Universität Wien, Vienna, Austria, 2010.
32. He, F.; Yi, W.; Bai, X. Investigation on Caloric Requirement of Biomass Pyrolysis Using TG-DSC Analyzer. *Energy Convers. Manag.* **2006**, *47*, 2461–2469. [CrossRef]
33. Habib, M.A.; Mokheimer, E.M.A.; Sanusi, S.Y.; Nemitallah, M.A. Numerical Investigations of Combustion and Emissions of Syngas as Compared to Methane in a 200 MW Package Boiler. *Energy Convers. Manag.* **2014**, *83*, 296–305. [CrossRef]
34. Basu, P. *Pyrolysis. Biomass Gasification, Pyrolysis and Torrefaction*; Academic Press: Cambridge, MA, USA, 2013; pp. 147–176. [CrossRef]
35. Scott, S.A.; Dennis, J.S.; Hayhurst, A.N.; Brown, T. In Situ Gasification of a Solid Fuel and CO_2 Separation using Chemical Looping. *AIChE* **2006**, *52*, 3325–3328. [CrossRef]
36. Cabello, A.; Abad, A.; Mendiara, T.; Izquierdo, M.T.; de Diego, L.F. Outstanding Performance of a Cu-Based Oxygen Carrier Impregnated on Alumina in Chemical Looping Combustion. *Chem. Eng. J.* **2023**, *455*, 140484. [CrossRef]
37. Navajas, A.; Mendiara, T.; Goñi, V.; Jiménez, A.; Gandía, L.M.; Abad, A.; García-Labiano, F.; de Diego, L.F. Life Cycle Assessment of Natural Gas Fuelled Power Plants Based on Chemical Looping Combustion Technology. *Energy Convers. Manag.* **2019**, *198*, 111856. [CrossRef]
38. European Platform on LCA | EPLCA Developer Environmental Footprint. Available online: https://eplca.jrc.ec.europa.eu/LCDN/developerEF.xhtml (accessed on 13 February 2024).
39. Saskatchewan Province Web Harvesting Surplus Cereal Straw. Available online: https://www.saskatchewan.ca/business/agriculture-natural-resources-and-industry/agribusiness-farmers-and-ranchers/crops-and-irrigation/field-crops/cereals-barley-wheat-oats-triticale/harvesting-surplus-cereal-straw (accessed on 9 November 2023).
40. European Aluminium. *Environmenatl Profile Report—Life Cycle Inventory Data for Aluminium Production and Transformation Processes in Europe February 2022*; European Aluminium: Brussels, Belgium, 2022.
41. International Energy Agency Greenhouse Gas R&D Programme. *Capturing CO2*; International Energy Agency: Paris, France, 2007.
42. Saidur, R.; Abdelaziz, E.A.; Demirbas, A.; Hossain, M.S.; Mekhilef, S. A Review on Biomass as a Fuel for Boilers. *Renew. Sustain. Energy Rev.* **2011**, *15*, 2262–2289. [CrossRef]