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# Life-cycle assessment of hydrogen production via catalytic gasification of wheat straw in the presence of straw derived biochar catalyst --Manuscript Draft--

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Abstract:	The environmental footprints of H 2 production via catalytic gasification of wheat straw using straw-derived biochar catalysts were examined. The functional unit of 1 kg of H 2 was adopted in the system boundaries, which includes 5 processes namely biomass collection and pre-treatment units (P1), biochar catalyst preparation using fast pyrolysis unit (P2), two-stage pyrolysis-gasification unit (P3), products separation unit (P4), and H 2 distribution to downstream plants (P5). Based on the life-cycle assessment, the hot spots in this process were identified, the sequence was as follows: P4 > P2 > P1 > P3 > P5. The end-point impacts score for the process was found to be 93.4017 mPt. From benchmarking analysis, the proposed straw-derived biochar catalyst was capable of offering almost similar catalytic performance with other metal-based catalysts with a lower environmental impact.

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August 10, 2021

Professor Ashok Pandey (Editor-in-chief) and Guest Editors ELSEVIER Special Issue of Bioresource Technology,

Subject: Submission of research article for the VSI: RABRA-2021 in ELSEVIER Bioresource Technology "Recent Advances in Biochar Research and Applications"

Dear Guest Editor,

On behalf of my co-authors, I am submitting the revised article entitled 'Life cycle assessment of hydrogen production via catalytic gasification of wheat straw in the presence of straw derived biochar catalyst'. I am the corresponding author of this study and would be held responsible for all aspects of this paper during and after the publication process. The manuscript has not been submitted for publication nor has it been published before in whole or in part elsewhere. The other co-authors and I had agreed to submit this article to this journal. This work reported represents the results and findings from joint efforts with researchers from several institutions

The authors are in the opinion that the enclosed article fits well within the scope of ELSEVIER Bioresource Technology "**30,080 Life cycle analysis of biofuel and 70,030 Gasification**" that demonstrates the sustainable and renewable approach of thermo catalytic approach using biochar as catalyst. Most importantly, this manuscript is well fitted the theme of the special issue "Environmental benefits/impacts of emerging applications of biochar".

We thank the reviewers for the valuable comments that enabled us to enhance the quality of the manuscript. The manuscript has been revised to a great extent by incorporating all the comments/ suggestions from the reviewers. We believe our work is of broad interest and reference to researchers and engineers especially from the biomass industry and biochar utilization. Thus, we consider our work is of sufficient originality, applicability, and impact to appeal to the readership of this journal.

Thank you for considering the manuscript for publication in your prestigious journal.

The declaration and ethical statement are as follows:

- Screening of similarity index by Turnitin to 13% similarity in total which excludes the references, acknowledgement and author affiliation.

- Word count: Abstract (130), and Full article (8114 words, 32 pages)

- Number of Figures – 4, and Number of Tables - 2

Sincerely,

Adrian Loy

Manuscript Number: BITE-D-21-04350R2

Title: Life cycle assessment of hydrogen production via catalytic gasification of wheat straw in the presence of straw derived biochar catalyst.

We thank the editors and reviewers for the valuable comments that enabled us to enhance the quality of the manuscript. The following sections summarize our responses to all comments from the reviewers. The changes in revised manuscript were shown in **RED** font.

#### **Editor**

No.	Comment	Action/Response
1.	E-supplementary figures and tables	• Thank you for the comment. We have
	cannot be quoted in text as Fig S1Table	amended the changes accordingly.
	S1, etc. These should be mentioned as	- Line 178-179 (see supplementary
	(see supplementary material) in the text	material)
	at relevant places and after the	- Line 531, after the conclusion- We
	conclusion in a sentence as "E-	have added the sentence "E-
	supplementary data for this work can be	supplementary data for this work can
	found in e-version of this paper online".	be found in e-version of this paper
		online"



Highlights

- 1) The environmental impacts based on P5 unit are found to be negligible.
- 2) P4 unit poses the highest environmental impact, especially on human health category.
- 3) The whole process environmental impact is found to be 93.4017 mPt.
- 4) "Wheat straw loading" parameter contributes the most to global warming potential.
- 5) Straw biochar catalysts offer competitive H<sub>2</sub> yield and lower environmental impact.

1	Life-cycle assessment of hydrogen production via catalytic
2	gasification of wheat straw in the presence of straw
3	derived biochar catalyst
4	
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28	

- 29 Abstract (130 words)
- 30

The environmental footprints of H<sub>2</sub> production *via* catalytic gasification of wheat straw using 31 straw-derived biochar catalysts were examined. The functional unit of 1 kg of H<sub>2</sub> was adopted 32 33 in the system boundaries, which includes 5 processes namely biomass collection and pretreatment units (P1), biochar catalyst preparation using fast pyrolysis unit (P2), two-stage 34 pyrolysis-gasification unit (P3), products separation unit (P4), and H<sub>2</sub> distribution to 35 downstream plants (P5). Based on the life-cycle assessment, the hot spots in this process were 36 identified, the sequence was as follows: P4 > P2 > P1 > P3 > P5. The end-point impacts score 37 for the process was found to be 93.4017 mPt. From benchmarking analysis, the proposed straw-38 derived biochar catalyst was capable of offering almost similar catalytic performance with 39 other metal-based catalysts with a lower environmental impact. 40

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43 Keywords: Life-cycle analysis; Biochar; Gasification; Hydrogen; Biomass

45 1. Introduction

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With the alarming demand of global energy and rapid growth of the world population 47 across the globe, the necessity in searching for alternative renewable and carbon-neutral energy 48 sources is vital to meet the soaring global energy needs. From both economic and 49 50 environmental standpoints, valorization of agricultural crop residues to platform chemicals is deemed as a feasible and attractive approach to achieve a circular carbon economy (Alhazmi 51 & Loy, 2021). Owing to the infinite, cheap, and environmentally friendly properties of 52 agricultural crops, its extensive utilization as renewable energy resources can be observed 53 lately with the emerging closed-loop economy and the on-going transition towards post-fossil-54 carbon societies (Giuntoli et al., 2013). According to the UN Food and Agriculture 55 56 Organization (FAO) 2018, the global production of agricultural crops is growing exponentially 57 due to the drastic demand from human mankind, specifically the agricultural crops of wheat, maize, and rice (Roser, 2020). Among the agricultural crop residues reported in the literature, 58 59 wheat straw is one of the most widespread residues readily available in Europe, America, and Western Asia continents with an annual global production of 132.59 million tonnes per year 60 (Ingrao et al., 2021). 61

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Instead of landfilling or direct combustion of wheat straw (after harvesting), such 63 abundant lignocellulosic wastes can be transformed into sustainable renewable bio-based 64 products via thermochemical methods. Among all the thermochemical pathways, gasification 65 is one of the key technologies that has been extensively investigated. Over the years, many 66 experimental studies have successfully demonstrated a high production of H<sub>2</sub> from biomass 67 gasification process, including wheat straws as feedstock. In 2017, Cao and co-authors have 68 investigated supercritical water gasification of wheat straw soda black liquor in a batch reactor 69 system (Cao et al., 2017). Notably, high yield of  $H_2$  (62.38 mol/kg) with carbon content 70

71 (98.17%) was attained at 1023 K with a diluted black liquor of 2.5 wt% as reactant. Another 72 similar finding reported by Hu and co-authors, showing that 36 vol% of H<sub>2</sub> was attained with 73 the aid of 60%  $Fe_2O_3/Al_2O_3$  at 5g of wheat straw, reaction time of 10 min, and temperature of 74 1123 K (Hu et al., 2018).

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76 Over the decades, non-noble metal-based catalysts (e.g. Ni, Cu, Co) have been reported as the best reforming catalysts for industrial applications in biomass gasification (Cao et al., 77 2020). They have shown great potential as reforming catalysts given its high selectivity, cheap 78 79 cost, and high availability. Nevertheless, some drawbacks (e.g. large amount of loading, short lifespan, and easy scaling) are inevitable. Whereas, noble metals (e.g. Pt, Ru, and Rh) have 80 81 both high catalytic activity and long lifespan, but they cannot be applied on a large scale due 82 to economic consideration (Cheah et al., 2021). In this sense, the search for an affordable and 83 highly active reforming catalyst is essential to support the realization of the circular gasification economy. 84

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Lately, biochar has emerged as a new class of biomass-derived functional materials that 86 can be applied as a catalyst in various energy recovery applications (Do Minh et al., 2020; 87 Waqas et al., 2018). The rise of the application of biochar as a support material for the 88 89 preparation of tar cracking/reforming catalysts, particularly, for the synthesis of char-supported 90 metal nanoparticles has attracted large interest from both industrial and academic communities (You et al., 2018; Guo et al., 2020). For instance, Yao and co-authors have investigated the 91 effect of Ni-based biochar catalysts for H<sub>2</sub> production via gasification process (Yao et al., 92 93 2016). Notably, cotton-char supported Ni catalyst demonstrated the highest catalytic activity of H<sub>2</sub> production (64.02 vol.%) as compared to its counterparts (rice husk char, activated carbon 94 95 char, and wheat straw char). In 2021, Farooq et al. reported that the presence of silica in the

96 rice husk chars can reduce coke formation in Ni- char supported catalysts (Farooq et al., 2021). 97 Most importantly, the metal oxides in the rice husk char induced a positive synergistic effect 98 to pure Ni catalyst and thus, a higher tar conversion and H<sub>2</sub> yield were obtained in contrast to 99 the bi-functional Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Emerging knowledge and evidence on the applications of biochar 100 as a reforming catalyst with high effectiveness in tar cracking, and low cost, suggesting that 101 the valorization of biochar can be a feasible alternative that can improve the overall economic 102 and environmental values of a gasification system.

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104 To the best of the authors' knowledge, the analysis of environmental impacts of H<sub>2</sub> production from gasification of wheat straw using straw-derived biochar catalyst is still yet to 105 106 be reported in the literature. The environmental aspect of a wheat straw-based gasification plant 107 is important to be examined since it is one of the key considerations for future technology 108 investment. Thereby, the whole gasification process starting from the raw materials to the end product should be analyzed and optimized from the perspective of the life-cycle of resource 109 and environment performance. Hence, this work aims to assess and identify the possible 110 environmental impacts of carbon chain of wheat straw gasification from the beginning 111 (biomass collection and pre-treatment of wheat straw) until the end process (H<sub>2</sub> distribution to 112 petrochemical plant). Based on this framework, the hypothesis of "the monetary value of the 113 environmental impact of biochar production and the application as as biochar catalyst" can be 114 115 elucidated. Moreover, the comprehensive performance of each process unit on the environmental impact can be evaluated without value-choices based weighting factor (Li et al. 116 (2020). 117

118

The case study was modeled based on a gate-to-gate view, taking consideration from
biomass collection and pre-treatment units (P1), biochar catalysts production in fast pyrolysis

121 unit (P2), two-step pyrolysis -gasification units (P3), products separation unit (P4), and lastly H<sub>2</sub> product distribution to downstream plants (P5). Furthermore, a sensitivity analysis was also 122 performed to identify and ascertain the most significant input parameters in affecting the 123 environmental impacts based on the gate-to-gate LCA boundaries. This study provides a 124 postulated assessment of the environmental impacts with regards to catalytic gasification 125 process of wheat straws using straw-derived biochar catalyst and knowledge to support future 126 decision-making in moving towards higher TRL based on the LCA with the selected 127 boundaries. 128

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131 2. Methodology

132 2.1 Method

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According to the ISO 14040 (Principle and framework) and 14044 standards (Requirement and 134 guidelines), the LCA method comprises of four independent phases: (1) goal and scope 135 definition; (2) life-cycle inventory analysis; (3) impact assessment; and (4) interpretation 136 137 (Alhazmi & Loy, 2021). This LCA case study was carried out based on the IMPACT 2002+, where the environmental impact categories include but not limited to global warming potential, 138 ozone depletion potential, aquatic acidification potential, aquatic eutrophication, aquatic 139 140 ecotoxicity, terrestrial ecotoxicity, ionizing radiation, mineral extraction, non-renewable, land occupation, and respiratory inorganics were analyzed. The damage categories such as human 141 health, ecosystem quality, climate changes, and resources were also being investigated. Most 142 researchers have applied IMPACT 2002+ in their study because this method considers the 143 environmental impacts on both a midpoint and endpoint level (Hong, Li, & Zhaojie, 2010; 144 Jolliet et al., 2003). 145

147 2.2 Goal and Scope Definition

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The goal of the present LCA study was to evaluate the environmental assessment of H<sub>2</sub> 149 150 production in catalytic wheat straw gasification using straw-derived biochar catalysts. The environmental footprints of all input processes of the defined life-cycle from raw material pre-151 152 treatment to the final product (H<sub>2</sub>) were included in this study (Fig. 1). The system boundary 153 of this case study was adopting a 'gate-to-gate' approach. It includes biomass collection and 154 pre-treatment units (P1), biochar catalyst production using fast pyrolysis unit (P2), two-stage pyrolysis- gasification unit (P3), products separation units (P4), and H<sub>2</sub> distribution to 155 156 downstream plants (P5).

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#### 158 2.3 Life-cycle inventory (LCI)

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Wheat is one of the most important staple grains in the Kingdom of Saudi Arabia where most 160 161 of it is consumed in the form of pita or bread. According to the U.S. Department of Agricultures' Foreign Agricultural Service (FAS), wheat production in Saudi Arabia is 162 expected to escalate in the next two market years due to intensive government policy to reduce 163 irrigation. The production is forecasted to increase by 40 % in the year 2019-2020 relative to 164 production capacity of 500,000 tonnes in 2018-2019 (World Grain, 2021). The pilot-scale 165 catalytic gasification plant was proposed to be located at Al-Hasa Oasis, Saudi Arabia, which 166 has about 30,000 acres of agricultural land that are irrigated by the flow of more than 60 artesian 167 springs. More importantly, there are a few downstream plants located nearby. 168

169

Meanwhile, the data of biochar catalyst production was adopted based on authors' previous
works (Loy, et al.(a), 2018; Loy, et al.(b), 2018) and the remaining units was retrieved from

literature (Kalinci, Hepbasli, & Dincer, 2012; Wang, You, Lu, Chen, & Xu, 2020; Yao et al., 172 2016) and Ecoinvent database v3.6. All the data used were based on the optimum conditions 173 of the bench to pilot scale experimental work. The environmental performance of H<sub>2</sub> 174 production from the catalytic gasification was evaluated following the LCA approach. Note 175 that the functional unit was fixed at 1 kg of H<sub>2</sub>, while the project lifespan is assumed to be 15 176 years with an annual operating day of 300 days. The plant capacity is assumed to be 200,000 177 tonnes of wheat straw per year. Full details on input and output of the whole process (see 178 supplementary material), and the explanation of each process are shown in the following 179 180 section.

181

182 2.3.1 Biomass collection and pre-treatment units (P1)

Pre-treatment process is an important stage in upgrading biomass to reduce its size; thus 183 increaseing the accessible surface area (Chiaramonti et al., 2012). The wheat straw was sieved 184 to approximately 50 mm<sup>2</sup> using a vibration ball milling machine; to increase the reaction 185 surface area (Kumar et al., 2020). After milling, the wheat straw was fed into the mixing tank 186 to wash out the unwanted alkali and alkaline earth metals using a diluted acid mixture of 187 188 hydrochloric acid solution (30 vol.%), which can lower the reagent cost without affecting its effectiveness (Solarte-Toro et al., 2019). Then, the wheat straw and the acid mixture were then 189 transferred into an ultrafilter (50  $m^2$  of active surface per module) to remove the impurities 190 (Waste 1). "Waste 1" mainly includes chlorides, water, alkali, and alkaline metals. Whereas 191 the drying process was modeled to produce wheat straw (dry basis) at less than 2% w.c. In 192 order to produce 36.23 kg of wheat straw at 2% w.c. (Base = wheat straw at 5 % w.c), 3.46 kg 193 of water (unremoved waste) was assumed to be evaporated. 194

**196** 2.3.2 Biochar catalyst production using fast pyrolysis unit (P2)

Fast pyrolysis is reported to be a suitable technology to produce microporous and fragmented 197 198 chars that are potentially favorable for biochar catalyst usage (Brewer et al. 2009). Thus, the biochar catalyst in this work was produced *via* fast pyrolysis of wheat straw in a semi pilot-199 scale tube furnace at 773 K (Yao et al., 2016). In order to gasify 36.23 kg of wheat straw, a 200 201 30.81 kg biochar catalyst (i.e., biochar catalyst-to-feedstock ratio= 1:0.85) was required (Yao et al., 2016). Meanwhile, the wheat straw loading (205.4 kg) was calculated based on Pfitzer's 202 study (Pfitzer et al., 2016), where approximately 15 wt% of biochar can be obtained via fast 203 204 pyrolysis of wheat straw. The electricity consumption of the semi-pilot pyrolysis unit was assumed to be 0.0281 kWh per kg biomass as reported (Brassard, Godbout, & Hamelin, 2021). 205 The carbon emissions attributed to catalyst loading was assumed to be negligible since it will 206 only be conducted manually once after every few years (Montoya et al., 2020; Gholizadeh et 207 208 al., 2021).

209

#### 210 2.3.3 Two-stage pyrolysis-gasification unit (P3)

The catalytic gasification process of wheat straw was operated in a two-stage fixed bed; thereby 211 it has the advantage of producing gaseous products with higher calorific value as compared to 212 conventional gasifiers (Kosov and Zaichenko, 2016). During the first stage, the feedstock was 213 pyrolyzed under inert condition. Then, the pyrolysis volatiles were catalytic steam reformed in 214 the presence of biochar catalyst to enhance the yield of H<sub>2</sub>. Nitrogen flow (99.99%) was 215 216 supplied as carrier gas to prevent any unwanted oxidation in the pyrolysis zone (773 K). Whereas, the gasification temperature was set to be 1173 K, while steam was introduced into 217 the system to aid the water gas shift, catalytic reforming, and boudouard's reactions (Loy, et 218 219 al., 2018 (a)). The H<sub>2</sub> yield attained was reported to be 27.61 g/kg biomass or 52.35 wt.%, respectively. 220

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222 2.3.4 Product separation units (P4)

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This process can be divided into 3 sub-processes, namely 1) cyclone separation unit (biochar),
2) condensation unit (biooil) and, 3) gas separation unit (biogas). The full explanation of each
unit operation is discussed in the section below:

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228 2.3.5.1 Cyclone separation unit

Among all the industrial cyclone separators, square cyclone separators have vast advantages 229 230 that include simplicity, lower cost, small volume, shorter start time, and shorter separation time compared to the single stage and two stages cyclones (Zhang et al., 2021). Thus, a square 231 cyclone separation unit was selected in this study to remove the biochar produced from the 232 catalytic two-stage pyrolysis-gasification process. Three-square aluminum steel cyclone was 233 modeled with a thickness of 0.002 m based on the functional units. The energy consumption 234 of the side channel cyclone blower was 1.5 kW/hr and single phase (220-240 V) (Venkatesh et 235 al., 2021). 236

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238 2.3.5.2 Condensation unit

The condensation process was proposed for the condensable vapors produced from the catalytic gasification of wheat straw using biochar catalyst (Brassard et al., 2021). In order to calculate the energy consumption of water pumping, a submersible pump of 1 HP with a capacity of 10 L/min at 20 PSI was modeled (a typical submersible pump of 1 HP with a capacity of 43.2 L/min at 20 PSI and 20-foot depth was selected (Monarch Industries, Model MST5-100). Based on the catalytic gasification experiments of 1 kg of wheat straw per hour using a water flow of 180 Lwater/h, it was estimated that 6521 L of water was pumped and recirculated for the gasification of 36.23 kg of wheat straw (Brassard et al., 2021). The electricity consumption of the pumps (in MJ) was calculated by the total energy consumption of the pump (0.7 kW) with the time needed to pump 6521 L of water (~12 hr) and divided by a factor of 3.6. Also, it was assumed that 5000 L of water per year was used in each condenser (1<sup>st</sup> condenser: 100 % water and 2<sup>nd</sup> condenser: 50/50 ratio water to ethylene glycol to prevent boiling issue). The specific volume of each liquid annually was attained using Eq. (1) as shown:

253 
$$Unit volume (L Mg^{-1}) = \frac{Total volume (L year^{-1})}{200000 Mg_{biomss} year^{-1}}$$
(1)

254

The water circulating in the two condensers was maintained at 393 K and 278 K, respectively. In the 1<sup>st</sup> condenser, the temperature was set to beat 333 K and 393 K each day, considering that the heat losses were compensated by hot gases heating during pyrolysis. For the 2<sup>nd</sup> condenser, the temperature has to be in the range of 294 K to 278 K each day. The energy consumption was calculated based on Eq. (2) as shown:

260

$$261 \qquad Q = mCp\Delta T \tag{2}$$

where m is the mass of water circulated in the condenser for 36.23 kg of biomass,  $\Delta t$  is the difference of temperature for heating or cooling (in K) and Cp = 4.185 kJ kg<sup>-1</sup> K<sup>-1</sup>.

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265 2.3.5.3 Gas separation unit

In this gas separation phase, the dry syngas (16.12 kg) was fed to a pressure swing adsorption (PSA) unit where H<sub>2</sub> was fully adsorbed on the adsorbent (e.g. zeolite and silica) of the unit, before being transferred to the petrochemical plants (Kohlheb et al., 2020). The electricity of the PSA was found to be around 1.26-1.52 kWh/Nm<sup>3</sup>-CO<sub>2</sub> depending on the capacity of H<sub>2</sub>
production. The unadsorbed flue gases (e.g 9.07 CH<sub>4</sub> vol%, 26.31 CO vol%, 18.01 CO<sub>2</sub> vol%)
can be incinerated in a flame oxidation burner which can be utilized as an energy source.
However, in this study, we did not consider the fraction gaseous mixture as a source of energy.

274 2.3.5 H<sub>2</sub> distribution to downstream plants (P5)

There are a few downstream petrochemical plants located at or near to Al-Hasa Oasis region such as Saudi Aramco and SATORP. As such, the average pipeline distance was calculated based on Eq. (3). The calculated pipeline distance from the gasification site to the downstream plant in terms of -kilometers was around 2-km, and the pipeline was assumed to be made of chromium steel 18/8 – GLO steel 9.

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281 
$$r = \frac{1}{6}\tau \sqrt{\frac{F}{yf}} (\sqrt{2} + \ln(1 + \sqrt{2}))$$
 (3)

where r = average pipeline distance, F is the H<sub>2</sub> delivered annually to the plant (t/year); *y* is the annual yield of feedstock (t/year); *f* is the fraction of acreage around the plant devoted to feedstock production;  $\tau$  is the ratio of the actual distance to the straight-line distance from the plant.

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Sensitivity analysis was carried out to examine the effects of individual input parameters on the environmental impacts based on the gasification process. A  $\pm$  20 % variation of the input parameters, including the feedstock transportation distance, biochar loading, syngas yield, and wheat straw loading was studied. With the sensitivity analysis, process engineers and academicians will have a better overview of the evaluation by minimizing the uncertaintyattributed to the empirical data.

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295 3. Results and discussion

**296** 3.1 Interpretation of LCIA results

**297** 3.1.1 Impact 2002+ Midpoint Categories

The results of LCIA of the 5 different processes involved in catalytic biomass gasification for H<sub>2</sub> production using biochar-derived catalyst are reported in Table 1 in terms of Impact 2002+ midpoint categories. Significant midpoints that contributed to the damage categories in section 3.1.2 have been elucidated in the following:

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303 With respect to aquatic ecotoxicity, the environmental impact was found to be the most significant among all categories, whereby the major contributions were dominated by P2 unit 304 (4443 kg TEG water), followed by biomass collection and pre-treatment unit (4138 kg TEG 305 306 water), products separation unit (3800 kg TEG water) and two-stage pyrolysis-gasification unit (403 kg TEG water). Although the Environment Protection Agency (EPA) has not published 307 any water quality guidelines for TEG, there are still several aspects with relation to the 308 309 environmental readiness level of the whole process from the point of view of legislation should be incorporated (EPA, 2006). Since the outputs from P2, P3, and P4 units include biooil, which 310 contains organic aromatic compounds that were acidic in nature, whereby the low pH of biooil 311 obtained was expected to produce significant ecotoxicity upon exposure to aquatic organisms 312 and systems (Oasmaa, Elliott, & Korhonen, 2010). On the other hand, the toxic effect of 313 biomass pre-treatment was due to the washing out of alkali and alkaline earth metals from the 314

315 biomass. A substantial quantity of alkali and alkaline metals, such as Si (31.86 wt%), K (19 wt%), Ca (4.14 wt%), Cl (2.67 wt%), and Mn (1.10 wt%), was being removed into Waste 1. It 316 has been reported that the Si component, which can be easily oxidized into silica, contributes 317 318 to total suspended solid (TSS) in water. Thus, it should be carefully practiced to meet the 10 mg/L as regulated by "2003-Ministry of Municipal and Rural Affairs (MMRA)" and '2006-319 Ministry of Water and Electricity (MWE) of Saudi Arabia" (MMRA, 2003; MWE, 2006). In 320 addition, the washed ions in the wastewater, typically, sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium 321  $(Ca^{2+})$ , and chlorides  $(Cl^{-})$ , that are released into aquatic ecosystems have been reported to be 322 323 responsible for physiological irregularities of aquatic lives while distracting ion regulatory mechanism in the living organisms (Hansen, Olsen, & Rosenkilde, 1996). 324

325

326 Another environmental impact that demonstrates a significant point was terrestrial ecotoxicity. Although it was consistently less severe as compared to aquatic ecotoxicity from all processes, 327 the impact on terrestrial ecosystems was considered high and should never be neglected. The 328 environmental impact towards terrestrial ecotoxicity was found to be mostly contributed by P1 329 (2892.09 kg TEG soil) and P2 (1482.92 kg TEG soil). The terrestrial ecotoxicity potential value 330 331 from P1 was about 10-fold that of P3, due to the attribution of the presence of alkaline earth metals in wheat straw that may potentially affect soil ecosystems. Previous study has reported 332 that poor quality irrigation water that contains certain ions at concentrations above the threshold 333 values (>3.00 dS/m) can cause plant toxicity problems by impairing growth, reducing yield, 334 changing morphology of agriculture plants (Memon, Kuboi, Fuji, Ito, & Yatazawa, 1983). 335

336

337 Viewing from the aspect of terrestrial acid and aquatic acidification, the midpoint impact point338 was found to be smaller than the ecotoxicity potential. The processes that contribute the most

339 to acidification were product separation, and catalyst preparation. These processes produce biooil and biogas that contain mainly acid components and gases, such as SO<sub>X</sub> and NO<sub>X</sub>. These 340 gas components were accumulated in the atmosphere to be captured by the moisture to form 341 342 acid rain that contributed to terrestrial and aquatic acidification ultimately (Plens, Monaro, & Coutinho, 2015). This shall be given utmost consideration since EPA has regulated Primary 343 National Ambient Air Quality Standard (NAAQS) for SO<sub>X</sub> and NO<sub>X</sub> to be at a maximum 344 concentration of 75 ppm and 100 ppm for 1 hr, respectively (EPA, 2010, 2018). It was seen 345 that the midpoint score that originates from carcinogens (<0.5 kg C<sub>2</sub>H<sub>3</sub>Cl eq.) was smaller in 346 347 impact points as compared to non-carcinogens (<1.4 kg C<sub>2</sub>H<sub>3</sub>Cl eq.) consistently. The EPA has regulated the toxicity threshold of  $C_2H_3Cl$  to  $1\times10^{-4}$  mg/L since it has been demonstrated to be 348 highly potential to induce cancer (EPA, 2000) and therefore, exhibiting detrimental health 349 350 effects. The impact of carcinogens was mostly from P1 process since it involves washing out 351 of alkali and alkaline earth metals that are toxic to the environment (Ge & Li, 2018). In addition, it was found that the presence of chloride in the wastewater may lead to the generation of toxic 352 353 and carcinogenic by-products (Prasse, von Gunten, & Sedlak, 2020). In a similar manner, the contribution from ionizing radiation was found to be from P1, followed by P3 that exhibited a 354 very similar impact point. The apparent impact from P1 was due to the diesel fuel used in wheat 355 straw transportation, while P3 produce aromatic hydrocarbons biooil that have ionizing 356 357 radiation potential. On the other hand, impact of non-carcinogens was found to be consistently 358 higher than the carcinogenic counterparts and were mainly contributed by P2, followed by P1 and P4, respectively. This has been attributed to usage of electricity that consumes sources of 359 energy in these processes, such as 577.17 and 342.51 kWh, for catalyst preparation and product 360 361 separation, respectively. The electricity consumption and reactions involved in the processes emit substances, such as PM<sub>10</sub>, SO<sub>X</sub> and NO<sub>X</sub>, that are not categorized as carcinogens but 362 363 detrimental to human health with prolonged and high dosage exposure (Lock et al., 2019).

364

On the other hand, ozone layer depletion demonstrated a negligible effect with minimum 365 gaseous emission from fossil fuels and chlorofluorocarbons (CFCs) from the utilization of 366 renewable biomass resources, which aligns with the initiative of Montreal Protocol to alleviate 367 ozone depletion issue (OEQ, 1988). By evaluating the effect of global warming, it was found 368 369 that the processes contributed to moderate consequences with the dominant phase originating from P4, while P1, P2, and P3 demonstrated a similar impact. P5 acts as an indirect GHG 370 through its effect on hydroxyl radicals (Derwent et al., 2006). As a whole, the results from the 371 372 environmental indicators show that both aquatic acidification depletion and global warming potential have remarkably influenced the life-cycle environmental performance of the 373 gasification system. Thus, both parameters were selected for the sensitivity analysis to provide 374 375 an in-depth understanding of the relationship between the input variables with both individual environmental impacts. 376

377

378 3.1.2 Impact 2002+ Damage Categories

All midpoint scores as discussed in section 3.1 were related to the four damage categories, 379 which are human health, ecosystem quality, climate change, and resources, respectively. The 380 percentage contribution of each mid-point impact to the four end-point impacts for H<sub>2</sub> 381 production via catalytic gasification of wheat straw using biochar as catalyst is shown in Fig. 382 2. The "human health" damage category is the sum of the midpoint categories "carcinogenic 383 and non-carcinogenic toxicity", "organic and inorganic respiratory effects", "ionizing 384 radiation", and "ozone layer depletion". The "ecosystem quality" damage category is the sum 385 of the midpoint categories from "aquatic ecotoxicity", "terrestrial ecotoxicity", "terrestrial and 386 aquatic acidification", "land occupation", and "aquatic eutrophication". On the other hand, the 387

damage category "climate change" is the same category as the midpoint category "global
warming". Finally, the damage category "resources" is the summation of the midpoint
categories from "non-renewable energy consumption" and "mineral extraction".

391

The damage assessment based on the 5 different processes involved in catalytic biomass gasification for H<sub>2</sub> production using straw-derived biochar catalyst is summarized in Table 2. In this context, the value was calculated as the average person's annual share of the environmental impacts of the entire population in Europe. The scale was chosen in such a manner that the value of milli-point (mPt) represents one thousandth of the annual load from one average European inhabitant. The purpose of normalization was to facilitate interpretation and comparison between respective shares of each impact to the overall damage.

399

400 From Fig. 3, it was found that the impact of the different processes was in the order of P4>P2> P1>P3>P5. Based on the findings, the most detrimental contributing criterion that exemplifies 401 402 impact of the different processes arises, particularly from the human health, resources, and 403 climate change damage categories. The damage impact of P5 was considered minor and negligible as compared to the other units Since the human health category was dominated by 404 respiratory effects caused by substances emitted into air, the product separation phase that has 405 406 the highest middle point category exhibited the greatest damage potential. In a similar manner, P4 yielded the highest point due to the generation of GHG radicals and components from the 407 408 process that can be potentially inhaled. Resource depletion impact was also the highest from the P4 since it utilizes several equipment, such as cyclones, pumps, condensers, and PSA, that 409 410 requires energy consumption from combustion of non-renewable fuels. In addition, it also involves the usage of water with high capacity for the condensation process to convert 411

412 condensable vapours into biooil. The findings pinpoint that the feasibility and sustainable
413 circular carbon benefits of catalytic biomass gasification for H<sub>2</sub> production using biochar
414 catalysts can be enhanced by improving the separation efficiency of the process.

415

Subsequently, P2 has the second highest damage potential from the Impact 2002+ assessment, 416 with the greatest point contributed by human health, climate change, and ecosystem quality, 417 respectively. Human health was significant due to similar reasoning attributed to respiratory 418 effects due to the emission of organic and inorganic substances, such as PM<sub>10</sub> and VOCs. 419 Energy consumption was also necessary for the catalyst preparation phase, which produces 420 potential GHG components, typically CO<sub>2</sub> and CH<sub>4</sub>. The ecosystem quality carries the third-421 422 highest contribution in the damage assessment since it produces several air emissions and 423 organic compounds that can potentially affect the aquatic and terrestrial balance.

424

P1 was the third-highest contributor to the damage assessment with the most detrimental impact 425 426 originating from the resources, human health, and climate change. The highest contributor from 427 resource utilization inherited similar points to product separation and two-stage pyrolysisgasification units. This has been attributed to the similar usage of energy, water, and feedstocks 428 from wheat in these processes. Viewing from the impact of human health, the biomass pre-429 430 treatment was found to be much lower as compared to the product separation and catalyst preparation phases. This demonstrates that although the biomass pretreatment involves the 431 production of wastewater with alkali and alkaline earth metals, the ultimate impact was not 432 dominant since it has a lower score point for respiratory substances. 433

434

435 Fourthly, P3 exhibited the damage impact in the order of human health > climate change > resources. In fact, the score points between two-stage pyrolysis-gasification and biomass pre-436 treatment were quite similar when comparing the contribution by these two categories. The 437 438 difference lies in lower contribution in the two-stage pyrolysis- gasification via the ecosystem quality since it has a smaller impact that originates from lower aquatic and terrestrial 439 ecotoxicity as well as acidification properties. The reasoning has been attributed to lower 440 441 concentrations of emissions and organic outputs from the process. In addition, on the contrary, climate change contributes to a higher score in the impact assessment since the process still 442 443 emits greenhouse pollutants albeit at lower concentrations. Based on the findings, the main trade-off concerning environmental impacts was not found to be associated with the initial 444 upstream nor end-user distribution units but with the downstream separation unit (P4). This 445 446 suggests that more emphasis on the strategic tactical and operational planning on this unit is required to produce a more environmentally friendly catalytic gasification system. 447

448

#### 449 3.2 Sensitivity Analysis

Sensitivity analysis of significant parameters in the input for aquatic acidification depletion 450 and global warming potential of H<sub>2</sub> production via catalytic gasification of wheat straw is 451 depicted in Fig. 4. From Fig. 4 (a), it can be seen that a 20 % reduction in the feedstock 452 transportation distance has the highest decrease of aquatic acidification. The findings suggest 453 454 that the soot emissions from vehicles during transportation, which contain NOx, SO<sub>X</sub>, and CO<sub>2</sub>, contribute to acid gas formation. Such environmental impact can be reduced by strategically 455 456 locating the plant site (i.e., locate at a closer vicinity). It is then followed by the syngas yield, where its reduction will result in a significant drop in the acidification potential. This is due to 457 the presence of acidic NOx, SO<sub>X</sub>, and CO<sub>2</sub> gases in the compositions. On the contrary, the 458 459 reduction of the biochar and feedstock loading by 20 % increased the aquatic acidification with 460 the biochar loading showed a more significant impact. The analysis highlights the importance of having sufficient biochar and feedstock to facilitate efficient conversion performance as well 461 as minimize the production and emission of acidic NOx and SOx. On the other hand, a 20 % 462 463 increment in the syngas yield and distance of feedstock transportation could lead to an approximately similar increment in the aquatic acidification potential. The increment in aquatic 464 acidification potential with increasing feedstock transportation distance by 20 % was found to 465 466 be not that significant as compared to its counterpart when the distance was decreased. In a similar manner, the 20 % increment in biochar and feedstock loading leads to the opposite 467 468 impact in the reduction of aquatic acidification, whereby the decrement was exceptionally observed with the alteration in feedstock loading, due to the enhancement in reaction efficiency 469 470 of catalytic biomass gasification.

471

From Fig. 4(b), it was found that the decrement in the input parameters by 20 % caused a 472 473 reduction in global warming potential consistently with the descending order of feedstock 474 transportation distance > syngas yield > biochar loading > wheat straw loading. The decrement in the transportation distance and syngas yield demonstrated a higher reduction due to a 475 reduction in CO<sub>2</sub> produced during the process. On the other hand, CO<sub>2</sub> emission was less 476 affected by the reduction of biochar and wheat straw loading, mainly attributed to the nature 477 of the reactions involved in the biomass gasification that produce GHG. The increment in 20 478 % of the input parameters was depicted to be increasing persistently in the order of wheat straw 479 loading > feedstock transportation distance > biochar loading > syngas yield. The wheat straw 480 loading was found to be much higher in increment as compared to the other input parameters. 481 The findings suggest that a high loading necessitates a bigger capacity and consumption of 482 resources that release an exemplified amount of GHG to the atmosphere. 483

484

As a whole, the most significant input parameter that contributes to a reduction of aquatic 485 acidification depletion and global warming potential with a 20 % decrease was the feedstock 486 transportation distance. Whereas, with an increment in the inputs by 20 %, the most significant 487 parameters were found to be biogas yield and wheat straw loading to aquatic acidification 488 489 depletion and global warming gas potential, respectively. From the sensitivity analysis, different uncertainty factors in the system with respect to environmental burdens have been 490 determined. The integration of the sensitivity analysis with energy and exergy assessment 491 492 should be carried out to provide a bigger picture of the biomass sustainability frontier.

493

#### 494 3.3 Benchmarking study

This subsection aims to benchmark the proposed biochar-based catalytic gasification of wheat 495 straw to other existing relevant works. Based on the findings, although the studies are not 496 conducted under the same conditions, it can still be seen that the straw-derived biochar catalysts 497 proposed in this work, are capable of offering a decent H<sub>2</sub> yield as compared to other studied 498 catalysts for wheat straw gasification. It is interesting to note that H<sub>2</sub> yielded through straw-499 500 derived biochar gasification (25.59 g H<sub>2</sub>/kg wheat straw) is comparable to other metal oxide catalysts such as Ni-based catalysts (5.6~ 25.3 g H<sub>2</sub>/kg wheat straw), Rh-based catalyst (8.4 g 501 502 H<sub>2</sub>/kg wheat straw), and Fe-based catalyst (16.02-23.93 g H<sub>2</sub>/kg wheat straw). Moreover, biochar catalysts are known as a promising substitute for traditional metal-based catalysts, 503 504 given their cost effectiveness and environmentally friendly-nature (Lee, Kim, & Kwon, 2017). Given that there is only a scarce amount of literature that has performed LCA study for a wheat 505 straw catalytic gasification process, benchmarking analysis on the environmental performance 506 is difficult to be performed. Nevertheless, one can still qualitatively justify the environmental 507

508 benefit of using char-based catalysts as compared to other metal-based catalysts in two ways. Firstly, its relatively high H<sub>2</sub> yield simply indicates a more efficient use of resources (e.g. lower 509 amount of feedstock required, and lower energy consumed), which further results in lower 510 environmental impacts. Secondly, the catalysts are derived purely from biogenic resources 511 which do not add significant burden to the carbon cycle. This, therefore, leads to a lower 512 environmental impact as compared to metal-based catalysts. Using Ni catalyst as an example, 513 every kg of Ni contributes 13 kg CO<sub>2</sub>-eq (LCA, 2020)), which is about 7.7 times higher than 514 that of the proposed straw-derived char catalysts (equivalent to 1.69 kg CO<sub>2</sub>.eq/kg catalyst). 515 516 This is in agreement with the comparative study made by Frazier et al. (Frazier RS, 2015)), where the GWP of metal-based catalysts is significantly higher (>10 folds) than that of the 517 char-based catalysts. As the world is marching towards sustainable development, the use of 518 519 catalysts that were derived from natural renewable resources are deemed favourable. 520 Policymakers can put efforts in encouraging such applications to promote green economy development in the industry sector including the hydrogen production industry. 521

522

#### 523 4. Conclusions

The LCA results showed that environmental impact of the different processes was in the descending order of P4 > P2 > P1 > P3 > P5. The P4 was found to be the targeted hotspot in this study, which yields the highest greenhouse gas and resource depletion impacts. Thus, it is recommended to take into consideration the "separation unit, P4" thoughtfully in any decision making of scaling up this process. Also, future research direction should be pivoted towards metal-based supported biochar catalysts to provide a more in-depth understanding of the feasibility of biochar catalyst application.

\*E-supplementary data for this work can be found in e-version of this paper online

### 532

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539 540	6. References
541 542 543 544	[1] Alhazmi, H., & Loy, A. C. M. (2021). A review on environmental assessment of conversion of agriculture waste to bio-energy via different thermochemical routes: Current and future trends. <i>Bioresource Technology Reports</i> , 14, 100682.
545 546 547 548	[2] Brassard, P., Godbout, S., & Hamelin, L. (2021). Framework for consequential life cycle assessment of pyrolysis biorefineries: A case study for the conversion of primary forestry residues. <i>Renewable and Sustainable Energy Reviews</i> , 138, 110549.
549 550 551	[3] Brewer, C., Schmidt-Rohr., Klaus, S., Justinus, R. (2009). Characterization of Biochar from Fast Pyrolysis and Gasification Systems. Environmental Progress & Sustainable Energy. 28. 386 - 396. 10.1002/ep.10378.
553 554 555	[3] Cao, C., Xu, L., He, Y., Guo, L., Jin, H., & Huo, Z. (2017). High-Efficiency Gasification of Wheat Straw Black Liquor in Supercritical Water at High Temperatures for Hydrogen Production. <i>Energy &amp; Fuels</i> , 31(4), 3970-3978.
557 558 559 560	[4] Cao, L., Yu, I. K. M., Xiong, X., Tsang, D. C. W., Zhang, S., Clark, J. H., Ok, Y. S. (2020). Biorenewable hydrogen production through biomass gasification: A review and future prospects. Environmental Research, 186, 109547.
561 562 563 564 565	[5] Cheah, K. W., Yusup, S., Loy, A. C. M., How, B. S., Skoulou, V., & Taylor, M. J. (2021). Recent advances in the catalytic deoxygenation of plant oils and prototypical fatty acid models compounds: Catalysis, process, and kinetics. <i>Molecular Catalysis</i> , 111469.
566 567 568 569	[6] Chiaramonti, D., Prussi, M., Ferrero, S., Oriani, L., Ottonello, P., Torre, P., & Cherchi, F. (2012). Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. <i>Biomass and Bioenergy</i> , 46, 25-35.

570	[7] Derwent, R., Simmonds, P., O'Doherty, S., Manning, A., Collins, W., & Stevenson, D.
571	(2006). Global environmental impacts of the hydrogen economy. Int. J. Nuclear
572	Hydrog. Prod. Appl., 1(1), 57 - 67.
573	
574	[8] Do M, T., Song, J., Deb, A., Cha, L., Srivastava, V., & Sillanpää, M. (2020). Biochar
575	based catalysts for the abatement of emerging pollutants: A review. Chemical
576	Engineering Journal, 394, 124856.
577	
578	[9] EPA. (2006). National Recommended Water Quality Criteria. from United States
579	Environmental Protection Agency.
580	
581	[10] Farooq, A., Jang, SH., Lee, S. H., Jung, SC., Rhee, G. H., Jeon, BH., & Park, YK.
582	(2021). Catalytic steam gasification of food waste using Ni-loaded rice husk derived
583	biochar for hydrogen production. <i>Chemosphere</i> , 130671.
584	
585	[11] Frazier RS, J. E., Kumar A., (2015). Life Cycle Assessment of Biochar versus Metal
586	Catalysts Used in Syngas Cleaning Energies 621-644
587	Calarysis Osed in Syngas Creaning. Energies, 621 677.
588	[12] Ge V & Li Z (2018) Application of Lignin and Its Derivatives in Adsorption of
580	Heavy Metal Ions in Water: A Review ACS Sustain Cham Eng. 6(5) 7181-7192
505	$Teavy Wetar fons in water. Tr Review. Tes Sustain. Chem. Eng., O(5), T101^{-7}192.$
590	[13] Guo E. Jia X. Liang S. Zhou N. Chan P. & Puan P. (2020) Development of
291	[15] Ouo, F., Jia, A., Liang, S., Zhou, N., Chen, F., & Kuan, K. (2020). Development of
592	biochar-based hanocatarysts for tar cracking/reforming during biomass pyrorysts and
593	gasification. <i>Bioresource Technology</i> , 298, 122263.
594	
595	[14] Mortaza G., Hu, X and Liu, Q. (2021) Progress of using biochar as a catalyst in thermal
596	conversion of biomass" Reviews in Chemical Engineering, vol. 37, no. 2, pp. 229-
597	258.
598	
599	[15] Giuntoli, J., Boulamanti, A. K., Corrado, S., Motegh, M., Agostini, A., & Baxter, D.
600	(2013). Environmental impacts of future bioenergy pathways: the case of electricity
601	from wheat straw bales and pellets. GCB Bioenergy, 497-512.
602	
603	[16] Hansen, H. J. M., Olsen, A. G., & Rosenkilde, P. (1996). The effect of Cu on gill and
604	esophagus lipid metabolism in the rainbow trout Oncorhynchus mykiss. Comp.
605	Biochem. Physiol. C Toxicol. Pharmacol., 113(1), 23-29.
606	
607	[17] Hong, J., Li, X., & Zhaojie, C. (2010). Life cycle assessment of four municipal solid
608	waste management scenarios in China. Waste Management, 30(11), 2362-2369.
609	
610	[18] Hu, J., Li, C., Guo, O., Dang, J., Zhang, O., Lee, DJ., & Yang, Y. (2018), Syngas
611	production by chemical-looping gasification of wheat straw with Fe-based oxygen
612	carrier Bioresource Technology 263 273-279
613	
614	[19] Ingrao C. Matarazzo A. Gorijan S. Adamczyk I. Failla S. Primerano P. &
615	Huisingh D (2021) Wheat_straw derived bioethanol production: A raview of Life
616	Cycle Assessments Science of The Total Environment 146751 146771
617	Cycle Assessments. Science of the total Environment, 140/51-140//1.
01/	

618 619 620	<ul> <li>[20] Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., &amp; Rosenbaum, R. (2003). IMPACT 2002+: A new life cycle impact assessment methodology. <i>The</i> <i>International Journal of Life Cycle Assessment</i>, 8(6), 324.</li> </ul>
621	
622	[21] Kalinci, Y., Hepbasli, A., & Dincer, I. (2012). Life cycle assessment of hydrogen
623	production from biomass gasification systems. International Journal of Hydrogen
624	Energy 37(19) 14026-14039
625	Lhergy, 57(17), 1+020-1+057.
626	[22] Kohlheh N. Wluka M. Bezama A. Thrän D. Aurich A. & Müller P. A. (2020)
627	[22] Kommed, N., Wiuka, M., Dezama, A., Tinan, D., Aurich, A., & Muner, K. A. (2020). Environmental Economic Assessment of the Pressure Swing Adsorption Bioges
627	Linvironmental-Economic Assessment of the Fressure Swing Adsorption Diogas
628	Opgrading Technology. <i>BioEnergy Research</i> .
629	
630	[23] Kumar, M., Xiong, X., Wan, Z., Sun, Y., Isang, D. C. W., Gupta, J., OK, Y. S.
631	(2020). Ball milling as a mechanochemical technology for fabrication of novel
632	biochar nanomaterials. <i>Bioresource Technology</i> , 312, 123613.
633	
634	[24] LCA, N. m. (2020). Nickel metal LIFE CYCLE DATA
635	https://nickelinstitute.org/policy/nickel-life-cycle-management/nickel-life-cycle-data/
636	(accessed 08062021).
637	
638	[25] Li, Q., Song, G., Xiao, J., Hao, J., Li, H., & Yuan, Y. (2020). Exergetic life cycle
639	assessment of hydrogen production from biomass staged-gasification. Energy, 190,
640	116416.
641	[26] Lee I Kim K H & Kwon F F (2017) Biocher as a Catalyst Renewable and
641	[20] Lee, J., Killi, KII., & Kwoli, E. E. (2017). Diochai as a Catalyst. <i>Renewable and</i>
642	Sustainable Energy Reviews, 77, 70-79.
643	[27] Lock S. S. M. Lau, K. K. Shariff A. M. Veong, V. F. Ban, Z. H. & Tay, W. H.
645	(2010) Process simulation and ontimization of ovygan anriched combustion using
645	(2019). The standard and optimization of oxygen enficiency computation using this polymeric membranes: affect of thickness and temperature dependent physical
640	aging L Cham Tashnal Bistschol 04(0) 2844 2868
047 C10	aging. J. Chem. Technol. Diolechol., 94(9), 2044-2808.
040 640	[28] Lov A C M Con D K W Vugun S Chin P I E Lom M K Shabbar M
649	[20] LOY, A. C. M., Oall, D. K. W., Tusup, S., Chill, D. L. F., Lalli, M. K., Shahoaz, M., Dianawati, E. (2018a). Thermogravimatric kinetic modelling of in situ estalutio
650	Rianawau, E. (2018a). Thermogravimetric kinetic moderning of in-situ catalytic
651	pyrolytic conversion of fice nusk to bioenergy using fice null ash catalyst.
652	Bioresource Technology, 201, 213-222.
653	
654	[29] Loy, A. C. M., Yusup, S., Lam, M. K., Chin, B. L. F., Shahbaz, M., Yamamoto, A., &
655	Acda, M. N. (2018b). The effect of industrial waste coal bottom ash as catalyst in
656	catalytic pyrolysis of rice husk for syngas production. Energy Conversion and
657	Management, 165, 541-554.
658	
659	[30] Memon, A., Kuboi, T., Fuji, K., Ito, S., & Yatazawa, M. (1983). Taxonomic character of
660	plant species in absorbing and accumulating alkali and alkaline earth metals grown in
661	temperate forest of Japan. Plant Soil, 70(3), 367-389.
662	
663	[31] Montoya, D. B, Xiaolei Z., Jun L., Vivek R., Simão M., Marco G., (2020)Performance
664	of biochar as a catalyst for tar steam reforming: Effect of the porous structure, Applied
665	Energy,259.
666	

667 [32] Nanda, S., Reddy, S. N., Dalai, A. K., & Kozinski, J. A. (2016). Subcritical and supercritical water gasification of lignocellulosic biomass impregnated with nickel 668 nanocatalyst for hydrogen production. International Journal of Hydrogen Energy, 669 41(9), 4907-4921. 670 671 [33] Nanda, S., Reddy, S. N., Vo, D. N., Sahoo, B. N., & Kozinski, J. A. (2018). Catalytic 672 673 gasification of wheat straw in hot compressed (subcritical and supercritical) water for hydrogen production. Energy Science & Engineering, 448-459. 674 675 676 [34] Oasmaa, A., Elliott, D. C., & Korhonen, J. (2010). Acidity of Biomass Fast Pyrolysis Bio-oils. Energy Fuels, 24(12), 6548-6554. 677 678 679 [35] OEQ. (1988). The Montreal Protocol on Substances That Deplete the Ozone Layer. Office of Environmental Quality. 680 681 [36] Pfitzer, C., Dahmen, N., Tröger, N., Weirich, F., Sauer, J., Günther, A., & Müller-682 683 Hagedorn, M. (2016). Fast Pyrolysis of Wheat Straw in the Bioliq Pilot Plant. Energy & Fuels, 30(10), 8047-8054. 684 685 686 [37] Plens, A. C., Monaro, D. L., & Coutinho, A. R. (2015). Adsorption of SOx and NOx in activated viscose fibers. An. Acad. Bras. Ciênc., 87(2), 1149-1160. 687 688 689 [38] Prasse, C., von Gunten, U., & Sedlak, D. L. (2020). Chlorination of Phenols Revisited: Unexpected Formation of  $\alpha,\beta$ -Unsaturated C4-Dicarbonyl Ring Cleavage Products. 690 691 Env. Sci. Technol., 54(2), 826-834. 692 [39] Roser, H. R. a. M. (2020). "Agricultural Production". Published online at 693 694 OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/agricultural-695 production' [Online Resource]. 696 [40] Shang, S., Guo, C., Lan, K., Li, Z., He, W., Qin, Z., & Li, J. (2020a). Hydrogen-rich 697 Syngas Production via Catalytic Gasification of Sewage Sludge and Wheat Straw 698 699 Using Corn Stalk Char-supported Catalysts. 2020, 15(2), 20. 700 [41] Shang, S., Qin, Z., Lan, K., Wang, Y., Zhang, J., Xiong, T., . . . Li, J. (2020b). 701 702 Hydrogen-rich Syngas Production via Catalytic Gasification of Biomass Using Ni/Zr-703 MOF Catalyst. 2020, 15(1), 16. 704 705 [42] Solarte-Toro, J. C., Romero-García, J. M., Martínez-Patiño, J. C., Ruiz-Ramos, E., 706 Castro-Galiano, E., & Cardona-Alzate, C. A. (2019). Acid pretreatment of lignocellulosic biomass for energy vectors production: A review focused on 707 operational conditions and techno-economic assessment for bioethanol production. 708 Renewable and Sustainable Energy Reviews, 107, 587-601. 709 710 711 [43] Venkatesh, S., Sivapirakasam, S. P., Sakthivel, M., Ganeshkumar, S., Mahendhira Prabhu, M., & Naveenkumar, M. (2021). Experimental and numerical investigation in 712 the series arrangement square cyclone separator. Powder Technology, 383, 93-103. 713 714 [44] Kosov, V., & Zaichenko (2016) J. Phys.: Conf. Ser. 774 012135. 715 716

717	[45] Wang, J., You, S., Lu, Z., Chen, R., & Xu, F. (2020). Life cycle assessment of bio-based
/18	levoglucosan production nom cotton straw through fast pyrorysis. <i>Bioresource</i>
719	Technology, 307, 123179.
720	
721	[46] Waqas, M., Aburiazaiza, A. S., Miandad, R., Rehan, M., Barakat, M. A., & Nizami, A.
722	S. (2018). Development of biochar as fuel and catalyst in energy recovery
723	technologies. Journal of Cleaner Production, 188, 477-488.
724	
725	[47] Yao, D., Hu, Q., Wang, D., Yang, H., Wu, C., Wang, X., & Chen, H. (2016). Hydrogen
726	production from biomass gasification using biochar as a catalyst/support. Bioresource
727	Technology, 216, 159-164.
728	
729	[48[You, S., Ok, Y. S., Tsang, D. C. W., Kwon, E. E., & Wang, CH. (2018). Towards
730	practical application of gasification: a critical review from syngas and biochar
731	perspectives. Critical Reviews in Environmental Science and Technology, 48(22-24),
732	1165-1213.
733	
734	[49] Zhang, Y., Jin, R., Dong, S., Wang, Y., Dong, K., Wei, Y., & Wang, B. (2021).
735	Heterogeneous condensation combined with inner vortex broken cyclone to achieve
736	high collection efficiency of fine particles and low energy consumption <i>Powder</i>
750	Tashralam 292 420 420
151	<i>1c</i> ( <i>m</i> ) <i>i</i> 0 <i>gy</i> , <i>3</i> 02, 420-430.
720	



Fig. 1. a) Sankey diagram of the product distribution of catalytic gasification of wheat straw. b) System boundaries of catalytic gasification of wheat straw using straw derived biochar catalyst, which includes biomass collection and pre-treatment units (P1), catalyst preparation using fast pyrolysis unit (P2), two-stage pyrolysis and gasification unit (P3), and products separation units (P4) as well as hydrogen distribution to downstream plant (P5)



Fig 2: Comparison of the life-cycle environmental impacts of P1, P2, P3, P4 and P5 processes.



Fig. 3. Contribution analysis of human health, ecosystem quality, climate change and resources in 5 different units.


Fig. 4. Sensitivity analysis of significant parameters for aquatic acidification depletion (AP, a) and global warming potential (GWP, b) of hydrogen production *via* catalytic gasification of wheat straw

Impact category	Unit (per kg H <sub>2</sub> )	P1	P2	Р3	P4	Р5
Carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0.5016	0.1286	0.0141	0.0410	2.13E-05
Non- carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0.9625	1.3562	0.0586	0.7091	2.08E-04
Respiratory inorganics	kg PM2.5 eq	0.04613	0.09582	0.0390	0.1078	1.77E-05
Ionizing radiation	Bq C-14 eq	404.7977	105.1269	108.3498	27.1100	1.10 E-04
Ozone layer depletion	kg CFC-11 eq	9.23E-06	8.76E-07	2.26E-07	3.43E-07	9.41E-12
Respiratory organics	kg C <sub>2</sub> H <sub>4</sub> eq	0.0222	13.8634	6.7869	18.092	4.98E-06
Aquatic ecotoxicity	kg TEG water	4138.1792	4442.6763	403.3099	3800.3279	1.3023
Terrestrial ecotoxicity	kg TEG soil	2892.09	1482.9228	26.5880	326.6058	0.0266
Terrestrial acid	kg SO <sub>2</sub> eq	0.9848	3.6619	1.4891	3.9373	4.12 E-04
Land occupation	m2org.arable	6.9382	29.3288	0.0315	6.1323	3.93E-06
Aquatic acidification	kg SO <sub>2</sub> eq	0.2031	0.7801	0.2747	0.7683	1.79 E-04
Aquatic eutrophication	kg PO <sub>4</sub> P-lim	0.0079	0.0066	6.6 E-0.4	0.0023	7.89E-08
Global warming	kg CO <sub>2</sub> eq	52.8928	51.9777	50.4356	81.347	1.98E-02

Table 1. Mid-point impacts of hydrogen production via catalytic gasification of wheat straw

2							
Damage category	Unit	P1	P2	P3	P4	P5	Total
Human health	mPt	5.1516	14.2103	5.9234	16.3716	1.84 E-03	41.6587
Ecosystem quality	mPt	2.3119	3.48427	0.1324	0.98939	5.18E-05	6.91801
Climate change	mPt	5.3421	5.24974	5.0939	8.2161	2.00 E-03	23.9038
Resources	mPt	5.5492	3.05417	4.4793	7.8366	1.90 E-0.3	20.9212

1 Table 2. End-point impacts of catalytic gasification of wheat straw using biochar catalyst.

<u>±</u>

1	Life-cycle assessment of hydrogen production via catalytic
2	gasification of wheat straw in the presence of straw
3	derived biochar catalyst
4	
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28	

- 29 Abstract (130 words)
- 30

The environmental footprints of H<sub>2</sub> production *via* catalytic gasification of wheat straw using 31 straw-derived biochar catalysts were examined. The functional unit of 1 kg of H<sub>2</sub> was adopted 32 33 in the system boundaries, which includes 5 processes namely biomass collection and pretreatment units (P1), biochar catalyst preparation using fast pyrolysis unit (P2), two-stage 34 pyrolysis-gasification unit (P3), products separation unit (P4), and H<sub>2</sub> distribution to 35 downstream plants (P5). Based on the life-cycle assessment, the hot spots in this process were 36 identified, the sequence was as follows: P4 > P2 > P1 > P3 > P5. The end-point impacts score 37 for the process was found to be 93.4017 mPt. From benchmarking analysis, the proposed straw-38 derived biochar catalyst was capable of offering almost similar catalytic performance with 39 other metal-based catalysts with a lower environmental impact. 40

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42

43 Keywords: Life-cycle analysis; Biochar; Gasification; Hydrogen; Biomass

45 1. Introduction

46

With the alarming demand of global energy and rapid growth of the world population 47 across the globe, the necessity in searching for alternative renewable and carbon-neutral energy 48 sources is vital to meet the soaring global energy needs. From both economic and 49 50 environmental standpoints, valorization of agricultural crop residues to platform chemicals is deemed as a feasible and attractive approach to achieve a circular carbon economy (Alhazmi 51 & Loy, 2021). Owing to the infinite, cheap, and environmentally friendly properties of 52 agricultural crops, its extensive utilization as renewable energy resources can be observed 53 lately with the emerging closed-loop economy and the on-going transition towards post-fossil-54 carbon societies (Giuntoli et al., 2013). According to the UN Food and Agriculture 55 56 Organization (FAO) 2018, the global production of agricultural crops is growing exponentially 57 due to the drastic demand from human mankind, specifically the agricultural crops of wheat, maize, and rice (Roser, 2020). Among the agricultural crop residues reported in the literature, 58 59 wheat straw is one of the most widespread residues readily available in Europe, America, and Western Asia continents with an annual global production of 132.59 million tonnes per year 60 (Ingrao et al., 2021). 61

62

Instead of landfilling or direct combustion of wheat straw (after harvesting), such 63 abundant lignocellulosic wastes can be transformed into sustainable renewable bio-based 64 products via thermochemical methods. Among all the thermochemical pathways, gasification 65 is one of the key technologies that has been extensively investigated. Over the years, many 66 experimental studies have successfully demonstrated a high production of H<sub>2</sub> from biomass 67 gasification process, including wheat straws as feedstock. In 2017, Cao and co-authors have 68 investigated supercritical water gasification of wheat straw soda black liquor in a batch reactor 69 system (Cao et al., 2017). Notably, high yield of  $H_2$  (62.38 mol/kg) with carbon content 70

71 (98.17%) was attained at 1023 K with a diluted black liquor of 2.5 wt% as reactant. Another 72 similar finding reported by Hu and co-authors, showing that 36 vol% of H<sub>2</sub> was attained with 73 the aid of 60%  $Fe_2O_3/Al_2O_3$  at 5g of wheat straw, reaction time of 10 min, and temperature of 74 1123 K (Hu et al., 2018).

75

76 Over the decades, non-noble metal-based catalysts (e.g. Ni, Cu, Co) have been reported as the best reforming catalysts for industrial applications in biomass gasification (Cao et al., 77 2020). They have shown great potential as reforming catalysts given its high selectivity, cheap 78 79 cost, and high availability. Nevertheless, some drawbacks (e.g. large amount of loading, short lifespan, and easy scaling) are inevitable. Whereas, noble metals (e.g. Pt, Ru, and Rh) have 80 81 both high catalytic activity and long lifespan, but they cannot be applied on a large scale due 82 to economic consideration (Cheah et al., 2021). In this sense, the search for an affordable and 83 highly active reforming catalyst is essential to support the realization of the circular gasification economy. 84

85

Lately, biochar has emerged as a new class of biomass-derived functional materials that 86 can be applied as a catalyst in various energy recovery applications (Do Minh et al., 2020; 87 Waqas et al., 2018). The rise of the application of biochar as a support material for the 88 89 preparation of tar cracking/reforming catalysts, particularly, for the synthesis of char-supported 90 metal nanoparticles has attracted large interest from both industrial and academic communities (You et al., 2018; Guo et al., 2020). For instance, Yao and co-authors have investigated the 91 effect of Ni-based biochar catalysts for H<sub>2</sub> production via gasification process (Yao et al., 92 93 2016). Notably, cotton-char supported Ni catalyst demonstrated the highest catalytic activity of H<sub>2</sub> production (64.02 vol.%) as compared to its counterparts (rice husk char, activated carbon 94 95 char, and wheat straw char). In 2021, Farooq et al. reported that the presence of silica in the

96 rice husk chars can reduce coke formation in Ni- char supported catalysts (Farooq et al., 2021). 97 Most importantly, the metal oxides in the rice husk char induced a positive synergistic effect 98 to pure Ni catalyst and thus, a higher tar conversion and H<sub>2</sub> yield were obtained in contrast to 99 the bi-functional Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Emerging knowledge and evidence on the applications of biochar 100 as a reforming catalyst with high effectiveness in tar cracking, and low cost, suggesting that 101 the valorization of biochar can be a feasible alternative that can improve the overall economic 102 and environmental values of a gasification system.

103

104 To the best of the authors' knowledge, the analysis of environmental impacts of H<sub>2</sub> production from gasification of wheat straw using straw-derived biochar catalyst is still yet to 105 106 be reported in the literature. The environmental aspect of a wheat straw-based gasification plant 107 is important to be examined since it is one of the key considerations for future technology 108 investment. Thereby, the whole gasification process starting from the raw materials to the end product should be analyzed and optimized from the perspective of the life-cycle of resource 109 and environment performance. Hence, this work aims to assess and identify the possible 110 environmental impacts of carbon chain of wheat straw gasification from the beginning 111 (biomass collection and pre-treatment of wheat straw) until the end process (H<sub>2</sub> distribution to 112 petrochemical plant). Based on this framework, the hypothesis of "the monetary value of the 113 environmental impact of biochar production and the application as as biochar catalyst" can be 114 115 elucidated. Moreover, the comprehensive performance of each process unit on the environmental impact can be evaluated without value-choices based weighting factor (Li et al. 116 (2020). 117

118

The case study was modeled based on a gate-to-gate view, taking consideration from
biomass collection and pre-treatment units (P1), biochar catalysts production in fast pyrolysis

121 unit (P2), two-step pyrolysis -gasification units (P3), products separation unit (P4), and lastly H<sub>2</sub> product distribution to downstream plants (P5). Furthermore, a sensitivity analysis was also 122 performed to identify and ascertain the most significant input parameters in affecting the 123 environmental impacts based on the gate-to-gate LCA boundaries. This study provides a 124 postulated assessment of the environmental impacts with regards to catalytic gasification 125 process of wheat straws using straw-derived biochar catalyst and knowledge to support future 126 decision-making in moving towards higher TRL based on the LCA with the selected 127 boundaries. 128

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130

131 2. Methodology

132 2.1 Method

133

According to the ISO 14040 (Principle and framework) and 14044 standards (Requirement and 134 guidelines), the LCA method comprises of four independent phases: (1) goal and scope 135 definition; (2) life-cycle inventory analysis; (3) impact assessment; and (4) interpretation 136 137 (Alhazmi & Loy, 2021). This LCA case study was carried out based on the IMPACT 2002+, where the environmental impact categories include but not limited to global warming potential, 138 ozone depletion potential, aquatic acidification potential, aquatic eutrophication, aquatic 139 140 ecotoxicity, terrestrial ecotoxicity, ionizing radiation, mineral extraction, non-renewable, land occupation, and respiratory inorganics were analyzed. The damage categories such as human 141 health, ecosystem quality, climate changes, and resources were also being investigated. Most 142 researchers have applied IMPACT 2002+ in their study because this method considers the 143 environmental impacts on both a midpoint and endpoint level (Hong, Li, & Zhaojie, 2010; 144 Jolliet et al., 2003). 145

147 2.2 Goal and Scope Definition

148

The goal of the present LCA study was to evaluate the environmental assessment of H<sub>2</sub> 149 150 production in catalytic wheat straw gasification using straw-derived biochar catalysts. The environmental footprints of all input processes of the defined life-cycle from raw material pre-151 152 treatment to the final product (H<sub>2</sub>) were included in this study (Fig. 1). The system boundary 153 of this case study was adopting a 'gate-to-gate' approach. It includes biomass collection and 154 pre-treatment units (P1), biochar catalyst production using fast pyrolysis unit (P2), two-stage pyrolysis- gasification unit (P3), products separation units (P4), and H<sub>2</sub> distribution to 155 156 downstream plants (P5).

157

### 158 2.3 Life-cycle inventory (LCI)

159

Wheat is one of the most important staple grains in the Kingdom of Saudi Arabia where most 160 161 of it is consumed in the form of pita or bread. According to the U.S. Department of Agricultures' Foreign Agricultural Service (FAS), wheat production in Saudi Arabia is 162 expected to escalate in the next two market years due to intensive government policy to reduce 163 irrigation. The production is forecasted to increase by 40 % in the year 2019-2020 relative to 164 production capacity of 500,000 tonnes in 2018-2019 (World Grain, 2021). The pilot-scale 165 catalytic gasification plant was proposed to be located at Al-Hasa Oasis, Saudi Arabia, which 166 has about 30,000 acres of agricultural land that are irrigated by the flow of more than 60 artesian 167 springs. More importantly, there are a few downstream plants located nearby. 168

169

Meanwhile, the data of biochar catalyst production was adopted based on authors' previous
works (Loy, et al.(a), 2018; Loy, et al.(b), 2018) and the remaining units was retrieved from

literature (Kalinci, Hepbasli, & Dincer, 2012; Wang, You, Lu, Chen, & Xu, 2020; Yao et al., 172 2016) and Ecoinvent database v3.6. All the data used were based on the optimum conditions 173 of the bench to pilot scale experimental work. The environmental performance of H<sub>2</sub> 174 production from the catalytic gasification was evaluated following the LCA approach. Note 175 that the functional unit was fixed at 1 kg of H<sub>2</sub>, while the project lifespan is assumed to be 15 176 years with an annual operating day of 300 days. The plant capacity is assumed to be 200,000 177 tonnes of wheat straw per year. Full details on input and output of the whole process (see 178 supplementary material), and the explanation of each process are shown in the following 179 180 section.

181

182 2.3.1 Biomass collection and pre-treatment units (P1)

Pre-treatment process is an important stage in upgrading biomass to reduce its size; thus 183 increaseing the accessible surface area (Chiaramonti et al., 2012). The wheat straw was sieved 184 to approximately 50 mm<sup>2</sup> using a vibration ball milling machine; to increase the reaction 185 surface area (Kumar et al., 2020). After milling, the wheat straw was fed into the mixing tank 186 to wash out the unwanted alkali and alkaline earth metals using a diluted acid mixture of 187 188 hydrochloric acid solution (30 vol.%), which can lower the reagent cost without affecting its effectiveness (Solarte-Toro et al., 2019). Then, the wheat straw and the acid mixture were then 189 transferred into an ultrafilter (50  $m^2$  of active surface per module) to remove the impurities 190 (Waste 1). "Waste 1" mainly includes chlorides, water, alkali, and alkaline metals. Whereas 191 the drying process was modeled to produce wheat straw (dry basis) at less than 2% w.c. In 192 order to produce 36.23 kg of wheat straw at 2% w.c. (Base = wheat straw at 5 % w.c), 3.46 kg 193 of water (unremoved waste) was assumed to be evaporated. 194

**196** 2.3.2 Biochar catalyst production using fast pyrolysis unit (P2)

Fast pyrolysis is reported to be a suitable technology to produce microporous and fragmented 197 198 chars that are potentially favorable for biochar catalyst usage (Brewer et al. 2009). Thus, the biochar catalyst in this work was produced *via* fast pyrolysis of wheat straw in a semi pilot-199 scale tube furnace at 773 K (Yao et al., 2016). In order to gasify 36.23 kg of wheat straw, a 200 201 30.81 kg biochar catalyst (i.e., biochar catalyst-to-feedstock ratio= 1:0.85) was required (Yao et al., 2016). Meanwhile, the wheat straw loading (205.4 kg) was calculated based on Pfitzer's 202 study (Pfitzer et al., 2016), where approximately 15 wt% of biochar can be obtained via fast 203 204 pyrolysis of wheat straw. The electricity consumption of the semi-pilot pyrolysis unit was assumed to be 0.0281 kWh per kg biomass as reported (Brassard, Godbout, & Hamelin, 2021). 205 The carbon emissions attributed to catalyst loading was assumed to be negligible since it will 206 only be conducted manually once after every few years (Montoya et al., 2020; Gholizadeh et 207 208 al., 2021).

209

#### 210 2.3.3 Two-stage pyrolysis-gasification unit (P3)

The catalytic gasification process of wheat straw was operated in a two-stage fixed bed; thereby 211 it has the advantage of producing gaseous products with higher calorific value as compared to 212 conventional gasifiers (Kosov and Zaichenko, 2016). During the first stage, the feedstock was 213 pyrolyzed under inert condition. Then, the pyrolysis volatiles were catalytic steam reformed in 214 the presence of biochar catalyst to enhance the yield of H<sub>2</sub>. Nitrogen flow (99.99%) was 215 216 supplied as carrier gas to prevent any unwanted oxidation in the pyrolysis zone (773 K). Whereas, the gasification temperature was set to be 1173 K, while steam was introduced into 217 the system to aid the water gas shift, catalytic reforming, and boudouard's reactions (Loy, et 218 219 al., 2018 (a)). The H<sub>2</sub> yield attained was reported to be 27.61 g/kg biomass or 52.35 wt.%, respectively. 220

222 2.3.4 Product separation units (P4)

223

This process can be divided into 3 sub-processes, namely 1) cyclone separation unit (biochar),
2) condensation unit (biooil) and, 3) gas separation unit (biogas). The full explanation of each
unit operation is discussed in the section below:

227

228 2.3.5.1 Cyclone separation unit

Among all the industrial cyclone separators, square cyclone separators have vast advantages 229 230 that include simplicity, lower cost, small volume, shorter start time, and shorter separation time compared to the single stage and two stages cyclones (Zhang et al., 2021). Thus, a square 231 cyclone separation unit was selected in this study to remove the biochar produced from the 232 catalytic two-stage pyrolysis-gasification process. Three-square aluminum steel cyclone was 233 modeled with a thickness of 0.002 m based on the functional units. The energy consumption 234 of the side channel cyclone blower was 1.5 kW/hr and single phase (220-240 V) (Venkatesh et 235 al., 2021). 236

237

238 2.3.5.2 Condensation unit

The condensation process was proposed for the condensable vapors produced from the catalytic gasification of wheat straw using biochar catalyst (Brassard et al., 2021). In order to calculate the energy consumption of water pumping, a submersible pump of 1 HP with a capacity of 10 L/min at 20 PSI was modeled (a typical submersible pump of 1 HP with a capacity of 43.2 L/min at 20 PSI and 20-foot depth was selected (Monarch Industries, Model MST5-100). Based on the catalytic gasification experiments of 1 kg of wheat straw per hour using a water flow of 180 Lwater/h, it was estimated that 6521 L of water was pumped and recirculated for the gasification of 36.23 kg of wheat straw (Brassard et al., 2021). The electricity consumption of the pumps (in MJ) was calculated by the total energy consumption of the pump (0.7 kW) with the time needed to pump 6521 L of water (~12 hr) and divided by a factor of 3.6. Also, it was assumed that 5000 L of water per year was used in each condenser (1<sup>st</sup> condenser: 100 % water and 2<sup>nd</sup> condenser: 50/50 ratio water to ethylene glycol to prevent boiling issue). The specific volume of each liquid annually was attained using Eq. (1) as shown:

253 
$$Unit volume (L Mg^{-1}) = \frac{Total volume (L year^{-1})}{200000 Mg_{biomss} year^{-1}}$$
(1)

254

The water circulating in the two condensers was maintained at 393 K and 278 K, respectively. In the 1<sup>st</sup> condenser, the temperature was set to beat 333 K and 393 K each day, considering that the heat losses were compensated by hot gases heating during pyrolysis. For the 2<sup>nd</sup> condenser, the temperature has to be in the range of 294 K to 278 K each day. The energy consumption was calculated based on Eq. (2) as shown:

260

$$261 \qquad Q = mCp\Delta T \tag{2}$$

where m is the mass of water circulated in the condenser for 36.23 kg of biomass,  $\Delta t$  is the difference of temperature for heating or cooling (in K) and Cp = 4.185 kJ kg<sup>-1</sup> K<sup>-1</sup>.

264

265 2.3.5.3 Gas separation unit

In this gas separation phase, the dry syngas (16.12 kg) was fed to a pressure swing adsorption (PSA) unit where H<sub>2</sub> was fully adsorbed on the adsorbent (e.g. zeolite and silica) of the unit, before being transferred to the petrochemical plants (Kohlheb et al., 2020). The electricity of the PSA was found to be around 1.26-1.52 kWh/Nm<sup>3</sup>-CO<sub>2</sub> depending on the capacity of H<sub>2</sub>
production. The unadsorbed flue gases (e.g 9.07 CH<sub>4</sub> vol%, 26.31 CO vol%, 18.01 CO<sub>2</sub> vol%)
can be incinerated in a flame oxidation burner which can be utilized as an energy source.
However, in this study, we did not consider the fraction gaseous mixture as a source of energy.

274 2.3.5 H<sub>2</sub> distribution to downstream plants (P5)

There are a few downstream petrochemical plants located at or near to Al-Hasa Oasis region such as Saudi Aramco and SATORP. As such, the average pipeline distance was calculated based on Eq. (3). The calculated pipeline distance from the gasification site to the downstream plant in terms of -kilometers was around 2-km, and the pipeline was assumed to be made of chromium steel 18/8 – GLO steel 9.

280

281 
$$r = \frac{1}{6}\tau \sqrt{\frac{F}{yf}} (\sqrt{2} + \ln(1 + \sqrt{2}))$$
 (3)

where r = average pipeline distance, F is the H<sub>2</sub> delivered annually to the plant (t/year); *y* is the annual yield of feedstock (t/year); *f* is the fraction of acreage around the plant devoted to feedstock production;  $\tau$  is the ratio of the actual distance to the straight-line distance from the plant.

286

Sensitivity analysis was carried out to examine the effects of individual input parameters on the environmental impacts based on the gasification process. A  $\pm$  20 % variation of the input parameters, including the feedstock transportation distance, biochar loading, syngas yield, and wheat straw loading was studied. With the sensitivity analysis, process engineers and academicians will have a better overview of the evaluation by minimizing the uncertaintyattributed to the empirical data.

294

295 3. Results and discussion

**296** 3.1 Interpretation of LCIA results

**297** 3.1.1 Impact 2002+ Midpoint Categories

The results of LCIA of the 5 different processes involved in catalytic biomass gasification for H<sub>2</sub> production using biochar-derived catalyst are reported in Table 1 in terms of Impact 2002+ midpoint categories. Significant midpoints that contributed to the damage categories in section 3.1.2 have been elucidated in the following:

302

303 With respect to aquatic ecotoxicity, the environmental impact was found to be the most significant among all categories, whereby the major contributions were dominated by P2 unit 304 (4443 kg TEG water), followed by biomass collection and pre-treatment unit (4138 kg TEG 305 306 water), products separation unit (3800 kg TEG water) and two-stage pyrolysis-gasification unit (403 kg TEG water). Although the Environment Protection Agency (EPA) has not published 307 any water quality guidelines for TEG, there are still several aspects with relation to the 308 309 environmental readiness level of the whole process from the point of view of legislation should be incorporated (EPA, 2006). Since the outputs from P2, P3, and P4 units include biooil, which 310 contains organic aromatic compounds that were acidic in nature, whereby the low pH of biooil 311 obtained was expected to produce significant ecotoxicity upon exposure to aquatic organisms 312 and systems (Oasmaa, Elliott, & Korhonen, 2010). On the other hand, the toxic effect of 313 biomass pre-treatment was due to the washing out of alkali and alkaline earth metals from the 314

315 biomass. A substantial quantity of alkali and alkaline metals, such as Si (31.86 wt%), K (19 wt%), Ca (4.14 wt%), Cl (2.67 wt%), and Mn (1.10 wt%), was being removed into Waste 1. It 316 has been reported that the Si component, which can be easily oxidized into silica, contributes 317 318 to total suspended solid (TSS) in water. Thus, it should be carefully practiced to meet the 10 mg/L as regulated by "2003-Ministry of Municipal and Rural Affairs (MMRA)" and '2006-319 Ministry of Water and Electricity (MWE) of Saudi Arabia" (MMRA, 2003; MWE, 2006). In 320 addition, the washed ions in the wastewater, typically, sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium 321  $(Ca^{2+})$ , and chlorides  $(Cl^{-})$ , that are released into aquatic ecosystems have been reported to be 322 323 responsible for physiological irregularities of aquatic lives while distracting ion regulatory mechanism in the living organisms (Hansen, Olsen, & Rosenkilde, 1996). 324

325

326 Another environmental impact that demonstrates a significant point was terrestrial ecotoxicity. Although it was consistently less severe as compared to aquatic ecotoxicity from all processes, 327 the impact on terrestrial ecosystems was considered high and should never be neglected. The 328 environmental impact towards terrestrial ecotoxicity was found to be mostly contributed by P1 329 (2892.09 kg TEG soil) and P2 (1482.92 kg TEG soil). The terrestrial ecotoxicity potential value 330 331 from P1 was about 10-fold that of P3, due to the attribution of the presence of alkaline earth metals in wheat straw that may potentially affect soil ecosystems. Previous study has reported 332 that poor quality irrigation water that contains certain ions at concentrations above the threshold 333 values (>3.00 dS/m) can cause plant toxicity problems by impairing growth, reducing yield, 334 changing morphology of agriculture plants (Memon, Kuboi, Fuji, Ito, & Yatazawa, 1983). 335

336

337 Viewing from the aspect of terrestrial acid and aquatic acidification, the midpoint impact point338 was found to be smaller than the ecotoxicity potential. The processes that contribute the most

339 to acidification were product separation, and catalyst preparation. These processes produce biooil and biogas that contain mainly acid components and gases, such as SO<sub>X</sub> and NO<sub>X</sub>. These 340 gas components were accumulated in the atmosphere to be captured by the moisture to form 341 342 acid rain that contributed to terrestrial and aquatic acidification ultimately (Plens, Monaro, & Coutinho, 2015). This shall be given utmost consideration since EPA has regulated Primary 343 National Ambient Air Quality Standard (NAAQS) for SO<sub>X</sub> and NO<sub>X</sub> to be at a maximum 344 concentration of 75 ppm and 100 ppm for 1 hr, respectively (EPA, 2010, 2018). It was seen 345 that the midpoint score that originates from carcinogens (<0.5 kg C<sub>2</sub>H<sub>3</sub>Cl eq.) was smaller in 346 347 impact points as compared to non-carcinogens (<1.4 kg C<sub>2</sub>H<sub>3</sub>Cl eq.) consistently. The EPA has regulated the toxicity threshold of  $C_2H_3Cl$  to  $1\times10^{-4}$  mg/L since it has been demonstrated to be 348 highly potential to induce cancer (EPA, 2000) and therefore, exhibiting detrimental health 349 350 effects. The impact of carcinogens was mostly from P1 process since it involves washing out 351 of alkali and alkaline earth metals that are toxic to the environment (Ge & Li, 2018). In addition, it was found that the presence of chloride in the wastewater may lead to the generation of toxic 352 353 and carcinogenic by-products (Prasse, von Gunten, & Sedlak, 2020). In a similar manner, the contribution from ionizing radiation was found to be from P1, followed by P3 that exhibited a 354 very similar impact point. The apparent impact from P1 was due to the diesel fuel used in wheat 355 straw transportation, while P3 produce aromatic hydrocarbons biooil that have ionizing 356 357 radiation potential. On the other hand, impact of non-carcinogens was found to be consistently 358 higher than the carcinogenic counterparts and were mainly contributed by P2, followed by P1 and P4, respectively. This has been attributed to usage of electricity that consumes sources of 359 energy in these processes, such as 577.17 and 342.51 kWh, for catalyst preparation and product 360 361 separation, respectively. The electricity consumption and reactions involved in the processes emit substances, such as PM<sub>10</sub>, SO<sub>X</sub> and NO<sub>X</sub>, that are not categorized as carcinogens but 362 363 detrimental to human health with prolonged and high dosage exposure (Lock et al., 2019).

On the other hand, ozone layer depletion demonstrated a negligible effect with minimum 365 gaseous emission from fossil fuels and chlorofluorocarbons (CFCs) from the utilization of 366 renewable biomass resources, which aligns with the initiative of Montreal Protocol to alleviate 367 ozone depletion issue (OEQ, 1988). By evaluating the effect of global warming, it was found 368 369 that the processes contributed to moderate consequences with the dominant phase originating from P4, while P1, P2, and P3 demonstrated a similar impact. P5 acts as an indirect GHG 370 through its effect on hydroxyl radicals (Derwent et al., 2006). As a whole, the results from the 371 372 environmental indicators show that both aquatic acidification depletion and global warming potential have remarkably influenced the life-cycle environmental performance of the 373 gasification system. Thus, both parameters were selected for the sensitivity analysis to provide 374 375 an in-depth understanding of the relationship between the input variables with both individual environmental impacts. 376

377

378 3.1.2 Impact 2002+ Damage Categories

All midpoint scores as discussed in section 3.1 were related to the four damage categories, 379 which are human health, ecosystem quality, climate change, and resources, respectively. The 380 percentage contribution of each mid-point impact to the four end-point impacts for H<sub>2</sub> 381 production via catalytic gasification of wheat straw using biochar as catalyst is shown in Fig. 382 2. The "human health" damage category is the sum of the midpoint categories "carcinogenic 383 and non-carcinogenic toxicity", "organic and inorganic respiratory effects", "ionizing 384 radiation", and "ozone layer depletion". The "ecosystem quality" damage category is the sum 385 of the midpoint categories from "aquatic ecotoxicity", "terrestrial ecotoxicity", "terrestrial and 386 aquatic acidification", "land occupation", and "aquatic eutrophication". On the other hand, the 387

damage category "climate change" is the same category as the midpoint category "global
warming". Finally, the damage category "resources" is the summation of the midpoint
categories from "non-renewable energy consumption" and "mineral extraction".

391

The damage assessment based on the 5 different processes involved in catalytic biomass gasification for H<sub>2</sub> production using straw-derived biochar catalyst is summarized in Table 2. In this context, the value was calculated as the average person's annual share of the environmental impacts of the entire population in Europe. The scale was chosen in such a manner that the value of milli-point (mPt) represents one thousandth of the annual load from one average European inhabitant. The purpose of normalization was to facilitate interpretation and comparison between respective shares of each impact to the overall damage.

399

400 From Fig. 3, it was found that the impact of the different processes was in the order of P4>P2> P1>P3>P5. Based on the findings, the most detrimental contributing criterion that exemplifies 401 402 impact of the different processes arises, particularly from the human health, resources, and 403 climate change damage categories. The damage impact of P5 was considered minor and negligible as compared to the other units Since the human health category was dominated by 404 respiratory effects caused by substances emitted into air, the product separation phase that has 405 406 the highest middle point category exhibited the greatest damage potential. In a similar manner, P4 yielded the highest point due to the generation of GHG radicals and components from the 407 408 process that can be potentially inhaled. Resource depletion impact was also the highest from the P4 since it utilizes several equipment, such as cyclones, pumps, condensers, and PSA, that 409 410 requires energy consumption from combustion of non-renewable fuels. In addition, it also involves the usage of water with high capacity for the condensation process to convert 411

412 condensable vapours into biooil. The findings pinpoint that the feasibility and sustainable
413 circular carbon benefits of catalytic biomass gasification for H<sub>2</sub> production using biochar
414 catalysts can be enhanced by improving the separation efficiency of the process.

415

Subsequently, P2 has the second highest damage potential from the Impact 2002+ assessment, 416 with the greatest point contributed by human health, climate change, and ecosystem quality, 417 respectively. Human health was significant due to similar reasoning attributed to respiratory 418 effects due to the emission of organic and inorganic substances, such as PM<sub>10</sub> and VOCs. 419 Energy consumption was also necessary for the catalyst preparation phase, which produces 420 potential GHG components, typically CO<sub>2</sub> and CH<sub>4</sub>. The ecosystem quality carries the third-421 422 highest contribution in the damage assessment since it produces several air emissions and 423 organic compounds that can potentially affect the aquatic and terrestrial balance.

424

P1 was the third-highest contributor to the damage assessment with the most detrimental impact 425 426 originating from the resources, human health, and climate change. The highest contributor from 427 resource utilization inherited similar points to product separation and two-stage pyrolysisgasification units. This has been attributed to the similar usage of energy, water, and feedstocks 428 from wheat in these processes. Viewing from the impact of human health, the biomass pre-429 430 treatment was found to be much lower as compared to the product separation and catalyst preparation phases. This demonstrates that although the biomass pretreatment involves the 431 production of wastewater with alkali and alkaline earth metals, the ultimate impact was not 432 dominant since it has a lower score point for respiratory substances. 433

434

435 Fourthly, P3 exhibited the damage impact in the order of human health > climate change > resources. In fact, the score points between two-stage pyrolysis-gasification and biomass pre-436 treatment were quite similar when comparing the contribution by these two categories. The 437 438 difference lies in lower contribution in the two-stage pyrolysis- gasification via the ecosystem quality since it has a smaller impact that originates from lower aquatic and terrestrial 439 ecotoxicity as well as acidification properties. The reasoning has been attributed to lower 440 441 concentrations of emissions and organic outputs from the process. In addition, on the contrary, climate change contributes to a higher score in the impact assessment since the process still 442 443 emits greenhouse pollutants albeit at lower concentrations. Based on the findings, the main trade-off concerning environmental impacts was not found to be associated with the initial 444 upstream nor end-user distribution units but with the downstream separation unit (P4). This 445 446 suggests that more emphasis on the strategic tactical and operational planning on this unit is required to produce a more environmentally friendly catalytic gasification system. 447

448

#### 449 3.2 Sensitivity Analysis

Sensitivity analysis of significant parameters in the input for aquatic acidification depletion 450 and global warming potential of H<sub>2</sub> production via catalytic gasification of wheat straw is 451 depicted in Fig. 4. From Fig. 4 (a), it can be seen that a 20 % reduction in the feedstock 452 transportation distance has the highest decrease of aquatic acidification. The findings suggest 453 454 that the soot emissions from vehicles during transportation, which contain NOx, SO<sub>X</sub>, and CO<sub>2</sub>, contribute to acid gas formation. Such environmental impact can be reduced by strategically 455 456 locating the plant site (i.e., locate at a closer vicinity). It is then followed by the syngas yield, where its reduction will result in a significant drop in the acidification potential. This is due to 457 the presence of acidic NOx, SO<sub>X</sub>, and CO<sub>2</sub> gases in the compositions. On the contrary, the 458 459 reduction of the biochar and feedstock loading by 20 % increased the aquatic acidification with 460 the biochar loading showed a more significant impact. The analysis highlights the importance of having sufficient biochar and feedstock to facilitate efficient conversion performance as well 461 as minimize the production and emission of acidic NOx and SOx. On the other hand, a 20 % 462 463 increment in the syngas yield and distance of feedstock transportation could lead to an approximately similar increment in the aquatic acidification potential. The increment in aquatic 464 acidification potential with increasing feedstock transportation distance by 20 % was found to 465 466 be not that significant as compared to its counterpart when the distance was decreased. In a similar manner, the 20 % increment in biochar and feedstock loading leads to the opposite 467 468 impact in the reduction of aquatic acidification, whereby the decrement was exceptionally observed with the alteration in feedstock loading, due to the enhancement in reaction efficiency 469 470 of catalytic biomass gasification.

471

From Fig. 4(b), it was found that the decrement in the input parameters by 20 % caused a 472 473 reduction in global warming potential consistently with the descending order of feedstock 474 transportation distance > syngas yield > biochar loading > wheat straw loading. The decrement in the transportation distance and syngas yield demonstrated a higher reduction due to a 475 reduction in CO<sub>2</sub> produced during the process. On the other hand, CO<sub>2</sub> emission was less 476 affected by the reduction of biochar and wheat straw loading, mainly attributed to the nature 477 of the reactions involved in the biomass gasification that produce GHG. The increment in 20 478 % of the input parameters was depicted to be increasing persistently in the order of wheat straw 479 loading > feedstock transportation distance > biochar loading > syngas yield. The wheat straw 480 loading was found to be much higher in increment as compared to the other input parameters. 481 The findings suggest that a high loading necessitates a bigger capacity and consumption of 482 resources that release an exemplified amount of GHG to the atmosphere. 483

As a whole, the most significant input parameter that contributes to a reduction of aquatic 485 acidification depletion and global warming potential with a 20 % decrease was the feedstock 486 transportation distance. Whereas, with an increment in the inputs by 20 %, the most significant 487 parameters were found to be biogas yield and wheat straw loading to aquatic acidification 488 489 depletion and global warming gas potential, respectively. From the sensitivity analysis, different uncertainty factors in the system with respect to environmental burdens have been 490 determined. The integration of the sensitivity analysis with energy and exergy assessment 491 492 should be carried out to provide a bigger picture of the biomass sustainability frontier.

493

#### 494 3.3 Benchmarking study

This subsection aims to benchmark the proposed biochar-based catalytic gasification of wheat 495 straw to other existing relevant works. Based on the findings, although the studies are not 496 conducted under the same conditions, it can still be seen that the straw-derived biochar catalysts 497 proposed in this work, are capable of offering a decent H<sub>2</sub> yield as compared to other studied 498 catalysts for wheat straw gasification. It is interesting to note that H<sub>2</sub> yielded through straw-499 500 derived biochar gasification (25.59 g H<sub>2</sub>/kg wheat straw) is comparable to other metal oxide catalysts such as Ni-based catalysts (5.6~ 25.3 g H<sub>2</sub>/kg wheat straw), Rh-based catalyst (8.4 g 501 502 H<sub>2</sub>/kg wheat straw), and Fe-based catalyst (16.02-23.93 g H<sub>2</sub>/kg wheat straw). Moreover, biochar catalysts are known as a promising substitute for traditional metal-based catalysts, 503 504 given their cost effectiveness and environmentally friendly-nature (Lee, Kim, & Kwon, 2017). Given that there is only a scarce amount of literature that has performed LCA study for a wheat 505 straw catalytic gasification process, benchmarking analysis on the environmental performance 506 is difficult to be performed. Nevertheless, one can still qualitatively justify the environmental 507

508 benefit of using char-based catalysts as compared to other metal-based catalysts in two ways. Firstly, its relatively high H<sub>2</sub> yield simply indicates a more efficient use of resources (e.g. lower 509 amount of feedstock required, and lower energy consumed), which further results in lower 510 environmental impacts. Secondly, the catalysts are derived purely from biogenic resources 511 which do not add significant burden to the carbon cycle. This, therefore, leads to a lower 512 environmental impact as compared to metal-based catalysts. Using Ni catalyst as an example, 513 every kg of Ni contributes 13 kg CO<sub>2</sub>-eq (LCA, 2020)), which is about 7.7 times higher than 514 that of the proposed straw-derived char catalysts (equivalent to 1.69 kg CO<sub>2</sub>.eq/kg catalyst). 515 516 This is in agreement with the comparative study made by Frazier et al. (Frazier RS, 2015)), where the GWP of metal-based catalysts is significantly higher (>10 folds) than that of the 517 char-based catalysts. As the world is marching towards sustainable development, the use of 518 519 catalysts that were derived from natural renewable resources are deemed favourable. 520 Policymakers can put efforts in encouraging such applications to promote green economy development in the industry sector including the hydrogen production industry. 521

522

## 523 4. Conclusions

The LCA results showed that environmental impact of the different processes was in the descending order of P4 > P2 > P1 > P3 > P5. The P4 was found to be the targeted hotspot in this study, which yields the highest greenhouse gas and resource depletion impacts. Thus, it is recommended to take into consideration the "separation unit, P4" thoughtfully in any decision making of scaling up this process. Also, future research direction should be pivoted towards metal-based supported biochar catalysts to provide a more in-depth understanding of the feasibility of biochar catalyst application.

531 \*E-supplementary data for this work can be found in e-version of this paper online

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539 540	6. References
541 542 543 544	[1] Alhazmi, H., & Loy, A. C. M. (2021). A review on environmental assessment of conversion of agriculture waste to bio-energy via different thermochemical routes: Current and future trends. <i>Bioresource Technology Reports</i> , 14, 100682.
545 546 547 548	[2] Brassard, P., Godbout, S., & Hamelin, L. (2021). Framework for consequential life cycle assessment of pyrolysis biorefineries: A case study for the conversion of primary forestry residues. <i>Renewable and Sustainable Energy Reviews</i> , 138, 110549.
549 550 551	[3] Brewer, C., Schmidt-Rohr., Klaus, S., Justinus, R. (2009). Characterization of Biochar from Fast Pyrolysis and Gasification Systems. Environmental Progress & Sustainable Energy. 28. 386 - 396. 10.1002/ep.10378.
553 554 555	[3] Cao, C., Xu, L., He, Y., Guo, L., Jin, H., & Huo, Z. (2017). High-Efficiency Gasification of Wheat Straw Black Liquor in Supercritical Water at High Temperatures for Hydrogen Production. <i>Energy &amp; Fuels</i> , 31(4), 3970-3978.
557 558 559 560	[4] Cao, L., Yu, I. K. M., Xiong, X., Tsang, D. C. W., Zhang, S., Clark, J. H., Ok, Y. S. (2020). Biorenewable hydrogen production through biomass gasification: A review and future prospects. Environmental Research, 186, 109547.
561 562 563 564 565	[5] Cheah, K. W., Yusup, S., Loy, A. C. M., How, B. S., Skoulou, V., & Taylor, M. J. (2021). Recent advances in the catalytic deoxygenation of plant oils and prototypical fatty acid models compounds: Catalysis, process, and kinetics. <i>Molecular Catalysis</i> , 111469.
566 567 568 569	[6] Chiaramonti, D., Prussi, M., Ferrero, S., Oriani, L., Ottonello, P., Torre, P., & Cherchi, F. (2012). Review of pretreatment processes for lignocellulosic ethanol production, and development of an innovative method. <i>Biomass and Bioenergy</i> , 46, 25-35.

570	[7] Derwent, R., Simmonds, P., O'Doherty, S., Manning, A., Collins, W., & Stevenson, D.
571	(2006). Global environmental impacts of the hydrogen economy. Int. J. Nuclear
572	Hydrog. Prod. Appl., 1(1), 57 - 67.
573	
574	[8] Do M, T., Song, J., Deb, A., Cha, L., Srivastava, V., & Sillanpää, M. (2020). Biochar
575	based catalysts for the abatement of emerging pollutants: A review. Chemical
576	Engineering Journal, 394, 124856.
577	
578	[9] EPA. (2006). National Recommended Water Quality Criteria. from United States
579	Environmental Protection Agency.
580	
581	[10] Farooq, A., Jang, SH., Lee, S. H., Jung, SC., Rhee, G. H., Jeon, BH., & Park, YK.
582	(2021). Catalytic steam gasification of food waste using Ni-loaded rice husk derived
583	biochar for hydrogen production. <i>Chemosphere</i> , 130671.
584	
585	[11] Frazier RS, J. E., Kumar A., (2015). Life Cycle Assessment of Biochar versus Metal
586	Catalysts Used in Syngas Cleaning Energies 621-644
587	Calarysis Osed in Syngas Creaning. Energies, 621 677.
588	[12] Ge V & Li Z (2018) Application of Lignin and Its Derivatives in Adsorption of
580	Heavy Metal Ions in Water: A Review ACS Sustain Cham Eng. 6(5) 7181-7192
505	$Teavy Wetar fons in water. Tr Review. Tes Sustain. Chem. Eng., O(5), T101^{-7}192.$
590	[13] Guo E. Jia X. Liang S. Zhou N. Chan P. & Puan P. (2020) Development of
291	[15] Ouo, F., Jia, A., Liang, S., Zhou, N., Chen, F., & Kuan, K. (2020). Development of
592	biochar-based hanocatarysts for tar cracking/reforming during biomass pyrorysts and
593	gasification. <i>Bioresource Technology</i> , 298, 122263.
594	
595	[14] Mortaza G., Hu, X and Liu, Q. (2021) Progress of using biochar as a catalyst in thermal
596	conversion of biomass" Reviews in Chemical Engineering, vol. 37, no. 2, pp. 229-
597	258.
598	
599	[15] Giuntoli, J., Boulamanti, A. K., Corrado, S., Motegh, M., Agostini, A., & Baxter, D.
600	(2013). Environmental impacts of future bioenergy pathways: the case of electricity
601	from wheat straw bales and pellets. GCB Bioenergy, 497-512.
602	
603	[16] Hansen, H. J. M., Olsen, A. G., & Rosenkilde, P. (1996). The effect of Cu on gill and
604	esophagus lipid metabolism in the rainbow trout Oncorhynchus mykiss. Comp.
605	Biochem. Physiol. C Toxicol. Pharmacol., 113(1), 23-29.
606	
607	[17] Hong, J., Li, X., & Zhaojie, C. (2010). Life cycle assessment of four municipal solid
608	waste management scenarios in China. Waste Management, 30(11), 2362-2369.
609	
610	[18] Hu, J., Li, C., Guo, O., Dang, J., Zhang, O., Lee, DJ., & Yang, Y. (2018), Syngas
611	production by chemical-looping gasification of wheat straw with Fe-based oxygen
612	carrier Bioresource Technology 263 273-279
613	
614	[19] Ingrao C. Matarazzo A. Gorijan S. Adamczyk I. Failla S. Primerano P. &
615	Huisingh D (2021) Wheat_straw derived bioethanol production: A raview of Life
616	Cycle Assessments Science of The Total Environment 146751 146771
617	Cycle Assessments. Science of the total Environment, 140/51-140//1.
01/	

618 619 620	<ul> <li>[20] Jolliet, O., Margni, M., Charles, R., Humbert, S., Payet, J., Rebitzer, G., &amp; Rosenbaum,</li> <li>R. (2003). IMPACT 2002+: A new life cycle impact assessment methodology. <i>The</i> <i>International Journal of Life Cycle Assessment</i>, 8(6), 324.</li> </ul>
621	
622	[21] Kalinci, Y., Hepbasli, A., & Dincer, I. (2012). Life cycle assessment of hydrogen
623	production from biomass gasification systems International Journal of Hydrogen
624	Energy 37(19) 14026-14039
625	Lh(rgy, 57(17), 1+020-1+057).
626	[22] Kohlheb N. Wluka M. Bezama A. Thrän D. Aurich A. & Müller P. A. (2020)
627	[22] Kollineo, N., Wiuka, M., Dezalia, A., Tilial, D., Aureli, A., & Muller, K. A. (2020). Environmental Economic Assessment of the Pressure Swing Adsorption Bioges
027	Linvitolimental-Economic Assessment of the Fressure Swing Ausorption Diogas
628	Opgrading Technology. BioEnergy Research.
629	[22] Kannan M. X'ana, X. Wan, Z. Gan, X. Tarana, D. C. W. Carata, L. Ola, V. C
630	[23] Kumar, M., Xiong, X., Wan, Z., Sun, Y., Isang, D. C. W., Gupta, J., OK, Y. S.
631	(2020). Ball milling as a mechanochemical technology for fabrication of novel
632	biochar nanomaterials. <i>Bioresource Technology</i> , 312, 123613.
633	
634	[24] LCA, N. m. (2020). Nickel metal LIFE CYCLE DATA
635	https://nickelinstitute.org/policy/nickel-life-cycle-management/nickel-life-cycle-data/
636	(accessed 08062021).
637	
638	[25] Li, Q., Song, G., Xiao, J., Hao, J., Li, H., & Yuan, Y. (2020). Exergetic life cycle
639	assessment of hydrogen production from biomass staged-gasification. <i>Energy</i> , 190,
640	116416.
641	[26] Lee J Kim K-H & Kwon F E (2017) Biochar as a Catalyst Renewable and
6/2	Sustainable Fnergy Reviews 77 70-79
6/3	Sustainable Energy Reviews, 77, 70 79.
644	[27] Lock S. S. M. Lau, K. K. Shariff, A. M. Yeong, Y. F. Ban, Z. H. & Tay, W. H.
645	(2019) Process simulation and ontimization of oxygen enriched combustion using
646	thin polymeric membranes: effect of thickness and temperature dependent physical
647	aging I Chem Technol Biotechol 94(9) 2844-2868
648	
649	[28] Lov A C M Gan D K W Yusun S Chin B L F Lam M K Shahbaz M
650	Rianawati F (2018a) Thermogravimetric kinetic modelling of in-situ catalytic
651	nyrolytic conversion of rice husk to bioenergy using rice hull ash catalyst
652	Rioresource Technology 261 213-222
653	<i>Dioresource reennology</i> , 201, 215 222.
654	[29] Lov A C M Yusun S Lam M K Chin B I F Shahhaz M Yamamoto A &
655	Acda M N (2018b) The effect of industrial waste coal bottom ash as catalyst in
656	catalytic pyrolysis of rice busk for syngas production <i>Energy Conversion and</i>
657	Management 165 541-554
658	Management, 105, 541-554.
650	[30] Memon A. Kuboi T. Fuji K. Ito S. & Vatazawa M. (1083). Taxonomic character of
660	[50] Mellioli, A., Kubol, T., Fuji, K., 10, S., & Tatazawa, M. (1983). Taxonomic character of
661	temperate forest of Japan <i>Plant Soil</i> 70(3) 367 380
662	temperate forest of Japan. T tuni Soli, $70(3)$ , $307-383$ .
662	[31] Montova D B Xizolai Z Jun L Vivak P Simão M Marco G (2020) Parformanco
664	of higher as a catalyst for tar steam reforming. Effect of the porous structure Applied
665	Energy 259
666	$\operatorname{Encr}{\operatorname{Sy}}(23)$ .
550	

667 [32] Nanda, S., Reddy, S. N., Dalai, A. K., & Kozinski, J. A. (2016). Subcritical and supercritical water gasification of lignocellulosic biomass impregnated with nickel 668 nanocatalyst for hydrogen production. International Journal of Hydrogen Energy, 669 41(9), 4907-4921. 670 671 [33] Nanda, S., Reddy, S. N., Vo, D. N., Sahoo, B. N., & Kozinski, J. A. (2018). Catalytic 672 673 gasification of wheat straw in hot compressed (subcritical and supercritical) water for hydrogen production. Energy Science & Engineering, 448-459. 674 675 676 [34] Oasmaa, A., Elliott, D. C., & Korhonen, J. (2010). Acidity of Biomass Fast Pyrolysis Bio-oils. Energy Fuels, 24(12), 6548-6554. 677 678 679 [35] OEQ. (1988). The Montreal Protocol on Substances That Deplete the Ozone Layer. Office of Environmental Quality. 680 681 [36] Pfitzer, C., Dahmen, N., Tröger, N., Weirich, F., Sauer, J., Günther, A., & Müller-682 683 Hagedorn, M. (2016). Fast Pyrolysis of Wheat Straw in the Bioliq Pilot Plant. Energy & Fuels, 30(10), 8047-8054. 684 685 686 [37] Plens, A. C., Monaro, D. L., & Coutinho, A. R. (2015). Adsorption of SOx and NOx in activated viscose fibers. An. Acad. Bras. Ciênc., 87(2), 1149-1160. 687 688 689 [38] Prasse, C., von Gunten, U., & Sedlak, D. L. (2020). Chlorination of Phenols Revisited: Unexpected Formation of  $\alpha,\beta$ -Unsaturated C4-Dicarbonyl Ring Cleavage Products. 690 691 Env. Sci. Technol., 54(2), 826-834. 692 [39] Roser, H. R. a. M. (2020). "Agricultural Production". Published online at 693 694 OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/agricultural-695 production' [Online Resource]. 696 [40] Shang, S., Guo, C., Lan, K., Li, Z., He, W., Qin, Z., & Li, J. (2020a). Hydrogen-rich 697 Syngas Production via Catalytic Gasification of Sewage Sludge and Wheat Straw 698 699 Using Corn Stalk Char-supported Catalysts. 2020, 15(2), 20. 700 [41] Shang, S., Qin, Z., Lan, K., Wang, Y., Zhang, J., Xiong, T., . . . Li, J. (2020b). 701 702 Hydrogen-rich Syngas Production via Catalytic Gasification of Biomass Using Ni/Zr-703 MOF Catalyst. 2020, 15(1), 16. 704 705 [42] Solarte-Toro, J. C., Romero-García, J. M., Martínez-Patiño, J. C., Ruiz-Ramos, E., 706 Castro-Galiano, E., & Cardona-Alzate, C. A. (2019). Acid pretreatment of lignocellulosic biomass for energy vectors production: A review focused on 707 operational conditions and techno-economic assessment for bioethanol production. 708 Renewable and Sustainable Energy Reviews, 107, 587-601. 709 710 711 [43] Venkatesh, S., Sivapirakasam, S. P., Sakthivel, M., Ganeshkumar, S., Mahendhira Prabhu, M., & Naveenkumar, M. (2021). Experimental and numerical investigation in 712 the series arrangement square cyclone separator. Powder Technology, 383, 93-103. 713 714 [44] Kosov, V., & Zaichenko (2016) J. Phys.: Conf. Ser. 774 012135. 715 716

717	[45] Wang, J., You, S., Lu, Z., Chen, R., & Xu, F. (2020). Life cycle assessment of bio-based
/18	levoglucosali productioni nom cotton straw through fast pyrorysis. <i>Bioresource</i>
719	Technology, 307, 123179.
720	
721	[46] Waqas, M., Aburiazaiza, A. S., Miandad, R., Rehan, M., Barakat, M. A., & Nizami, A.
722	S. (2018). Development of biochar as fuel and catalyst in energy recovery
723	technologies. Journal of Cleaner Production, 188, 477-488.
724	
725	[47] Yao, D., Hu, Q., Wang, D., Yang, H., Wu, C., Wang, X., & Chen, H. (2016). Hydrogen
726	production from biomass gasification using biochar as a catalyst/support. Bioresource
727	<i>Technology, 216</i> , 159-164.
728	
729	[48[You, S., Ok, Y. S., Tsang, D. C. W., Kwon, E. E., & Wang, CH. (2018). Towards
730	practical application of gasification: a critical review from syngas and biochar
731	perspectives. Critical Reviews in Environmental Science and Technology, 48(22-24),
732	1165-1213.
733	
734	[49] Zhang, Y., Jin, R., Dong, S., Wang, Y., Dong, K., Wei, Y., & Wang, B. (2021).
735	Heterogeneous condensation combined with inner vortex broken cyclone to achieve
736	high collection efficiency of fine particles and low energy consumption <i>Powder</i>
700	Tashnalagy 382 420 420
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Fig. 1. a) Sankey diagram of the product distribution of catalytic gasification of wheat straw. b) System boundaries of catalytic gasification of wheat straw using straw derived biochar catalyst, which includes biomass collection and pre-treatment units (P1), catalyst preparation using fast pyrolysis unit (P2), two-stage pyrolysis and gasification unit (P3), and products separation units (P4) as well as hydrogen distribution to downstream plant (P5)



Fig 2: Comparison of the life-cycle environmental impacts of P1, P2, P3, P4 and P5 processes.



Fig. 3. Contribution analysis of human health, ecosystem quality, climate change and resources in 5 different units.



Fig. 4. Sensitivity analysis of significant parameters for aquatic acidification depletion (AP, a) and global warming potential (GWP, b) of hydrogen production *via* catalytic gasification of wheat straw

Impact category	Unit (per kg H <sub>2</sub> )	P1	P2	Р3	P4	Р5
Carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0.5016	0.1286	0.0141	0.0410	2.13E-05
Non- carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0.9625	1.3562	0.0586	0.7091	2.08E-04
Respiratory inorganics	kg PM2.5 eq	0.04613	0.09582	0.0390	0.1078	1.77E-05
Ionizing radiation	Bq C-14 eq	404.7977	105.1269	108.3498	27.1100	1.10 E-04
Ozone layer depletion	kg CFC-11 eq	9.23E-06	8.76E-07	2.26E-07	3.43E-07	9.41E-12
Respiratory organics	kg C <sub>2</sub> H <sub>4</sub> eq	0.0222	13.8634	6.7869	18.092	4.98E-06
Aquatic ecotoxicity	kg TEG water	4138.1792	4442.6763	403.3099	3800.3279	1.3023
Terrestrial ecotoxicity	kg TEG soil	2892.09	1482.9228	26.5880	326.6058	0.0266
Terrestrial acid	kg SO <sub>2</sub> eq	0.9848	3.6619	1.4891	3.9373	4.12 E-04
Land occupation	m2org.arable	6.9382	29.3288	0.0315	6.1323	3.93E-06
Aquatic acidification	kg SO <sub>2</sub> eq	0.2031	0.7801	0.2747	0.7683	1.79 E-04
Aquatic eutrophication	kg PO <sub>4</sub> P-lim	0.0079	0.0066	6.6 E-0.4	0.0023	7.89E-08
Global warming	kg CO <sub>2</sub> eq	52.8928	51.9777	50.4356	81.347	1.98E-02

Table 1. Mid-point impacts of hydrogen production via catalytic gasification of wheat straw
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Damage category	Unit	P1	P2	P3	P4	P5	Total
Human health	mPt	5.1516	14.2103	5.9234	16.3716	1.84 E-03	41.6587
Ecosystem quality	mPt	2.3119	3.48427	0.1324	0.98939	5.18E-05	6.91801
Climate change	mPt	5.3421	5.24974	5.0939	8.2161	2.00 E-03	23.9038
Resources	mPt	5.5492	3.05417	4.4793	7.8366	1.90 E-0.3	20.9212

1 Table 2. End-point impacts of catalytic gasification of wheat straw using biochar catalyst.

Supplementary Interactive Plot Data (CSV)

Click here to access/download Supplementary Interactive Plot Data (CSV) LCA\_Supplementary\_08072021.docx

## **CRediT** author statement

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## **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: