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Phenolic-rich bio-oil production by microwave catalytic pyrolysis of switchgrass: Experimental study, life cycle assessment, and economic analysis

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Abstract

 This study aims to determine the environmental impacts and feasibility of optimizing the 35 production of phenolic-rich bio-oil, via switchgrass microwave catalytic pyrolysis. K_3PO_4 (Tripotassium phosphate) was used as the catalyst, at different temperatures, throughout this life cycle assessment (LCA) study. Results were compared with non-catalytic microwave 38 pyrolysis (SiC-400) and conventional pyrolysis. K_3PO_4 (KP) was used as the microwave absorber and catalyst to enhance the low microwave absorption of switchgrass during microwave pyrolysis, and to improve the bio-oil quality and selectivity for phenolics production. Pyrolysis temperatures made a considerable difference to the LCA. There was an 42 86% reduction in the pyrolysis time when heating the sample to 300° C (KP-300), as compared to 400°C (KP-400), resulting in a significant reduction of the amount of energy required, and GHG's emitted. The total global warming potential (GWP) for microwave catalytic pyrolysis is observed within 159−223 kg CO2-eq/1000 kg of dried switchgrass (SG), with the baseline case (SiC-400) being the highest, and KP-300 being the lowest. Using the produced biochar, which is rich in nutrients for soil application, brings the net GWP to negative values through carbon sequestration. KP-300 also showed the highest selectivity for phenol and alkylphenols production, which increased by 252% and 420% respectively, 50 compared to the baseline. The results clearly indicate that introducing K_3PO_4 showed great potential for accelerating microwave heating, and improving bio-oil selectivity towards alkylphenols, which can be used to replace petroleum-based phenol. This in turn can reduce GHG emissions, due to higher conversion efficiencies and lower energy consumption compared with non-catalytic microwave pyrolysis and conventional pyrolysis.

 Keywords: *Catalytic microwave pyrolysis optimization; Life cycle assessment; Phenolic-rich bio-oil; K3PO4; Carbon sequestration; Switchgrass*

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 Due to population explosion and up-grading the quality of life (Chan et al., 2020), fossil- based energy consumption has risen to alarming levels (Basafa and Hawboldt, 2021). The intensive usage of fossil fuel to meet the energy demand by both industrial and domestic sectors is boosting carbon emissions, which has remarkably increased the issues of global warming (Mohamed et al., 2022a). This extensive consumption is exhausting fossil fuel resources and has resulted in many environmental concerns. Therefore, the production and consumption of petroleum-based products such as phenols will be limited (Ma et al., 2020). Phenol and its derivatives are essential industrial chemical compounds, required for the production of multitudes of industrial products including resins (Bu et al., 2012). Therefore, valorizing renewable energy resources and phasing out petroleum-based resources for phenol production is a crucial need of our time (Chan et al., 2020).

 Pyrolysis is a thermochemical degradation of material in an inert atmosphere that generates a variety of products such as non-condensable gases (NCG), biochar, and bio-oil, within a brief reaction time (Hu et al., 2021). Production of bio-oil from agricultural wastes (Chan et al., 2020) and wood wastes (Shu et al., 2019) is regarded as a cost-efficient and viable process. However, in a typical conventional pyrolytic process, bio-oil quality drops due to its poor selectivity (Wang et al., 2018) and complex chemical composition (Chan et al., 2020), making bio-oil unfavorable for fuel or chemical extraction applications (Lu et al., 2018). Bio-oil is characterized as a complex mixture, comprising almost all species of highly oxygenated organic compounds (Uzoejinwa et al., 2018) such as ketones, phenols, aromatic hydrocarbons, organic acids, aliphatic hydrocarbons, esters, ethers, aldehydes, and alcohols (Bu et al., 2012). The major challenge with bio-oil is high oxygen content, which affects its 82 stability and lowers its energy density, in addition to being highly corrosive ($pH = -2.5$) and viscous. These properties limit bio-oil usage in internal combustion engines (Lu et al., 2018), and therefore limit its potential application as a fuel replacement for fossil fuels (Chan et al., 2020).

 However, bio-oil can be upgraded to produce several bio-based chemicals that have a variety of uses in many industries. For instance, biochemicals (e.g., phenolics and ketones) are used as resins and solvents (Chan et al., 2020), while aromatic hydrocarbons are employed as both fuels and solvents in industrial applications (Bu et al., 2012). Among bio- oil fractions, phenols are the most commercially useful compounds. They can be used as raw materials in many industries such as fine chemicals, pharmaceutical industry, resin manufacturing, and food processing (Chan et al., 2020). Extensive research has been carried out to assess the efficiency of hydro-deoxygenation (HDO) and catalytic fast pyrolysis for transforming bio-oils into higher-grade biofuels. HDO is a widely used method to transform low-value products into biofuels. However, the stability of benzene structure makes the transformation of oxygenated phenolic compounds very difficult (Kim, 2015), and thus research on phenolic compounds is an important consideration (Shu et al., 2019). Recently, several studies have suggested that phenolic compounds can be isolated from bio-oils (Basafa and Hawboldt, 2021), and this significantly facilitates the industrialization of the phenol production from biomass (Kim, 2015).

 Phenolic compounds can be generated by fast pyrolysis of lignin-based biomass, which possess potential commercial value as they can be employed as a phenol substitute in manufacturing phenolic resins (Basafa and Hawboldt, 2021). For obtaining aromatic and phenolic compounds from bio-oil, catalytic pyrolysis was found as an effective process for upgrading bio-oil selectivity and increasing its commercial value (Ma et al., 2020). It is noteworthy that several studies in the literature focused on the production of phenolic 107 compounds at high pyrolysis temperatures $(> 400 °C)$ (Wang et al., 2021).

 To make pyrolysis more effective, microwave pyrolysis has been investigated as an efficient method to enhance the quality of biochar, bio-oil, and syngas (Ma et al., 2020).

 Several studies have highlighted that the catalytic upgrading of liquid bio-oils (i.e., pyrolytic vapors) can produce bio-oils rich in phenols (Lu et al., 2018). Further, mixing activated carbon as a microwave absorber with biomass at high loads (> 40 wt%) can produce phenolic-rich bio-oil under microwave pyrolysis (Wang et al., 2019). However, activated carbon is very expensive (Mohamed et al., 2022b), which can cost > 10 US\$/kg (Fingolo et al., 2020), increasing bio-oil production cost remarkably, and limiting the potential industrial application of the microwave pyrolysis process. No previous studies focused on microwave 117 pyrolysis of biomass at low pyrolytic temperatures $(< 350^{\circ}$ C) for producing phenol-rich bio- oils and biochar rich in nutrients (Ma et al., 2021). Therefore, to achieve a higher yield of phenolic products at a reduced cost (Periyasamy et al., 2022), it is imperative to select the appropriate catalysts for enhancing bio-oil activity and optimizing phenolic production (Wang et al., 2021). In order to promote a circular economy of biomass microwave catalytic pyrolysis, the quality of the bio-oil and biochar should be simultaneously improved to decrease production costs.

124 In our previous studies, it was found that mixing K_3PO_4 (Tripotassium phosphate) with switchgrass enhanced the poor microwave absorption of switchgrass, boosted the microwave heating rate (Mohamed et al., 2021a), and produced efficient biochar with high sorption 127 affinity for heavy metals (Mohamed et al., 2017) and increasing water holding capacity of sandy soils (Mohamed et al., 2016a), and rich in nutrients (Mohamed et al., 2021b). To the best of our knowledge, no previous studies have investigated the possibility of producing phenolic-rich bio-oil at low temperatures or determined the feasibility and environmental impacts of the process. To determine the sustainability and feasibility of the microwave catalytic pyrolysis process for industrial application, life cycle assessment (LCA) and economic analysis are highly need. Therefore, the objectives of this study are to (a) 134 investigate the effectiveness of K_3PO_4 as a catalyst for promoting the catalytic microwave pyrolysis of biomass to produce phenolic-rich bio-oil at different pyrolysis temperatures; and

 (b) to quantify the environmental impacts and determine the feasibility of the production of phenolic-rich bio-oil, and nutrient-rich biochar, through microwave catalytic pyrolysis of switchgrass under different temperatures, in comparison with the conventional pyrolysis. For the first time, this study provides a more detailed comparison to guide future research and development on bio-oil and biochar production from microwave catalytic pyrolysis in a more comprehensive manner. Pyrolysis temperature, liquid product yields, and bio-oil properties are examined to determine their effects on phenolic production and selectivity, and to quantify the environmental impacts of phenolic-rich bio-oil production under different operating conditions.

 To assess the potential of microwave catalytic pyrolysis for producing phenolic-rich bio- oil, the environmental impacts such as human toxicity potential (HTP), acidification potential (AP), global warming potential (GWP), eutrophication potential (EP), and photo-oxidant formation potential (POCP) are determined based on switchgrass microwave catalytic pyrolysis process though cradle-to-gate life-cycle assessment, and contrasted with those from the non-catalytic microwave pyrolysis, and those from conventional pyrolysis in the literature.

2. Materials and methods

 Switchgrass (SG) was used in this study for its bioenergy application potential. SG is a C4 plant that could be grown in a wide geographic areas to enhance the productivity of soil with less amounts of water and nutrients, and it was identified as a model energy crop by the US Department of Energy (Keshwani and Cheng, 2010). Most biomass materials have a low dielectric loss compared with that of good absorbers (e.g., activated carbon). Therefore, a microwave absorber is required to enhance microwave heating (Mohamed et al., 2022c). Thus, K_3PO_4 (Tripotassium phosphate) was incorporated with SG as a microwave absorber and catalyst to improve the poor microwave absorption of SG and hence expedite the heating rate of the catalytic pyrolysis process, thereby optimizing the characteristics of the biochar and gas and producing phenolic-rich bio-oil. Silicon carbide (SiC), an inert chemical and efficient microwave absorber, was incorporated with SG to enhance the weak microwave absorption by SG (Mohamed et al., 2016b). Pre-mixed SG catalyst samples were transferred into the 168 reactor, and N_2 was supplied to create an anoxic environment at 1.5 L/min for nearly 30 minutes. The microwave was powered at 750 W and the sample's temperature was set to be 170 300 or 400°C (Mohamed et al., 2021b). To avoid the reflection of microwaves, collection of un-absorbed microwave was done by a water-cooling system. More information about experimental setup and procedures can be found in previous studies (Mohamed et al., 2021a). 16 162

2.1. Products characterization

To study the effects of K_3PO_4 on the bio-oil selectivity and deoxygenation performance, gas chromatography with mass spectrometer (GC/MS, Agilent 7820A GC and mass spectrometry detector Agilent 5975 Series MSD) was used to analyze the chemical composition of the whole bio-oil, including organic and aqueous components (Mohamed et al., 2021a). Helium (99.999% purity) was used as the carrier gas at a flow rate of 1 mL/min. C, H, N, and S contents of biochars were determined using a CHNS analyzer (PerkinElmer

 2400Series-II), and oxygen was determined by difference. More information on bio-oil and biochar characterizations can be found in previous studies (Mohamed et al., 2021a).

2.2. Life cycle assessment of catalytic microwave pyrolysis

 Life cycles assessment (LCA) was adopted in order to determine the environmental impacts associated with catalytic microwave pyrolysis of SG. The environmental impacts were measured using LCA data based on the experimental results, literature review, and data from other energy-related organizations. In compliance with the methods defined in ISOs 14040 and 14044, the environmental impacts were determined. It is assumed that the process is established in Canada.

2.2.1. Goal and scope

 The purpose of this LCA analysis is to determine the environmental consequences and the greenhouse gas (GHG) emissions of the production of phenolic-rich bio-oil and nutrient- rich biochar produced through SG microwave catalytic pyrolysis under different temperatures in comparison with the non-catalytic microwave pyrolysis and conventional pyrolysis. Contribution analysis was conducted to identify the processes contributing drastically to energy consumption, GWP, and other environmental impacts. The standardized methodology of life LCA was followed using Open LCA with Ecoinvent version 3.71 Unit Process database (Alengebawy et al., 2022). The method for the life cycle impact assessment (LCIA) for this study is ReCiPe 2016 Midpoint (H). 1000 kg of dried switchgrass material (DM) was used as a functional unit. The system boundary includes the following processes: 1) Transport of switchgrass, 2) Drying, 3) Grinding and Screening, 5) Storage, 6) Feeding, 7) Pyrolysis, 8) Cooling, and 9) Transport of products (bio-oil and biochar) (Figure 1).

2.2.2. Life cycle inventory

 The LCA is performed based on SG pyrolysis process cradle-to-gate and contrasted with the non-catalytic microwave pyrolysis and conventional pyrolysis from literature. The noncondensable gases (NCG) can be used for energy recovery using the combined heat and

 power (CHP) system; however, their environmental impacts are not taken into consideration because the combustion data are not available. To investigate the acidification, eutrophication, and human toxicity potential as well as to calculate the specific GHG emissions of microwave catalytic pyrolysis of SG, the life cycle inventory (LCI) was compiled from primary data collected from the experimental work and different literatures (Mong et al., 2021). The electricity consumed for the drying stage was determined assuming initial moisture of 25 wt% for SG, which is thermally dried to 8 wt% before being grinded, screened, and fed into the reactor (Huang et al., 2022). Pyrolysis is conducted at 300 or 400 °C, and vapors are condensed to produce bio-oil, biochar and NCG. For transportation, it is assumed that SG is transported from 50 km distance, and bio-oil and biochar are sold to local customers within 25 km distance from the production site using a 16-tonne truck.

2.2.3. Biochar and carbon sequestration

 The carbon sequestered in the biochars was determined based on the elemental composition of the biochars (Leng et al., 2021). The stability of the biochar and available environmental credit could be predicted depending on the H/C and O/C ratios in the char products (Enders et al., 2012). It has been shown that the relationship between oxygen and carbon in the biochar and carbonaceous materials structure governs stability: carbonaceous materials with an O/C molar ratio of less than 0.2 (e.g. graphite, some biochars) are typically the most stable, possessing an estimated half-life of more than 1000 years; biochar with an O/C ratio of 0.2–0.6 (most biochars) have intermediate half-lives (100–1000 years); and, finally biochar with an O/C ratio of greater than 0.6 (biomass) possess a half-life within 100 years (Méndez et al., 2012). The O/C molar ratio for KP-300 and KP-400 biochars are 0.32 and 0.37, respectively as shown in Table 1, demonstrating that the carbon in biochars would last for more than 100 years.

2.2.4. Impact assessment and sensitivity analysis

 For determining the impacts of microwave pyrolysis systems on global warming, the 235 main GHGs carbon dioxide (CO_2) , methane (CH_4) and nitrous oxide (N_2O) were considered, 236 using $CO₂$ equivalence factors (mass basis) for a 100-year time horizon with a global 237 warming potential (GWP) of 298 for N_2O and 25 for CH₄. The avoided GHGs emissions through carbon sequestration of biochar in soil, the replacement of GHG emissions related to 239 fuel oil combustion #2 (2570 g CO_2 -eq/L) are included in the estimated GHG emissions (Brassard et al., 2018). The NCG from microwave pyrolysis can be recovered to provide energy for drying the wet switchgrass, which can be used to replace hydroelectricity. For biochar-400, it is assumed that 85% of the C in biochar remains in soil for 100 years (BC+100 of 85%), and 90% of the C in biochar remains in soil for 100 years for biochar KP- 300 (BC+100 of 90%) based on their O/C and H/C molar ratios (Brassard et al., 2018). To determine the energy balance for pyrolyzing 1000 kg of dried SG, the energy inputs including energy consumption for drying, grinding and screening, feeding, pyrolysis, and 247 quenching, in addition to energy output from NCG and bio-oil were also included. NCG can be used to substitute hydroelectricity to produce heat. The conversion efficiency from NCG to heat is estimated to 75% (Brassard et al., 2018), which can be used to substitute hydroelectricity (Huang et al., 2022).

2.2.5. Economic analysis

 A preliminary assessment of the annual production cost and profit from selling the pyrolysis products was performed for all scenarios to see if the processes are economically viable throughout the operating period. The costs of raw materials and the pyrolysis products are presented in Table S1 in the supplementary material. Since the cost of raw materials, electricity pricing, the selling prices for pyrolysis products vary widely, three cases were considered for the economic assessment, including low-case, base-case, and high-case values, which are summarized in Table S1. Based on the provided economic analysis results, the

 proportion of the operational cost for all scenarios is set at 36% of the utility cost (Barry et al., 2019). The total production cost (TPC) was calculated based on the costs of utility, raw materials, including chemicals, and operational cost. The net profits of the scenarios are then determined based on income from product sales after deducting TPC.

3. Results and discussion

3.1. Effect of K3PO⁴ on heating behaviour and pyrolysis products

 It was found that SG absorbs microwaves ineffectively, and the maximum temperature recorded was < 150°C (Mohamed et al., 2016b). Thus, no bio-oil or biochar was produced 268 from SG without a catalyst. However, mixing K_3PO_4 with SG enhanced the microwave heating, significantly, reaching 300 and 400°C in 2.10 and 15.30 min, respectively. The KP-270 400 sample took a longer time to reach 400°C, because of the oxygenated coke deposition on the catalyst surfaces, as a result of hemicellulose inhibition (Mohamed et al., 2019a). Oxygenated coke deposition on catalyst surfaces was found to reduce microwave absorption, remarkably (Mohamed et al., 2019b). For the effect of temperature on the distribution of pyrolysis products, K3PO⁴ increased biochar and reduced bio-oil yields at higher temperature because of the coke deposition (Table 1). In contrast, there are several microwave absorbing materials that have been used for enhancing the microwave absorption of biomass materials, including carbonaceous materials such as activated carbon, graphene (Dong et al., 2019), graphite (Zhang et al., 2020), and carbon nanotubes (Wei et al., 2020). However, most of these materials are relatively expensive (Wang and Wang, 2019) and do not have high 280 catalytic activity for producing high-quality phenolic-rich bio-oil. Whereas, K_3PO_4 can enhance the microwave heating, produce phenolic-rich bio-oil, and remain in the produced biochars to serve as source of nutrients for plants.

3.2. Effect of K3PO⁴ on bio-oil selectivity and phenol production

286 When compared with the baseline sample $(SiC-400)$, K_3PO_4 demonstrated a greater deoxygenation potential, with remarkable reduction of the highly reactive oxygenated compounds, including acetic acid, and furans, and the complete removal of the other oxygenates including aldehydes and anhydro-sugars (Table 2). The detailed compositions of bio-oil for different KP samples compared with the baseline, are presented in Table 3. The 291 acidic compounds responsible for bio-oil acidity were reduced by \sim 75% under both pyrolysis temperatures, compared with the baseline. Furan compounds were significantly reduced by 85% and 79%, in comparison with the baseline, for KP-300 and KP-400, respectively. However, K3PO⁴ improved bio-oil selectivity towards phenolic production, and the phenolic and aromatic compounds were dramatically increased by 385% and 303% for KP-300 and KP-400. This eventually enhanced the energy density and stability of the bio-oil. These 297 findings agree with previous studies (Lu et al., 2018), in which K_3PO_4 measurably increased phenolics content in bio-oil (Lu et al., 2013). Commercial activated carbon has been found to improve bio-oil selectivity towards phenolic production (Ma et al., 2020). Similarly, HZSM-5 was also found to increase phenolics content through the conversion of furan compounds into aromatics, and then converting aromatics into phenolics on catalytic surfaces (Wang et al., 2019). HZSM-5 was also found promote alkylation reactions, which increased the production of alkylated phenols (Yathavan and Agblevor, 2013). It was also reported that combining bentonite and HZSM-5 improved bio-oil selectivity by creating more aromatics than HZSM- 5 without bentonite (He et al., 2018). However commercial activated carbon and HZSM-5 are very expensive (Müller et al., 2015), and coke coverage could decrease catalytic conversion efficiency and deactivate the catalysts irreversibly (Wang et al., 2014). Ma and coworkers 308 studied the effects of using $Ni/SiO₂$, $Ca/SiO₂$, and $Ni–Ca/SiO₂$ for producing phenolic-rich bio-oil from waste chilli stem biomass, and Ni–Ca/SiO₂ showed high catalytic activity for increasing phenolics by 150% compared with the sample without a catalyst (Ma et al., 2021).

 MgO and biomass-derived activated carbon catalysts were used to produce phenolic-rich bio- oil from Douglas fir and it was found that oxygenated phenols dominated, accounting for up to 80% of the phenols (Huo et al., 2020).

 In contrast, a significant increase was observed in the generation of phenolics, and many other aromatics compounds, due to the catalysts used, where KP-300 indicated the highest production in phenolics. Subsequently, a complete elimination of hemicellulose derived compounds, including linear aldehydes, occurred during the pyrolysis reactions. Through catalytic pyrolysis, oxygenated substances such as acetic acid, furfuryl alcohol, furans, and furfurals are easily transformed to aromatics (Carlson et al., 2010). The results of the kinetic 320 analysis revealed that K_3PO_4 greatly catalyzed tar cracking, and promoted lignin decomposition (Mohamed et al., 2020), which helps to explain the remarkable increase in phenolics content, compared with the baseline data.

323 The effects of catalytic microwave pyrolysis, using K_3PO_4 on phenolic and aromatic 324 species under different pyrolysis temperatures, are shown in Figure 2. It is found that K_3PO_4 enhanced bio-oil selectivity for the production of phenolic compounds including phenol and alkylphenols, and KP-300 showed the highest selectivity for the production of phenol and alkylphenols, which increased by 252% and 420% in comparison with the baseline, whereas phenol and alkylphenols increased by only 9% and 18% compared to KP-400. Although phenolic-rich bio-oils lack reactivity for synthesizing phenolic resins, they possess a high content of phenolic compounds and offer an effective replacement of phenol produced from fossil fuel. Most bio-oils reported in previous studies, were composed of a small amount of reactive phenol and a mix of phenolics that include aromatic ethers and alkylated phenol. This complex nature makes it less attractive when compared to pure phenol (Kim, 2015). However, the addition of phenolic-rich bio-oil for the production of formaldehyde phenolic- resin, demonstrated a good capability for substituting fossil fuel phenols (Kim, 2015). It was found that phenol synthesis is significantly impacted by the pyrolytic conditions, such as

 catalyst type, temperature, and catalyst content (Lu et al., 2018). Phenol production and phenol yield were observed to be higher from pinewood rather than poplar wood. In order to lower the extra hydrogen supplied, mixed pyrolysis gas was utilized to maintain a uniform provision of hydrogen atmosphere for phenol production (Lu et al., 2018).

 Vanillin is one of the most unstable and reactive oxygenated phenolic compounds (Chen et al., 2020), which has a poor stability in comparison to other phenolics (Oh et al., 2017). Consequently, the removal of such reactive compounds can progressively increase the chemical stability of the bio-oil. Due to their similar properties with phenol, alkylphenols are regarded as commercially beneficial chemicals. For instance, it is widely applied in the production of polymer building blocks. Alkylphenols can be employed as a cost-effective solvent for isolating oxygenated compounds from aqueous solutions, derived by biomass that include furfural compounds, levulinic acid, and gamma-valerolactone. Hence, alkylphenols have a great ability to be used as a chemicals platform, it is thus important to create a viable approach to produce bio-oils rich in alkylphenols (Shu et al., 2019). Octane number and heating value are higher in alkylated phenols than oxygenated phenols, which makes them preferable compounds to be extracted from bio-oils (Zabeti et al., 2012). For instance, methyl phenol and phenol have similar heating values of 34.15 and 33.11 MJ/kg, respectively (Zabeti et al., 2012). Aromatic hydrocarbons, specifically those compounds having a higher octane number, are useful chemicals that can be employed as octane enhancers in gasoline (Rezaei et al., 2014).

3.3. Life cycle assessment

 The total estimated energy consumption for bio-oil production including drying, grinding and screening, feeding, pyrolysis, etc. are 727, 1,125, and 1,260 KWh/1000 kg dried SG for KP-300, KP-400, and SiC-400, respectively (Table 1). The drying stage for the raw material contributed by 22% and 14%, while the microwave pyrolysis process contributed by 76% and 85% for KP-300 and KP-400, respectively, confirming that initial drying of the feedstock

 material requires a significant amount of energy. These findings are in line with the other studies in the literature, revealing that other drying methods such as solar drying could be utilized to further reduce the energy consumption of the process. The percentage of the environmental impacts for each process involved in the production of bio-oil including transporting the raw material and final products (bio-oil and biochar) is shown in Figure 3. Drying and pyrolysis stages contributed remarkably to GWP for all cases, while the transportation of SG and pyrolysis products (bio-oil and biochar) is the major contributor to all other environmental indicators, except the GWP (Figure 3). This is in agreement with other reported studies in literature, in which transportation has been found to have a major influence on the eutrophication potential (EP) (Peters et al., 2015) and acidification potential (AP) (Roberts et al., 2010). The breakdown values of the environmental impacts for each process are presented in Table 4. For EP, the values ranged from 0.024 to 0.041 kg $PO4³$ 375 eq/1000 kg DM, while AP values ranges are 0.136–0.151 kg SO₂ eq/1000 kg DM. These EP values are remarkably low when compared with conventional pyrolysis, in which 377 conventional pyrolysis could contribute to EP by 1.39 kg $PO₄³$ eq/1000 kg DM and for AP 378 by 0.045 kg SO_2 eq/1000 kg DM, respectively (Wang et al., 2015). The remarkable effects of drying and microwave pyrolysis on GWP (Table 4 and Figure 3) are due to their significant energy consumption. However, microwave catalytic pyrolysis has less impact on GWP (159−223 kg CO2-eq/1000 kg DM) when compared to conventional pyrolysis, in which the 382 GWP from conventional pyrolysis ranged from 737 CO_2 -eq/1000 kg DM (Wang et al., 2015) to 1,295 kg CO2-eq/1000 kg DM (Muñoz et al., 2017). Other studies found that reducing pyrolysis temperatures from 400 to 300°C resulted in a remarkable reduction in the negative environmental impacts, including human toxicity, and freshwater eutrophication, which reduced the impacts by 38% and 56%, respectively (Muñoz et al., 2017).

 Acidification potential, which has a substantial influence on the environment, is linked with emissions of compounds, such as SO_2 , NOX , NH_3 , and hydrocarbons. Those acidic

 chemicals (excluding NH3) could react to create acid rain with other atmospheric components. Acid rain may decrease the pH of soil and water (Johansson et al., 2008) and damage environments for many living organisms (Vienescu et al., 2018). The EP is described 392 as the rise in organic matter input in the environment. The $PO₄³$ equivalents are assessed 393 based on NH₃ and NO_x levels (PO₄³⁻ eq). The EP examines all the consequences on the air, water, and soil environments released by high macronutrients levels (Vienescu et al., 2018). Microwave heating has been claimed to decrease energy use by more than 50% in comparison with conventional heating systems (Mohamed et al., 2016b). However, this mainly depends on microwave absorption ability of a feedstock, and a good microwave

 absorber should be mixed with the feedstocks having poor absorption ability for microwaves. In microwave pyrolysis, the sample is heated immediately, as microwaves directly transmit electromagnetic energy, leading to immediate and volumetric heating (Kostas et al., 2017). As a result, microwave pyrolysis of large particles is possible without the requirement for an energy-intensive grinding to produce smaller particle sizes (Zhou et al., 2013). It was claimed that the energy required for pre-treatment processes accounted for up to 55% of the energy required for the complete conventional pyrolysis process. This considerable quantity of energy might be conserved in part by employing a microwave pyrolysis technique, resulting in a large cost reduction (Beneroso et al., 2017).

 Figure 4 compares CO² generated from microwave catalytic pyrolysis of SG with avoided $CO₂$ credits from utilizing pyrolysis products through carbon sequestration and fuel replacement, and the net value of GWP under different pyrolysis temperatures was also 410 compared. It is shown that most of the avoided $CO₂$ credits were achieved through replacing bio-oil with the diesel fuel for the KP-400 sample, while the credit obtained from NCG is the lowest (\sim 8.9 kg CO₂-eq/kg 1000 kg DM) assuming that NCG is used on-site to replace hydroelectricity. However, the emission from NCG combustion are not considered according to previous studies (Muñoz et al., 2017), and thus future studies should focus on determining

 the actual emissions from NCG combustion. If NCG is used to replace natural gas, then the value remarkably increases, leading to a remarkable increase in the net avoided GWP. It was 417 found that the avoided $CO₂$ credit of NCG for replacing electricity produced by natural gas 418 combined-cycle power generation system is 527 kg $CO₂$ -eq/kg 1000 kg DM (Mong et al., 2021). The biochar produced at low pyrolysis temperature (KP-300) contributed more to 420 avoided carbon with the highest net negative GWP of -665 CO_2 -eq per 1000 kg dried SG (Figure 5). This is because of its higher carbon content and high aromaticity, which is confirmed by the low O/C ratio. Also, the biochars from KP-300 and KP-400 contain high amounts of essential nutrients including K (304−385 g/kg), P (168−195 g/kg), Ca (14.2−23.3 g/kg), and other nutrients (Mohamed et al., 2021b), which make the biochars more desirable for soil application.

 Generally, the results show that the total net avoided GWP for KP-300 is higher than that of KP-400; this result is due to the reduction in microwave energy consumption and increased credit for biochar carbon sequestration. The LCA analysis reveals that microwave catalytic pyrolysis is a potential novel approach for SG utilization that may help reduce the GWP through sustainable utilization of agricultural wastes.

3.4. Sensitivity analysis

 The sensitivity analysis for GWP is conducted on the basis of environmental analysis to examine the effects of the main factors on sustainability of the process. The analysis includes SG initial moisture content and microwave pyrolysis, as illustrated in Figure 5. The total GWP is observed to range from 159 to 223 CO2-eq per 1000 kg dried SG, as shown in Table 4. The moisture content of the collected SG imposed a great impact on the overall GWP (Figure 3). The overall GWP would be lowered by 11−14% if SG is dried by sun to a moisture level of 15 wt%. Further, reducing the consumed electricity through microwave pyrolysis by 25% decreases the GWP by 15% when compared with the original case. This can be achieved by mixing another good microwave absorber with K_3PO_4 to trigger

 synergistic effects for expediting microwave heating. Our previous studies showed that mixing two catalysts with biomass can trigger synergetic effects (Mohamed et al., 2020), which resulted in expediting microwave heating and improving bio-oil quality and selectivity (Mohamed et al., 2021a). The produced bio-oils are rich in phenolics that can be used for substituting fossil fuel phenols. The bio-oil can be used for diesel fuel replacement; however, upgrading is essential to further increase its calorific value and reduce the oxygen content of the bio-oil. Bio-oil upgrading can further enhance energy recovery, which largely depends on the calorific value and bio-oil oxygen content. Nevertheless, bio-oil upgrading is an energy- intensive process (Peters et al., 2015) and therefore, requires more energy inputs than the recovered energy from the upgraded bio-oil (Zhang, 2014). Bio-oil from this study can then be used for phenols extraction due to its high phenolic content. Further investigation is needed to evaluate whether it is a reasonable decision to implement bio-oil upgrading.

3.5. Economic analysis

 The economic analysis results of the microwave pyrolysis scenarios with different estimates (i.e., low-case, high-case, and base-case) are summarized in Table 5. When considering the low-case estimates for selling pyrolysis products, only KP-300 was found to provide a low marginal net profit. However, for other pyrolysis scenarios, no revenues were generated from pyrolysis products, resulting in a negative profit. Previous studies found that slow and fast pyrolysis processes are not profitable when considering high electricity price (Kung et al., 2013). However, in this study, the cost of the chemicals contributes remarkably to the TPC, therefore, lowering the mixing ratio of the chemicals can result in a positive profit. Whereas, all pyrolysis scenarios generated revenues from pyrolysis products, resulting in a positive profit after considering the base-case and high selling prices for pyrolysis products (Table 5). For all cases, the gas products earned the lowest amount of money (Shahbeig and Nosrati, 2020), in which the revenue was determined based on electricity credit. According to other studies in literature, the bio-oil produced did not yield considerable

 income, owing to their low quality (Iribarren et al., 2012; Kung et al., 2013). The bio-oil and biochar yields, and their market values are significant factors in the process net profit. In order to make the process more profitable, the marketable values should be at least within the base-case estimated prices.

 Considering the three ranges of the estimates, the TPC cost ranges from 526−1,220 US\$/1000 kg dried SG with KP-300 being the lowest and SiC-400 being the highest. The cost 473 of chemicals (i.e., K_3PO_4 , SiC) is the major contributor to TPC, which ranges from 37%−55%. The microwave pyrolysis costs are also similar to numbers proposed by previous studies, which estimated the production cost to be ~640 US\$/1000 kg for fast pyrolysis (Brown et al., 2011).

 The main limitation of this study is that other environmental effects resulting from using biochar on land application, such as the release of GHG emissions, were not considered. The limited boundary in this study also should be considered, and future studies should compare different routes for extracting phenols from bio-oil and compare the feasibility and profitability of different processes. Future studies should also focus on the environmental impacts of extracting phenolic compounds from bio-oil, and determine the feasibility of the process, compared with phenols derived from fossil fuel sources.

4. Conclusions

 This study employed the life cycle analysis method to analyze the climate change and energy effect from microwave catalytic pyrolysis of switchgrass at different pyrolysis temperatures, for producing phenolic-rich bio-oil. The results show that microwave catalytic pyrolysis, using K3PO4 can produce a phenolic rich bio-oil at lower temperatures compared with conventional pyrolysis. KP-300, which was pyrolyzed at 300°C, showed the highest selectivity for phenol and alkylphenols production, which increased by 252% and 420% in comparison with the baseline (SG with SiC but without K_3PO_4). The total GWP is observed

 to range from 159 to 223 kg CO2-eq per 1000 kg dried SG, with KP-300 being the lowest. Sensitivity analysis shows that drying and microwave pyrolysis are the most important parameters that can be optimized during microwave catalytic pyrolysis to further reduce the negative environmental burdens. The produced biochar is rich in nutrients, which can be used for soil applications, leading to further reduction in the GWP through carbon sequestration. 498 The highest negative GWP of -398 kg CO_2 -eq per 1000 kg dried SG was found for KP-300. The economic analysis shows that microwave catalytic pyrolysis is an eco-friendly and profitable process for recycling biomass feedstocks. This study demonstrates that the catalytic microwave pyrolysis of switchgrass has lower environmental effects than non-catalytic microwave pyrolysis and conventional pyrolysis because of the greater conversion efficiency and lower energy consumption, lowering the carbon footprint while simultaneously improving the quality of bio-oil and biochar.

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Conflict of interest

 The authors declare that the research was conducted without any influence of financial or personal relationships that can potentially be the source of conflict of interest.

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 Table 2. The concentrations of lumped main products of bio-oil from microwave pyrolysis of SG for KP-300 and KP-400 cases compared with SG mixed with SiC (baseline). 1 739

 Table 3. Chemical composition of bio-oil (peak area %) produced from KP-300 and KP-400 cases compared with SG mixed with SiC (baseline).

	GWP (kg $CO2$ eq)			EP (kg PO ₄ ³⁻ eq)			AP (kg $SO2$ eq)			HTP (kg DCB eq)			POCP ($kg C2H4$ eq)		
	SiC-	KP-	KP-	SiC-	KP-	KP-	SiC-	KP-	KP-	SiC-	KP-	KP-	SiC-	KP-	KP-
	400	300	400	400	300	400	400	300	400	400	300	400	400	300	400
Drying	5.73E	5.73E	5.73E	1.28E-	3.03E-	3.03E-	$1.28E-$	$1.28E-$	$1.28E-$	2.56E-	2.56E-	2.56E-	7.61E-	$7.61E -$	7.61E-
	$+01$	$+01$	$+01$	02	03	03	02	02	02	02	02	02	04	04	04
Grinding $+$ Screening	9.91E	9.91E	9.91E	$2.21E-$	5.22E-	5.22E-	$2.21E-$	2.21E-	2.21E-	4.43E-	4.43E-	4.43E-	1.31E-	1.31E-	1.31E-
	$+00$	$+00$	$+00$	03	04	04	03	03	03	03	03	03	04	04	04
Feeding	2.18E-	2.18E-	2.18E-	4.88E-	1.15E-	1.15E-	4.88E-	4.88E-	4.88E-	9.79E-	9.79E-	9.79E-	2.89E-	2.89E-	2.89E-
	01	01	01	05	05	05	05	05	05	05	05	05	06	06	06
Microwave Pyrolysis	1.37E	7.27E	1.10E	1.20E-	$6.11E-$	9.62E-	4.12E-	2.60E-	3.30E-	6.48E-	5.18E-	5.18E-	$2.32E-$	1.53E-	1.85E-
	$+02$	$+01$	$+02$	02	03	03	02	02	02	02	02	02	03	03	03
Cooling	2.95E-	3.03E-	2.81E-	6.70E-	7.37E-	6.38E-	2.85E-	2.31E-	2.71E-	6.22E-	4.61E-	5.92E-	7.99E-	5.42E-	7.61E-
	01	01	01	06	06	06	05	05	05	05	05	05	06	06	06
Transport (SG, bio-oil	1.79E	1.85E	1.56E	1.39E-	$1.42E-$	1.21E-	9.42E-	9.54E-	8.19E-	1.31E-	$1.33E-$	1.14E-	6.68E-	6.93E-	5.81E-
and biochar)	$+01$	$+01$	$+01$	02	02	02	02	02	02	01	01	01	03	03	03
Total	2.23E	1.59E	1.93E	4.10E-	2.39E-	$2.52E-$	1.51E-	1.36E-	1.30E-	2.26E-	$2.15E -$	1.96E-	9.90E-	9.36E-	8.57E-
	$+02$	$+02$	$+02$	02	02	02	01	01	01	01	01	01	03	03	03
Conventional pyrolysis															
(Muñoz et al., 2017)	1.30E+03 kg CO_2 -eq			1.40E-03 kg $PO43$ eq/1000			1.35E+00 kg DCB								
	/1000 kg DM			kg DM			eq/1000 kg DM								
(Wang et al., 2015)	$7.37E+02$ kg CO_2 -eq			1.39E+00 kg $PO43$			4.50E-02 kg SO_2 eq/1000			1.49E+00 kg DCB			4.08E-03 kg C_2H_4		
	/1000 kg DM			eq/1000 kg DM			kg DM			eq/1000 kg DM			eq/1000 kg DM		

Table 4. Environmental impacts of different stages involved in the microwave catalytic pyrolysis of 1000 kg of dried SG for KP-300 and KP-400 cases compared with the baseline (SiC-400) and conventional pyrolysis from literature.

KP: K3PO4, SG: switchgrass, SiC: silicon carbide, GWP: global warming potential, EP: eutrophication potential, AP: acidification potential, HTTP: human toxicity potential, POCP: photo-oxidant formation potential

		SiC-400			KP-300		KP-400			
	Low	Base- Case	High	Low	Base- Case	High	Low	Base- Case	High	
Total										
Production	651.52	935.39	1,220	526.48	696.48	866.31	642.83	842.00	1,041	
Cost (US\$)										
Utilities	97.02	121.34	146.03	55.98	70.01	84.26	86.78	108.53	130.62	
Raw										
Material	285.00	477.00	668.00	315.00	432.00	548.00	315.00	432.00	548.00	
Costs										
Operation	269.50	337.05	405.65	155.50	194.47	234.05	241.05	301.47	362.83	
cost										
Product Sales	503.87			538.80						
(US\$)		1,217	1,999		1,517	2,495	532.38	1,484	2,437	
Bio-oil	215.76	644.25	1,073	228.27	681.58	1,135	205.76	614.38	1023	
Biochar	257.31	534.63	880.57	283.11	800.92	1,320	292.36	827.10	1,362	
NCG	30.80	38.52	46.36	27.43	34.31	41.29	34.27	42.85	51.58	
Net Profit (US\$)	-147.65	282.01	779.98	12.33	820.33	1,629	-110.45	642.33	1,395	

Table 5: Economic analysis results of microwave catalytic pyrolysis scenarios for KP-300 and KP-400 cases compared with the baseline (SiC-400).

KP: K3PO4, SiC: silicon carbide, NCG: non-condensable gases,

Figure 1. Structure of the production phenolic-rich bio-oil by microwave catalytic pyrolysis of switchgrass.

Table 2. Phenol, alkylated phenol, oxygenated phenol, and aromatic concentrations of bio-oil from microwave pyrolysis of SG for KP-300 and KP-400 cases compared with SG mixed with SiC (baseline).

Figure 3. Breakdown of the environmental impacts of different stages involved in the microwave catalytic pyrolysis of 1000 kg dried SG for KP-300 and KP-400 cases compared with the baseline (SiC-400).

Figure 4. CO₂ generated from microwave catalytic pyrolysis and avoided CO₂ from utilizing pyrolysis products.

Figure 5. Sensitivity analysis of various parameters affecting GWP based on 1000 kg dried SG, and the changes are presented as percentage relative to the baseline.