

Generating Energy and Greenhouse Gas Inventory Data of Activated Carbon Production Using Machine Learning and Kinetic Based Process Simulation

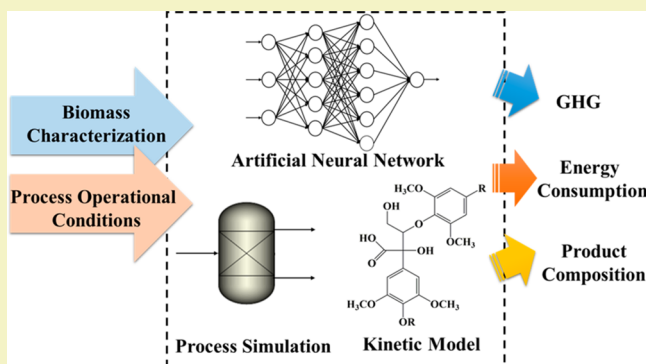
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Supporting Information

ABSTRACT: Understanding the environmental implications of activated carbon (AC) produced from diverse biomass feedstocks is critical for biomass screening and process optimization for sustainability. Many studies have developed Life Cycle Assessment (LCA) for biomass-derived AC. However, most of them either focused on individual biomass species with differing process conditions or compared multiple biomass feedstocks without investigating the impacts of feedstocks and process variations. Developing LCA for AC from diverse biomass is time-consuming and challenging due to the lack of process data (e.g., energy and mass balance). This study addresses these knowledge gaps by developing a modeling framework that integrates artificial neural network (ANN), a machine learning approach, and kinetic-based process simulation. The integrated framework is able to generate Life Cycle Inventory data of AC produced from 73 different types of woody biomass with 250 characterization data samples. The results show large variations in energy consumption and GHG emissions across different biomass species (43.4–277 MJ/kg AC and 3.96–22.0 kg CO₂-eq/kg AC). The sensitivity analysis indicates that biomass composition (e.g., hydrogen and oxygen content) and process operational conditions (e.g., activation temperature) have large impacts on energy consumption and GHG emissions associated with AC production.

KEYWORDS: Activated carbon, Biomass, Life Cycle Assessment, Machine learning, Artificial neural network, Kinetics, Process simulation



INTRODUCTION

Activated carbon (AC) is a carbonaceous material with high porosity, absorptivity, and surface reactivity and has high value-added applications in water purification, industrial processes, and flue gas cleanup.^{1,2} AC also has many emerging applications such as functional materials used for electrode, catalyst, and carbon capture.³ The worldwide consumption of AC was 12.8 million metric tons in 2015,⁴ and the annual growth rate of the AC market was projected as 6.31% from 2019 to 2024.⁵ AC can be produced from diverse carbonaceous sources such as coal (the main current source of commercial AC) and biomass (e.g., agricultural waste, wood, and herbaceous plants).^{3,6} Given a large number of potential feedstocks for AC production and rapid growth of AC demand, it is critical to understand the environmental implications of producing AC from alternative biomass feedstocks, especially given that AC production is one of the largest contributors to the overall environmental impacts of relevant technologies such as wastewater treatment based on previous Life Cycle Assessment (LCA) studies.^{7–10} This understanding will enable more informed decision-making related to biomass selection, technology investment, process design, and optimization.

Many LCA studies evaluated the environmental implications of AC produced from diverse sources. A comprehensive literature review of previous studies is provided in Supporting Information (SI), section 1. The review indicates large variations in the environmental burdens associated with AC production from different biomass feedstocks (see Table S1). Given that most previous studies focused on a specific biomass feedstock, it is difficult to apply their results for other biomass feedstocks or make generic comparisons.^{11–13} Developing LCAs for AC produced from a variety of biomass is challenging due to the lack of Life Cycle Inventory (LCI) data. Rapid and reliable estimation of LCI data for AC produced from diverse biomass sources is essential to screen different types of biomass feedstock and support early stage technology development and process design for sustainable AC production. It also significantly reduces the time and efforts needed for the gate-to-gate LCI data collection for manufacturing processes that is usually the most time-consuming phase for LCA.¹⁴ A few

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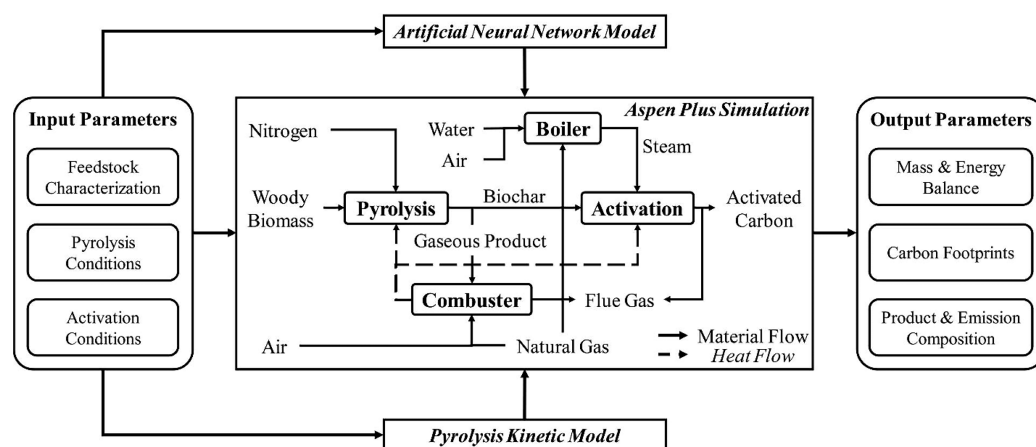


Figure 1. Schematic diagram of the integrated modeling framework in this study.

previous studies have investigated different approaches for the rapid generation of LCI data of production processes. For example, Parvatker and Eckelman¹⁵ reviewed different methods that have been used for LCI estimation, such as process simulation tools,^{16,17} process design calculations,^{18,19} stoichiometry, proxy method,²⁰ molecular structure-based models,²¹ and hybrid LCI.^{22,23} Other studies have used other process simulations in conjunction with other techniques such as dynamic model,²⁴ kinetic model,²⁵ network approaches,²⁶ and knowledge-based models.²⁷ Applying previous approaches to estimate LCI for AC produced from diverse biomass feedstocks is challenging due to the lack of quantitative understandings of the relationships between LCI and large variations in biomass compositions and process operations, which are further discussed in the following two paragraphs. A few studies have tried to use machine learning (ML), a technique that does not rely on preknown knowledge, to directly generate LCI data²¹ or environmental impacts.^{28–30} However, these applications of ML techniques are limited to commercialized chemicals/products with abundant LCI data. Thus, it is challenging to apply ML alone to AC production that lacks LCI data for different biomass feedstocks.

Previous studies indicate that energy consumptions and greenhouse gas (GHG) emissions are mainly driven by the AC production stage that usually has large variations due to differences in the types and composition of biomass, process operational conditions, and sources of energy.^{9,13} A few studies have tried to explore such variations by investigating AC production scenarios by varying process parameters. For example, Sepúlveda-Cervantes et al. conducted a gate-to-gate LCA of soybean shell-based AC production using zinc chloride activation.³¹ By varying the operational conditions (i.e., activation temperature, time, and impregnation ratio), the electricity consumption of AC production changed from 17 to 50 MJ/kg AC, and the GHG emissions varied between 5.86 to 47.2 kg CO₂-eq/kg AC.³¹ Arena et al. analyzed the impacts of different energy sources on the environmental footprints of coconut shell AC, which showed a significant reduction of most environmental impact categories (60–80%) by using electricity from renewable sources.¹² For feedstock variations, most studies^{13,32,33} developed LCA for individual biomass with a limited set of operational conditions then made a comparative analysis. To the best of the authors' knowledge, none of the previous studies have correlated LCA results with parameters related to biomass characteristics and process

operations. Thus, it is challenging to use previously developed LCA models to obtain quantitative understandings of the impacts of feedstocks and process variations or screen biomass and perform process optimization for AC production from an environmental perspective.

One additional, and significant, liability of many studies is that they have assumed a fixed composition for the gas and vapor product generated by the activation process,^{11,12,31} whose accuracy cannot be ensured in the scenarios with varying feedstocks and operating conditions. The composition of these gas and vapor can have a significant effect on LCI.^{11,12,31} The composition of gases and vapors will vary depending on both the composition of the starting biomass and operational conditions.^{31,34}

To address the gaps discussed above, this study integrated kinetic-based process simulation and artificial neural network (ANN), a machine learning approach, to estimate environmental footprints of AC produced from a variety of biomass feedstocks. Specifically, primary energy consumption and GHG emissions of AC production, two most commonly used indicators in previous LCAs for AC production,^{11–13} were parametrized by process models that used large data sets collected from literature (e.g., ultimate analysis of biomass, in total 250 data samples) and predicted by ANN (e.g., total AC yield). As the focus is to demonstrate the functionality of the integrated framework in generating the LCI data for AC produced from different biomass, the system boundary of this work is gate-to-gate. This system boundary is also consistent with most of the previous LCAs of AC.^{9–12,31–33,35–42} The influences of biomass feedstock characteristics were investigated by correlating the feedstock compositions with energy consumption and GHG emissions.

This study can be used for screening a diverse array of biomass feedstocks useful for AC production, enhancing options for feedstock selection, process design, and process optimization. Although this work focuses on AC production, the integration of ANN and kinetic-based simulation can be applied to other production systems to generate LCI data for rapid LCA analysis, especially for emerging technologies whose LCI data is not available. These combined models will allow future research and production on biomass-based AC to clearly understand the environmental sustainability implications of their process choices. Furthermore, the sensitivity analysis was constructed to identify the key biomass properties and operational parameters driving the energy and GHG

emissions, which are valuable information for future process optimization and improvement.

MATERIALS AND METHODS

This study focuses on steam activation, a common technology for AC production.³ The steam AC production process consists of two steps. In the first step, dried biomass is treated at high temperature (400–850 °C) and inert atmosphere in a slow pyrolysis process that produces solid biochar, syngas, and condensable bio-oil.² In the second step, the biochar is placed in a high-temperature reactor without air, and superheated steam is injected to activate the biochar. A series of complex chemical reactions are involved in both steps, and it is challenging to directly determine the yields and composition of the products of each step. Yet the yield and composition of the gases and vapors are required to estimate the energy consumption and GHG emissions of AC production.⁴³ To address this challenge, previous studies used either experiments or literature data for specific feedstocks with a limited set of activation conditions.^{12,13,33,35,44} However, such data cannot be accurately extended to a broad array of different feedstocks. Although some recent studies tried to use ANN models to predict the LCI data or LCIA (life cycle impact assessment) results,^{21,28–30} it is very challenging to use ANN alone to estimate the environmental burdens of AC production that does not have sufficient data samples for different biomass feedstocks and process operational conditions. This work addressed this challenge by first using kinetic-based process models to estimate pyrolysis yield and gas composition and then using trained ANN models to predict the activation yield, and Aspen Plus process simulation to generate gate-to-gate LCI data such as energy consumption and air emissions (see Figure 1).^{45,46}

Three types of input parameters were used in this modeling framework, including biomass characterization (i.e., ultimate analysis data), pyrolysis conditions (i.e., temperature and reaction time), and activation conditions (i.e., steam to biochar mass ratio, activation time, and temperature). These data were used as the input of the ANN model to predict the total yield of AC production. The training process is detailed in our prior work.⁴⁵ This study focuses on woody biomass, given that it is one of the most abundant biomass resources in the world.⁴⁷ This also has the practical advantage of limiting the effects of ash, in particular active alkali, which can have a significant impact on the initial slow pyrolysis reactions and be significant in herbaceous or agricultural feedstocks. The data of ultimate analysis (a type of chemical analysis commonly used for biomass and fuels, it provides composition information such as the contents of carbon, hydrogen, and oxygen)⁴⁸ combined with the pyrolysis time and temperature were then used as the inputs to the pyrolysis kinetic model adapted from the previous study,⁴⁶ producing data on the quantity and composition of pyrolysis products. Both ANN and kinetic models were run independently, although they used the same data sets for biomass characterization and operational conditions. Then the data generated by the kinetic model (gas and solid products from pyrolysis) and ANN model (total AC yield) were used in an Aspen Plus process simulation that ultimately provided the energy and mass balance data needed to estimate the environmental burdens of AC.⁴⁹ A list of input and output parameters is provided in Table S2. As this study mainly focused on energy and GHG emissions, energy consumption and GHG in the gas products were mainly tracked for the process simulation. However, the integrated modeling framework is capable to provide the full list of inputs and outputs that can be used as LCI to estimate other environmental impact categories such as acidification and eutrophication that other researchers may be interested in.

Pyrolysis Kinetic Model. Many mechanistic studies have attempted to investigate biomass thermochemical conversion processes. Four types of mechanisms were commonly used, including (1) three-step reaction mechanism, (2) two-stage semiglobal reaction mechanism, (3) Broido-Shafizadeh reaction mechanism, and (4) multistep reaction mechanism (MSRM).⁵⁰ The MSRM framework was chosen in this study given its capability of predicting the

composition of the biochar solid and the product gases and vapors.^{50,51} MSRM assumes that biomass is composed of the lignocellulosic components (i.e., cellulose, hemicellulose, and lignin) and thermal degradations happen on these components and derived products. Then the MSRM based model suggests a series of reactions, related to the decomposition of the individual biomass components, where the overall reaction rate can be determined by the kinetic equation shown in eq 1:

$$r = kT^n e^{-E/RT} \quad (1)$$

where r is the rate of reaction, k is the pre-exponential factor, T is the reaction temperature, n is the exponential factor of temperature, E is the activation energy of the reaction, and R is the ideal gas constant. The k , n , and E are given for each reaction included in the MSRM model,⁵² and thus the product compositions can be calculated based on a given combination of temperature, time and starting biomass composition. See Table S3 for parameter values associated with each reaction included in this model. In total, the kinetic model includes 5 reactions for cellulose, 10 for hemicellulose, 12 for lignin, 8 for metaplastic compounds, and 13 for gas-phase tar cracking.

In this study, the pyrolysis kinetic model was developed based on the MSRM model published in 2017.⁴⁶ Modifications were made by considering gas-phase tar cracking reactions and the differences between softwood and hardwood.^{53,54} Extractive components of biomass were not considered in this study as previous studies indicated that the extractive content of woody biomass is generally low (1–5% for softwood and 2–8% for hardwood), and there is limited interaction between the reactions of these extractives and the bulk of the biomass.^{55–58} The triangulation method (see eqs 1–5 in the SI) was used to estimate the lignocellulosic composition of biomass (used as the inputs of MSRM) from the ultimate analysis data of biomass.⁵⁸ This method was used due to the lack of lignocellulosic composition data from the literature and database. It is recognized that the use of triangulation method may lead to some deviations, for example, the cellulose and hemicellulose in woody biomass perform similar elemental composition but different decomposition pathways.⁵⁹ This limitation can be addressed in the future when more lignocellulosic composition data is available. Even with this limitation, the pyrolysis yield of biochar generated by the kinetic model ranges from 20.8 to 39.1% that is well-aligned with industrial pyrolysis operations.^{60,61}

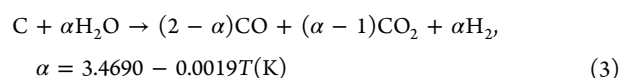
Artificial Neural Network. A key parameter needed by the Aspen Plus process simulation is the yield of AC. The MSRM kinetic model provides the yield of the intermediate biochar (pyrolysis yield), but it does not provide the final yield of AC from biochar (activation yield). In this study, the yield of the final AC product from the starting biomass (biomass yield) was estimated by using ANN as outlined in our prior work.⁴⁵ The ANN model was trained using eight input variables, including five process variables (i.e., pyrolysis time, pyrolysis temperature, activation time, activation temperature, and steam to biochar ratio) and three biomass characterization variables (i.e., biomass carbon content, hydrogen content, and oxygen content). The output variable is the total AC yield based on the total biomass input of the entire AC production process.⁴⁵ The ANN model demonstrated a high accuracy ($R^2 = 0.971$) and showed high consistency with independent experimental data through an additional model validation step.⁴⁵

Aspen Plus Process Simulation. In this study, the process simulation model was developed using Aspen Plus⁴⁹ (Aspen Plus V10) to generate energy and mass balances. The process flowsheets of pyrolysis and steam activation are provided in Figure S3 and S4, and the detailed model is shown in SI, section 2.3. One key parameter needed for the process simulation of steam activation is the activation yield that is defined as the AC produced divided by the total biochar input to the activation process.⁶² The activation yield could have large variations depending on the quantity and quality of biochar (that are driven by pyrolysis process and biomass feedstock) and process operational conditions.⁶³ To take such variations into consideration, this study calculated the activation yield using eq 2, where the total AC yield is given by the ANN model and the pyrolysis yield of

biochar was provided by the kinetic model. The calculated activation yields range from 29.0 to 94.8%, which is consistent with the activation yields derived from literature.⁶³

$$\text{activation yield} = \frac{\text{total AC yield}}{\text{pyrolysis yield of biochar}} \times 100\% \quad (2)$$

In addition to the data provided by the ANN and kinetic models discussed previously, another key piece of information is the composition of flue gas coming from the steam activation. This gas needs to be counted as an air emission. Previous LCA studies have assumed that the only steam-carbon reaction occurs without CO₂ generation,¹² which is not consistent with experimental measurements.^{13,33} Other reactions such as the water–gas shift reaction, methanation reactions, steam-reforming reactions, and the Boudouard reaction also occur.^{64,65} In this study, those reactions were considered by using the model from Martín-Gullón et al.⁶⁶ as shown in eq 3.



The Aspen Plus database has property data, which can be used to model gas-phase reactions and estimate the reaction products including gases (e.g., hydrogen, methane, carbon monoxide and carbon dioxide) and vapors (e.g., alkanes, alkenes and oxygenates).^{67,68} However, the property data for solid components (e.g., woody biomass, biochar, and AC), lignocellulosic components (e.g., cellulose, hemicellulose and lignin) and monosaccharides (e.g., glucose and xylose) are not included in Aspen databases. The relevant physical property parameters for lignocellulosic components and monosaccharides were collected from the literature.⁶⁹ For solid components, the thermodynamic data was calculated based on previous studies^{54,70} and documented in SI, section 2.4. Key process parameters used in the Aspen Plus simulation are listed in Table 1.

Table 1. Key Process Parameters Used in the Process Simulation Model

parameter	value	ref
heat capacity of biomass feedstock (J/(kg K))	1500 + T^a	71
heat capacity of biochar and AC (J/(kg K))	420 + 2.09 T – 6.85 × 10 ^{−4} T^{2a}	71
pyrolysis gas residence time (s)	2	52
pyrolysis nitrogen gas mass flow	1/6 of feedstock mass flow	44
pyrolysis thermal efficiency (%)	90	72
combustor excess air rate (%)	30	12
pyrolysis nonsolid product combustion rate (%)	80	73
steam boiler thermal efficiency (%)	82	74
activation furnace thermal efficiency (%)	90	72
pyrolysis temperature (K) ^b	773	
pyrolysis time (min) ^b	60	
activation temperature (K) ^b	1073	
activation time (min) ^b	60	
steam to biochar ratio (kg/kg) ^b	2	

^a T represents the absolute temperature in Kelvin. ^bThese parameters were used in the sensitivity analysis with ranges provided in Table S5.

In this study, the natural gas was combusted in the combustor to provide the heat for pyrolysis and activation, given that natural gas is the most commonly used fuel type to supply heat in the U.S. manufacturing industry.⁷⁵ A few studies used electricity to supply heat, but all of them were based on lab-scale AC production/experiments.^{11,31,36,39} Electricity could be used for ancillary facilities or purposes (e.g., process monitoring and control), but the electricity consumption for those purposes is generally negligible^{13,33,35} and

needs to be assessed on a case-by-case basis given the specific equipment used. Thus, this study does not include ancillary electricity consumption and the primary energy consumption is reported in the form of natural gas. Meanwhile, all of the gaseous byproducts from the initial pyrolysis process were combusted with an 80% combustion rate to produce process energy. The combustion rate is the ratio of pyrolysis products that can be fully combusted, and 80% was used based on the ratio of unidentified and hard-to-combust substances of nonsolid pyrolysis products.⁷³ The energy content in the flue gases from the activation process are estimated to be minor,¹³ so they were not combusted. To understand the impacts of energy recovery, scenarios with and without burning gas products were evaluated using energy recovery ratio (ERR) calculated by eq 4:

$$\text{ERR} = \frac{\text{energy recovered}}{\text{total energy consumption}} \times 100\% \quad (4)$$

Understanding the Impacts of Biomass Feedstock. To investigate the impact of the composition of the woody biomass feedstock, a large data set (250 data samples) containing the characterization data of woody biomass feedstocks was collected from Bioenergy Feedstock Library,⁷⁶ Phyllis2 database,⁷⁷ and the literature.^{78–112} The entire data set is provided in Table S6. The Aspen Plus process simulation was run for each sample with the fixed operational conditions shown in Table 1, allowing for comparisons among different feedstocks, as well as an initial quantification of the variations in energy and GHG emissions for individual species of biomass sources. In addition, the sensitivity analysis was conducted to understand the impacts of varied biomass composition and operational conditions on the energy and GHG emissions of AC. The typical value and upper/lower bounds of all parameters were determined by the literature review and documented in Table S5.^{45,63,113–115}

Fossil-based and biogenic GHG were tracked separately in this study given the debate of accounting biogenic GHG.¹¹⁶ Some studies set the characterization factor of biogenic CO₂ as zero according to the carbon-neutral assumption.^{13,117,118} Fossil-based GHG emissions were generated from burning natural gas that was assumed to be the sole fossil fuel used in the AC production.¹¹⁹ Biogenic GHG emissions were generated from both energy recovery (burning pyrolysis gas products) and the activation process (GHG as byproducts). Both fossil-based and biogenic GHGs were converted to the same unit (kg CO₂ eq/kg AC) by applying the latest 100-year Global Warming Potential (GWP) conversion factors from IPCC, which distinguishes methane from biogenic and fossil sources (the GWP conversion factor is 30 for fossil methane and 28 for biogenic methane).¹²⁰

RESULTS AND DISCUSSION

Table 2 lists the average, minimum, maximum, and standard deviation (STD) for 250 data samples of different biomass feedstocks. These ranges are consistent with the results of previous LCA studies using woody biomass (Table S1). Some observations can be identified in Table 2. First, there are large variations in energy consumption and fossil-based/biogenic GHG emissions of steam AC production across different types of biomass. Second, although the average energy consumption and GHG emissions of softwood are higher than that of hardwood, there are large overlaps between the softwood and hardwood for the min-max results across all categories. The differences between hardwood and softwood could be more remarkable if more characterization data is available (e.g., textural properties, lignocellulose composition, morphology). Third, energy recovery reduces the primary energy consumption and fossil-based GHG emissions by burning gas byproducts as biogenic fuel sources (and as a result biogenic GHG emissions increase). The detailed LCI generated by this

Table 2. Variability in Primary Energy Consumption, Fossil-Based and Biogenic GHG Emissions

	softwood		hardwood		total	
	average (min-max)	STD ^a	average (min-max)	STD ^a	average (min-max)	STD ^a
E_{NRE} (MJ/kg AC)	101(43–224)	32	88(43–277)	32	93(43–277)	33
E_{RE} (MJ/kg AC)	65(25–155)	23	57(23–208)	24	60(23–207)	24
fossil GHG _{NRE} (kg CO ₂ -eq/kg AC)	8.7(4.2–18.8)	2.6	7.4(4.0–22)	2.4	7.9(4.0–22)	2.6
fossil GHG _{RE} (kg CO ₂ -eq/kg AC)	4.0(1.7–9.3)	1.4	3.5(1.5–12)	1.4	3.7(1.5–12)	1.4
biogenic GHG _{NRE} (kg CO ₂ -eq/kg AC)	5.1(2.7–12)	1.5	4.3(2.4–13)	1.4	4.6(2.4–13)	1.5
biogenic GHG _{RE} (kg CO ₂ -eq/kg AC)	6.7(3.4–14)	1.9	5.9(3.4–16)	1.8	6.2(3.4–16)	1.9

^aSTD: Standard deviation; RE: with energy recovery; NRE: without energy recovery.

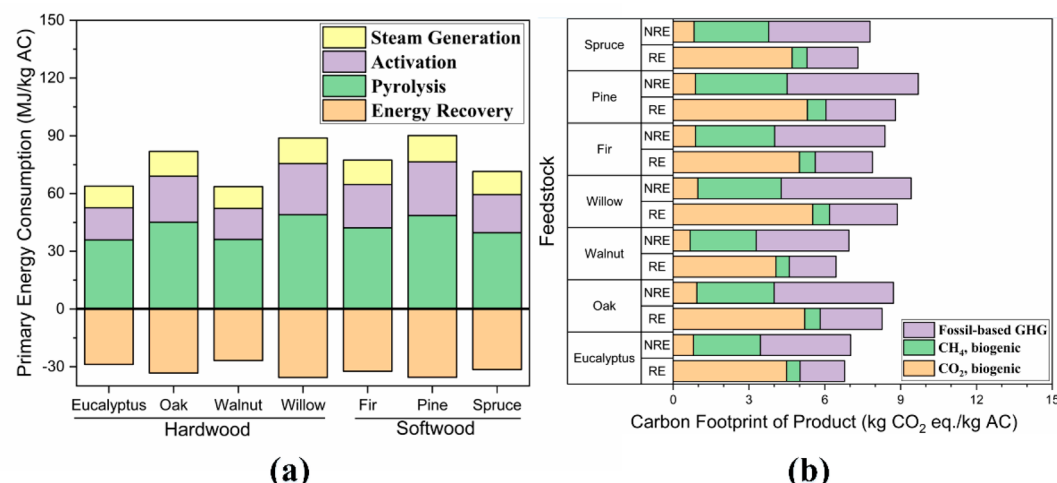


Figure 2. Average primary energy consumption (a) and carbon footprint (b) of steam AC production from different woody biomass species.

study for each of the 250 data samples were provided in the EXCEL file supplemented as one of the SI documents.

To understand the major contributors to both energy and GHG emissions results, the breakdown results of four types of common hardwood (i.e., eucalyptus, oak, walnut, and willow) and three types of common softwood (i.e., fir, pine, and spruce) were shown in Figure 2. Because more than one data sample of biomass characterization was collected from the literature, the average values of the results for each type of wood were shown.

In Figure 2a, the energy demand by different unit processes in the AC production is shown as positive and the energy recovered by burning flue gas is shown as negative. Figure 2a shows that across all different biomass species, pyrolysis has the largest energy demand (53–57% without energy recovery), which is consistent with the literature.^{33,38,44} Across seven feedstocks, 72–80% of the pyrolysis energy consumption can be supplied by the energy recovered from flue gas, which is also consistent with the previous study (~75%).⁶⁷ For the entire AC production process, at most 45% of the primary energy consumption can be recovered by burning flue gas from pyrolysis, indicating the importance of including energy recovery in AC production.

Figure 2b shows the average results of the carbon footprint of AC production from seven types of woody biomass. The CO₂ and CH₄ from pyrolysis and steam activation as byproducts, and in the case of energy recovery from flue gas combustion of the pyrolysis gases, are considered as biogenic as the carbon is originally from biomass. Figure 2b shows that without energy recovery most of the GHG emissions were from natural gas combustion. When energy recovery from

pyrolysis gas combustion is included most of the GHG emissions come from biogenic sources. The biogenic carbon emission can be sequestered by the regrowth of the plant, which was not included in this study as the carbon sequestration capacity of different wood species is highly variable and depends on regional climate and forest management practices. However, carbon sequestration could be easily incorporated into this framework in future work. Given the large contribution of biogenic carbon in the results (69–74%) it is clear that the GHG emissions of AC production with energy recovery will be much lower if carbon sequestration from biomass is included.

To further understand the impacts of biomass feedstocks on AC production energy and carbon footprints, the results of 250 data samples were plotted with different biomass compositions (see Table S6). The results indicated that hydrogen content and hydrogen/carbon ratio (H/C ratio) are two parameters strongly correlated with GHG emissions (Figures S6–S7) and primary energy consumption as shown in Figure 3a,b. For both softwood and hardwood, increasing the hydrogen content increases the primary energy consumption, except for a few samples that show decreased energy consumption with hydrogen content higher than 6.5%. Since the carbon contents for these outliers are relatively higher than other data samples, Figure 3b plots energy consumption and H/C ratio to eliminate the influence of the carbon content, which shows similar trends as Figure 3a but with a more scattered distribution of results. The results of the scenario without energy recovery have similar trends and shown in Figure S7.

The large impacts of hydrogen and H/C ratios can be explained by their impacts on the AC yields. A high H/C ratio

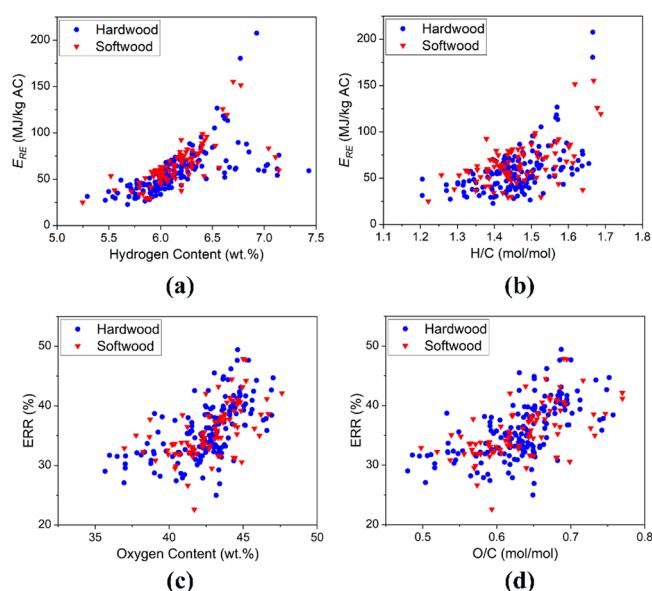


Figure 3. Impacts of feedstock characteristics on the primary energy consumption ((a) hydrogen content and (b) hydrogen to carbon ratio) and energy recovery ratio ((c) oxygen content and (d) oxygen to carbon ratio).

in biomass feedstock usually indicates a lower percentage of aromatic carbon, which may lead to low AC yields given the important role of aromatic carbon in steam activation.^{2,121} Such information could be helpful for future biomass selection and process design, it also demonstrates the unique capability of the modeling framework presented in this study.

A similar approach was applied to ERR, the indicator of energy recovery (see Figure S9). Two parameters, oxygen content and O/C ratio, show correlations with ERR as shown in Figure 3c,d. For both hardwood and softwood, the higher oxygen content of biomass or atomic O/C ratio, the higher ERR in the steam AC production process. This higher O/C ratio is indicative of higher carbohydrate content, and hemicellulose in particular are known to be less stable and generate more gas and vapor products under pyrolysis conditions.¹²² Thus, feedstocks with higher O/C ratios will produce more gases and vapors that are important for energy recovery. Based on the discussion above, one conclusion is that choosing biomass with lower hydrogen contents, H/C ratio, and higher oxygen contents, O/C ratio is beneficial from energy and GHG emissions perspectives.

In addition to biomass characteristics, another set of parameters that have large impacts on pyrolysis and steam activation processes are operational conditions. To understand the impacts of these parameters, a sensitivity analysis was performed using the ranges shown in Table S5 and the results for primary energy consumption and biogenic GHG emissions are shown in Figure 4 (see Figure S10 for the results without energy recovery and the results for fossil-based GHG emissions). Figure 4 indicates that among different biomass characteristics, hydrogen content and ash content are both important. The importance of hydrogen is already discussed previously. The effects of ash are complex. Active alkali ash species (e.g., sodium, potassium, calcium, etc.) can impact the decomposition of the biomass carbohydrate fraction in particular during the pyrolysis process, which in turn will affect the ratio of biochar to pyrolysis vapors and thus the final AC yield will also be affected.¹²³

Among different operating parameters, the activation temperature has the greatest impact. This is due to its large impact on the final AC yield, and associated heat duty on the furnace and boiler. In general, choosing biomass with low hydrogen contents and setting the low temperature for steam activation and pyrolysis processes are beneficial from energy and GHG emissions perspectives.

There are some limitations of the modeling framework presented in this study. While understanding the primary energy consumption and GHG emissions for AC production are useful, the AC product must meet a series of performance specifications demanded by the market. For example, the adsorption capacity of AC is a key parameter determining the effectiveness of applications such as contamination removal in water and associated prices. This parameter was not included in this study due to the lack of data. The authors previously published a study that used ANN to predict the BET surface area of AC, which could be used as an initial proxy of the adsorption capacity of AC.⁴⁵ In that study, a contribution analysis was conducted to understand the impacts of variations in feedstocks and process operations on the yields and BET surface area of AC produced. The results indicated that both yields and BET surface area of AC are highly driven by the variations of feedstock compositions (e.g., ash and carbon content) and operational conditions of steam activation (e.g., activation temperature and steam to carbon ratio). Depending on the applications, other performance specifications may be expected for AC such as iodine number and methylene blue index.¹²⁴ Previous literature indicated that these specifications are affected by process and feedstock variations, which could

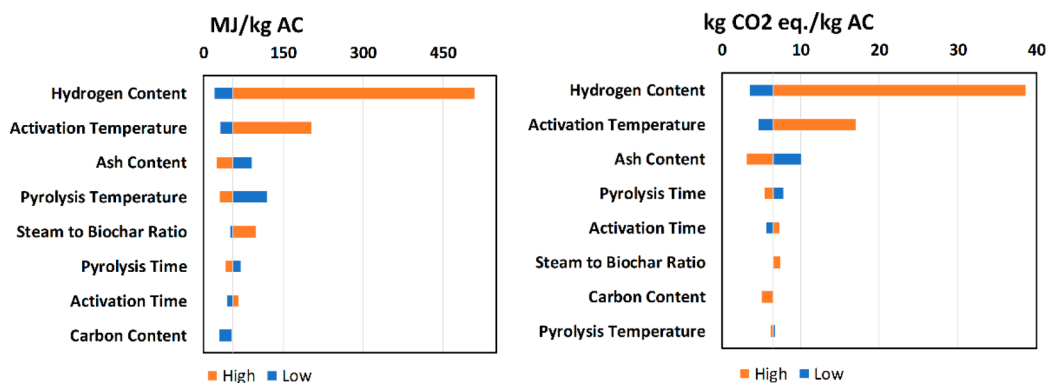


Figure 4. Sensitivity analysis for the energy consumption and biogenic GHG emissions (with energy recovery) of the steam AC production process

be the future research direction for the authors if sufficient experimental data are available. Another limitation is the procedure used to estimate the quality and heating value of the intermediate pyrolysis gases, which could be further improved with the improvement of pyrolysis kinetic models in the future. Finally, this study does not include other biomass-related parameters such as particle size due to their relative low impacts on the results based on previous studies.¹²⁵ In addition, the oven-dried biomass used in the present study avoided the influence of the moisture content, which may have some impact and needs additional clarification when evaluating the cradle-to-gate AC production process that is a larger system boundary than this gate-to-gate study. This limitation can be addressed by adding additional drying processes in future work.

In conclusion, this work developed a modeling framework that integrates ANN and kinetic-based process simulation models to estimate the gate-to-gate primary energy consumption and GHG emissions across a variety of woody biomass. The LCI generated by the integrated models can be used as data sources for future LCAs of AC or industrial systems using AC materials. To understand opportunities for reducing energy consumption and GHG emissions from AC production, the key driving factors were identified and the impacts of variations were quantified. Furthermore, the results of this study indicated the importance of feedstock selection and operation of AC production from an environmental sustainability perspective. Both the results and modeling framework can be used by engineers and project managers to select biomass feedstocks and improve process operations. Although this study focused on woody biomass and AC production, the modeling framework can be applied to other types of biomass and other biomass utilization technologies. The ranges and distributions of the primary energy consumption and GHG emissions estimated in this study can also be used as transparent and reliable data sources for future LCA and Techno-Economic Assessment.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06522>.

Detailed information on literature review, modeling framework and settings, feedstock data set, additional results, and references (PDF)

Detailed Life Cycle Inventory generated for AC production using different biomass species (XLSX)

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Generating Energy and Greenhouse Gas Inventory Data of Activated Carbon Production Using Machine Learning and Kinetic Based Process Simulation

Supporting Information

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1. Literature Review of LCA and Relevant Analysis for Activated Carbon

Production

Previous studies have estimated the energy consumption and Global Warming Potential (GWP) of activated carbon (AC) produced from different feedstock and technological routes as shown in Table S1. All of these data were normalized to the functional unit as 1 kg of AC product. Since different energy sources are provided by different studies, the energy consumption from electricity was converted to primary energy consumption using the efficiency of 32.9%.¹

Table S1 Primary Energy Consumption (PEC) and Global Warming Potential (GWP) of Activated Carbon Production (Functional Unit: 1 kg of AC)

Ref.	System Boundaries	Feedstock	Activating Agent	PEC (MJ/kg)	GWP (kg CO ₂ -eq./kg)
²	Activation	Coal	Steam	30.71 ^a	5.321
	Gate-to-gate	Coal	Steam	-	11.00
³	Gate-to-gate	Coal	Steam	196.2 ^a	-
⁴	Gate-to-gate	Coal	Steam	-	8.292
⁵	Gate-to-gate	Coal	Steam	-	8.410
⁶	Gate-to-gate	Coal	Steam	-	9.423
⁷	Gate-to-gate	Coal	Steam	-	9.620
	Gate-to-gate	Wood	Steam	-	1.790
⁸	Drying	Olive Waste	H ₃ PO ₄	47.47	2.777
	Pyrolysis	Olive Waste	H ₃ PO ₄	43.67	3.388
	Impregnation	Olive Waste	H ₃ PO ₄	52.15	3.317
	Gate-to-gate	Olive Waste	H ₃ PO ₄	167.6	11.10
⁹	Gate-to-gate	Coconut shell	Steam	10.40-11.80 ^b	0.8752-1.000
¹⁰	Drying	Soybean shell	ZnCl ₂	0.3900 ^a	-
	Pyrolysis	Soybean shell	ZnCl ₂	7.560-10.25 ^a	-
	Impregnation	Soybean shell	ZnCl ₂	43.16-143.8 ^a	-
	Gate-to-gate	Soybean shell	ZnCl ₂	51.68-152.0 ^a	5.860-47.15
¹¹	Chipping	Wood waste	Steam	2.168	0.003246
	Drying	Wood waste	Steam	1.252 ^a	0.05661
	Pyrolysis	Wood waste	Steam	7.613	0.01136
	Activation	Wood waste	Steam	2.271 ^a	0.01652
	Gate-to-gate	Wood waste	Steam	13.30 ^a	0.08814
	Gate-to-gate	Coconut shell	Steam	-	1.150
¹²	Chipping	Poplar	Steam	0.2564	-

	Drying	Poplar	Steam	11.36	1.564
	Pyrolysis	Poplar	Steam	1.325	0.1821
	Activation	Poplar	Steam	0.7791	0.1092
	Gate-to-gate	Poplar	Steam	13.72	1.853
¹³	Activation	Wood chip	Steam	106.4 ^a	-
	Activation	Wood chip	Steam	73.50 ^c	-
	Activation	Coal	Steam	141.9 ^a	8.520
	Cradle-to-gate	Wood chip	Steam	158.3	8.600
	Cradle-to-gate	Coal	Steam	241.6	18.28
¹⁴	Pyrolysis	Hazelnut shell	Steam	23.18 ^d	-
	Activation	Hazelnut shell	Steam	20.00 ^d	-
¹⁵	Pyrolysis	Coconut shell	Steam	85.64	-
	Activation ^e	Coconut shell	Steam	-7.821	-
¹⁶	Drying	Corn stover	Steam	5.950	-
	Pyrolysis ^f	Corn stover	Steam	18.45	-
	Activation	Corn stover	Steam	11.90	-
¹⁷	Gate-to-gate	Eucalyptus wood	ZnCl ₂	118.6	8.581
	Gate-to-gate	Eucalyptus wood	H ₃ PO ₄	153.8	5.575

^a Assume the electricity is purchased from the grid and the average energy efficiency is 32.9%¹

^b The study assumed that flue gas is fully combusted to compensate the energy use

^c Activation in an upscaled reactor with a capacity of 33.3 kg biochar per hour, the result fixed the yield from the LCI of the present study¹³

^d The theoretical energy consumptions presented by the author are considered and normalized to the functional unit

^e The activation step was mixed with some oxygen to achieve partial oxidation

^f The carbonization step applied fast pyrolysis

Bayer et al. completed the first life cycle assessment (LCA) study of AC production from coal in 2005.² Steam activation was implemented to convert hard coal to granular activated carbon (GAC). In this study, 3 metric tons of hard coal and 1,600 kWh were needed to produce 1 ton of GAC. In addition, 330 m³ of natural gas was combusted to provide 12 tons of steam as the activating agent for 1 ton GAC. The cradle-to-gate GWP of GAC production in this study was 11.0 kg CO₂ eq./kg AC.² However, if the GAC can be recycled and used as the feedstock of GAC production, the GWP of the process was reduced to 1.17 kg CO₂ eq./kg AC.²

Many studies then have developed LCA models for coal-based AC based on the process data by Bayer et al.² In these studies, the GWP of coal-based AC varied between 8.29-9.62 kg CO₂ eq./kg AC.⁴⁻⁷ Manda et al. made a comparison between the coal-based GAC and wood-based GAC using the data from Azargohar.¹⁸ The normalized results showed a significant reduction (81.4%) of GWP by changing the feedstock from coal to wood.⁷

A few studies have developed LCA models for AC from biomass. Hjaila et al. developed an LCA model for AC produced from olive waste cake using phosphoric acid as the activation agent.⁸ In this study, the system boundary is gate-to-gate, including all processes from the acquisition of olive waste cake to the production of AC.⁸ The LCI was developed based on the experimental data and the results were compared to coal-based AC.⁸ Arena et al. constructed the LCA of coconut shell based AC production via steam activation with the similar system boundary as Hjaila et al. Different scenarios were developed to compare different energy sources, coconut shell applications, and different byproduct disposal strategies.^{8,9} In this study, the life cycle inventory (LCI) data was developed based on the literature data.^{9,19} The study highlighted the potential of low-carbon electricity energy sources and environmental management methods in reducing the environmental impact of AC production.⁹

Some researchers have tried to generate detailed process data using experimental studies. Sepúlveda-Cervantes et al. developed an LCA for AC from soybean shell using zinc chloride activation, and the LCI data were developed based on the lab-scale experiments. The experiments and optimal operational conditions for high AC yields were determined by response surface methodology (RSM).¹⁰ A similar approach was used in another study for AC from corn pericarp by potassium hydroxide activation.²⁰ The brew waste-based AC produced by sulfuric acid activation is also studied by the lab-scale experiments and LCA.²¹ In this study, it is

concluded that the impact of AC disposal is ignorable and the impact of untreated brew waste disposal is significant.²¹ Gu et al. used steam to activate wood chip derived biochar in a pilot-scale test calciner (1.54 or 1.13 kg/h biochar precursor) and an upscaled commercial calciner (33.6 kg biochar precursor).¹³ The cradle-to-gate LCA results demonstrate that the cumulative energy demand (CED) and GWP of wood chip-based AC production are 158.33 MJ/kg AC product and 8.60 kg CO₂ eq./kg AC product, respectively.¹³ The CED and GWP were higher for AC from hard coal.¹³ A similar process was established by Kim et al. at a larger scale (4 tons a day).¹¹ In this study, the steam AC production from wood waste showed lower energy consumption and environmental impact compared with previous LCA studies.^{9,11,13}

Some studies have used simulations and/or experiments to quantify the energy consumption of AC production. Hung simulated the AC production using coconut shell and steam activation processes by ChemCAD for an industrial-scale fluidized bed reactor (14.5 tons a day).¹⁵ Since the steam activation was implemented with high-pressure, the activation in the fluidized bed reactor was exothermic rather than endothermic.¹⁵ Another study simulated an industrial scale steam AC production using corn stover feedstock and fast pyrolysis.¹⁶ Sharifan used a lab-scale experiment to investigate the energy consumption of steam AC production from hazelnut shell.¹⁴

Table S1 shows large variations for both primary energy consumption and GWP of AC production. These variations could be caused by different system boundaries, feedstock, and technologies (e.g., activation agent as shown in Table S1). Note that a few studies estimated energy consumption based on theoretical energy demand without considering the energy efficiency of energy end uses such as boilers.¹⁴ In this study, the energy and mass balance was simulated in Aspen Plus based on the input variables collected either from literature or ANN models. The energy efficiency of different energy end uses was considered. The energy

efficiency of the reactor was assumed to be 90%, the efficiency of the boiler was assumed to be 82%.^{22,23}

2. Modeling Framework Methods

The input and output parameters of the modeling framework developed in this study are listed in Table S2.

Table S2 Model Input and Output Parameters

Input Parameters	
Parameters	Unit
<i>Feedstock Properties</i>	
Carbon Content	wt%, dry basis
Hydrogen Content	wt%, dry basis
Oxygen Content	wt%, dry basis
Ash Content	wt%, dry basis
<i>Pyrolysis</i>	
Pyrolysis Time	minute
Pyrolysis Temperature	K
<i>Activation</i>	
Activation Time	minute
Activation Temperature	K
Steam to Biochar Mass Ratio	kg/kg
Output Parameters	
Parameters	Unit
<i>Pyrolysis Reactor</i>	
Feedstock – Woody Biomass	kg/kg AC
Product – Biochar	kg/kg AC
Syngas – Carbon Dioxide	kg/kg AC
Syngas – Methane	kg/kg AC
Thermal Energy Consumption	MJ/kg AC
<i>Combustor</i>	
Flue Gas – Carbon Dioxide	kg/kg AC
Flue Gas – Methane	kg/kg AC
Thermal Energy Recovery	MJ/kg AC
<i>Steam Boiler</i>	
Water Consumption	kg/kg AC
Thermal Energy Consumption	MJ/kg AC
<i>Activation Furnace</i>	
Flue Gas – Carbon Dioxide	kg/kg AC

Thermal Energy Consumption	MJ/kg AC
<i>Biochar Properties</i>	
Carbon Content	wt%, dry basis
Hydrogen Content	wt%, dry basis
Oxygen Content	wt%, dry basis
Ash Content	wt%, dry basis
<i>Activated Carbon Properties</i>	
Carbon Content	wt%, dry basis
Hydrogen Content	wt%, dry basis
Oxygen Content	wt%, dry basis
Ash Content	wt%, dry basis

2.1 The Kinetic Model for Pyrolysis

The reactions in the slow pyrolysis stage were simulated by the multi-step reaction mechanism where biomass is decomposed to lignocellulosic components (cellulose, hemicellulose and lignin). Model compounds were chosen to represent major biomass lignocellulosic components based on literature.²⁴ Glucose ($C_6H_{10}O_5$) was chosen to represent cellulose and xylose ($C_5H_8O_4$) was chosen to represent hemicellulose. Given the complexity of lignin structure, three types of chemical compounds were chosen to present lignin: Lignin-C, lignin-O and lignin-H. The structures of these compounds are shown in Figure S1.

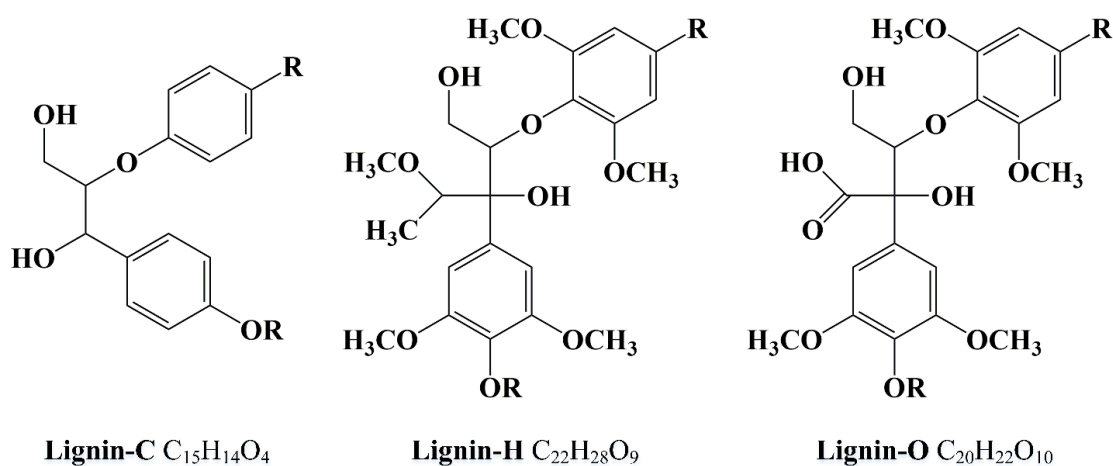


Figure S1 Structures and Chemical Formulas of lignin-C, lignin-O and lignin-H²⁴

Since only ultimate analysis data were collected in the present study, the contents of these model compounds should be estimated by the ultimate analysis data. The triangle method developed by Debiagi et al. was used in this study as shown in Figure S2.²⁵ Considering the chemical composition of model compounds, the contents of different model compounds can be calculated by Equation 1-5. Then the triangle method was used to construct 3 reference components to replace 5 model compounds in order to reduce the degree of freedom in Equation 1-5 to be solvable.

$$x_{CELL}C_{CELL} + x_{HEMI}C_{HEMI} + x_{LIGC}C_{LIGC} + x_{LIGH}C_{LIGH} + x_{LIGO}C_{LIGO} = C_{BIOMASS} \quad (1)$$

$$x_{CELL}H_{CELL} + x_{HEMI}H_{HEMI} + x_{LIGC}H_{LIGC} + x_{LIGH}H_{LIGH} + x_{LIGO}H_{LIGO} = H_{BIOMASS} \quad (2)$$

$$x_{CELL}O_{CELL} + x_{HEMI}O_{HEMI} + x_{LIGC}O_{LIGC} + x_{LIGH}O_{LIGH} + x_{LIGO}O_{LIGO} = O_{BIOMASS} \quad (3)$$

$$x_{CELL} + x_{HEMI} + x_{LIGC} + x_{LIGH} + x_{LIGO} = 1 \quad (4)$$

$$x_{CELL}, x_{HEMI}, x_{LIGC}, x_{LIGH}, x_{LIGO} \geq 0 \quad (5)$$

Note for equations: x_t – Mass fraction of compound t ; C_t – Carbon content of compound t ; H_t – Hydrogen content of compound t ; O_t – Oxygen content of compound t ; *CELL* – Cellulose; *HEMI* – Hemicellulose; *LIGC* – Lignin-C; *LIGH* – Lignin-H; *LIGO* – Lignin-O.

However, some biomass samples in Figure S2 are outside the model compounds. In this study, the components of model compounds in the samples outside the range were determined by fixing the variables in Equation 1-5 (fix x_{CELL} and x_{HEMI}) by the experimental compositional analysis result of the corresponding biomass sample, and then solve the Equation 1-4. Since some solution may be negative when Equation 5 is not considered, these negative values are set as 0 and the remaining positive values are normalized to satisfy Equation 5.

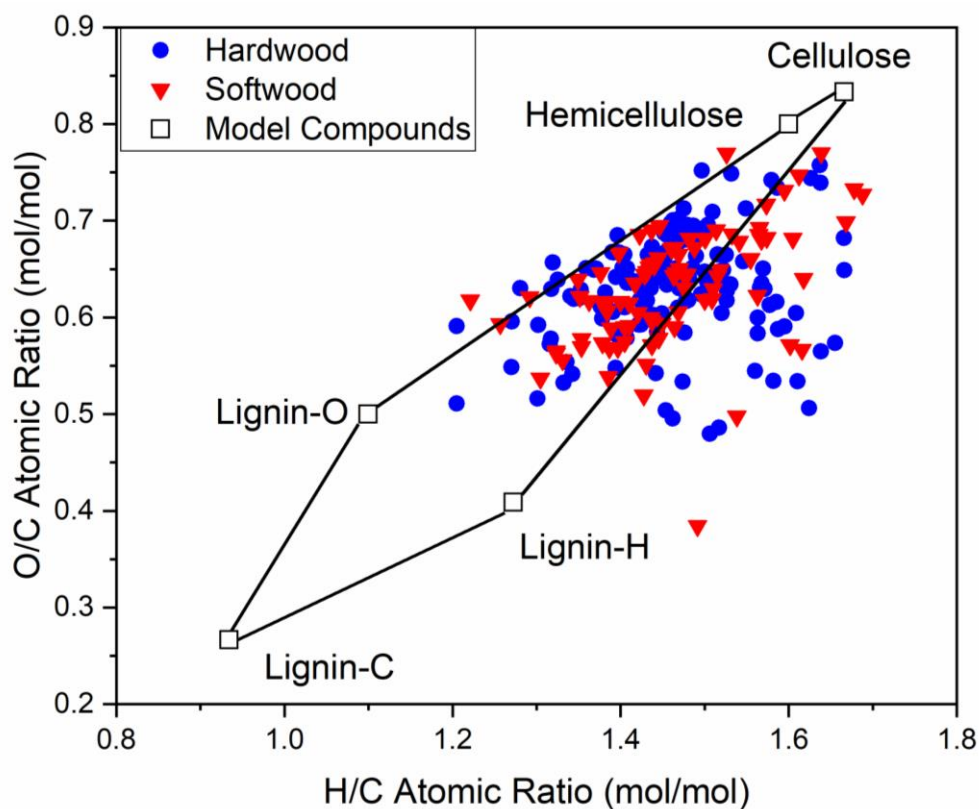


Figure S2 Biomass characterization representation for model compounds and collected woody biomass samples by Krevelen diagram

After determining the model compounds of the woody biomass samples, the kinetic model was developed based on the multi-step reaction mechanism that provides a series of reactions. The reactants are model compounds and corresponding products. In this study, the pyrolysis kinetic model was based on the model developed by Anca-Couce et al.²⁶, which was modified by adding gas-phase tar cracking reactions²⁷ and fitting the differences between different types of biomass.²⁸ The reactions, corresponding kinetic parameters, and other relevant parameters are listed in Table S3.

Table S3 Pyrolysis Kinetic Model Reactions and Parameters^{26–28}

Primary Kinetic Reactions (T = Pyrolysis Temperature, t = Pyrolysis Time)					
Reactions			k (s^{-1})	n	E (kJ/mol)
<i>Cellulose ($x_{CELL} = 0.1$)</i>					
CELL	→	CELLA	4×10^{13}	0	188.37
CELLA	→	$(1-x_{CELL}) \cdot (0.45 \text{ HAA} + 0.2 \text{ GLYOX} + 0.3 \text{ C}_3\text{H}_6\text{O} + 0.25 \text{ HMFU} + 0.05 \text{ H}_2 + 0.31 \text{ CO} + 0.41 \text{ CO}_2 + 0.4 \text{ CH}_2\text{O} + 0.15 \text{ CH}_3\text{OH} + 0.1 \text{ CH}_3\text{CHO} + 0.83 \text{ H}_2\text{O} + 0.02 \text{ HCOOH} + 0.05 \text{ G-H}_2 + 0.2 \text{ G-CH}_4 + 0.61 \text{ Char})$	2×10^6	0	80.0
CELLA	→	$x_{CELL} \cdot (5.5 \text{ Char} + 4 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	2×10^6	0	80.0
CELLA	→	$(1-x_{CELL}) \cdot (0.45 \text{ HAA} + 0.2 \text{ GLYOX} + 0.3 \text{ C}_3\text{H}_6\text{O} + 0.25 \text{ HMFU} + 0.05 \text{ H}_2 + 0.31 \text{ CO} + 0.41 \text{ CO}_2 + 0.4 \text{ CH}_2\text{O} + 0.15 \text{ CH}_3\text{OH} + 0.1 \text{ CH}_3\text{CHO} + 0.83 \text{ H}_2\text{O} + 0.02 \text{ HCOOH} + 0.05 \text{ G-H}_2 + 0.2 \text{ G-CH}_4 + 0.61 \text{ Char})$	4	1	41.86
CELLA	→	$x_{CELL} \cdot (5.5 \text{ Char} + 4 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	4	1	41.86
<i>Hemicellulose (XYHW for hardwood; GMSW for softwood; $x_{HCE} = 0.2$)</i>					
GMSW	→	0.7 HCE1 + 0.3 HCE2	1×10^{10}	0	129.70
XYHW	→	0.35 HCE1 + 0.65 HCE2	1.25×10^{11}	0	131.38
HCE1	→	$(1-x_{HCE}) \cdot (0.5 \text{ CO} + 0.5 \text{ CO}_2 + 0.325 \text{ CH}_4 + 0.8 \text{ CH}_2\text{O} + 0.1 \text{ CH}_3\text{OH} + 0.25 \text{ C}_2\text{H}_4 + 0.125 \text{ ETOH} + 0.025 \text{ H}_2\text{O} + 0.025 \text{ HCOOH} + 0.275 \text{ G-CO}_2 + 0.4 \text{ G-COH}_2 + 0.125 \text{ G-H}_2 + 0.45 \text{ G-CH}_3\text{OH} + 0.875 \text{ Char})$	1.2×10^9	0	125.58
HCE1	→	$x_{HCE} \cdot (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	1.2×10^9	0	125.58
HCE1	→	$(1-x_{HCE}) \cdot (0.1 \text{ CO} + 0.8 \text{ CO}_2 + 0.3 \text{ CH}_2\text{O} + 0.25 \text{ H}_2\text{O} + 0.05 \text{ HCOOH} + 0.15 \text{ G-CO}_2 + 0.15 \text{ G-CO} + 1.2 \text{ G-COH}_2 + 0.2 \text{ G-H}_2 + 0.625 \text{ G-CH}_4 + 0.375 \text{ G-C}_2\text{H}_4 + 0.875 \text{ Char})$	0.15	1	33.5
HCE1	→	$x_{HCE} \cdot (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	0.15	1	33.5
HCE1	→	$(1-x_{HCE}) \cdot (0.5 \text{ CO} + 0.5 \text{ CO}_2 + 0.325 \text{ CH}_4 + 0.8 \text{ CH}_2\text{O} + 0.1 \text{ CH}_3\text{OH} + 0.25 \text{ C}_2\text{H}_4 + 0.125 \text{ ETOH} + 0.025 \text{ H}_2\text{O} + 0.025 \text{ HCOOH} + 0.275 \text{ G-CO}_2 + 0.4 \text{ G-COH}_2 + 0.125 \text{ G-H}_2 + 0.45 \text{ G-CH}_3\text{OH} + 0.875 \text{ Char})$	3	1	46.05
HCE1	→	$x_{HCE} \cdot (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	3	1	46.05
HCE2	→	$(1-x_{HCE}) \cdot (0.2 \text{ HAA} + 0.175 \text{ CO} + 0.275 \text{ CO}_2 + 0.5 \text{ CH}_2\text{O} + 0.1 \text{ ETOH} + 0.2 \text{ H}_2\text{O} + 0.025 \text{ HCOOH} + 0.4 \text{ G-CO}_2 + 0.925 \text{ G-COH}_2 + 0.25 \text{ G-CH}_4 + 0.3 \text{ G-CH}_3\text{OH} + 0.275 \text{ G-C}_2\text{H}_4 + \text{Char})$	5×10^9	0	138.14
HCE2	→	$x_{HCE} \cdot (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	5×10^9	0	138.14

<i>Lignin ($x_{LIG} = 0.3$)</i>					
LIG-C	→	0.35 LIG-CC + 0.1 pCoumaryl + 0.08 PHENOL + 0.32 CO + 0.3 CH ₂ O + H ₂ O + 0.7 G-COH ₂ + 0.495 G-CH ₄ + 0.41 G-C ₂ H ₄ + 5.735 Char	1.33×10^{15}	0	203.02
LIG-H	→	LIG-OH + 0.25 HAA + 0.5 C ₃ H ₆ O + 0.5 G-C ₂ H ₄	6.7×10^{12}	0	156.97
LIG-O	→	LIG-OH + CO ₂	3.3×10^8	0	106.74
LIG-CC	→	(1-x _{LIG})*(0.35 HAA + 0.3 pCoumaryl + 0.2 PHENOL + 0.4 CO + 0.65 CH ₄ + 0.6 C ₂ H ₄ + 0.7 H ₂ O + 0.4 G-CO + G-COH ₂ + 6.75 Char)	3×10^7	0	131.86
LIG-CC	→	x _{LIG} *(15 Char + 4 H ₂ O + 3 H ₂)	3×10^7	0	131.86
LIG-OH	→	LIG + 0.55 CO + 0.05 CO ₂ + 0.1 CH ₄ + 0.6 CH ₃ OH + 0.9 H ₂ O + 0.05 HCOOH + 0.6 G-CO + 0.85 G-COH ₂ + 0.1 G-H ₂ + 0.35 G-CH ₄ + 0.3 G-CH ₃ OH + 0.2 G-C ₂ H ₄ + 4.15 Char	1×10^8	0	125.58
LIG	→	(1-x _{LIG})*FE2MACR	4	1	50.2
LIG	→	x _{LIG} *(10.5 Char + 3 H ₂ O + 0.5 CO ₂ + 3 H ₂)	4	1	50.2
LIG	→	(1-x _{LIG})*(0.2 C ₃ H ₆ O + CO + 0.2 CH ₄ + 0.2 CH ₂ O + 0.4 CH ₃ OH + 0.2 CH ₃ CHO + 0.95 H ₂ O + 0.05 HCOOH + 0.45 G-CO + 0.5 G-COH ₂ + 0.4 CH ₄ + 0.65 C ₂ H ₄ + 5.5 Char)	4×10^8	0	125.58
LIG	→	x _{LIG} *(10.5 Char + 3 H ₂ O + 0.5 CO ₂ + 3 H ₂)	4×10^8	0	125.58
LIG	→	(1-x _{LIG})*(0.4 CO + 0.2 CH ₄ + 0.4 CH ₂ O + 0.6 H ₂ O + 0.2 G-CO + 2 G-COH ₂ + 0.4 CH ₄ + 0.4 G-CH ₃ OH + 0.5 C ₂ H ₄ + 6 Char)	0.083	1	33.5
LIG	→	x _{LIG} *(10.5 Char + 3 H ₂ O + 0.5 CO ₂ + 3 H ₂)	0.083	1	33.5
<i>Metaplastic ($x_G = 0.4$)</i>					
G-CO ₂	→	CO ₂	4×10^5	0	100.46
G-CO	→	(1-x _G)*CO + x _G *(0.5 Char + 0.5 CO ₂)	3×10^{13}	0	209.3
G-COH ₂	→	0.75 G2-COH ₂ + 0.25*(H ₂ + 0.5 CO + 0.25 CO ₂ + 0.25 Char)	1×10^6	0	100.46
G-H ₂	→	H ₂	1×10^{12}	0	313.96
G-CH ₄	→	CH ₄	2×10^{13}	0	300.0
G-CH ₃ OH	→	(1-x _G)*CH ₃ OH + x _G *(Char + H ₂ O + H ₂)	1.2×10^{13}	0	209.3
G-C ₂ H ₄	→	0.3 C ₂ H ₄ + 0.7 CH ₄ + 0.7 Char	1×10^6	0	100.46
G2-COH ₂	→	0.2 G3-COH ₂ + 0.8*(H ₂ + CO)	1.5×10^9	0	209.3
Gas Phase Tar Cracking Reactions (T = Pyrolysis Temperature, t = Gas Residence Time)					
Reactions (with $k = 3.08 \times 10^3 \text{ s}^{-1}$, $n = 0$, $E = 66.3 \text{ kJ/mol}$)					
HAA	→	1.5 H ₂ + 1.5 CO + 0.25 CO ₂ + 0.25 CH ₄			
GLYOX	→	H ₂ + 2CO			

C ₃ H ₆ O	→	0.5 CO ₂ + C ₂ H ₄ + 0.5 CH ₄
C ₃ H ₄ O ₂	→	CO ₂ + C ₂ H ₄
HMFU	→	3 CO + 1.5 C ₂ H ₄
pCoumaryl	→	2 CO + 1.5 C ₂ H ₄ + CH ₄ + 3 Char
PHENOL	→	CO + C ₂ H ₄ + 0.5 CH ₄ + 2.5 Char
FE2MACR	→	4 CO + C ₂ H ₄ + 2 CH ₄ + 3 Char
CH ₂ O	→	H ₂ + CO
CH ₃ OH	→	1.5 H ₂ + 0.5 CO + 0.25 CO ₂ + 0.25 CH ₄
CH ₃ CHO	→	CO + CH ₄
ETOH	→	H ₂ + CO + CH ₄
HCOOH	→	H ₂ + CO ₂

Note1 (Solid): CELL – Cellulose; CELLA – Activated cellulose; XYHW – Hardwood hemicellulose; GMSW – Softwood hemicellulose; HCEA1 or HCEA2 – Activated hemicellulose 1 or 2; LIG-C – Carbon rich lignin (Lignin-C); LIG-H – Hydrogen rich lignin (Lignin-H); LIG-O – Oxygen rich lignin (Lignin-O); LIG-CC – Carbon rich lignin 2; LIG-OH – OH rich lignin; LIG – Intermediate lignin; G-X – Trapped substance X; Char – Biochar.

Note2 (Volatiles): HAA – Hydroxyacetaldehyde acid; HCOOH – Formic acid; GLYOX – Glyoxal; C₃H₆O – Acetone; C₃H₄O₂ – Propanedial; HMFU – 5-hydroxymethyl-furfural; pCoumaryl – Paracoumaryl alcohol; PHENOL – Phenol; FE2MACR – Sinapaldehyde; CH₂O – Formaldehyde; ETOH – Ethanol.

2.2 Artificial Neural Network

The integration of machine learning (ML) methods and LCA has been developed in recent years. Nabavi-Pelesaraei et al. integrated artificial neural network (ANN) models with LCA to estimate process energy output and environmental impacts of agricultural processes (e.g., paddy and sugarcane production).^{29,30} However, this type of integration of LCA and ML is still limited by data availability. Therefore in this section, we coupled the ML with the simulation model to provide the required data for LCA, since the availability of the combination of ML and process simulation has been identified by the previous studies.³¹

In the presented study, ANN was used to predict the total yield of the overall steam AC production for different biomass feedstocks. The details of the trained ANN were documented in the authors' previous publication.³² Then the yield of the biochar-to-AC process can be determined using Equation 6 and the biomass-to-biochar yield provided by the kinetic model. In

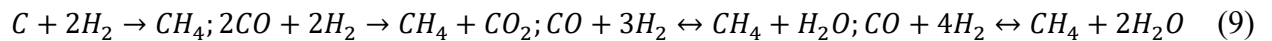
addition, it was assumed that the ash content from the biomass feedstock is retained in the biochar and the AC. Hence, the burn-off rate of organic components in biochar, which is the ratio of mass loss in the activation stage to the ash-free biochar mass, should be calculated by Equation 6.

$$\text{Burn-off} = \left(1 - \frac{\text{Total AC Yield} - \text{Ash Content}}{\text{Pyrolysis Yield} - \text{Ash Content}}\right) \times 100\% \quad (6)$$

The main reaction in the steam activation is shown in Equation 7:



Previous LCA of steam AC production assumed that only steam-carbon reaction exists in the activation process and as a result, the activation flue gas should not contain any CO₂.⁹ However, experimental studies showed significant carbon dioxide content in the activation flue gas, which contradicts with this assumption.^{11,13} One study indicated that different types of reactions may happen in the steam activation process, including water-gas shift reaction (Equation 8), methanation reactions and steam-reforming reactions (Equation 9), and Boudouard reaction (Equation 10).³³ However, the extent of these reactions in the specified temperature and time was hard to determine. Therefore, in this study, the reaction formula developed by Martín-Gullón et al. was used, which covered all products occurred in Equation 8-10.³⁴ Even the aforementioned formula was established by fitting the data from bituminous coal-based AC production, it can be transferred to the biomass-based AC production due to the similar reaction mechanism of steam activation for coal and biochar.³³





2.3 Aspen Plus Simulation

The pyrolysis kinetic model and ANN provide essential data inputs of Aspen Plus process simulation models. Aspen Plus software provides different types of reactor, including RYield, RGibbs, RCSTIR, RStoic and RBatch.³⁵ In this study, RBatch is chosen as it is a common reactor type for pyrolysis simulations.³⁶ The process flowsheet of pyrolysis was shown in Figure S3.

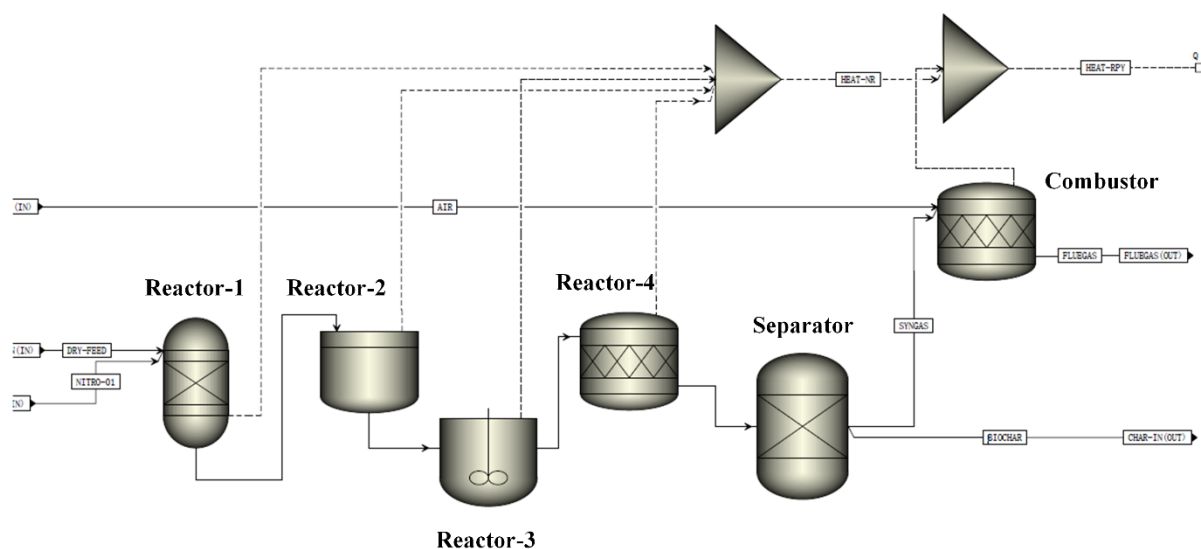


Figure S3 Process Flowsheet of Pyrolysis

The pyrolysis reaction process consists of four continuous sub-reactors. The Reactor-1, which is set as RYield reactor, decomposed the biomass feedstock into model compounds and ash content. Then the primary kinetic reactions mentioned in Table S3 were implemented in the Reactor-2 (RBatch). The Reactor-3 calculated gas-phase tar cracking reactions in Table S3.

Finally, the RStoic Reactor-4 converted the remaining metaplastic components into biochar. After the pyrolysis kinetic reactions, the Separator unit moved the solid components out and the hot volatiles was sent to the Combustor unit. The Combustor unit was set as RStoic, which oxidized all of the combustible components in the syngas with the burn-off rate of 80%. The heat generated from the Combustor unit was recovered to compensate for the energy consumption of Reactor units. The components of output flows from Separator and Combustor were tracked to generate the Life Cycle Inventory (LCI) data.

The assumed reaction provided by Martín-Gullón et al. can be directly simulated by the RStoic reactor in Aspen Plus, thus the process flowsheet of steam activation of biochar can be constructed, which is shown in Figure S4. The steam boiler rises the temperature of water from the room temperature to the desired temperature in order to generate the superheated steam. The Activation Reactor unit was set as the RStoic reactor, which implemented the reaction between water and biochar with the predefined reaction extent. Detailed information of the unit operations presented in Figure S3 and S4 are given in Table S4.

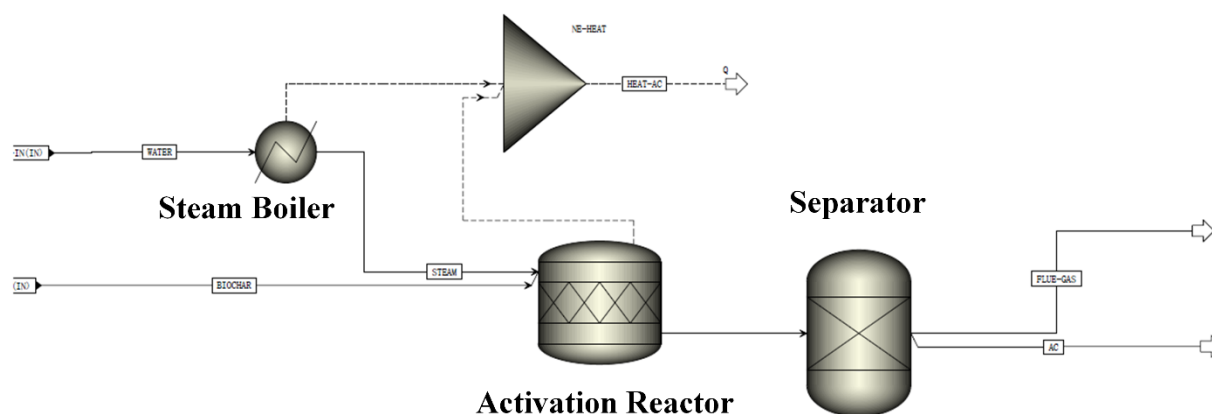


Figure S4 Process Flowsheet of Activation

Table S4 Parameter Settings for Unit Operators in the Aspen Process Simulation

Parameters	Values
<i>Figure S3 – Reactor-1</i>	
Reactor Type	RYield
Temperature ^a	773 K
Pressure	1 atm
Reactions	Conversion of biomass to lignocellulosic components and ash
<i>Figure S3 – Reactor-2</i>	
Reactor Type	RBatch
Temperature ^a	773 K
Pressure	1 atm
Catalyst Loading	0 kg
Reaction time ^b	3600 s
Reactions	Primary kinetic reactions in Table S3
<i>Figure S3 – Reactor-3</i>	
Reactor Type	RCSTR
Temperature ^a	773 K
Pressure	1 atm
Residence Time	2 s
Reactions	Gas phase tar cracking reactions in Table S3
<i>Figure S3 – Reactor-4</i>	
Reactor Type	RStoic
Temperature ^a	773 K
Pressure	1 atm
Reactions	Conversion of trapped substances (see notes in Table S3) to biochar
<i>Figure S4 – Activation Reactor</i>	
Temperature ^c	1073 K
Pressure	1 atm
Reactions	Activation reactions

^a Pyrolysis temperature in Table S2; ^b Pyrolysis time in Table S2; ^c Activation temperature in Table S2.

Note: The values for parameters that are indexed ^{a,b,c} are the default value.

The Aspen Simulation Workbook was used to automatically inputs the results of ANN models into the Aspen Plus simulation. Aspen Simulation Workbook was the plugin in the Microsoft excel which allows running simulations with different input parameters automatically. The thermal efficiencies of reactors and pyrolysis combustion rate can be seen in Table 1 in the manuscript. The combustion rate is set as 80% due to the heavy oil products from slow pyrolysis that is hard to combust. By fitting the characterization of products from slow pyrolysis of beech

at 500°C, around 20% of the non-solid products cannot be identified, which are considered as the heavy oil products.³⁶ Therefore the combustion rate is set as 80% in the present study.

When the simulation is finished, LCI of AC production can be established from the simulation results. An example AC production process material and energy flow chart that is generated from Aspen Plus simulation data is shown in Figure S5, and additional LCI information of the simulation scenarios are summarized in the attached excel file.

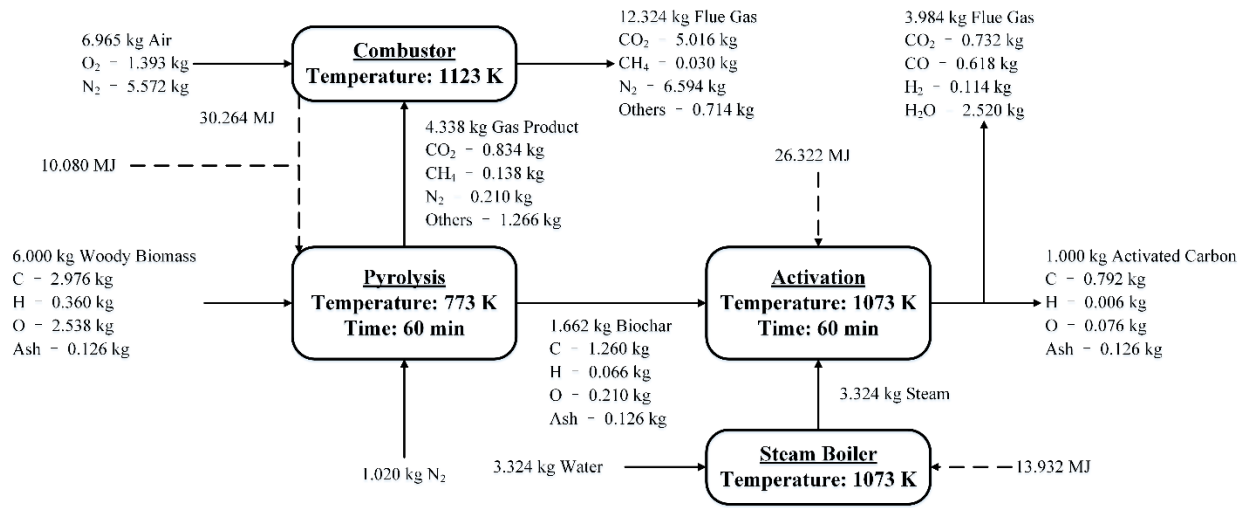


Figure S5 An Example of Material and Energy Flows of AC Production

2.4 Other Assumptions

The thermodynamic properties of the substances were collected from the Aspen Plus databank or the report from National Renewable Energy Laboratory (NREL).^{37,38} The higher heating value (HHV) of solid compounds, a key parameter needed to calculate the DHSFRM parameters for process simulation³⁹, was calculated by Dulong's equation (Equation 11), where m_C , m_H and m_O represent the weight percentage (wt.%) of carbon, hydrogen, and oxygen in the biochar or AC.⁴⁰

$$HHV(MJ / kg) = 0.338m_C + 1.442m_H - 0.182m_O \quad (11)$$

For the HHV of woody biomass, the equation was modified by Demirbaş in order to reflect the effect of considerable nitrogen content in the biomass.⁴¹ The updated equation was shown in Equation 12:

$$HHV(MJ / kg) = 0.335m_C + 1.423m_H - 0.154m_O - 0.145m_N \quad (12)$$

Based on the previous equations, the ultimate analysis data of biochar and AC are needed. The pyrolysis kinetic model generates some metaplastic substances which trap the volatile components into the biochar. Therefore, based on the method developed by Debiagi et al., the carbon, hydrogen and oxygen content of biochar can be determined by normalizing the elemental composition of char (elemental carbon) and trapped substances (containing carbon, hydrogen, and oxygen).²⁸ In this study, the elemental compositions of AC were derived from the biochar by Equation 13-15, whose constants are fitted by the literature data.⁴² All these data are in the dry-ash-free basis.

$$C_{AC} = 1.097 * C_{Biochar} \quad (13)$$

$$H_{AC} = 0.215 * H_{Biochar} \quad (14)$$

$$O_{AC} = 100 - C_{Biochar} - H_{Biochar} \quad (15)$$

With these equations, the produced AC contains higher carbon content and lower hydrogen content, which is consistent with the literature.^{13,42} One limitation is that Equation 13-15 were derived based on activation temperature – 1073K, activation time – 60 min, and steam to biochar ratio – 2 kg/kg. More experimental data are needed if the operational conditions are changed.

Besides, the Aspen Plus software also requires the parameters for the calculation of viscosity, which are categorized as VSPOLY parameters. In the present study, the VSPOLY parameters for

the substances were assumed to be either the default values in Aspen Plus database or from literature data.^{37,38,43}

2.5 Sensitivity Analysis

The sensitivity analysis was conducted in this study using the baseline and upper and lower bounds of parameters as shown in Table S5. For feedstock characteristics, the average value were used as baselines. For the operational conditions, the typical values used in literature were used. The upper and lower bound of biomass characteristics were determined based on the maximum and minimum value of feedstock datasets. The upper bound and lower bound of operational conditions were establish by referencing several literature conditions.^{32,44–47}

Table S5 The baseline and ranges of input parameters used in the sensitivity analysis

	Baseline	Lower Bound	Upper Bound	Ref.
Carbon Content (wt%)	49.59	42.55	55.52	^a
Hydrogen Content (wt%)	6.02	5.05	7.19	^a
Ash Content (wt%)	2.14	0.1	10.62	^a
Pyrolysis Temperature (°C)	500	300	700	44
Pyrolysis Time (min)	60	10	120	32
Activation Temperature (°C)	800	750	900	45
Activation Time (min)	60	45	75	46
Steam to Biochar Ratio (kg/kg)	2	1.35	5.4	47

^a Based on the dataset

3. Woody Biomass Feedstock Characterization Dataset

In this study, large datasets of woody biomass characterization samples were collected from different databases and publications as shown in Table S6. The lignocellulosic components calculated based on ultimate analysis data and the triangle method were also presented in the

same table. There are four different data sources in this study: The biomass feedstock composition and property database from National Renewable Energy Laboratory⁴⁸, the bioenergy feedstock library from Idaho National Laboratory⁴⁹, the Phyllis2 database for biomass and waste from ECN⁵⁰, and other literature references.²⁵ These data were used to create different simulation scenarios in order to understand the impacts of biomass feedstock. All these data are listed in Table S6, which can be useful in replicating the results and becoming the basis of further researches.

Table S6 Woody Biomass Feedstock Characterization Dataset

		Raw Data (dry basis, wt%)					Triangle Method Result (dry basis, wt%)				
Feedstock	Type	C	H	O	N	Ash	CELL	HEMI	LIGC	LIGH	LIGO
Data from National Renewable Energy Laboratory ⁴⁸											
Ailanthus	HW	50.77	6.36	42.05	0.31	0.51	42.87	30.71	6.27	1.22	18.43
Pistachio	HW	48.79	5.91	43.41	0.56	1.28	45.08	32.04	2.44	0.49	18.66
White Ash	HW	49.75	6.91	43.04	0.00	0.30	45.22	32.06	2.88	0.54	19.00
Manzanita	HW	48.27	5.95	44.77	0.17	0.82	47.03	33.28	0.66	0.20	18.02
Robinia	HW	50.86	5.72	42.04	0.57	0.80	42.07	29.63	7.90	1.20	18.40
Teak	HW	51.60	6.00	40.04	0.26	2.10	39.62	26.58	14.33	1.21	16.17
Almond	HW	48.31	6.00	42.73	0.68	2.24	48.56	32.37	2.23	0.00	14.59
Oak	HW	49.83	6.23	42.99	0.13	0.82	44.42	29.57	4.67	0.27	20.25
Almond	HW	47.12	5.97	40.07	1.19	5.55	43.14	28.23	0.06	11.70	11.30
Cherry tree	HW	50.03	5.87	42.41	0.31	1.36	43.32	27.94	6.93	0.25	20.19
Mixed	HW	49.09	5.93	42.49	0.33	2.10	44.23	27.89	5.32	0.09	20.38
Prune	HW	50.35	6.69	39.66	1.30	1.90	41.51	25.40	12.58	0.24	18.36
Spruce	SW	49.60	5.63	40.81	0.20	3.66	39.85	23.64	0.13	9.52	23.20
Eucalyptus	HW	48.20	5.30	42.20	0.00	4.30	44.03	26.11	5.83	0.00	19.73
Mixed	SW	50.30	5.80	40.65	0.42	2.80	37.87	21.77	0.18	6.82	30.57
Oak	HW	50.93	5.96	41.46	0.20	1.30	43.32	24.58	12.29	0.02	18.49
Spruce	SW	50.05	5.63	42.65	0.10	1.48	45.85	26.00	1.77	21.10	3.79
Olive	HW	51.38	6.32	40.02	0.45	1.69	39.01	22.06	4.29	31.71	1.25
Spruce	SW	50.90	6.40	42.00	0.00	0.70	44.95	25.07	2.99	21.57	4.72
Cedar	SW	48.80	6.40	44.40	0.00	0.40	53.77	29.55	0.00	11.95	4.33
Maple	HW	49.54	6.00	43.84	0.10	0.50	50.18	27.46	0.58	14.59	6.69
Larch	SW	50.67	6.38	42.51	0.00	0.45	46.46	25.18	2.99	17.77	7.16
Pine	SW	52.13	6.36	41.01	0.07	0.37	41.57	22.45	7.55	24.55	3.51
Douglas Fir	SW	52.30	6.30	40.32	0.10	0.98	39.97	21.35	9.67	26.08	1.94

Pine	SW	48.40	6.31	44.23	0.21	0.82	53.57	28.61	0.00	10.41	6.58
Olive	HW	45.15	5.63	37.56	1.55	10.01	41.45	22.09	3.66	15.70	7.10
Cotton	HW	48.48	6.12	41.48	0.97	2.85	46.80	24.91	2.14	14.66	8.64
Cotton	HW	48.48	6.12	41.48	0.97	2.85	46.80	24.91	2.14	14.66	8.64
Olive	HW	48.71	6.18	42.16	0.52	2.39	47.91	25.49	1.49	13.85	8.86
Pine	SW	50.10	6.00	38.17	0.10	5.63	37.33	19.84	10.39	26.02	0.80
Spruce	SW	48.82	5.84	42.44	0.17	2.73	47.44	24.95	1.85	13.46	9.57
Babassu	HW	50.38	5.38	42.35	0.26	1.59	44.75	23.44	5.31	16.83	8.08
Almond	HW	47.15	5.91	40.04	1.20	5.61	44.92	23.51	2.88	13.86	9.23
Cocoa	HW	46.31	5.57	36.12	3.21	8.60	38.30	19.99	9.70	20.21	3.20
Mulberry	HW	49.84	6.14	41.00	0.42	2.60	44.22	23.04	5.58	16.44	8.12
Ailanthus	HW	49.50	6.20	42.30	0.30	1.70	47.22	24.56	2.68	13.66	10.17
Birch	SW	48.74	6.26	44.09	0.19	0.54	52.28	26.98	0.00	9.83	10.38
Pine	SW	51.99	6.28	41.16	0.14	0.41	42.94	22.14	9.86	19.35	5.30
Olive	HW	50.77	5.90	37.07	1.36	4.61	34.30	17.53	13.78	29.78	0.00
Olive	HW	50.18	6.85	37.78	1.11	4.00	40.10	20.46	12.93	20.35	2.16
Willow	HW	49.29	5.98	42.72	0.57	1.38	48.03	24.39	2.42	11.89	11.89
Poplar	HW	50.19	6.06	40.43	0.60	2.70	43.33	21.81	8.95	15.67	7.54
Willow	HW	48.50	6.12	43.00	0.50	1.86	49.67	24.92	0.75	9.79	13.01
Douglas Fir	SW	50.63	6.23	42.54	0.12	0.47	46.78	23.38	5.02	12.79	11.56
Pine	SW	51.85	6.21	41.23	0.13	0.42	43.85	21.83	11.22	16.22	6.46
Pine	SW	51.48	6.16	41.14	0.16	0.97	43.97	21.75	10.86	15.29	7.16
Pistachio	HW	49.55	6.12	42.32	0.62	1.27	47.45	23.43	3.73	11.16	12.96
Peach	HW	51.21	6.14	41.14	0.40	1.07	44.27	21.78	10.43	14.56	7.89
Unidentified	SW	52.10	6.10	39.90	0.20	1.70	42.04	20.59	16.97	17.48	1.22
Cedar	SW	52.74	6.14	39.98	0.10	1.03	41.92	20.42	18.59	18.04	0.00
Almond	HW	48.60	5.70	37.51	0.62	7.46	40.05	19.49	15.30	15.39	2.31
Walnut	HW	51.00	6.04	40.31	0.78	1.78	43.46	21.13	13.01	14.68	5.94
Poplar	HW	49.93	6.10	42.26	0.29	1.36	46.94	22.76	4.97	10.80	13.18
Poplar	HW	47.67	6.15	45.29	0.20	0.68	56.36	27.22	0.00	5.04	10.70
Camphor	HW	50.30	6.10	42.50	0.10	0.80	47.24	22.38	5.72	9.90	13.96
Willow	HW	48.98	5.99	42.09	0.65	2.24	47.46	22.47	3.90	8.97	14.96
Palm	HW	47.28	6.25	38.82	2.83	4.59	41.83	33.02	3.91	2.92	13.73
Unidentified	HW	47.10	5.52	36.92	0.43	9.94	40.16	18.97	14.36	12.11	4.45
Fir	SW	50.35	6.14	43.18	0.05	0.28	48.30	22.74	4.32	9.02	15.35
Peanut	HW	45.77	5.46	39.56	1.63	7.46	45.05	21.20	3.60	8.17	14.52
Beech	SW	48.37	6.10	44.51	0.34	0.65	53.12	24.94	0.00	5.77	15.52
Spruce	SW	50.17	5.94	40.44	0.42	3.01	44.29	20.78	11.70	11.30	8.91
Eucalyptus	HW	50.43	6.01	41.53	0.17	1.76	45.85	21.24	9.33	9.87	11.95
Eucalyptus	HW	50.50	6.02	41.59	0.27	1.58	45.95	21.28	9.33	9.86	12.00
Maple	HW	50.64	6.02	41.74	0.25	1.35	46.16	21.25	9.44	9.58	12.23

Olive	HW	52.70	5.90	38.04	1.05	2.06	38.29	17.50	23.43	18.72	0.00
Oak	HW	48.82	6.06	44.17	0.15	0.78	51.25	23.37	0.04	5.80	18.75
Maple	HW	50.60	6.00	41.70	0.30	1.40	46.27	21.04	9.84	9.04	12.40
Walnut	HW	53.66	6.50	36.04	1.34	2.36	37.83	29.83	14.76	12.40	2.81
Unidentified	HW	50.48	6.04	42.43	0.17	0.78	47.34	21.51	7.31	8.35	14.71
Birch	SW	49.85	6.72	42.54	0.10	0.29	49.02	22.25	3.82	7.23	17.38
Kenaf (italy)	HW	46.60	5.80	42.62	1.00	3.67	50.74	23.00	0.00	4.97	17.62
Tan Oak	HW	48.50	6.08	44.98	0.05	0.35	53.86	24.40	0.00	4.49	16.90
Pine	SW	52.55	6.08	41.25	0.00	0.12	45.59	20.65	17.77	10.70	5.17
Oak	HW	48.78	6.09	44.98	0.00	0.15	53.41	24.19	0.00	4.75	17.50
Palm	HW	48.11	6.64	36.79	2.81	5.50	43.19	19.55	16.44	10.02	5.30
Peanut	HW	46.97	5.64	40.11	1.85	5.25	45.93	20.74	5.27	7.18	15.63
Spruce	SW	49.53	6.06	43.92	0.11	0.37	50.23	22.65	1.73	6.22	18.80
Birch	SW	48.89	6.04	44.43	0.22	0.35	51.81	23.19	0.00	5.12	19.53
Spruce	SW	50.20	5.90	41.14	0.20	2.56	45.79	20.46	11.01	8.34	11.84
Oak	HW	49.89	5.98	42.57	0.21	1.29	47.89	21.37	5.83	7.10	16.52
Mixed	HW	50.00	5.97	42.80	0.21	0.95	48.18	21.49	5.53	7.01	16.84
Casuarina	HW	48.59	5.94	43.37	0.45	1.62	50.00	22.14	1.30	5.38	19.56
Grape	HW	47.57	5.85	43.14	0.81	2.61	50.42	22.31	0.03	4.80	19.84
Spruce	SW	48.46	5.84	44.88	0.21	0.60	53.12	23.48	0.00	4.12	18.68
Cocoa	HW	49.21	5.34	33.87	3.04	8.42	31.42	13.87	23.88	22.41	0.00
Cocoa	HW	48.23	5.23	33.19	2.98	10.25	30.79	13.60	23.40	21.96	0.00
Oak	HW	49.74	5.96	42.56	0.23	1.47	48.04	21.17	5.67	6.54	17.11
Spruce	SW	48.39	5.55	41.67	0.10	4.19	46.73	20.59	5.47	6.35	16.67
Oak	HW	49.90	5.97	42.88	0.36	0.88	48.49	21.37	5.25	6.46	17.55
Fir	SW	49.00	5.98	43.91	0.05	1.04	50.52	22.22	1.03	5.11	20.07
Coconut	HW	50.29	5.05	39.63	0.45	4.14	36.26	15.91	5.79	0.27	37.62
Hazelnut	HW	51.00	5.40	40.50	1.30	1.80	31.13	13.66	7.08	0.32	46.01
Walnut	HW	53.52	6.52	35.37	1.53	2.95	34.14	14.98	6.18	40.81	0.94
Cypress	SW	54.98	6.54	38.08	0.00	0.40	33.42	14.66	6.65	42.56	2.31
Olive	HW	50.18	6.30	32.09	1.40	9.90	34.98	15.35	5.13	33.77	0.88
Grape	HW	54.01	6.83	35.00	1.46	2.50	39.85	17.48	5.18	34.95	0.04
Walnut	HW	47.86	5.75	34.60	1.07	10.62	32.77	14.38	5.44	36.56	0.23
Spruce	SW	51.10	5.50	42.30	0.10	1.00	38.88	17.06	5.71	0.23	37.12
Olive	HW	51.25	6.29	36.46	1.10	4.70	37.75	16.56	5.29	34.40	1.30
Almond	HW	48.55	5.33	40.74	0.81	4.50	37.73	16.55	5.46	0.19	35.56
Almond	HW	48.43	5.98	39.90	0.94	4.71	43.29	18.99	4.38	0.22	28.42
Grape	HW	45.72	5.05	38.95	1.07	9.13	38.46	16.87	4.71	0.24	30.58
Olive	HW	50.00	6.50	36.30	0.80	6.30	47.16	20.69	3.33	21.78	0.74
Peach	HW	53.15	7.19	35.86	0.60	3.20	55.60	24.39	2.17	14.59	0.06
Cherry	HW	53.41	7.04	38.05	0.30	0.90	52.35	22.97	3.07	20.07	0.64

Grape	HW	49.73	6.67	35.41	1.83	6.24	53.21	23.34	2.22	14.90	0.09
Pine	SW	52.60	7.02	40.07	0.00	0.31	56.99	25.00	2.28	15.31	0.11
Unidentified	SW	50.96	6.86	38.49	0.19	3.11	57.02	25.02	1.91	12.87	0.06
Olive	HW	49.85	6.59	39.06	0.70	3.40	54.14	23.75	2.41	15.91	0.39
Oak	HW	49.16	6.46	40.16	1.64	2.55	54.75	24.02	2.41	15.95	0.33
Elm	HW	50.35	6.57	42.34	0.00	0.74	55.07	24.16	2.58	17.45	0.00
Elm	HW	50.40	6.60	42.30	0.00	0.70	55.76	24.46	2.46	16.54	0.08
Oak	HW	50.44	6.59	42.73	0.00	0.24	55.91	24.53	2.49	16.29	0.54
Coconut	HW	50.64	5.09	39.91	0.45	3.75	40.33	31.54	8.13	5.05	11.21
Mixed	HW	50.09	5.94	42.30	0.26	1.31	47.63	20.87	7.48	6.76	15.95
Pistachio	HW	48.85	6.29	42.86	0.50	1.30	49.72	21.75	2.22	5.32	19.68
Poplar	HW	50.84	5.89	41.06	0.59	1.60	46.24	20.18	14.22	7.81	9.95
Peach	HW	53.00	5.90	39.14	0.32	1.59	42.36	18.43	25.69	11.93	0.00
Olive	HW	47.73	5.86	43.60	0.58	2.23	51.25	22.25	0.00	4.05	20.22
Fir	SW	51.36	5.99	42.20	0.06	0.36	47.35	20.52	11.79	7.17	12.82
Spruce	SW	50.25	5.99	43.36	0.10	0.30	49.09	21.24	5.11	5.77	18.49
Unidentified	SW	50.00	6.00	43.60	0.00	0.30	49.57	21.43	3.89	5.45	19.35
Almond	HW	48.04	5.79	42.32	0.72	3.06	48.66	21.04	2.75	5.03	19.47
Fir	SW	49.84	5.99	43.60	0.18	0.38	49.67	21.48	3.57	5.36	19.55
Eucalyptus	HW	48.29	5.93	44.28	0.39	1.10	52.18	22.53	0.00	3.81	20.37
Cotton	HW	44.88	5.54	41.57	1.04	6.66	50.16	21.64	0.00	3.20	18.34
Beech	SW	49.69	6.07	42.80	0.41	1.01	48.86	21.01	4.97	5.50	18.65
Peanut	HW	46.50	5.55	40.19	1.66	5.98	46.40	19.96	4.72	5.22	17.71
Prune	HW	49.47	6.25	42.67	0.58	0.96	49.13	21.12	4.31	5.33	19.15
Mixed	SW	49.73	5.95	43.40	0.22	0.67	49.45	21.25	3.89	5.23	19.50
Pine	SW	49.45	5.95	43.59	0.30	0.61	49.96	21.47	2.80	4.94	20.22
Madrone	HW	48.56	6.02	44.99	0.05	0.36	53.64	23.00	0.00	3.24	19.76
Unidentified	HW	50.52	5.80	40.35	0.40	2.86	45.80	19.63	16.51	7.19	8.01
Pine	SW	52.30	5.80	38.76	0.20	2.90	42.61	18.20	26.03	10.25	0.00
Sequoia	SW	52.30	5.90	40.30	0.20	1.30	46.45	19.82	24.01	7.72	0.71
Mixed	HW	50.49	5.95	42.83	0.16	0.54	48.47	20.61	7.60	5.65	17.14
Mixed	HW	50.48	5.94	42.80	0.16	0.54	48.46	20.59	7.66	5.63	17.11
Pine	SW	52.19	5.67	37.37	0.41	4.30	39.21	16.47	27.77	12.25	0.00
Sequoia	SW	50.67	5.98	42.91	0.05	0.36	48.68	20.44	7.95	5.26	17.32
Fir	SW	50.55	5.82	41.22	0.10	2.21	46.89	19.60	13.84	5.81	11.66
Poplar	HW	48.51	5.88	44.29	0.29	1.00	51.75	21.53	0.00	3.17	22.54
Eucalyptus	HW	48.50	5.89	44.43	0.28	0.75	52.22	21.72	0.00	3.05	22.26
Ecoblock	HW	51.48	5.92	42.03	0.14	0.43	47.87	19.88	14.08	5.66	12.08
Oak	HW	49.47	5.73	44.03	0.45	0.26	50.58	20.94	2.69	3.83	21.69
Coconut	HW	51.27	5.88	41.78	0.23	0.65	47.84	19.75	14.52	5.47	11.78
Fir	SW	50.40	5.80	41.40	0.10	2.20	47.23	19.49	12.96	5.22	12.90

Sequoia	SW	53.50	5.90	40.15	0.10	0.30	45.78	18.84	27.56	7.52	0.00
Eucalyptus	HW	49.04	5.88	44.01	0.30	0.76	50.95	20.95	1.48	3.35	22.51
Hazelnut	HW	47.79	5.78	43.79	0.76	1.43	51.86	21.31	0.00	2.77	22.64
Sequoia	SW	53.50	5.90	40.30	0.10	0.20	46.29	18.93	27.60	6.98	0.00
Eucalyptus	HW	48.32	5.89	45.12	0.15	0.52	54.18	22.10	0.00	1.97	21.24
Oak	HW	49.50	5.70	41.30	0.20	3.30	47.29	19.14	10.81	4.27	15.19
Cherry tree	HW	49.52	5.81	42.97	0.31	1.35	49.36	19.95	5.46	3.62	20.26
Unidentified	HW	49.00	6.00	44.60	0.00	0.30	52.14	20.90	0.10	2.42	24.14
Robinia	HW	48.73	5.66	41.71	1.00	2.90	48.28	19.28	7.36	3.49	18.68
Walnut	HW	49.86	5.83	43.30	0.22	0.78	49.80	19.88	5.57	3.30	20.68
Walnut	HW	49.80	5.82	43.25	0.22	0.85	49.76	19.87	5.56	3.29	20.66
Oak	HW	47.81	5.93	44.12	0.12	2.00	52.61	20.95	0.00	1.76	22.69
Fir	SW	48.52	5.81	44.66	0.25	0.72	52.72	20.73	0.00	1.75	24.08
Apricot	HW	51.39	6.29	41.82	0.20	0.20	49.07	19.26	14.29	3.65	13.53
Palm	HW	47.98	5.26	36.61	1.17	8.81	44.16	17.28	25.77	3.98	0.00
Olive	HW	49.20	5.40	37.90	0.70	6.60	46.06	17.90	25.99	3.45	0.00
Almond	HW	46.49	5.44	41.22	0.97	5.87	48.24	18.65	3.24	2.06	21.95
Spruce	SW	49.53	5.77	44.01	0.19	0.48	51.27	19.44	3.36	1.72	23.73
Vine	HW	48.15	5.61	42.84	0.81	2.59	50.23	19.05	3.14	1.67	23.33
Almond	HW	50.30	5.62	41.71	0.64	1.72	49.04	18.54	13.77	2.44	14.49
Almond	HW	48.85	5.51	40.94	0.80	3.90	48.30	18.01	11.73	1.95	16.10
Hazelnut	HW	52.90	5.60	38.70	1.40	1.40	45.44	16.82	32.09	4.25	0.00
Walnut	HW	49.98	5.71	43.35	0.21	0.71	50.68	18.75	6.85	1.50	21.51
Oak	HW	49.67	5.93	44.02	0.07	0.30	51.67	19.10	3.49	1.18	24.27
Spruce	SW	51.06	5.75	42.29	0.11	0.77	50.10	18.34	14.40	1.61	14.79
Cotton	HW	45.97	5.35	41.99	0.84	5.48	50.16	18.05	0.74	0.32	25.25
Oak	HW	49.76	5.40	39.29	0.15	5.30	48.48	17.44	23.89	1.00	3.89
Cherry tree	HW	46.93	5.97	39.29	1.11	6.63	47.74	17.12	9.47	0.92	18.12
Walnut	HW	49.74	5.63	43.16	0.37	1.08	50.93	18.25	7.25	0.81	21.69
Walnut	HW	49.72	5.63	43.14	0.37	1.07	50.94	18.25	7.25	0.81	21.69
Oak	HW	48.99	5.93	42.58	0.33	2.10	44.20	34.00	2.53	1.64	15.53
Kukui	HW	55.12	5.54	37.55	0.34	1.43	40.61	13.94	38.54	5.48	0.00
Leucaena	HW	47.89	5.84	43.29	0.41	2.50	50.29	21.72	0.43	4.30	20.78
Hickory	HW	49.70	6.50	43.10	0.00	0.70	45.14	34.61	2.22	1.47	15.86
Willow	HW	49.25	5.99	42.66	0.60	1.40	44.20	33.11	3.07	1.29	16.93
Maple	HW	49.88	6.09	43.26	0.14	0.60	44.59	33.22	3.09	1.21	17.30
Pine	SW	50.22	6.17	43.17	0.16	0.26	44.41	32.89	3.59	1.23	17.62
<i>Data from Idaho National Laboratory⁴⁹</i>											
Eucalyptus	HW	50.87	5.70	41.99	0.22	1.22	39.80	11.90	8.86	7.52	30.16
Hybrid Poplar	HW	49.95	6.12	41.98	0.31	1.64	52.24	15.87	8.08	22.16	0.00
Juniper	SW	52.67	6.08	37.83	0.55	2.87	34.79	8.91	7.77	45.66	0.00

Lodge Pole Pine	SW	50.25	6.54	41.70	0.14	1.36	52.47	7.51	0.00	38.66	0.00
Pine	SW	50.80	6.22	41.01	0.54	1.43	45.25	9.89	0.00	43.43	0.00
Pinyon Juniper	SW	50.98	5.89	38.61	0.27	4.25	34.44	11.94	6.98	39.19	3.16
Pinyon Pine	SW	52.62	6.27	38.69	0.55	1.87	37.79	8.96	2.85	48.53	0.00
Shrub Willow	HW	49.20	6.09	42.71	0.31	1.69	46.79	16.97	0.10	32.60	1.81
<i>Data from Phyllis2⁵⁰</i>											
Bamboo	HW	48.04	6.11	42.57	0.58	2.70	47.46	21.89	0.20	27.74	0.00
Bamboo	HW	44.16	5.64	44.08	0.75	5.37	45.78	20.01	0.00	11.13	17.70
Bamboo Sawdust	HW	46.06	5.75	46.18	0.19	1.83	43.37	28.03	0.00	1.90	24.86
Pine Wood	SW	48.23	6.30	43.75	0.13	1.59	45.15	39.36	2.92	10.97	0.00
Douglas Fir Wood	SW	49.95	6.31	42.80	0.17	0.77	56.93	14.03	3.77	24.49	0.00
Pyrenean Oak Wood	HW	48.87	6.37	38.01	2.70	4.05	49.79	12.31	0.20	33.65	0.00
Pyrenean Oak Wood	HW	48.71	6.53	39.25	2.51	3.00	51.44	17.21	0.00	28.35	0.00
<i>Literature Data</i> ^{41,51,60-69,52,70-79,53,80-86,54-59}											
Olive Branch	HW	48.77	6.08	40.59	1.06	3.50	34.67	24.02	0.00	37.81	0.00
Kiwi Branch	HW	49.01	5.59	42.42	0.78	2.20	32.98	34.24	14.30	0.00	16.27
Pine Bark	SW	51.00	5.19	42.02	0.69	1.10	32.81	14.46	12.69	0.00	38.94
Almond Tree Pruning	HW	50.63	6.42	40.82	0.79	1.34	42.19	25.17	2.88	28.42	0.00
Softwood bark	SW	51.87	5.85	39.39	0.39	2.50	22.40	22.28	7.13	31.92	13.52
Hardwood rich in fibres	HW	49.00	5.89	43.01	0.29	1.80	43.27	30.00	14.31	7.78	2.79
Softwood	SW	51.67	6.05	40.67	0.20	1.41	45.98	24.50	17.22	10.89	0.00
Hardwood	HW	49.11	6.27	41.53	0.39	2.70	44.79	31.01	4.48	17.02	0.00
Wood Bark	SW	52.25	6.00	39.95	0.19	1.60	24.80	29.80	13.60	30.20	0.00
Spruce Wood	SW	51.54	6.06	40.61	0.29	1.50	50.29	20.99	16.70	10.52	0.00
Beech Wood	HW	50.67	6.35	42.17	0.41	0.40	45.84	31.83	6.93	14.99	0.00
Beech Wood	HW	46.90	6.20	45.90	0.30	0.70	50.53	24.83	0.00	21.26	2.69
Spruce Wood	SW	48.30	6.30	44.60	0.40	0.40	47.59	22.89	0.00	29.12	0.00
Wood Chips	SW	46.17	5.87	47.39	0.08	0.48	38.31	38.31	0.00	2.47	20.42
Jatropha De-oiled Cake	SW	56.78	7.06	29.10	5.56	1.51	55.47	17.21	8.38	17.43	0.00
Willow	HW	49.55	6.45	39.62	2.68	1.70	57.90	16.91	3.53	19.96	0.00
Silver Fir	SW	50.96	6.37	42.00	0.20	0.47	53.46	15.39	5.07	25.61	0.00
Holm Oak	HW	46.78	5.75	44.44	0.49	2.54	40.32	27.56	0.00	8.14	21.43
Stone Pine	SW	50.01	5.95	42.96	0.30	0.78	44.08	21.61	9.38	15.06	8.93
Pyrenean Oak	HW	47.19	5.74	43.88	0.49	2.70	36.41	27.39	0.00	11.14	22.37
Bonbogori	HW	54.05	6.00	38.37	0.22	1.36	62.94	10.66	23.51	1.53	0.00
Moj	HW	51.35	6.09	40.58	0.30	1.68	63.48	7.56	15.55	11.73	0.00
Woody Waste	SW	48.09	6.68	44.80	0.10	0.33	41.42	31.96	0.00	26.29	0.00
Waste Square Timber	SW	46.94	6.56	45.85	0.10	0.55	44.17	24.26	0.00	31.03	0.00

Plywood	SW	42.55	5.81	43.68	1.69	6.27	40.77	24.58	0.00	21.37	7.01
Spruce Wood	SW	49.03	6.13	44.55	0.08	0.21	48.78	13.74	0.00	25.85	11.42
Pine	SW	48.55	5.76	44.37	0.02	1.30	48.15	22.20	9.04	0.00	19.31
Birch	HW	47.00	6.19	46.50	0.11	0.20	39.92	38.92	0.00	17.51	3.45
Spruce	SW	47.37	6.30	46.17	0.07	0.10	43.96	26.97	0.00	24.99	3.98
Pine	SW	46.87	6.30	46.67	0.07	0.10	42.96	26.97	0.00	24.03	5.94
Pine	SW	48.33	5.88	43.23	0.49	2.07	46.81	17.33	1.11	18.34	14.09
Beech	SW	49.73	6.29	43.04	0.40	0.53	46.15	31.53	5.39	16.39	0.00
Pinewood Sawdust	SW	49.19	6.10	44.08	0.08	0.56	53.70	21.88	8.82	15.05	0.00
Spruce	SW	48.76	6.23	44.60	0.15	0.26	49.38	22.66	0.00	27.71	0.00
Salix	HW	47.23	5.94	44.65	1.03	1.16	49.98	23.20	0.00	15.07	10.58
Poplar - Sapwood	HW	51.47	6.13	42.20	0.00	0.20	48.82	17.30	13.06	20.62	0.00
Poplar - Heartwood	HW	51.21	6.51	42.16	0.00	0.12	50.91	13.79	0.10	35.08	0.00
Norway Spruce	SW	50.28	6.20	43.19	0.10	0.23	42.33	26.20	4.86	26.38	0.00
Spruce Bark	SW	46.39	6.21	42.16	0.00	5.24	41.89	26.93	0.00	25.93	0.00
Eucalyptus Sawdust	HW	49.35	5.72	43.90	0.17	0.86	42.31	30.89	13.37	0.00	12.56
Pine	SW	49.33	6.39	43.44	0.20	0.63	38.77	24.21	0.00	36.38	0.00
Hybrid Poplar	HW	50.05	5.91	42.54	0.30	1.20	50.34	21.04	19.11	6.17	2.11
Subabul Wood	HW	48.16	5.89	45.06	0.00	0.89	44.57	26.88	2.51	7.00	17.83
Pine Chip	SW	47.19	6.64	45.74	0.17	0.27	53.87	16.85	0.00	29.01	0.00
Logging Residue Chip	SW	46.87	6.15	44.79	0.42	1.77	47.89	16.94	0.00	26.79	6.62
Fir Wood	SW	48.30	5.92	41.87	0.42	3.49	39.86	31.47	9.13	16.05	0.00
Pine Bark	SW	51.25	5.37	40.55	0.01	2.82	15.60	44.39	18.30	0.00	18.89
Bambusa vulgaris	HW	46.01	6.24	45.63	0.18	1.95	46.50	24.08	0.00	24.75	2.72
Bambusa vulgaris	HW	46.37	6.33	45.70	0.18	1.43	47.26	24.65	0.00	26.66	0.00
Bambusa vulgaris	HW	45.35	6.19	45.79	0.26	2.40	46.49	24.98	0.00	22.47	3.66
Lauan	HW	48.64	6.75	44.24	0.10	0.27	40.38	15.70	0.00	43.65	0.00
Patula Pine	SW	55.52	7.12	36.85	0.19	0.32	48.79	9.21	4.90	36.78	0.00

Note: db – dry basis; C – Carbon content; H – Hydrogen content; O – Oxygen content; N – Nitrogen content; Ash – Ash content; CELL – Cellulose content; HEMI – Hemicellulose content; LIGC – Lignin-C content; LIGH – Lignin-H content; LIGO – Lignin-O content.

4. Additional Results

4.1 Correlations between Simulation Results and Biomass Feedstock Properties

The correlations between different biomass characteristics and other indicators for AC production energy and carbon footprints are summarized in Figure S6-9. The biomass characteristics used in Figure S6-9 include the main elements of biomass ultimate analysis (Carbon, hydrogen and oxygen content), lignocellulosic components (cellulose, hemicellulose and lignin content), ash content and two other indicators derived from ultimate analysis (Hydrogen to carbon ratio (H/C) and oxygen to carbon ratio (O/C)). The value of all these variables can be found or deduced from the data given in Table S6. The indicators for Figure S6-9 are biogenic GHG emission, total GHG emission, primary energy demand and energy recovery ratio (ERR), respectively.

Besides the main insights that are concluded in the article, some additional findings can be summarized from Figure S6-9 with the given R-value (correlation coefficient) of each plot. Overall the correlation between most of the biomass characterization data and the proposed indicators are weak (with R-value < 0.2), except the hydrogen content, H/C ratio and ash content. In addition, the ash content is negatively correlated to all the proposed indicators, which is because ash has no reactions in the AC production process and retained in final AC production. However, the high ash content may reduce the quality of AC in some specific applications (e.g., adsorbent, supercapacitor).

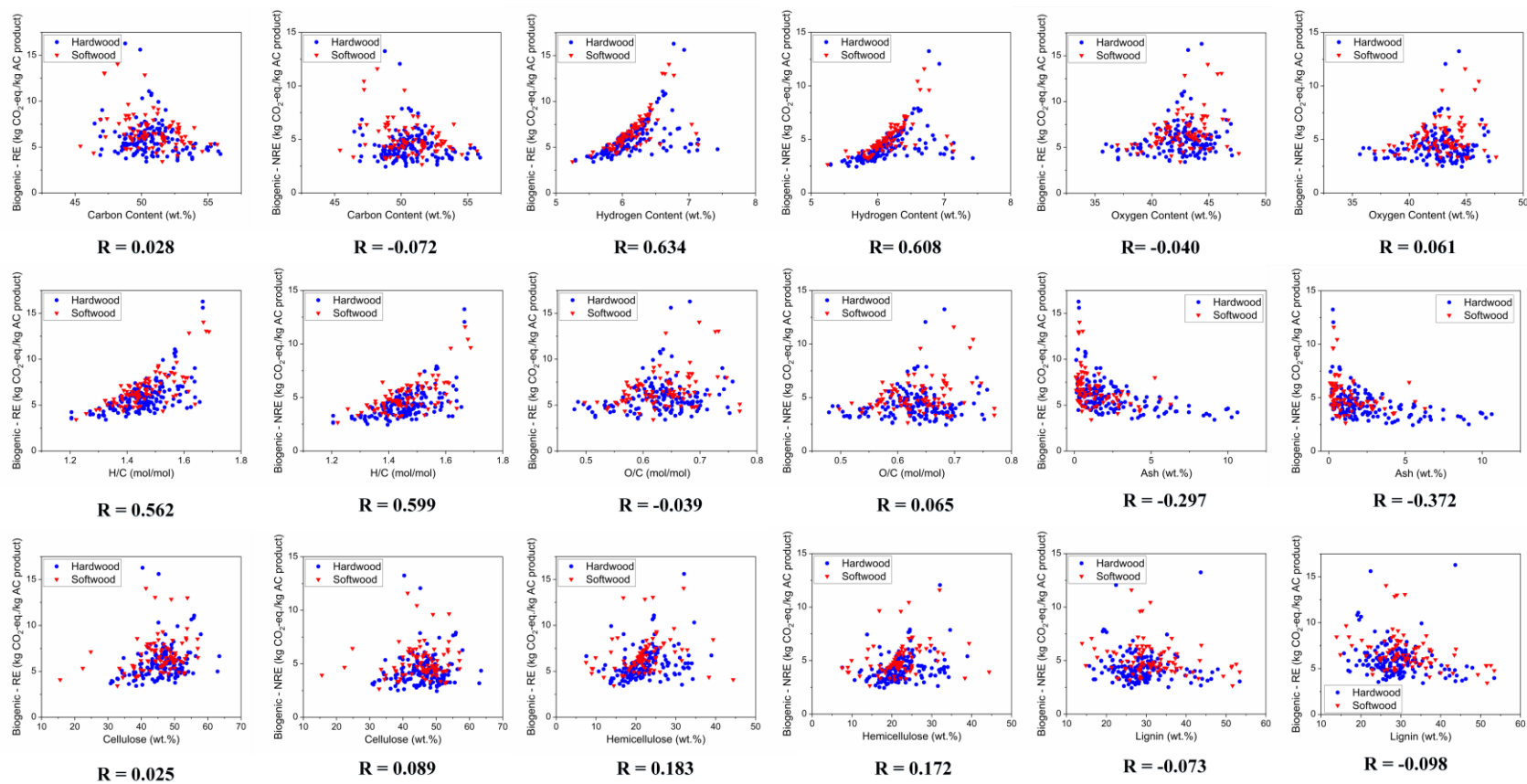


Figure S6 Correlations between the Biogenic GHG Emission of Steam AC Production and Feedstock Composition (RE: Process with Energy Recovery; NRE: Process without Energy Recovery)

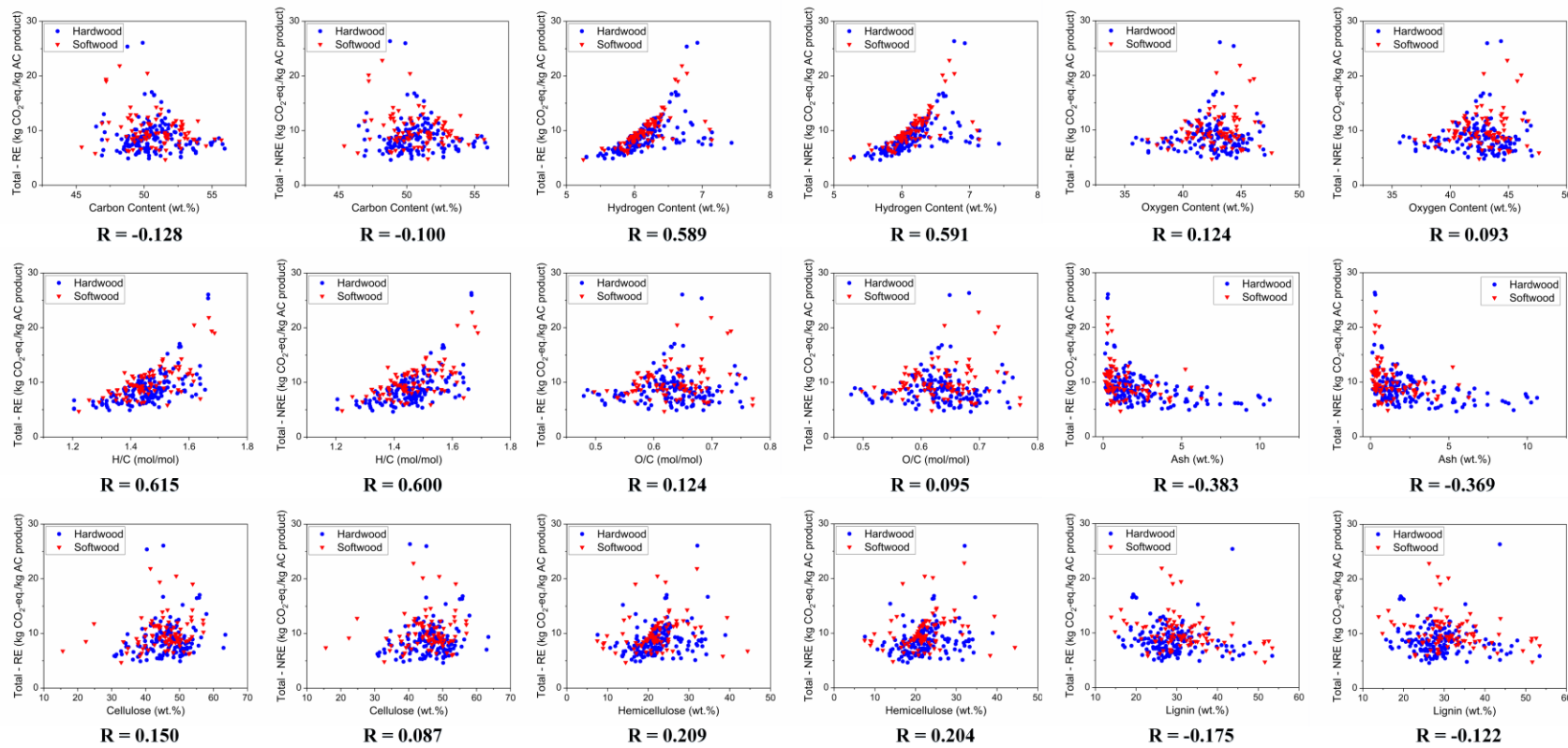


Figure S7 Correlations between the Total GHG Emission of Steam AC Production and Biomass Feedstock Composition (RE: Process with Energy Recovery; NRE: Process without Energy Recovery)

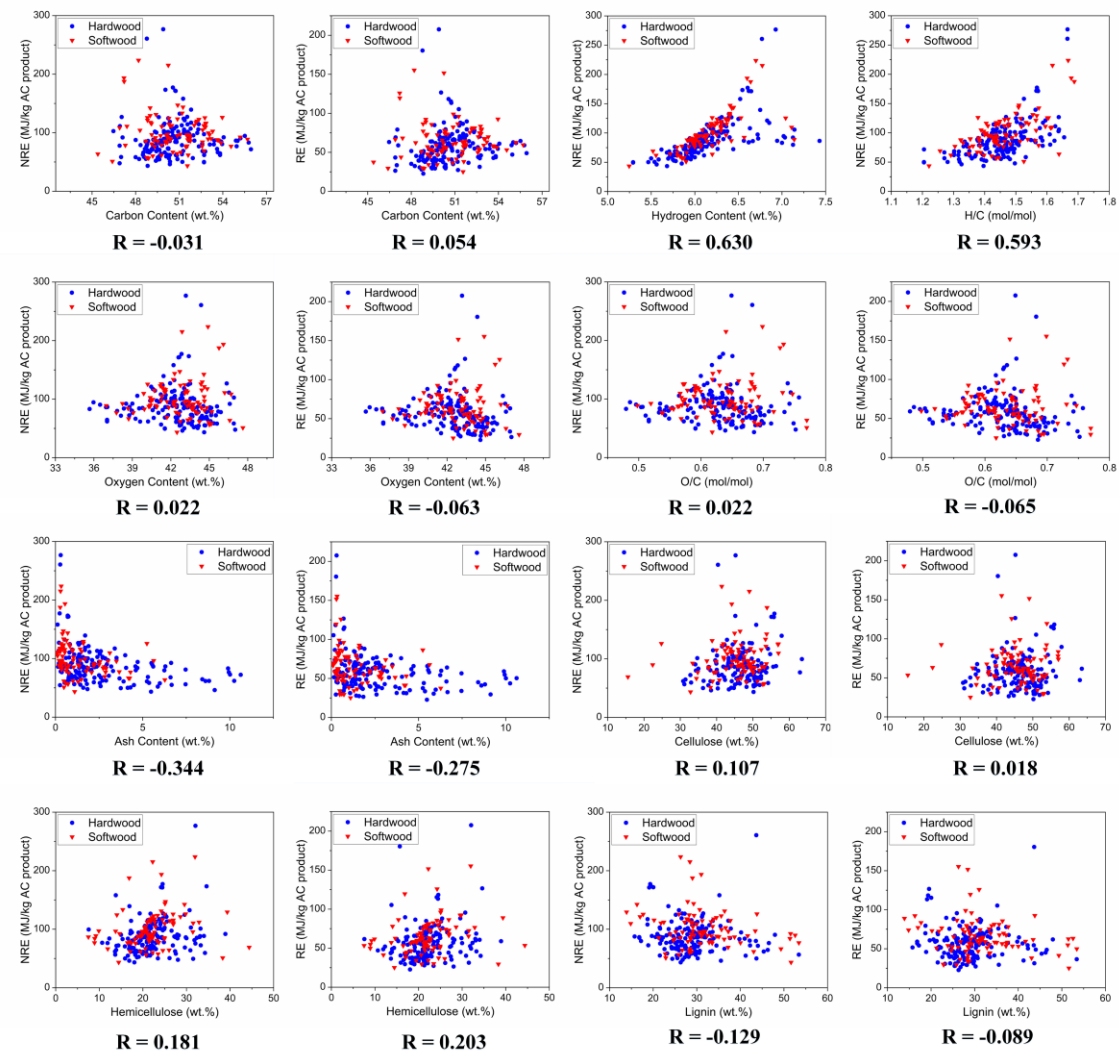


Figure S8 Correlations between Primary Energy Demand of Steam AC Production and Feedstock Composition (RE: Process with Energy Recovery; NRE: Process without Energy Recovery)

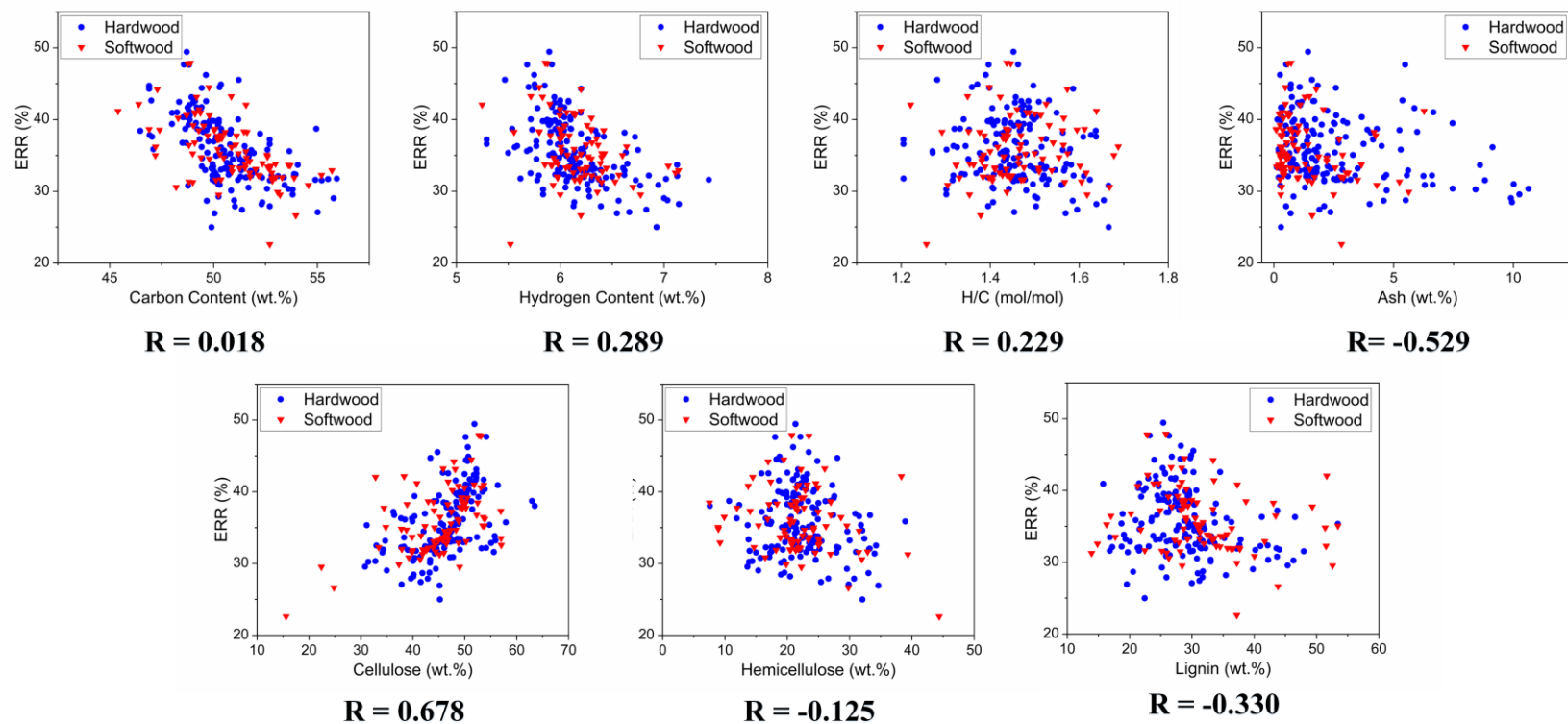


Figure S9 Correlations between Energy Recovery Ratio of Steam AC Production and Biomass Feedstock Composition

4.2 Additional Sensitivity Analysis Results

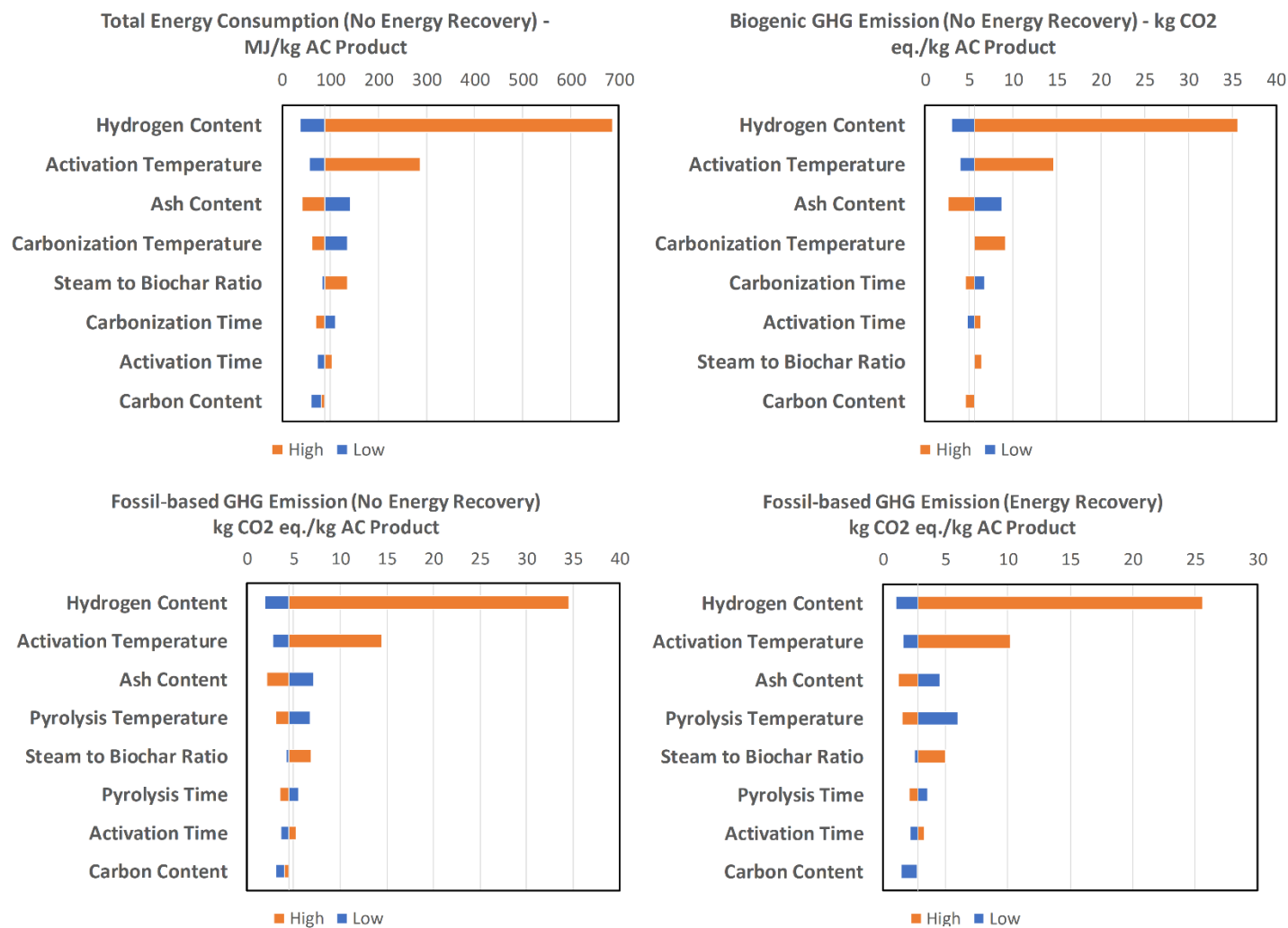


Figure S10 Sensitivity Analysis for the Energy Consumption, Biogenic GHG Emission (without Energy Recovery) and Fossil-based GHG Emission (with/without Energy Recovery) of Steam AC Production Process

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