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Development and Comparison of Thermodynamic Equilibrium and Kinetic Approaches for Biomass Pyrolysis Modeling

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Abstract: Biomass pyrolysis is considered as a thermochemical conversion system that is performed under oxygen-depleted conditions. A large body of literature exists in which thermodynamic equilibrium (TE) and kinetic approaches have been applied to predict pyrolysis products. However, the reliability, accuracy and predictive power of both modeling approaches is an area of concern. To address these concerns, in this paper, two new simulation models based on the TE and kinetic approaches are developed using Aspen Plus, to analyze the performance of each approach. Subsequently, the results of two models are compared with modeling and experimental results available in the literature. The comparison shows that, on the one hand, the performance of the TE approach is not satisfactory and cannot be used as an effective way for pyrolysis modeling. On the other hand, the results generated by the new model based on the kinetic approach suggests that this approach is suitable for modeling biomass pyrolysis processes. Calculation of the root mean square error (RMS), to quantify the deviation of the model results from the experiment results, confirms that this kinetic model presents superior agreement with experimental data in comparison with other kinetic models in the literature. The acquired RMS for the developed kinetic method in this paper varies within the span of 1.2 to 3.2 depending on temperature (400–600 °C) and various feedstocks (pine spruce sawdust, bagasse, wood bark, beech wood and paddy straw).

Keywords: biomass pyrolysis; biochar production; modeling; thermodynamic equilibrium; kinetic method

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1. Introduction

1.1. Necessity of the Matter

Climate change due to greenhouse gases (GHG) emitted by human activities is considered as a critical challenge for the environment, our societies and policy. Currently, most of the actions focusing on GHG emission reduction aim to reduce fossil fuel consumption, yet barely address the capturing of carbon dioxide released by fossil fuel combustion. Furthermore, some of these actions target activities in line with agricultural practices [1–3]. Despite some local achievements in decreasing emissions, the global emissions continue to increase. It was reported that 84% of the primary energy demand worldwide in 2019 was supplied by fossil fuels [4]. It is evident that fossil fuels are globally still a critical energy source. However, there are limited reserves of fossil fuels, and their overuse is accompanied by environmental degradation [5–7]. Thus, this situation encourages the use of renewable resources even more than before.

Renewable energy sources should be based on abundant sustainable resources with long-term availability. Furthermore, they should be available at a reasonable cost, and it should be possible to employ them for various tasks with little to no greenhouse gases or pollutant emissions into the environment. Among the different renewable energy sources, biomass has been recognized as a widely available, affordable and reliable source for fuel products [8–10]. Biomass energy products are produced by agricultural crops/residues, herbal/woody materials and organic wastes. Biomass could be incinerated to generate heat and power, or processed into refined energy products, such as biogas, biodiesel and bioethanol, which can be utilized as transportation fuels or for power and heat production. Biomass energy production could be a future growth sector, due to its renewable nature and relative abundance. However, currently the global share of biomass for primary energy generation is limited [11–14]. It should be noted that a large part of this is for heating and cooking in very poor countries. Thus, there are large gains in introducing new modern technologies for the utilization of biomass.

Several biological conversion systems (fermentation and anaerobic digestion) and thermochemical conversion processes (gasification, pyrolysis and liquefaction) can be applied to convert biomass feedstocks to fuel and chemicals. Among these processes, biomass pyrolysis has recently received much attention. Pyrolysis can produce a wide range of gas-, liquid- and solid-phase products (Figure 1) [15,16]. The solid product from pyrolysis is referred to as biochar. It is a porous, carbon-rich substance gained from thermochemical pyrolysis of biomass materials with little or no oxygen. Biochar could be used for several applications, such as fuel, in the preparation of activated carbon for wastewater treatment, for soil modification, and as a catalyst for industrial applications [17,18].

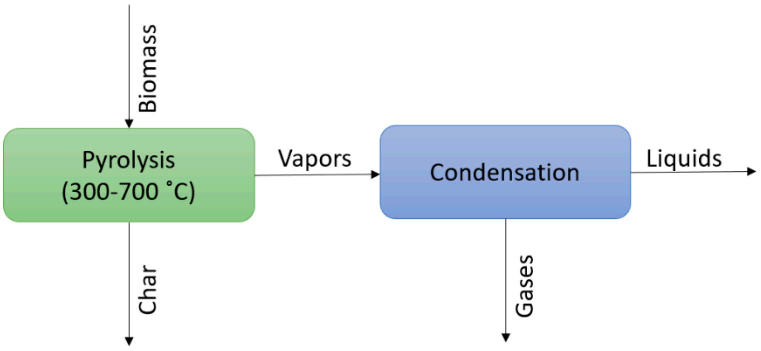

Figure 1. Schematic description of basic biomass pyrolysis system.

Pyrolysis systems are typically categorized into three forms: slow, fast and intermediate. The system type and the operational parameters of pyrolysis will greatly influence the relative contributions of the gas, liquid and solid products. For instance, the slow pyrolysis process is performed with a low heating rate and long vapor residence time, which are conditions that lead to maximum solid product yield [19,20]. The operator can achieve a desirable product mix by optimizing process parameters such as feedstock flow rate, moisture content of fuel, reactor temperature and pressure, heating rate through the pyrolyzer, and residence time within the reactor. Variations in any of these factors could significantly affect the product composition and the pyrolysis proficiency [21,22]. In addition, the permissible values for the biomass properties are tight due to the fact that the chemistry and fluid dynamics of pyrolysis are sensitive to changes in feedstock components, moisture, ash content and particle size [23,24]. In this way, laboratory and pilot experiments can be conducted to provide information about the optimal parameters and proper materials for a reactor. However, such experiments may need more time and cost in comparison to modeling [25,26].

In the literature, different modeling techniques such as computational fluid dynamics (CFD), artificial neural network (ANN) and process simulation via Aspen Plus, have been used for modeling biomass pyrolysis. However, among them, Aspen Plus has been favored recently because it avoids the modeling of intricate reaction mechanisms and processes, and it paves the way to establishing a simple model that contains the primary pyrolysis reactions [9,27]. Despite these benefits, the present authors are not aware of any published work that has simulated the biomass pyrolysis process in Aspen Plus with acceptable compliance using experimental data.

1.2. Approaches for Modeling of Pyrolysis and Simulation in Aspen Plus

Aspen Plus is recognized as a simulation software working toward the optimization of chemical processes using easily connectable unit operation blocks, such as heat exchangers, reactors, pumps, valves, etc. The operation blocks are linked together by applying the energy and mass streams to create a specific flowchart for the considered case. Physical properties of streams are provided as a database built in Aspen Plus. The program solves the governing equations by employing a sequential modular technique. This makes model development and model updating straightforward, because different parts of a complex process system can be evaluated as single modules before integration [28,29].

The models developed by Aspen Plus for biomass pyrolysis processes can be categorized as thermodynamic equilibrium (TE), kinetic models and fixed data (FD) models (see Figure 2a). A non-exhaustive survey of biomass pyrolysis modeling utilizing Aspen Plus from 2010 to 2021 found that approximately 63% of biomass pyrolysis simulations applied thermodynamic equilibrium models, and that the most-cited subset of this approach is the method relying on the minimum Gibbs free energy (MGFE) [30–43]. The remaining 14% and 23% used the kinetic approach [44–46] and FD [47–51], respectively (see Figure 2b).

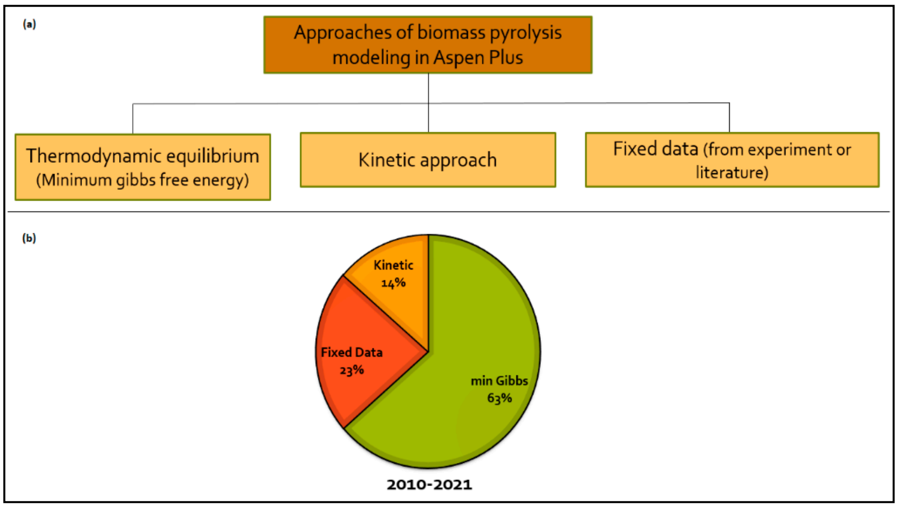

Figure 2. A categorization of biomass pyrolysis modeling types by Aspen Plus, (**a**): categorization of Aspen Plus biomass pyrolysis modeling approaches, (**b**): contribution of Aspen Plus biomass pyrolysis modeling approaches in the literature.

The thermodynamic equilibrium method forecasts the outlet product components under a set of important assumptions [52,53]:

- Substances are reacted in full mixed condition through unlimited time horizon;
- Temperature in the pyrolysis zone is constant;
- Chemical components are mixed perfectly.

Computation based on the TE approaches are simple and independent of the pyrolyzer design, in contrast to kinetic method. The TE method is considered attractive because of its simplicity, and because the general thermodynamic properties of materials, compounds and elements provides sufficient input. In contrast, a wide group of hard-to-establish factors are necessary for kinetic approaches. The factors make the equilibrium technique the most straightforward approach for studying the typical relations between biomass feedstock and process factors, and restricting product components and yields. Nevertheless, in practice, thermodynamic equilibrium mood is most likely not gained during pyrolysis operated at relatively modest temperatures, where reaction kinetics are slow. Furthermore, in some processes for fast pyrolysis, it is a desirable design feature to avoid reaching equilibrium. This is because the compounds that one seeks to produce, such as bio-oil, are not favored at equilibrium. Still, modeling relying on TE has been the most largely employed method because of the ease of calculation [53,54].

In order to accurately predict the product distributions in the pyrolysis unit, a non-equilibrium method, such as the kinetic model, is needed [44,55]. Kinetic models are able to calculate the product components and temperature profiles within different zones in the unit, as well as the evolution of these variables in time during non-steady-state operation. Kinetic models can be precise and detailed. However, these types of models are less flexible with respect to how they can be applied. Furthermore, it is difficult to achieve high accuracy because these models aim to define very complex phenomena, such as gas–solid reactions, gas–solid contacting processes and development of particle distributions, which are difficult to model reliably and accurately.

As mentioned above, the products of biomass pyrolysis include biochar, bio-oil and syngas. Biochar is a type of char containing mainly carbon and ash that is formed from biomass decomposition at a temperature between 300 °C to 700 °C under oxygen-deprived conditions. Bio-oil is an emulsion consisting of water (between 25–55 wt%) and organic fuel compounds such as alkanes, aromatic hydrocarbons, phenol derivatives and small amounts of ketones, esters, ethers, sugars, amines and alcohols. Syngas is a fuel gas mixture containing mainly H_2 and CO, small amounts of CO_2, CH_4 and C_2H_6, and trace amounts of other hydrocarbons.

The product yields (i.e., distribution of biochar, bio-oil and syngas) are the most important performance indicators of biomass pyrolysis technologies. They can be used for the evaluation of system performance and for sensitivity analysis, to determine the process conditions at which the products achieve their highest yields. Moreover, these indicators are used for validation of the developed models by experimental data to identify model accuracy and reliability. The product yields are calculated as follows:

$$\text{Biochar yield, } y_{biochar} = \frac{m_{biochar}}{m_{biomass}} \tag{1}$$

$$\text{Bio-oil yield, } y_{bio-oil} = \frac{m_{bio-oil}}{m_{biomass}} \tag{2}$$

$$\text{Syngas yield, } y_{syngas} = \frac{m_{syngas}}{m_{biomass}} \tag{3}$$

where $m_{biochar}$, $m_{\text{bio-oil}}$, m_{syngas} and $m_{biomass}$ are the mass flow rates of biochar, bio-oil, syngas and input biomass in kg/h, respectively.

For the simulation of the complete biomass pyrolysis process in Aspen Plus, three main parts need to be simulated; (i) biomass definition, (ii) decomposition part and (iii) pyrolysis reactor (Figure 3). In the TE method based on the MGFE, the biomass definition and the decomposition part are determined from the ultimate and proximate analysis of the biomass feedstocks, and such data are abundant in the literature. Moreover, the calculations for the pyrolysis reactor when applying this method rely on the minimum Gibbs energy distribution among the chemical species, for a given feed composition at the reaction temperature and pressure [54]. In the kinetic method, the biomass definition and decomposition are defined based on biochemical analysis of biomass feedstocks. Finally, computation in the pyrolysis reactor is primarily based on the reaction kinetics and hydrodynamics inside the pyrolyzer [55].

In the FD approach, the biomass is also defined using the ultimate and proximate analysis of biomass feedstocks, but the decomposition section and the pyrolysis reactor are considered as the fixed parts, and the required data for these units are gathered from the literature or experimental works. In fact, this method is only useful and valid for the biomass pyrolysis unit under study, which is integrated with other systems and cannot be used for other feedstocks or systems. For example, Zaini et al. [49] developed a simulation model of a biomass pyrolysis system coupled with steam reforming and the water–gas shift to produce hydrogen, biochar and bio-oil. The studied pyrolysis system in their work was fixed, and the required data, such as biomass compositions, pyrolysis temperature and pressure, and product yields, for this part were provided from the pilot plant of biomass pyrolysis currently operating at Envigas, Sweden. The remaining part (the hydrogen production unit) was simulated using Aspen Plus, and the system performance was investigated under different operating parameters. The strengths and weaknesses of the three different methods for biomass pyrolysis modeling by Aspen Plus are listed in Table 1.

Table 1. Features and weakness of pyrolysis modeling approaches.

	Strengths	**Weakness**
Thermodynamic equilibrium method	• Straightforward approach • It is not necessary to have chemical reactions • Helpful for assessment of complex systems that are difficult to perform in pilot unit • Highest yields of the products are achieved using this method • Not dependent on reactor structure • Pliable related to different feedstocks and process factors • Not sensitive to high temperatures • They are based on ultimate analysis of biomass; this type of data is abundant	• It is assumed that components are reacted under moderately mixed conditions with an unlimited time horizon • Tars/oils are not considered • Not useful for modest temperatures • Restriction for fluidized bed reactors • Not highly accurate results for all systems
Kinetics method	• Time or volume are considered finite • Precise results • Practical at low temperatures • Beneficial method for particle size effect assessment • Practical for fluidized bed reactors	• Sensitive to gas–solid contacting process • Sensitive to high temperatures • Computationally difficult and intensive. These are often difficult even for dedicated equipment manufactures, and require empirically derived models in most cases • Sensitive when deriving mass balance for several reactions • Limited applicability to different plants • Need to be defined for specific chemical reactions • Requires several databases for reaction constants and activation energy for each reaction • They are based on biochemical analysis of biomass; this type of data is scarce
Fixed data technique	• Useful for an available biomass pyrolysis unit • Useful for assessment of integrating other systems with pyrolysis	• It needs data for decomposition and pyrolysis parts • The model is only for a specific case and cannot be used for other feedstocks/systems

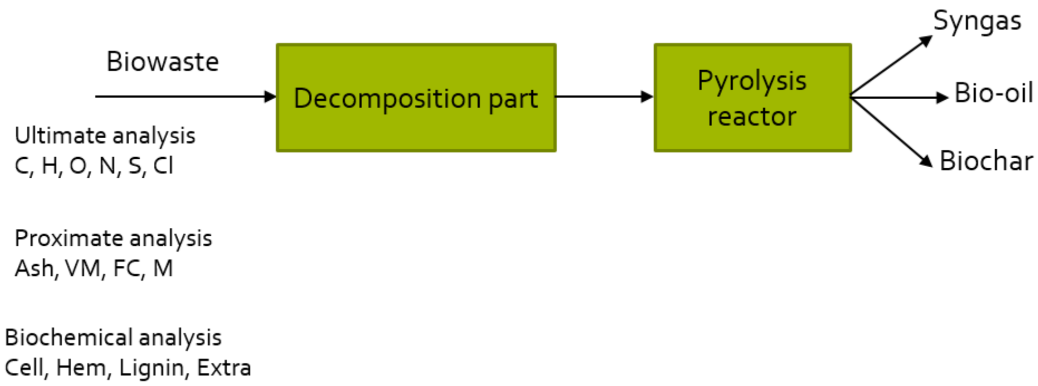

Figure 3. Main parts for simulation of biomass pyrolysis.

1.3. Aim of the Work

As mentioned above, both the thermodynamic equilibrium (TE) and kinetic approaches have been employed for biomass pyrolysis modeling using Aspen Plus. Clearly, most models relied on TE. It should be noted, however, that none of the TE-developed models have been validated by real or experimental data. They were only compared with other available TE model results, and claimed that these models have acceptable accuracy. Furthermore, in TE models, the science of pyrolysis chemistry, and model capability to simulate the exact conversion phenomena, are still unresolved issues [56].

Moreover, the authors are aware of only three peer-reviewed publications on biomass pyrolysis modeling based on the kinetic method in the period from 2010 to 2021 [44–46], and only one of them has been validated with existing experimental data [44]. In spite of the complexity of the kinetic model employed (by considering many chemical reactions and linear regression equations), this model could not be reproduced using only the presented data in the paper due to the limitations of the kinetic reactor model in Aspen Plus, as well as the lack of data regarding the decomposition part, reactor and biomass properties. Therefore, the objective of this paper is the development of two simulation models based on the TE and kinetic approaches, and the comparison of these two models with the available models and experimental results (from the literature) to investigate which method shows the smallest deviation from experimental results. To achieve this objective, in Section 2, the details regarding the developed TE model are explained, and its results are compared with the output results of other TE models and experimental works, and discussed. The same is carried out for the established kinetic model in Section 3; this section explains the details and structure of the developed kinetic model, after which the results of the comparison of this model with other kinetic modeling and experimental works are discussed. Finally, conclusions are drawn for both types of models in Section 4.

2. Thermodynamic Equilibrium (TE) Model

2.1. Model Description

The thermodynamic equilibrium model that was established in this paper is a replication of other TE models available in the literature [30–43]. In this work, the Penge Robinson equation of state with Boston–Mathias alpha function (PR-BM) was employed to calculate the physical properties of the conventional substances in the pyrolysis system. PR-BM approach can be applied for non-polar or mildly polar mixtures, and the alpha factor within the property package is a parameter dependent on temperature, which is useful for the correlation of vapor pressure of pure material when the temperature is very high. The enthalpy and density models chosen for biomass and ash as non-conventional substances were HCOALGEN and DCOALIGT. HCOALGEN and DCOALIGT are the available defined models in Aspen Plus for density and enthalpy calculations of non-conventional materials, such as biomass, ash and coal, which are not defined in the Aspen Plus database. HCOALGEN utilizes the proximate, ultimate and sulfur analysis to estimate the enthalpy.

The DCOALIGT model requires only the ultimate analysis and sulfur analysis. For the stream class, MCINCPSD stream is selected, which contains three substreams of MIXED, CIPSD and NCPSD class. MIXED is considered for the mixed streams that include conventional and non-solid materials, CIPSD is considered for solid components, such as carbon, which are formed from the biomass decomposition, and NCPSD is considered for non-conventional streams, such as biomass and ash [57,58].

Figure 4 presents the biomass pyrolysis process flowchart, simulated with Aspen Plus using the MGFE approach. Table 2 briefly shows a description of the unit operational blocks applied in the simulation. The BIOMASS flow is described as a non-conventional flow that is characterized by the chemical compositions and calorific value of the biomass feedstock, as achieved by proximate and ultimate analyses. Afterward, RYield, the Aspen Plus yield reactor, is utilized to simulate the feedstock decomposition. In this section, the feedstock is transformed from a non-conventional solid to volatile materials (VMs) and char. The VMs include hydrocarbons, oxygen, hydrogen, carbon monoxide and non-combustible gases, and the char is transformed to ash and carbon, by determent of the product distribution based on the various analyses of the biomass material. VM yield is equal to the volatile content in the biomass feedstock determined by the proximate analysis [59]. For the equilibrium simulation of the pyrolysis reactor, an RGibbs reactor is used to calculate the product compositions via minimizing the Gibbs free energy, which implies reaching full chemical equilibrium [60]. The pyrolysis reactor simulation is followed by a separator, in which char and ash are separated from the other products. It assumes that the REST stream contains aqueous- and gas-phase products (bio-oil and syngas) that can be separated from each other by passing through a cooler and a flash separator.

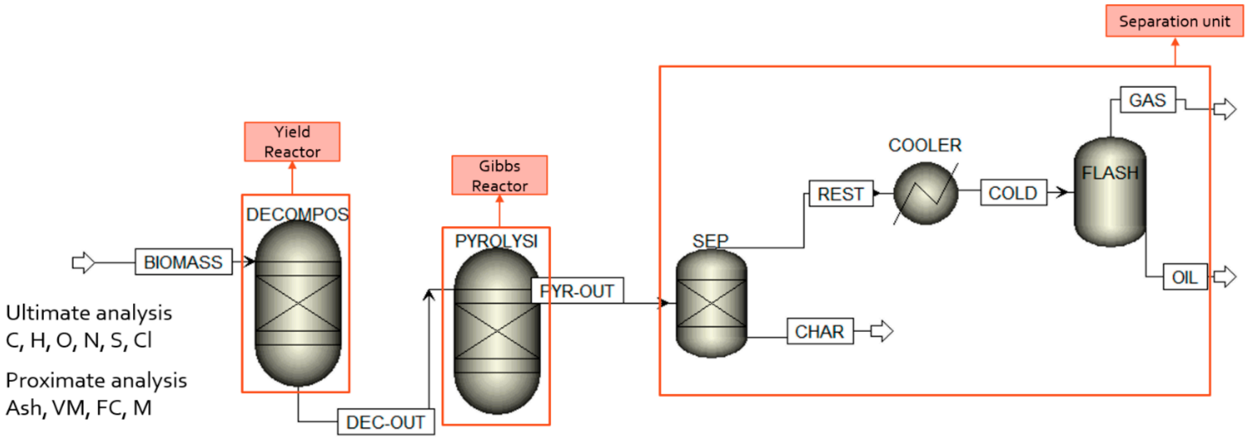

Figure 4. Flowchart of the simulation model for biomass pyrolysis developed using Aspen Plus based on the TE approach.

Table 2. Definition of Aspen Plus operational units employed in simulation.

Block	Name	Definition
RYield	DECOMPOS	Analysis of non-conventional biomass to conventional substances
RGibbs	PYROLYSIS	Rigorous equilibrium reactor based on minimum Gibbs free energy approach
Separator	SEP	Char and ash separation from the rest of steam via determination of split fractions
Exchanger	COOLER	To cool/reduce stream temperature
Flash/Separator	FLASH	One-stage separation process for splitting into two streams of non-condensates and condensates

2.2. Results and Comparison

2.2.1. Comparison with Shahbaz et al. (2020) TE Model

The product yields obtained from the Aspen Plus simulation based on the equilibrium method are verified by the equilibrium simulation values obtained from Shahbaz et al. [41]. In this research, biomass components—cellulose, hemicellulose and lignin—were used as feedstocks in the pyrolysis system at a temperature of 450 °C, a heating rate of 10 °C/min and a solid residence time of 30 min. The information utilized to define the biomass materials is provided in Table 3. Comparison of product (biochar, syngas and bio-oil) yields is shown in Table 4. On the one hand, it can be observed that the deviation of the present model from Shahbaz et al. is zero. On the other hand, if the TE model of biomass pyrolysis is compared only with other TE models, it can be concluded that, as expected, a near-perfect agreement has been achieved. However, to assure acceptable accuracy of the TE simulation of biomass pyrolysis, further comparison is carried out in this section.

Table 3. Analysis of feedstocks utilized within different TE models [33,41,61–63].

	Cellulose	Hemicellulose	Lignin	Biomass	Rice Husk	Bamboo	Bagasse
Proximate analysis (wt%)							
Moisture content	3	3	3	7.86	1.1	9.37 ± 0.80	13.2
Volatile matter (VM)	94.25	83.15	64.66	84.71	70.5	70.31 ± 0.44	71
Fixed carbon (FC)	5.75	16.85	32.47	13.94	16.6	17.75 ± 0.40	13.7
Ash content	0	0	2.87	1.35	12.9	2.57 ± 0.41	2.1
Ultimate analysis (wt% dry basis)							
Carbon	41.46	40.69	56.99	47.67	42	39 ± 3	51.71
Hydrogen	5.97	5.75	5.27	6.86	5.4	6.1 ± 0.2	5.32
Nitrogen	0.07	0.04	1.1	0.13	0.4	0.6 ± 0.3	0.33
Oxygen	52.48	53.49	33.52	43.98	39.3	54 ± 3	42.64
Sulfur	0.02	0.03	0.25	0.01	0	0.018 ± 0.006	0

Table 4. Comparison of product yields (wt%) for cellulose, hemicellulose and lignin.

	Cellulose		**Hemicellulose**		**Lignin**	
	Current Study	**Shahbaz et al. [41] Model**	**Current Study**	**Shahbaz et al. [41] Model**	**Current Study**	**Shahbaz et al. [41] Model**
Biochar	23	23	22	22	58	58
Bio-oil	26	26	26	26	3	3
Syngas	51	51	52	52	39	39

2.2.2. Comparison with Visconti et al. (2015) TE Model

The carbon content (wt%) in the biochar calculated with the present simulation model is compared with the TE model results of Visconti et al. [33] at different pyrolysis temperatures. The ultimate and proximate analyses of the used biomass in their work are shown in Table 3. Table 5 shows this comparison for a pyrolysis temperature range of 500 °C to 750 °C. Moreover, the molar percentage of syngas components obtained from the current study and the study by Visconti et al. are compared and shown in Table 6. Both comparisons in Tables 5 and 6 show good agreement for the TE simulation model developed in this paper, but the simulation results have not been compared with the real data, so it is yet to be proven as an effective and reliable method.

Table 5. Comparison of carbon content (wt%) in biochar.

	Current Study	**Visconti et al. [33] Model**
500 °C	95.55	95.6
650 °C	94.5	93
700 °C	93.5	93
750 °C	91.9	91.1

Table 6. Comparison of components (mol%) in syngas.

	Current Study	**Visconti et al. [33] Model**
CO	4.06	4
CO_2	28.1	28
H_2	39.4	40.5
H_2O	6.5	10
CH_4	21.8	18

2.2.3. Comparison with Alvarez et al. (2014) Experiment

In this subsection, the product yields calculated with the TE simulation model developed in this paper are compared with the experiment values achieved by Alvarez et al. [61]. In this paper, rice husk has been entered into a pyrolysis unit operating under atmospheric pressure and various temperatures. The main rice husk properties are summarized in Table 3. Four different temperatures were considered, and the comparison of product yields is provided in Figure 5. Noticeably, the deviation of the model results from the experimental data is high for all cases. It is evident that the Aspen Plus simulation model based on TE approach for biomass pyrolysis cannot be in an agreement with the experiment outputs. However, to be sure about this matter, other experimental results should be considered for comparison.

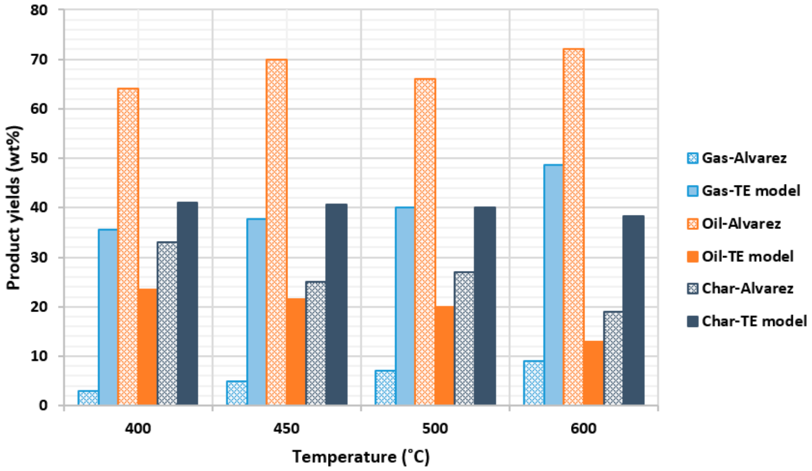

Figure 5. Comparison of product yields (wt%) for rice husk.

2.2.4. Comparison with Hernandez-Mena et al. (2014) Experiment

Comparison of the product yields obtained from the TE simulation model created in this paper and the experimental results of Hernandez-Mena et al. [62] are summarized in this section. In their work, pyrolysis of woody bamboo was investigated, and the biochar, bio-oil and syngas distributions were determined. The process was conducted in a fixed bed reactor at temperatures ranging from 300 to 600 °C and at a 10 °C/min heating rate. Table 3 displays the main characteristics of the studied biomass. Figure 6 shows the comparison of product yields at four different temperatures. This comparison again shows that the results of the TE modeling approach are not in agreement with the experimental results. As a limitation, it needs to be noted that the TE approach based on the minimum Gibbs free energy is not capable of predicting the liquid residues such as tar. In reality, bio-oil is a liquid fuel mixture consisting of several organic compounds, such as alkanes, aromatic hydrocarbons, phenol derivatives and small amounts of ketones, esters, ethers, sugars, amines and alcohols; conversely, the bio-oil output from the TE system contains only water, and none of the other components are considered using this type of method.

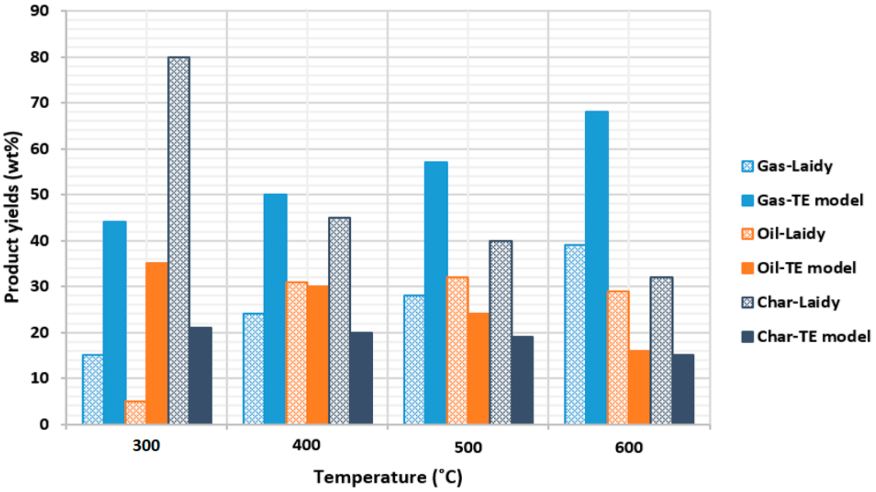

Figure 6. Comparison of product yields (wt%) for bamboo.

2.2.5. Comparison with Lee et al. (2013) Experiment

The product yields resulting from the TE modeling of biomass pyrolysis established in the present paper are compared with the experimental results of Lee et al. [63]. This experimental study evaluates the product distribution and characteristics at a pyrolysis temperature of 500 °C for several agricultural residues, such as sugarcane bagasse. The information regarding to the proximate and ultimate analysis of bagasse is listed in Table 3, and the comparison is summarized in Table 7, in which the deviation is calculated using the mean of the absolute error. The deviation is significant, which confirms the inadequacy of the TE method for the modeling of biomass pyrolysis systems.

Table 7. Comparison of product yields (wt%) for bagasse.

	Current Study	Lee et al. [63] Experiment	Deviation (%)
Biochar	30	24.5	18.33
Bio-oil	22	55.1	150.45
Syngas	49	20.4	58.37

Although the developed TE model perfectly matches with the results of other TE models in the literature, comparison with experimental results shows that the TE approach is not in agreement with these, and cannot be used as a reliable method for pyrolysis modeling. The reason for this is that the TE method applied in Aspen Plus is based on the minimum Gibbs free energy (G), which is calculated based on the chemical potential of a species in the mixture at constant temperature and pressure (Equation (4)) [36]:

$$dG = \sum_{i=1}^{K} \mu_i n_i dn_i \quad (4)$$

where n_i is the number of moles of species i, K is total number of chemical species in the reaction mixture, and μ_i is chemical potential of species i. The objective is to find the set of n_i values that will minimize the value of G. The chemical potential of a species is the energy that can be absorbed or released due to a change in the particle number of the given species, e.g., in a chemical reaction or phase transition. At pyrolysis operating temperatures, the chemical potential of, for example, liquid hydrocarbons, is higher than that of, for example, permanent gases. Hence, using the MGFE method, the output will be tilted towards simple gaseous products (CO, H_2, CO_2, CH_4, etc.), bio-oil will only contain water, and none of the organic compounds will be selected due to their high chemical potential.

In order to address this matter, the kinetic method, as another modeling approach, is studied in the next section.

3. Kinetic Model

3.1. Model Description

The authors are aware of only three published works that involve biomass pyrolysis modeling based on the kinetic method in Aspen Plus from 2010 to 2021 [44–46], only one of which has been validated with existing experimental data [44]. In this study, a novel simulation model based on the kinetic method is developed that can pyrolyze different biomass feedstocks under various operating conditions. In the following subsections, the model structure is explained, its results are compared with other modeling and experimental values, and finally, conclusions about the agreement of this method for biomass pyrolysis modeling are made.

Figure 7 shows the Aspen Plus flowchart of the biomass pyrolysis process using the kinetic method developed in the present paper. The FEED/BIOMASS stream is a non-conventional material that is defined by utilizing the biochemical analysis of the biomass (e.g., wt% of cellulose, hemicellulose, lignin and extra components). Thus, the required inputs for this part contain the biochemical analysis of biomass feedstock as well as inlet temperature and pressure, which are set to 25 °C and atmospheric pressure, respectively.

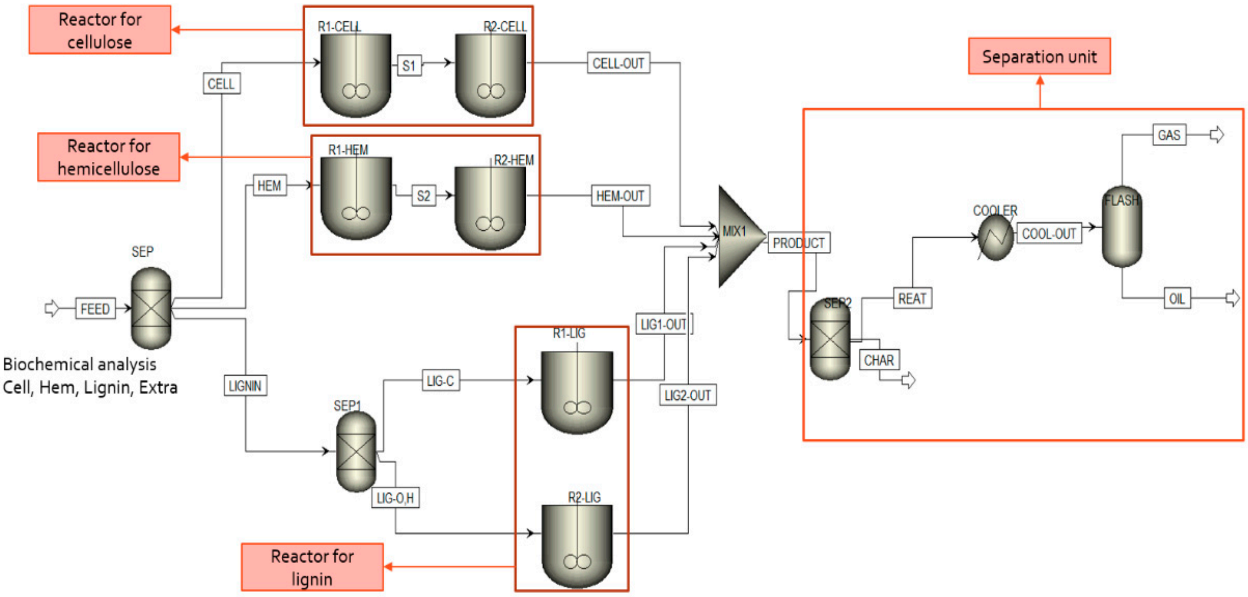

Figure 7. Flowchart of Aspen Plus kinetic simulation of biomass pyrolysis.

The biomass definition in the kinetic method differs from the one in the TE method. This is because all the studied individual reactions in the biomass pyrolysis are based on the cellulose, hemicellulose and lignin content of the biomass. Hence, it is necessary that biomass composition is determined based on its biochemical analysis. After the biomass definition, it is divided into the three streams of CELL (cellulose), HEM (hemicellulose) and LIGNIN (lignin) by passing through a separator.

CSTR, a continuous stirred tank reactor, is the most common reactor applied for kinetic process modeling in Aspen Plus. For the CSTR, two design variables are needed, pressure and temperature, or heat duty. The valid phases, and a reactor specification, need to be specified as well. The simulated CSTR in this work operates at atmospheric pressure and various temperatures in the window of 350 °C to −600 °C. Although, this kind of reactor is useful for modeling individual reactions of cellulose, hemicellulose and lignin, there are several difficulties to performing this correctly. The CSTR reactor model is not able to conduct a correct mass balance when several individual reactions are considered together in only one reactor. It is also sensitive to the solid–gas reactions and to operating under high temperature.

To overcome these challenges, some modeling strategies are applied. Three sets of reactors were considered for individual reactions of cellulose, hemicellulose and lignin. In this way, several reactions can be defined. The mass balances can now be solved correctly, and outputs related to each part can be easily evaluated individually. The chemical reactions considered for these parts are taken from the literature (Table 8) [64–66]. The reaction structure for biomass pyrolysis is shown in Figure 8. First, cellulose, by considering the kinetic parameters, is divided into two streams of activated cellulose (ACT-CELL) and cellulose (CELL), and for the reactions of each, one CSTR reactor has been simulated. The same is conducted for hemicellulose (Hem-1 and Hem-2). Lignin is divided into a LIG-C, LIG-H and LIG-O stream, and two series of reactors are defined, one for LIG-C and one for LIG-H and LIG-O reactions. At the next step, all the reactor outputs are combined in a mixer, after which, char and ash are separated from the rest of the products. Afterward, the REST stream containing liquid- and gas-phase products (i.e., bio-oil and syngas) are separated from each other by passing through a cooler and a flash separator (both operating at atmospheric pressure and 20 °C). Finally, molar and mass flow rates of biochar, bio-oil and syngas are the simulation outputs, and, using Equations (1)–(3), the product yields for each system can be calculated.

Table 8. Multi-step kinetics reactions in biomass pyrolysis.

	Reactions
Cellulose	CELL –> ACT-CELL ACT-CELL –> 0.95 GLYCOL-ALDEHYDE + 0.25 GLYOXAL+ 0.2 ACETALDEHYDE + 0.25 HYDROXYMETHYLFURFURAL + 0.16 CO_2+ 0.23 CO+ 0.9 H_2O+ 0.1 METHANE + 0.61 C + 0.2 ACETONE CELL –> 5 H_2O + 6 C
Hemicellulose	HEMICELL –> 0.4 HEM-1 + 0.6 HEM-2 HEM-1 –> 1.25 H_2 + 0.5 CO_2 + CO + 0.5 FORMALDEHYDE + 0.25 METHANOL + 0.125 ETHANOL + 2.125 H_2O + 2.3 C + 0.075 ETHYLENE + 0.05 METHANE HEM-2 –> XYLOS
Lignin	LIG-C –> 0.3 LIG-CC + 0.1 COUMARYL + 0.08 PHENOL + 0.41 ETHYLENE + H_2O + 0.495 METHANE + 0.82 CO + 6.985 C + 1.35 H_2 LIG-CC –> 0.3 COUMARYL + 0.2 PHENOL + 0.35 PROPENE-DIAL + 0.7 H_2O + 0.65 METHANE + 0.6 ETHYLENE + 7.4 C + 0.8 CO + H_2 LIG-H + LIG-O –> 2 LIG-OH + ACETONE + CO_2 LIG-OH –> PHENOL + 0.5 H_2O + METHANOL + 0.5 METHANE + ETHYLENE + 0.5 CO + 2.5 H_2 + 9 C LIG-OH –> 3 PHENOL + METHANE

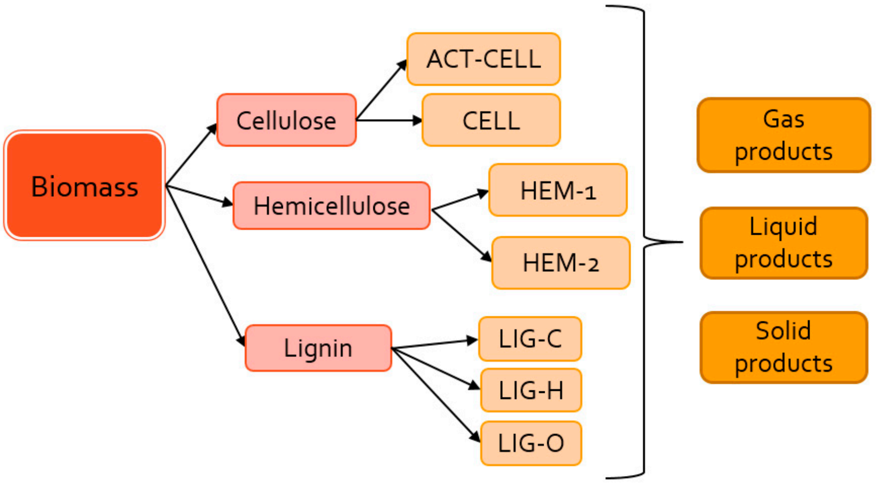

Figure 8. Reaction structure within biomass pyrolysis.

3.2. Results and Comparison

3.2.1. Comparison with Peters et al. (2017) Kinetic Model and Experiment

In this section, the product yields obtained from the kinetic-based Aspen Plus simulation model are compared with the kinetic simulation results of Peters et al. [44]. To the knowledge of the authors, this paper is the only published work containing kinetic simulation of biomass pyrolysis using Aspen Plus that has been validated with experimental data. They presented a kinetic reaction model for the biomass pyrolysis process that relied on the three main components of lignocellulosic biomass, i.e., cellulose, hemicellulose and lignin. However, their model is complex and not user-friendly; it considers 149 individual reactions describing the volatilization, decomposition and recomposition processes in the biomass pyrolysis, and several linear regression equations were created based on the experimental results. Moreover, this model cannot be reproduced due to the mentioned limitations of the kinetic reactor in Aspen Plus, as well as the lack of data concerning the decomposition part, reactor and biomass properties. In their work, beech wood was used as the feedstock in the pyrolysis system under various temperatures. The information used to describe this feedstock is presented in Table 9. They also verified their simulation results with experiments in a bench-scale pyrolysis plant.

Table 9. Biochemical composition of beech wood feedstock (%) [44].

Water	Cellulose	Hemicellulose	Lignin	Ash
12.95	40.26	21.68	19.91	1.62

Comparison of the product yields obtained in the present work with the model and the experimental results presented in Peters et al. [44] are shown in Table 10. The deviation of the obtained model results from the experiment data was calculated using the root mean square error (RMS). Two observations can be derived from the comparisons and RMS values in Table 10. Firstly, the Aspen Plus simulation model based on the kinetic approach could be a well-grounded method for the modeling of a biomass pyrolysis process, and the developed model in our paper presents a better agreement with the experimental results compared to the kinetic-based model of Peters et al. [44]. However, to be sure about the predictive power of the current model, it needs to be compared and verified with other experiments results.

Table 10. Comparison of product yields for beech wood (%).

	470 °C			**570 °C**		
	Current Study	**Experiment**	**Kinetic Simulation by Peters et al. [44]**	**Current Study**	**Experiment**	**Kinetic Simulation by Peters et al. [44]**
Gas	23.3	19.07	14.88	25.18	24.2	21.90
Oil	63	66.56	66.28	62.4	60.5	65.90
Char	13.8	14.27	18.82	12.4	10.3	12.03

At 470 °C, RMS-Peters et al. [44] & experiment = 3.57, At 570 °C, RMS-Peters et al. [44] & experiment = 3.53. **At 470 °C, RMS-Current study & experiment = 3.2, At 570 °C, RMS-Current study & experiment = 1.73**.

3.2.2. Comparison with Calonaci et al. (2010) Kinetic Model and Experiment

In this section, the product yields attained from the kinetic simulation model developed in this paper are compared with the kinetic modeling study of Calonaci et al. [66]. In this research, a kinetic model has been established that is run on several feedstocks, such as pine–spruce–sawdust. Table 11 shows the biochemical analysis of this biomass. Their model results have also been verified with experimental measurements. Comparison of the product yields achieved in the current work with the model and the experimental values presented in Calonaci et al. [66] are displayed in Table 12. The deviation (RMS) of the model results from the experimental measurements are also calculated. The RMS confirms that the kinetic simulation developed in this paper has better agreement with experiments in comparison with the model of Calonaci et al. [66].

Table 11. Biochemical composition of pine–spruce–sawdust feedstock (%) [66].

Water	**Cellulose**	**Hemicellulose**	**Lignin**
8	48.75	21.39	21.86

Table 12. Comparison of product yields for pine–spruce–sawdust feedstock (%).

	Current Study	**Experiment**	**Kinetic Model by Calonaci et al. [66]**
Syngas	19	17	17.20
Bio-oil	70	70	68.60
Biochar	11	12	14.10

RMS-Calonaci et al. [66] & experiments = 1.46. **RMS-Current study & experiments = 1.29**.

3.2.3. Comparison with Lee et al. (2013) Experiment

As the final step in this section, the product yields achieved from the kinetic simulation in this paper are verified by the experiment values of Lee et al. [63]. This study evaluates the distribution and characteristics of outcomes under a pyrolysis operating temperature of 500 °C for agricultural residues such as bagasse, paddy straw and wood bark. This comparison, and the deviations quantified using RMS, are shown in Table 13. The low RMS values prove that the kinetic simulation developed in this paper has good agreement. Finally, it can be concluded that, although the kinetic simulation method has several limitations and can be difficult to establish, it can be introduced as a reliable technique, with acceptable accuracy, for biomass pyrolysis modeling.

Table 13. Comparison of product yields for bagasse, paddy straw and wood bark (%).

	Bagasse		**Paddy Straw**		**Wood Bark**	
	Current Study	**Lee et al. [63] Experiment**	**Current Study**	**Lee et al. [63] Experiment**	**Current Study**	**Lee et al. [63] Experiment**
Syngas	26	24.5	41	41	29.6	31.9
Bio-oil	53	55.1	40	37.2	52	50.5
Biochar	20.7	20.4	19	21.8	18.2	17.6

RMS-Current study & Lee et al. [63] for bagasse = 1.5, for paddy straw = 2.29, for wood bark = 1.62.

4. Conclusions and Future Work

The conducted survey on biomass pyrolysis modeling approaches revealed that only two approaches are commonly used, namely thermodynamic equilibrium (TE) modeling and kinetic modeling. Both have been employed through the Aspen Plus process modeling software. The most common approach is TE modeling based on the minimum Gibbs free energy (MGFE) approach. However, there are still open questions about the accuracy and agreement with experimental results of these methods, and which of them can be brought forward as a reliable technique for pyrolysis R&D work, as well as fundamental studies. Therefore, in this paper, two simulation models were developed based on the TE-MGFE and kinetic approaches. The model results were then compared with models described in the literature and experimental results.

The TE method was considered as the simplest to apply because only general thermodynamic properties are employed for equilibrium modeling. In contrast, a kinetic or reaction model requires a wide range of hard-to-establish kinetic parameters and the definition of numerous reactions occurring simultaneously during the pyrolysis process. These factors have made equilibrium modeling the more convenient and more widely used technique. Nevertheless, the TE method is most likely to not have sufficiently high predictive power for modeling many pyrolysis applications, especially for reactors with relatively low operating temperatures.

The comparisons of results show that the TE model developed in this paper perfectly matches the available TE modeling results in the literature. However, comparison with experimental data shows that the TE approach has an unacceptable degree of agreement, and cannot be introduced as an effective way for pyrolysis modeling. The TE approach based on the minimum Gibbs free energy is not capable of generating predictions for many condensable products, such as tar. This is because such compounds are not at equilibrium, but are difficult to convert in ordinary reactors. Furthermore, the bio-oil output from TE modeling contains only water, and thus none of the organic components that are produced in real reactors. Moreover, the comparisons of the novel kinetic model developed in this paper with other kinetic modeling and experimental results in the literature confirm that the Aspen Plus simulation model based on the kinetic approach could be a well-grounded method for the modeling of the biomass pyrolysis process. Calculation of the root mean square error (RMS), for quantifying the deviation of the model results from the experiment results, confirms that this kinetic model presents superior agreement with experimental data upon comparison with other kinetic models in the literature. The acquired RMS for the developed kinetic method in this paper varies within the span of 1.2 to 3.2, depending on temperature (400–600 °C) and various feedstocks (pine–spruce–sawdust, bagasse, wood bark, beech wood and paddy straw).

In future work, the authors intend to carry out performance assessments and various sensitivity analyses of biomass pyrolysis systems under different pyrolysis conditions for various feedstocks by applying this model. Through this, the optimum conditions based on the final purpose (maximum biochar yield or bio-oil yield) for different biomass feedstocks can be found. Moreover, to assess the biomass pyrolysis system from different aspects of techno-economic, energy and environmental views, having a reliable and accurate model is critical. The model developed in this paper overcomes this problem and paves the way for the next step, that is, the techno-economic, energy and environmental assessment of the system.

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