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ORIGINAL ARTICLE

Prediction of pyrolytic product composition and yield for various grass biomass feedstocks

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Abstract
Pyrolysis is the fundamental thermochemical reaction for both combustion and gasification processes aimed at the conversion of a wide array of biomass wastes into many desirable products. The main products of biomass pyrolysis are biochar, bio-oil, and flue gases (which includes methane, carbon monoxide, hydrogen, and carbon dioxide). The present article is an attempt to observe the effect of temperature on the pyrolysis process by using elementary composition of biomass to estimate the product yield along with its composition. This study considered the grasses such as bamboo, kenaf, miscanthus, reed canary, and switch grasses as the biomass feedstock. The dependence of pyrolytic product (solid, liquid, gas) formation on variation of temperature and heating rate has been discussed. The results revealed that the amount of pyrolytic product formation is dependent on the elementary and biochemical composition of grass biomasses. Based upon the biomass composition, possibility of co-pyrolysis has been discussed in this paper. Validation of model results revealed that almost 99% similarity is observed in the case of miscanthus biochar yield; however, 10% dissimilarity in gas and water yield for miscanthus is observed between predicted and experimental yield. This modeling approach would not only help in optimizing the pyrolysis process, but also encouraged the utilization of the biomass feedstock efficiently for the production of desired products in a sustainable manner.

Keywords Biochar · Bio-oil · Flue gas · Pyrolysis · Mathematical modeling · Grasses

1 Introduction

Lignocellulosic materials are composed of biopolymers, mainly cellulose, hemicellulose, and lignin. The utilization of lignocellulosic material as chemical feedstock faces problems due to their complex structure and the difficulty to separate their components in an economically feasible way [1]. One of the simplest and oldest technologies to convert lignocellulosic materials to another class of chemicals is by the means of a thermochemical process named pyrolysis [2]. In this treatment, biomass goes through high temperature in the absence of oxygen, which results in physical and chemical changes in biomass ultimately lead to different products. The pyrolysis process consists of a very complex set of reactions that involve the formation of radicals. The products of the thermochemical processes are divided into three parts based on the product state, volatile fraction consisting gases which consists of hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and other hydrocarbon synthesis; a liquid product of bio-oil; and a carbon-rich porous solid material as biochar [3]. Due to high efficiency and good environmental performance in enhancing the energy density of bioresources, pyrolysis is attracting much attention. Modeling of the pyrolysis process assists in comprehending the process towards more economical and environment friendly.

The proportion of carbon stabilized in biochar, bio-oil, and flue gases are likely to be influenced by the proportion of cellulose, hemicellulose, and lignin content of biomass. Feedstock with high lignin content generates a maximum yield of biochar when undergoes pyrolysis around 500 °C [3]. As future research on biomass pyrolysis is aimed at high energy efficiency and specific product yield, the idea of parameters affecting the pyrolysis yield will play a crucial role.

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The pyrolysis yield is affected by feedstock type (biomass type, particle size, biomass pre-treatment), reaction condition (operational temperature, heating rate, pressure, residence time), reactor configuration, and presence/absence of catalysts [4]. However, operational temperature and heating rate are the most critical factors deciding the product yields [5]. If the purpose is to maximize the liquid product yield, process conditions are selected as low temperature and high heating rate. For high char yield, low temperature and low heating rate are required. In order to produce a high yield of gas products, high temperature, low heating rate, and long gas residence time should be applied [6].

The grasses under consideration in this paper are bamboo, miscanthus, reed canary, kenaf, and switch grass. India, China, and Myanmar have 19.8 million hectares of bamboo reserves which represent 80% of the world's bamboo forests. Forest area under bamboos in India was estimated at about 9.57 million hectares, which is nearly 12.8% of the total forest area of the country [7]. Since reed canary is an invasive species, it generally presents near lakes and other wetlands and thus inhabits other biological species and alters the ecosystem [8]. Switch grass is an adaptive plant and thus thrives in the majority of weather, soil type, and land conditions. It is found abundantly in the rocky mountain area of northern America and in parts of Mexico [9]. Kenaf is an industrial crop in Malaysia and mainly cultivated for its fiber in India, Bangladesh, USA, Indonesia, Thailand, and parts of Africa [10]. Hence, the discarded residues of grasses can be a potential source of feedstock for pyrolysis. Miscanthus originated from tropics and subtropics, but its presence had been detected throughout a wide climatic range in East Asia. The remarkable adaptability to different environments makes miscanthus suitable for cultivation in a range of North American and European climatic conditions [11]. Pyrolysis is one of the encouraging procedure used in waste management industry; it is the process in which harmful left-over like biowaste or automotive shredder residue (waste) is treated [12]. These products of pyrolysis have wide industrial and domestic applications, which are essentially needed for sustainable economic growth for developing countries like India [13, 14]. The volatile products can be cracked and partially combusted in reduced air supply to make producer gas that could be used for power generation [15], or in production of methanol or in heating processes, strategy like carbon capture and utilization (CCU) converts CO_2 into value-added products such as construction materials, plastics, fertilizers, and fuels [16]. The tarry liquid (pyrolysis oil or bio-oil) can be upgraded to high-grade hydrocarbon liquid fuels for internal combustion engine [17], commodity and specialty chemicals [18], substitute for the depleting petro-chemical sources as a conceivable way for adapting green technology [19]. Hence, the isolation of these chemicals is an additional consideration of biomass pyrolysis. Biochar has extreme porosity and surface area, which results in exceptional adsorption capacity to organic pollutants (herbicides, dyes, pesticides, antibiotics, heavy metals, and so on) [20]. Biochar have many applications such as in clean environment and sustainable energy, catalysis in transesterification reaction, super capacitor [21], reinforcement in rubber, in removal of phosphate, as asphalt flow modifier, helps in enzyme immobilization, and has an active role in drug delivery. Biochar has a potential application as a soil amendment in agriculture to improve nutrient adsorption, water retention capacity, cation exchange rate, and at the same time acts as an anthropogenic climate mitigation strategy [22]. Son et al. [23] have also discussed about the removal of heavy metal ions like Zn^{2+} using functionalized carbon nanotube and magnetic biochar.

Therefore, the modeling of pyrolysis system is the need of hour to predict the product distribution, which helps in scaling up the process based on operating reaction conditions [24]. These pyrolysis modeling could help researchers in order to get the vital outcomes by navigating through the process towards the specific products. One can get their desired pyrolytic products by manipulating different operating parameters like pyrolysis temperature, heating rate, etc.

An increasing amount of greenhouse gas (GHG) emissions like CO_2 and CO is a major global challenge, pyrolytic products (i.e., biochar) play a crucial role in carbon sequestering from the atmosphere, thus minimizing the GHG significantly [25]. Modeling of the pyrolysis could assist the researchers in developing the process economically viable, eco-friendly, and sustainable. It makes modeling of pyrolysis products from biomass crucial in the field of bioenergy and environmental biotechnology.

Mathematical modeling, simulation, and optimization are the best possible tools for analyzing and developing any complex process [26]. For the determination of quantitative composition of products, pyrolytic kinetics has to be understood. Kinetic modeling predicts the amount of pyrolytic products formed and the influence of technical parameters on pyrolysis process [27]. The outcome of pyrolysis modeling explores the economic feasibility of process by predicting the quantity of products and its by-products on a wide range of operating conditions of the temperature. Ample volume of work has been published on biomass pyrolysis regarding models, mechanism, process kinetics, and product distribution of pyrolysis with respect to parameters such as temperature and biomass composition. Different methodologies, operating conditions, fuel type, and measurement have varied widely among the studies. The prediction of product yield is possible by the development of numerous models that simulates the pyrolysis process. However, each model has its own pros and cons. Models are required to predict a simplified composition of pyrolysis products as a function of temperature.

One of the simplest and pioneering model was one-step global model, where the pyrolysis process was considered as single-step first-order reaction. These one-step models decompose the organic fuel into volatiles and coke with a fixed char yield. However, these models do not represent the real situation because it lacks the consideration of moisture content and char oxidation. Competing model is one of the classic models for wood pyrolysis. This model is empirical and was kept very simple. The cracking reaction is lumped into primary reaction, so there was no means to measure the secondary reaction, and thus, model has varying char yield [28].

One-stage multireaction model is used to determine product distribution by using simplified kinetic modeling. This model assumes that the biomass directly decomposes to its product excluding tar by a single and independent reaction. Although in this model it has been considered that the secondary reactions are parallelly taking place, it effects the yield of light gases, but such process and transport phenomenon were neglected. Two-stage, semi-global model indicates the consideration of primary and secondary stage of solid degradation process by using reaction kinetics with semi-global reaction mechanism. Here, primary reactions depend on temperature and are assumed to follow Arrhenius type equation. Secondary reactions are assumed to occur only in the gas/vapor phase. Although these assumptions simplified the pathway, yet, it only considered the phenomena occurring inside the solid and liquid phases and does not include the process occurring in the gas phase [29].

One of the models developed by Neves et al. [30], in which the plots of experimental data of CO/CO_2 and H_2/CO_2 have been used and total hydrocarbons and CO_2 to get the solutions of equations with degrees of freedom as zero. As a limitation to this model developed, one of the important parameters, (i.e.,) temperature, has not been considered for the prediction of char yield. Another economic trade-off model developed by Yoder et al. [31] for maximizing revenue with two products, bio-oil and biochar, emphasizes the heating value of biochar and bio-oil as a function of temperature. The model has focused on economic aspects of pyrolysis rather than the flue gas composition. One of the disadvantages of this model is not considering the biomass composition for the estimation of the pyrolytic product yield. Considering the unpredictability of responses engaged with the pyrolysis procedure, Song [32] has estimated the active parameters utilized in a gasifier reactor by considering the exact relations created by Neves et al. [30]. One of the upsides of this model is the temperature factor being considered while figuring the biochar quantity along with its C, H, and O proportion. Hence, the char yield shifts with the temperature. Biochar yield is directly calculated from the temperature and this yield is additionally used to compute the gas and tar yield.

In this study, the pyrolytic kinetic model planned by Song [32] was utilized to predict the production of biochar, flue gas, and tar produced in the reactor. The author considers the fuel belongs to lignocellulosic material whose main chemical constituents are cellulose, hemicellulose, and lignin. The dynamic framework of pyrolysis incorporates primary and secondary transformation procedures. Series and parallel reactions can be merged for an enhancement in the modeling process. In this paper, five various grass biomasses have been taken into consideration for further analysis of char, liquid, and flue gas yield.

2 Model development for predicting pyrolysis product yields and composition

As the biomass feedstock mainly comprises of hydrogen (H), carbon (C), and oxygen (O), the developed kinetic model utilizes the elemental characteristics (CHO) as input to predict the yield and composition of biochar, tar, and flue gas. The mathematical model was framed based on the existing literature of concepts explained for pyrolytic process as outlined in Neves et al. [30] and Song [32]. The postulates of the present mathematical model for predicting pyrolytic products are expressed underneath:

1. Drying and devolatilization of biomass quickly happen at the reactor bay
2. Oxygen is totally used up in a zone of insignificant thickness near to the inlet zone itself
3. Nitrogen does not take part in the pyrolytic reaction and so it is not taken into the consideration for elemental balance
4. Carbon gasification happens in a very much-blended isothermal reactor and the relating kinetic data can be utilized
5. Entrainment, scraps of the bed particles does not influence the reaction kinetics
6. Water gas shift response is considered as similar to its steady state
7. Biomass is in uniform size and well mixed in the reactor to ensure the representative sampling

In the foremost phase of pyrolysis, given biomass fuel (F) is taken as input and subjected to pyrolysis process for deriving numerous products such as biochar, tar, and flue gas. In the second phase, when pyrolysis occurring in high temperature, a portion of the volatiles discharged inside the molecule and can additionally participate in a secondary reaction that results in the generation of new products. The sequential and parallel response can occur either homogenously or heterogeneously as cracking, transforming, dehydration, compression, polymerization, oxidation, and gasification. In addition, the rise in pressure inside the reactor due to the gases present inside the chamber resulted in the recompression of gas to tar (fluid). Mainly secondary reactions are affected by heating temperature and vapor residence time [33]. The overall process of pyrolysis along with the possible secondary reactions is shown in Fig. 1.

The biochar yield is directly calculated by using Eq. 1. Liquid products comprise of water present as free moisture at surface, pyrolytic water (H_2O), and tar as given in Eq. 2. The flue gas consists of carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), and hydrogen gas (H_2) as depicted as in Eq. 3. C, H, and O amount in char and tar is calculated (Eqs. 4–9). Yield of H_2 is calculated by using effect of temperature (Eq. 10), which is further used to calculate the yield of CO (Eq. 11) and CH_4 (Eq. 12). Carbon, hydrogen, and oxygen mass balance has been carried out as shown in Eqs. 13–15, which has given the yield of tar, water, and carbon dioxide (Table 1). The detailed description on these equations could be referred from Swagathnath et al. [17]. The overall methodology adopted in the present study is depicted in Fig. 2, where the number in bracket indicates the equation no and T indicates the impact of temperature on the yields and CHO balance.

The elemental (ultimate analysis) composition of the desired biomass was given as input to the developed model for predicting the pyrolytic product yields. Although this model is applicable for all type of feedstock, however the present study considered the various grass biomasses as feedstocks such as kenaf grass, bamboo grass, miscanthus grass, reed canary grass, and switchgrass for the pyrolysis process. The elemental composition of the grass biomass as shown in Table 2 is retrieved from Vassilev et al. [34]. Table 3 represents the biochemical composition of grass biomasses used in the study.

The amount of energy required to increase the temperature of feedstock in a pyrolysis process from room temperature to highest reaction temperature and converting the biomass into different pyrolysis products (i.e., char, oil and gases) is defined as heat of pyrolysis [39]. The heat of pyrolysis or heating value of biomass is generally reported in two ways, higher heating value (gross calorific value) and lower heating value (net calorific value). The heat released from fuel combustion with original and generated water in a condensed state is higher heating value (HHV) and water in vapor state is called lower heating value (LHV) [40]. The corresponding HHV can be calculated using the ultimate analysis of respective biomass. Thus, the HHV (MJ kg^{-1}) of lignocellulosic materials including C, H, O, and N was calculated as outlined in Demirbas [41]. The heat of pyrolysis of considered grasses is given in Table 4.

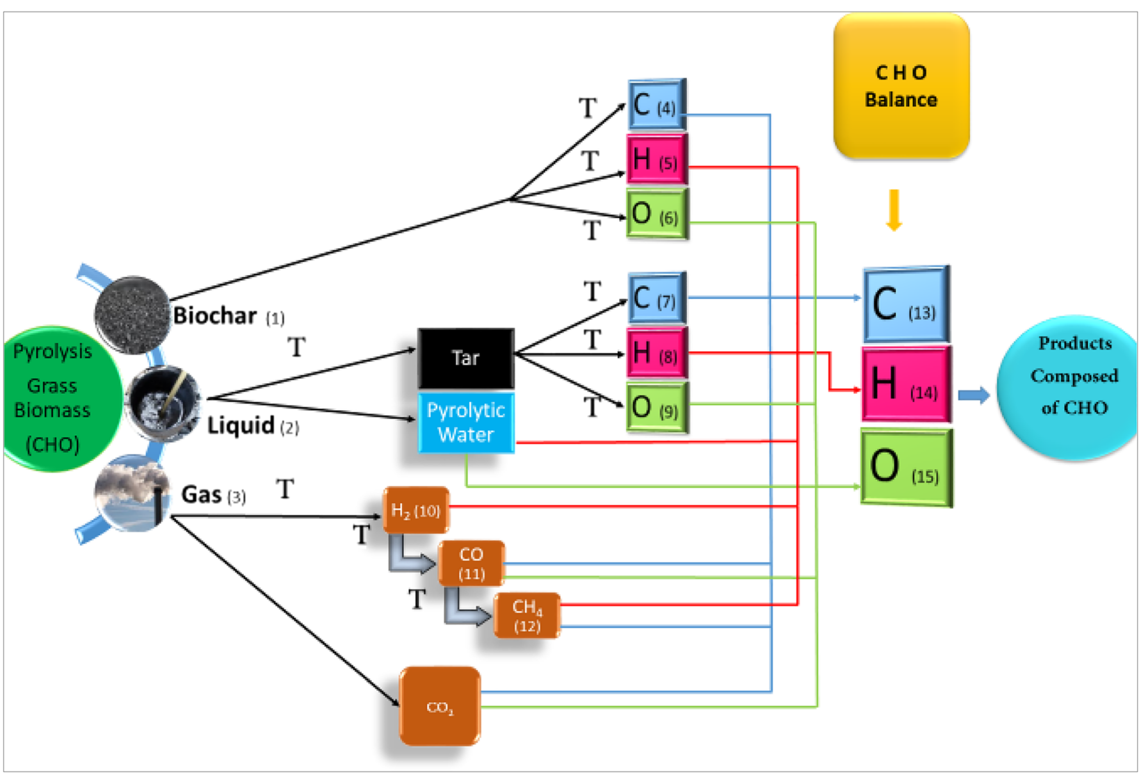

Fig. 1 Overall conceptual diagram of pyrolysis model to predict product yield and composition based on CHO balance. * Number in parentheses represents the corresponding equation in Table 1

Table 1 List of equations used in the current study to predict the yield of pyrolytic products

Description	Equation	Equation no.
Char yield from biomass	$Y_{ch,\ F} = 0.106 + 2.43 * exp\,(-0.66 * T * 10^{-2})$	1
Total liquid yield	$Total\ liquid\ yield = Y_{tar,F} + Y_{H_2O,F} + Moisture\ content\ of\ biomass$	2
Total gas yield	$Total\ volatile\ gas\ yield = Y_{H_2,F} + Y_{CO,F} + Y_{CH_4,F} + Y_{CO_2,F}$	3
Carbon content in char	$Y_{C,\ ch} = 0.93 - 0.92 * exp\,(-0.42 * T * 10^{-2})$	4
Hydrogen content in char	$Y_{H,\ ch} = (-0.41 * 10^{-2}) + (0.10 * exp\,(-0.24 * T * 10^{-2}))$	5
Oxygen content in char	$Y_{O,\ ch} = 0.07 + 0.85 * exp\,(-0.48 * T * 10^{-2})$	6
Carbon content in tar	$Y_{C,\ tar} = Y_{C,\ F} * (1.05 + (1.9 * T * 10^{-4}))$	7
Hydrogen content in tar	$Y_{H,\ tar} = Y_{H,\ F} * (0.93 + (3.8 * T * 10^{-4}))$	8
Oxygen content in tar	$Y_{O,\ tar} = Y_{O,\ F} * (0.92 - (2.2 * T * 10^{-4}))$	9
Hydrogen gas yield	$Y_{H_2,F} = 1.145*\left(1-exp\left(-0.11*T*10^{-2}\right)\right)^{9.384}$	10
Carbon monoxide gas yield	$Y_{CO,F} = Y_{H_2,F}/((3*10^{-4} + \left(\frac{0.0429}{\left(1+\frac{T}{632}\right)^{-7.23}}\right)$	11
Methane yield	$Y_{CH_4,F} = 0.146*Y_{CO,F}-\left(2.18*10^{-4}\right)$	12
Carbon balance	$Y_{C,F}-Y_{C,ch}*Y_{ch,F} = Y_{C,tar}*Y_{tar,F} + Y_{C,CH_4}*Y_{CH_4,F} + Y_{C,CO}*Y_{CO,F} + Y_{C,CO_2}*Y_{CO_2,F}$	13
Hydrogen balance	$Y_{H,F}-Y_{H,ch}*Y_{ch,F} = Y_{H,tar}*Y_{tar,F} + Y_{H,CH_4}*Y_{CH_4,F} + Y_{H,H_2}*Y_{H_2,F} + Y_{H,H_2O}*Y_{H_2O,F}$	14
Oxygen balance	$Y_{O,F}-Y_{O,ch}*Y_{ch,F} = Y_{O,tar}*Y_{tar,F} + Y_{O,CO}*Y_{CO,F} + Y_{O,CO_2}*Y_{CO_2,F} + Y_{O,H_2O}*Y_{H_2O,F}$	15

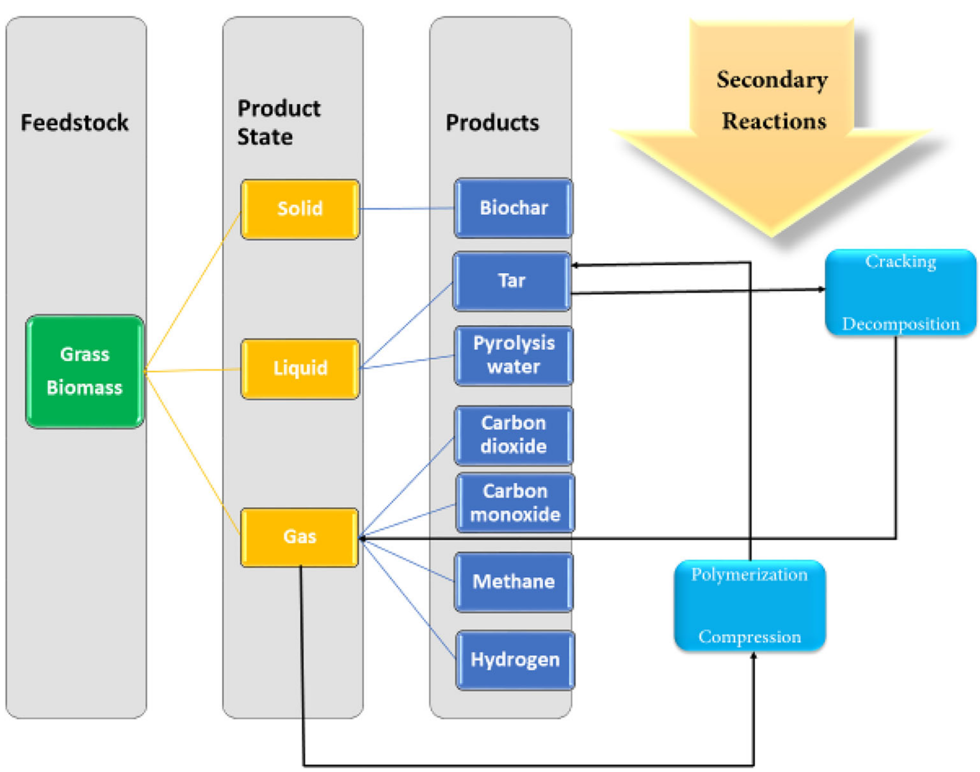

Fig. 2 Overall pyrolysis process of grass biomasses for various products including secondary reactions

Table 2 Elementary composition of different grass biomasses used in the study

Biomass (grasses)	Carbon	Oxygen	Hydrogen	Nitrogen	Sulfur
Kenaf	48.4	48.5	6.0	1.0	0.15
Bamboo	52.0	42.5	5.1	0.4	0.04
Miscanthus	49.2	44.2	6.0	1.0	0.15
Reed canary	49.4	42.7	6.3	1.5	0.15
Switch grass	49.7	43.4	6.1	0.7	0.11

Table 4 Heat of pyrolysis of grass biomasses by calculating higher heating value (HHV)

Biomass	Heat of pyrolysis, MJ kg^{-1}
Kenaf grass	17.13
Bamboo	18.07
Miscanthus	18.06
Reed canary	18.72
Switch grass	18.54

3 Results and discussion

The presented model predicts the amount of tar, char, and gas composition at known temperature for a given grass biomass. The model needs the percentage of C, H, and O (elementary composition) in biomass as the input. This model was executed on “MATLAB R2015b” to predict the yield of the various pyrolytic products. In this paper, the code for the pyrolysis temperature displayed from 200 to 1000 °C and the program yield (the relating estimate for the pyrolysis product) had been stored away in excel sheet and different examinations had been completed with this acquired information.

3.1 Pyrolysis product yield with respect to temperature

The present model predicts the general production pattern of biochar, tar, and volatile gases (like CO, CO_2, CH_4, H_2) with reference to operational temperature for any grass biomass. Figure 3 represents the prediction of various pyrolytic products for bamboo grass biomass as an example. The lower yield of biochar at higher temperature is a consequence of further decomposition of organic matter at a higher temperature, resulting in the release of volatile material. The tar amount intensified at the initial pyrolysis temperature and after that decreased because of secondary cracking. Variation in the yield of volatile gases over the temperature range could be due to different breakdown patterns of cellulose, hemicellulose, and lignin of biomass [42]. Among the gases, the amount of H_2, CO, and CH_4 was found to increase at higher pyrolytic temperature. As in Fig. 3, it was seen that a higher yield of water has been acquired at the pyrolytic temperature varying from 360 to 380 °C due to the release of moisture bound in the biomass. In case of volatile compounds, the increasing pattern of CO_2 release has been seen up to 800 °C and further increment in temperature exhibited decline profile. Similar patterns were observed in other grasses, which may be due to the fact that all the considered grasses were categorized under the lignocellulosic biomass with comparable, elementary, and biochemical composition.

3.2 Yield of liquid products

3.2.1 Tar yield

The examination of the pyrolysis model demonstrated that the considered grass sorts of biomass created a nearly a similar amount of tar and they pursue a similar pattern regarding temperature. Despite the fact that they have comparative patterns, reed canary grass creates a marginally more noteworthy measure of tar when contrasted with other grass biomasses. Kenaf grass released relatively lesser tar and all these differences might based on minimal distinctions in the biochemical composition of the biomasses. Figure 4a represents the variation of tar yield with reference to temperature for various grass biomasses. Reed canary and kenaf grasses have the most (42.6%) and least (21.5%) hemicellulose composition, respectively, which may identify with the variation of tar yield during the pyrolysis process. The presence of a higher proportion of hemicellulose in the biomasses might enhance the overall tar yield. High concentration of inorganic substance present in the biomass known to increased biochar devolatilization at high temperature at that point results in a greater yield of fluid and volatile gases [43].

Table 3 Biochemical composition of various grass biomasses used in the study

Grass biomass	Cellulose	Hemicellulose	Lignin	Reference
Kenaf	45–57	21.5	8–13	Akil et al. [35]
Bamboo	41.8	27.2	23.2	Chen et al. [36]
Miscanthus	50.4	26.5	12.2	Brosse et al. [37]
Reed canary	29.7	42.6	7.6	Dhyani and Bhaskar [38]
Switch grass	45.0	31.4	12.0	Dhyani and Bhaskar [38]

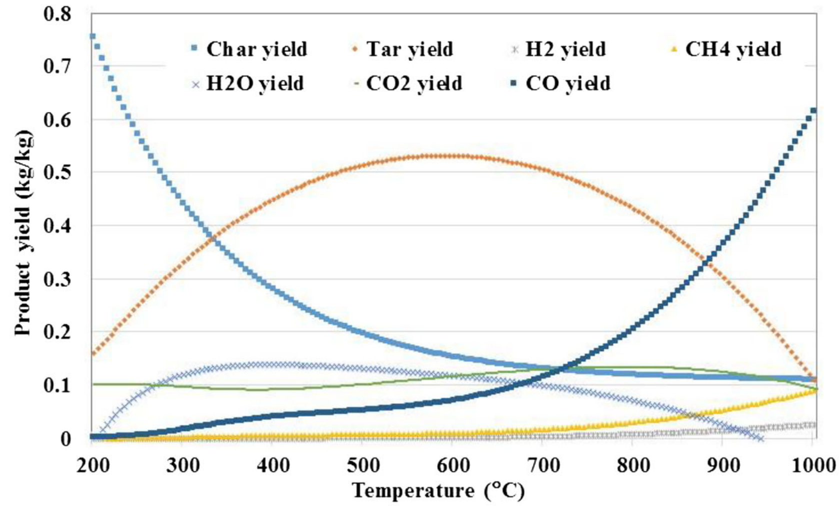

Fig. 3 Effect of pyrolysis temperature on various product yields obtained from bamboo grass

It may be very well concluded that the maximum amount of tar can be acquired at around 600 °C. The quantity of tar or oil declines as a function of temperature. Tar mainly comprises of benzene, toluene, styrene, phenol mixes, and a small measure of naphthalene [44]. At higher temperatures, specifically, tar compounds are broken down and result in a

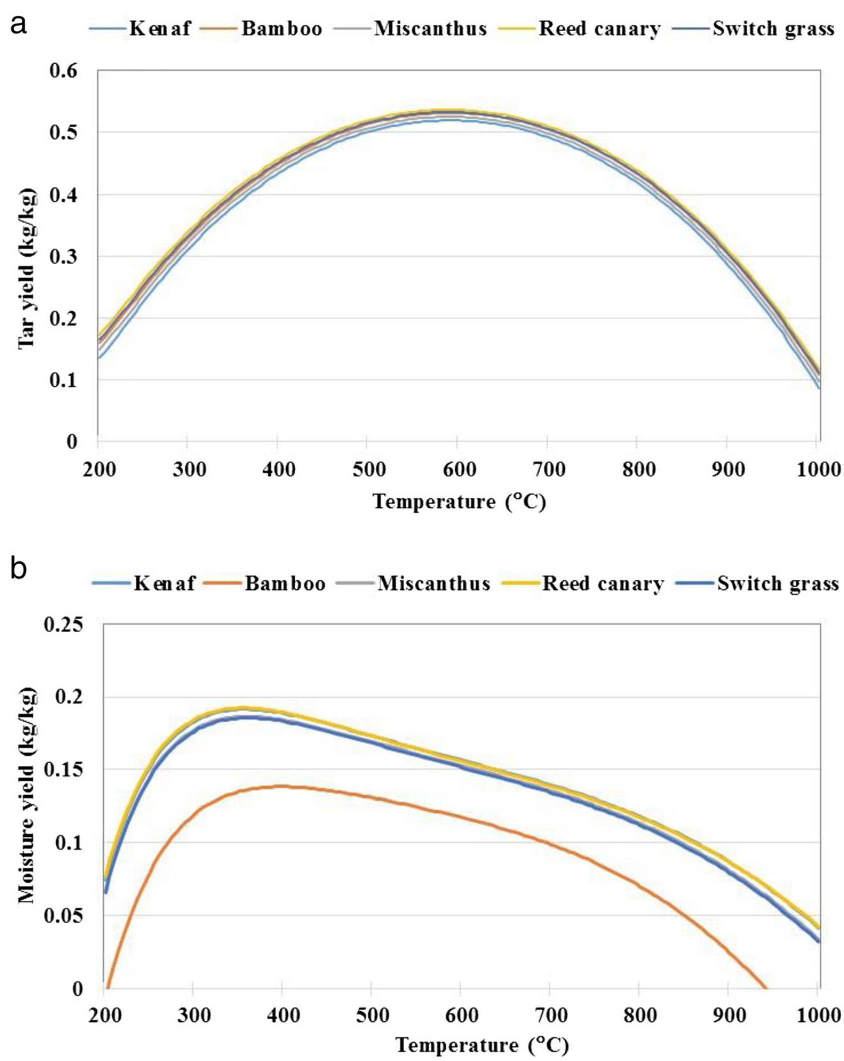

Fig. 4 Effect of pyrolytic temperature on **a)** tar yield and **b)** moisture yield from pyrolysis of grasses

decline in tar yield. Andrés et al. [45] reported that stable tar compounds with phenols and oxygenated tar species as a notable part are decomposed at high temperature in the range of 750–850 °C. Oxygen-containing phenolic compounds, for instance, phenol, cresol, and naphthols, are converted to volatile gases in the 700–850 °C temperature range. Non-oxygen-containing fragrant or polyaromatic compounds just crack at higher temperature of 850 to 1200 °C. Because of cracking during pyrolysis process, carbon dioxide, hydrogen, and carbon monoxide were released [46]. These outcomes could explain the increased yield of carbon dioxide and hydrogen in the temperature range of 750–850 °C.

3.2.2 Moisture yield

Free and bound moisture of the biomass adds to the overall pyrolytic moisture yield. Figure 4b demonstrates that the water yield increases till 350 °C, which is due to discharge of free followed by bound moisture particles of the biomass and afterward diminishes linearly till 1000 °C. At further higher temperature, the decline of moisture yield with an increment of H_2 and CH_4 could be observed [47]. Figure 4b shows with the exception of bamboo, every single different grass yield a practically equivalent amount of moisture. On account of bamboo, it yields overall less quantity of water when compared with different grasses under consideration.

3.3 Yield of gaseous products

The volatile gases and tar at higher temperature experience a progression of secondary reaction such as decarboxylation, deoxygenation, dehydrogenation, and cracking which further results in increment in flue gas. H_2 is generated from the splitting of hydrocarbons at a higher temperature. Emission of CO and CO_2 shows the presence of oxygen in the biomass. Those components fundamentally origin from the breaking of mostly oxygenated organic compounds. The measure of cellulose present in the biomass is an essential factor in deciding the measure of carbon oxides created. The light hydrocarbons such as CH_4, C_2H_4, and C_2H_6 might be produced because of the restructuring and breaking of heavier hydrocarbons and tar in the vapor stage [48]. Figure 5 portrays the effect of temperature on CO_2 yield. Around 800 °C, the carbon dioxide yield attains maxima and then decreases up to 1000 °C. Partial oxidation of carbon-to-carbon monoxide, rather than complete oxidation to carbon dioxide leads to this decline in CO_2 yield. The yield of hydrogen is high at a higher temperature but it is still produced in a very insignificant amount. At higher temperature, very high amount of carbon monoxide is supposed to release, which dictates that high-temperature pyrolysis process is non-environment friendly.

The bigger hydrocarbon molecules breakdown into smaller and simpler molecules might raised the methane production at higher temperature ($T > 700$ °C). Methane provides a great environmental benefit, producing more heat and light energy by mass than other hydrocarbon or fossil fuel. However, in the background of promoting energy conservation and environmental protection, it is of great significance to effectively reduce the methane release from the pyrolysis process [49]. Although the yield of biogases is less, their presence can be seen at higher operational temperature during pyrolysis.

3.4 Yield of solid char

The yield of char is greatly affected by operational temperature. Over the progress of reaction temperature, the char yield is declining at higher temperature, however with more carbon content. Because the elementary and biochemical composition is practically comparative for all grass biomass, distinct contrasts between the yields of biochar among the diverse grass biomasses were not observed. Yet, the little dissimilarity

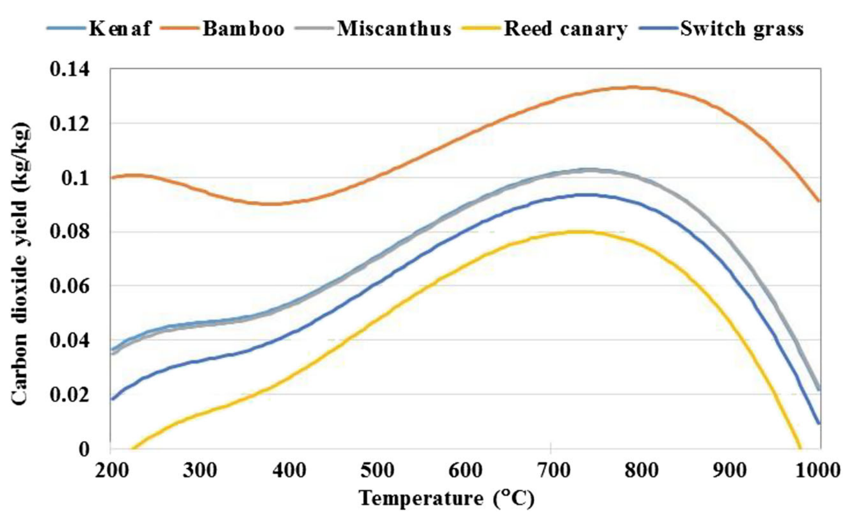

Fig. 5 Effect of pyrolytic temperature on yield of carbon dioxide from pyrolysis of grass biomasses

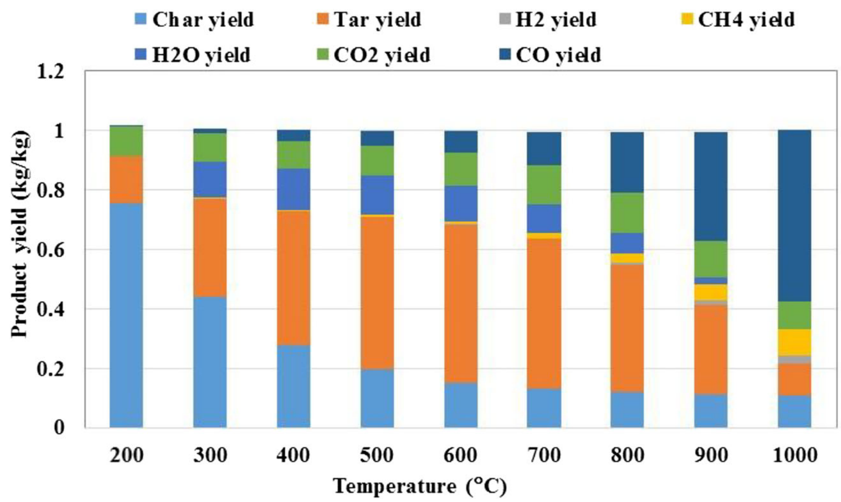

Fig. 6 Profile of pyrolytic product composition for bamboo grass with reference to reaction temperature

between the elemental composition of the considered biomass results in very insignificant variation in the char yield (Results not shown). By utilizing Eq. 16, the char yield was calculated.

$$\textit{Calculated char yield} = 1-\left(Y_{tar,F} + Y_{H_2O,F} + Y_{H_2,F} + Y_{CO,F} + Y_{CH_4,F} + Y_{CO_2,F}\right) \quad (16)$$

The biochar yield decreases with the increase in temperature, and at a higher temperature, the yield becomes constant as shown in Fig. 3. This char yield pattern shows the similarity to the result deduced by [50]. It might be due to the increase in the fixed carbon content at a higher temperature [51].

Figure 6 portrays the impact of temperature on pyrolytic products. At low temperature ($T \leq 400$ °C), biochar yielding is ruling, moderate temperature (400 °C $\leq T \leq$ 700 °C) favors bio-oil generation, and flue gas dominates the pyrolysis products at high temperature ($T \geq 700$ °C). It was observed from the present model that char yield is related to temperature in an exponentially negative fashion and the gas yield is exponentially proportion to the operational temperature. The presented model found non-linear relationship between the operational temperature and pyrolysis yields.

3.5 Effect of biomass on yield

The biochar yield of all the grass biomass is almost the same; nevertheless, a slight variation can be seen between the feedstock at a lower temperature. Bamboo, reed canary, and switchgrass have a marginally higher yield of biochar at a lower temperature. This is due to the higher fixed carbon content in Bamboo, reed canary, and switchgrass when contrasted with other grass biomasses. Bamboo, reed canary, and switchgrass have a moderately high carbon content of 52, 49.4, and 49.7%, respectively, while the grass average carbon content is 49.74%. The average C, H, and O composition of the grass biomass were found to be 49.74, 5.90, and 44.26%, respectively. When the deviation between elementary and average elementary composition is greater, then high variation in the biochar yield is observed. The high hydrogen amount (6.3%) of the reed canary grass leads to the higher moisture yield. Therefore, reed canary yields a higher amount of water compared to other biomass. Higher carbon amount (52%) of bamboo results in higher emission of carbon dioxide during the pyrolysis. The attributes of pyrolysis products incorporate the biochemical and elemental composition, thickness, permeable structure, and pH, shifts dependent on the feedstock biomass type [52].

Table 5 Validation of predicted pyrolytic yields with reported experimental data

Grass feedstocks	Pyrolysis	Biochar yield (%)		Bio-oil yield/organic (%)		Gas and pyrolytic water yield (%)		References
	Temp (°C)	Experimental	Predicted	Experimental	Predicted	Experimental	Predicted	
Bamboo	300	49.30	44.15	26.50	33.15	23.20	23.01	Chen et al. [55]
Miscanthus	500	19.17	19.56	61.31	50.80	20.03	29.06	Greenhalf et al. [56]
Reed canary	500	22.00	19.56	47.20	52.03	24.20	28.41	Fahmi et al. [57]
Switch grass	500	24.70	19.56	51.50	51.59	7.90	11.23	Greenhalf et al. [56]

Co-pyrolysis could be encouraged since all the grass biomasses have practically comparable elemental and biochemical composition. This energy efficient process can be used to compensate for the availability restrictions of the grass biomass. The char obtained after co-pyrolysis had high calorific incentive than standard pyrolysis as co-pyrolysis product has low water content of bio-oil, so the char obtained after co-pyrolysis had high calorific value than ordinary pyrolysis [53]. Enhancement of bio-oil produced from fast pyrolysis can be performed by co-pyrolysis in an economical and sustainable manner. Ideally, waste derived from co-pyrolysis would improve oil as well as char properties (as part of char by-product), and therefore, costs due to disposal in landfills or to the ocean and the associated environmental impact are mitigated [54].

3.6 Model validation

Table 5 compares the predicted yield from the present model with the real experimental yield that has been published in the scientific literature for different grass biomasses. The yields of the pyrolytic products were estimated by this mathematical model for wide range of operating temperature of pyrolysis process. In the instance of biochar yield, 5% difference is seen in switchgrass, in case of other grasses, dissimilarity between predicted and experimental yield is less than 5%. Switchgrass bio-oil yield is nearly the equivalent on account of experimental and predicted data. Ten percent difference were observed on account of gas and pyrolytic water yield in case of miscanthus grass. In the instance of flue gas generation, bamboo and miscanthus grasses show fundamentally the same as the result for the model prediction. For other grass biomass, the difference is insignificant. However, the kenaf grass experimental information is excluded in this paper because of the inaccessibility of information.

4 Conclusion

The present model evaluated the effect of operational temperature and elemental composition of biomass on the yield of pyrolytic products. The amount of heat required to accomplish the pyrolysis process is calculated by using the ultimate analysis of biomass. The model depicts similar output yield trends for all considered grasses (i.e., kenaf, bamboo, miscanthus, reed canary, and switchgrass). However, the slight differences were observed due to slighter variation on elementary and biochemical composition of biomass, which further encouraged for energy efficient co-pyrolysis process. Model was predominantly found to predict the yield of pyrolytic products with high accuracy of less than 5% and in few cases, the variation was around 10%. Though the present model was demonstration for grasses as feedstocks, it can be further extended to other lignocellulosic group of biomasses as well. Since pyrolysis is a complex process and its yield could be affected by various parameters, development of prediction models with better accuracy and user friendly need to be addressed.

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