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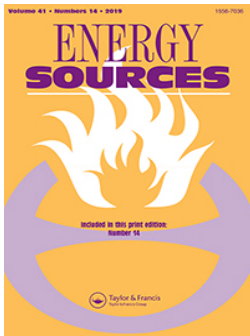
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Kinetic modeling and optimization of parameters for biomass pyrolysis: A comparison of different lignocellulosic biomass

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ABSTRACT

A primitive element for the development of sustainable pyrolysis processes is the study of thermal degradation kinetics of lignocellulosic waste materials for optimal energy conversion. The study presented here was conducted to predict and compare the optimal kinetic parameters for pyrolysis of various lignocellulosic biomass such as wood sawdust, bagasse, rice husk, etc., under both isothermal and non-isothermal conditions. The pyrolysis was simulated over the temperature range of 500–2400 K for isothermal process and for heating rate range of 25–165 K/s under non-isothermal conditions to assess the maximum pyrolysis rate of virgin biomass in both cases. Results revealed that by increasing the temperature, the pyrolysis rate was enhanced. However, after a certain higher temperature, the pyrolysis rate was diminished which could be due to the destruction of the active sites of char. Conversely, a decrease in the optimum pyrolysis rate was noted with increasing reaction order of the virgin biomass. Although each lignocellulosic material attained its maximum pyrolysis rate at the optimum conditions of 1071 K and 31 K/s for isothermal and non-isothermal conditions, respectively, but under these conditions, only wood sawdust exhibited complete thermal utilization and achieved final concentrations of 0.000154 and 0.001238 under non-isothermal and isothermal conditions, respectively.

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Introduction

The Policy Energy Act agreement (Demirbas, Sahin-Demirbas, and Hilal Demirbas 2004) followed by the Energy Independence and Security Act (Georgiou, Polatidis, and Haralambopoulos 2012) implies to achieve 36 billion gallons of biofuel production by the year 2022. Upsurge concern regarding depletion of fossil fuel and greenhouse gas emissions has eventuated an increased interest in nonconventional fuel technologies based on bio-renewable resources including starches, sugars, and lignocellulosic materials. Although sugar-based and corn-based raw materials are attractive substitutes for gasoline production, they are insufficient to supersede a major part of the one trillion gallons of fossil resources currently being exhausted worldwide per year (Limayem and Ricke 2012). Lignocellulosic biomass represents an alternative and clean energy source which transforms solar energy and atmospheric CO₂ into chemical energy via photosynthesis and plays a notable role in climate change alleviation and fossil fuel substitution (Mahmood et al. 2016a). Conversely, the large-scale supply of these nonfood cellulosic materials can

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be furnished from numerous low-cost raw materials such as wood sawdust, agricultural and forest residues, and industrial wastes with estimated annual production up to 146 billion tons worldwide (Wang et al. 2018).

Although numerous conventional techniques for the disposal of waste biomass have been evolved, the management of these wastes remains confronting. Furthermore, the methods to process these lignocellulosic materials such as landfill and incineration would provoke many potential supplementary hazards to the human health and the environment (Demirbas 2006). Accordingly, the development of efficient conversion processes of lignocellulosic materials for sustainable heat and power generation is the principal focus of scientific and industrial research. Pyrolysis, as the foremost stage during thermochemical conversion route of biomass (Mahmood et al. 2016b), is the thermal decomposition of complex lignocellulosic matrix into an array of liquid, solid, and gaseous products in the presence of an inert environment and has been extensively investigated in recent decades (Mahmood et al. 2017; Wang et al. 2018). It is a promising technique to process biomass and produce high-value-added products such as bio-oil, synthesis gas, and chemicals. Lignocellulosic biomass is a composite material, mainly composed of three biopolymers, namely, cellulose, hemicellulose, and lignin with relative distribution, and chemical structures depend on the certain species type and also development conditions. A careful description of lignocellulose pyrolysis accordingly includes various reactions. Such an extensive range of reactions will enhance the complexity of the models as well as the computational cost, since reactions will crop up over numerous characteristic times, impressing the overall stiffness of the system of equations (Ding et al. 2018). Nevertheless, accuracy and computational cost need to be balanced provoking the researchers to inevitably apply simplified models to subdue this challenge (Yiin et al. 2018). Therefore, kinetic of biomass pyrolysis has been investigated extensively in the recent decades.

The principal products of pyrolysis can be classified into tar, char, and volatile gases such as CH_4 , H_2 , CO , and CO_2 . The final composition and yield of pyrolysis products rely on lignocellulosic feedstock and operating parameters. A thermal kinetic model, which can efficiently predict all the products yield, is necessary in modeling, design, and scale-up of combustors and gasifiers (Babu and Chaurasia 2003). Conversely, since biomass mainly comprised of cellulose, hemicelluloses, and lignin, the expanse and rate of thermal disintegration of these components depend upon operating variables. Thus, it is also often indispensable to explore the impact of important parameters on product yield and instinct about their optimization. The most important operating parameters may include pyrolysis temperature, residence time, and rate of biomass heating. In general, lignocellulose conversion efficiency increases with increase in reaction temperature (Akhtar and Amin 2012). By increasing final temperature from 450°C to 700°C during flash pyrolysis of sunflower oil cake, 10.7% improvement in the conversion was reported (Yorgun, Şensöz, and Koçkar 2001). However, within same temperature interval (400–700°C), Ozbay et al. noted a higher decomposition rate of 17.5% for cottonseed cake pyrolysis (Ozbay, Pütün, and Pütün. 2006). On the other hand, residence times of few seconds to few minutes are often desirable to achieve optimum bio-oil yields through lignocellulose pyrolysis. Even so, it is arguable to conceive complete thermal utilization of biomass at very short residence times due to heat transfer limitations at particle surface (Akhtar and Amin 2012). The effect of heating rate on the pyrolysis yield of lignocellulosic biomass has also been elaborated. A 23.36% rise in liquid oil yield during rapid pyrolysis of soybean cake was observed by increasing heating rates from 5 to 700°C/min (Pütün et al. 2007). An interesting finding during rapid pyrolysis of cottonseed cake was reported by Ozbay et al. that liquid oil yield was enhanced at faster rates for initial heating rate interval of 0–300°C/min in contrast to the variations from 300 to 700°C/min. Optimum temperature for higher pyrolysis yield was also significantly affected the biomass heating rate (Ozbay, Pütün, and Pütün. 2006).

Technical enhancements of biomass contribution to cope with commercial energy demands are focused on improving the efficiency of conversion processes by optimization of the operating parameters. Large-scale development and optimization of pyrolysis and gasification systems necessitate kinetic modeling which allow quantitative representation of various reactions, and could be

a powerful tool for prediction of reactor performances, process design, assessment of pollutants evolution, and improved strategies for effective control. But, the absolute reaction mechanism of lignocellulose pyrolysis is exceedingly complex due to the formation of hundreds of intermediate products. Pyrolysis of lignocellulosic materials is, therefore, usually modeled based on the apparent kinetics (Zhang et al. 2009). An ideal thermal kinetic model should incorporate the primary reactions as well as the secondary disintegration reactions. Although substantial contributions have been made on kinetic modeling (Gao et al. 2017; Sheeba, Sarat Chandra Babu, and Jaisankar 2010), estimation and comparison of the optimum values of the important kinetic parameters affecting the pyrolysis process for numerous lignocellulosic materials are still lacking in the literature so far. In the present work, kinetic modeling and optimization of various parameters for pyrolysis of numerous lignocellulosic biomass including douglas fir bark, rice husk, peanut hull, and bagasse has been presented. A comparison of optimized parameters for different feedstocks with respect to thermal utilization, net heating rate, temperature, and final concentration has been conferred.

Method

The following is the two-step kinetic model proposed by Koufopoulos et al. for lignocellulosic biomass pyrolysis. The model was based on an experimental setup consisting of a tubular reactor 38 mm in diameter placed vertically into a tubular furnace heated electrically. The reactor furnished 100 mm long isothermal reaction belt with a maximum temperature difference of 10 K and negligible radial temperature distribution. The reaction proceeded under a nitrogen flowrate of 1667 cm³/min (at 101.3 kPa and 293 K), which was adequate to maintain a uniform temperature zone, depositing the oxygen and drive away the volatile and gaseous products from the reactor (Koufopoulos et al. 1991).

The kinetics of pyrolysis of all lignocellulosic biomass in the present study was simulated utilizing this model by taking the different decay order of each biomass which are found by modeling of thermogravimetric analysis elsewhere (Hashimoto et al. 2011).

The virgin biomass is thermally degraded with reaction order n_1 into primary volatile, gases, and solid char. These primary products react with each other to form secondary volatile, gases, and char. The kinetic equations for the above proposed model correlating the reaction rates with concentrations of five species are given below (Babu and Chaurasia 2003):

$$\frac{dC_B}{dt} = -k_1 C_B^{n_1} - k_2 C_B^{n_2} \quad (1)$$

$$\frac{dC_{G_1}}{dt} = -k_1 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (2)$$

$$\frac{dC_{C_1}}{dt} = k_2 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (3)$$

$$\frac{dC_{G_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (4)$$

$$\frac{dC_{C_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \quad (5)$$

where

n_1 = Reaction order for virgin biomass

n_2 = Reaction order for primary volatiles and gases = 1.5 (Babu and Chaurasia 2003; Gao and Li. 2008)

n_3 = Reaction order for primary solid char = 1.5 (Babu and Chaurasia 2003; Gao and Li. 2008)

This model is valid for isothermal as well as for non-isothermal conditions. For non-isothermal conditions, the temperature T can be replaced by a linear equation correlating the temperature as a function of heating rate H and time (Srivastava and Jalan 1996);

$$T = (H)t + T_o \quad (6)$$

where,

H = Heating rate in Kelvin per second (K/s)

T_o = Initial temperature in Kelvin (K)

At t = 0, only the virgin biomass is present and no primary or secondary products are formed. So the following set of initial conditions is applicable:

$$C_B = 1.0; C_{V1} = C_{C1} = C_{V2} = C_{C2} = 0$$

Simulation strategy

The model Equations (1)–(5) are solved by using the fourth-order RungeKutta method in Matlab-7 for each biomass with corresponding reaction order (Hashimoto et al. 2011; Hu, Jess, and Xu. 2007) for isothermal and Eqs. (1–6) for non-isothermal conditions. For isothermal conditions, the kinetic model is solved for a maximum simulation time of 20 s (Srivastava and Jalan 1994) for a specific biomass at a specific temperature starting from 500 up to 2400 K taking a step size of 10 K initially and then reducing it to even 1 K. For each simulated output, the pyrolysis rate of virgin biomass as well as the rate of char 1, volatile 1, etc., have been calculated. The optimum value of the temperature is based on the point where maximum pyrolysis rate of virgin biomass is attained. Once the optimized value of temperature is obtained, the model is again simulated at these optimized conditions to verify the optimum values of final concentration and pyrolysis rate of virgin biomass of primary and secondary species formed. The same strategy has been adopted for non-isothermal conditions for each biomass under heating rate range 25–165 K/s by taking a step size of 10 K/s initially and ultimately reducing it to 1 K/s. Table 1 summarizes the proximate and elemental analysis of different lignocellulosic materials studied in the present work.

Results and discussions

Non-isothermal conditions

The simulated concentration distributions of five species during biomass pyrolysis under non-isothermal conditions at the heating rate of 25 and 60 K/s are shown in Figure 1. The simulated results are found to have the same qualitative trends as already reported (Babu and Chaurasia 2003; Gao and Li. 2008).

The effect of heating rate on the pyrolysis rate of different biomass is shown in Figure 2a. Pyrolysis rate indicates the fractional mass change of the biomass material per unit time due to thermal disintegration during pyrolysis (Yang et al. 2006). Pyrolysis rate first increases with heating rate, but this trend is observed up to a certain value of heating rate; after that the pyrolysis rate decreases with heating rate providing an optimum value of heating rate at which the pyrolysis rate is maximum. This is attributed due to the destruction of active sites of char as a result of increase in

Table 1. Proximate and ultimate analysis of the lignocellulosic materials.

| Sr. No. | Lignocellulosic material | Proximate analysis (Weight %, dry basis) | | | Ultimate analysis (Weight %, dry basis) | | | Reference |
|---------|--------------------------|---|-------|-------|--|------|-------|---------------------------------------|
| | | FC | VM | Ash | C | H | O | |
| 1 | Douglas fir bark | 32.79 | 65.46 | 1.75 | 53.10 | 6.10 | 40.60 | (Parikh, Channiwala, and Ghosal 2007) |
| 2 | Peanut hull | 21.09 | 73.02 | 5.89 | 45.77 | 5.46 | 39.56 | (Parikh, Channiwala, and Ghosal 2007) |
| 3 | Bagasse | 14.95 | 73.78 | 11.27 | 44.80 | 5.35 | 39.55 | (Channiwala and Parikh 2002) |
| 4 | Wood sawdust | 15.00 | 82.70 | 2.30 | 47.50 | 6.07 | 43.88 | (Parikh, Channiwala, and Ghosal 2007) |
| 5 | Rice husk | 16.95 | 61.81 | 21.24 | 38.50 | 5.20 | 34.61 | (Channiwala and Parikh 2002) |

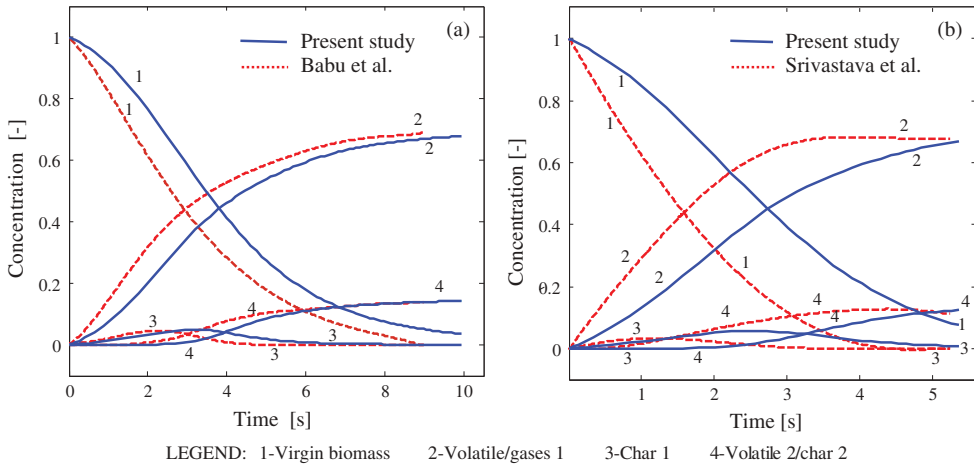


Figure 1. Simulated concentration distributions for wood sawdust under non-isothermal conditions at heating rate $H = 60$ K/s (a) and 25 K/s (b).

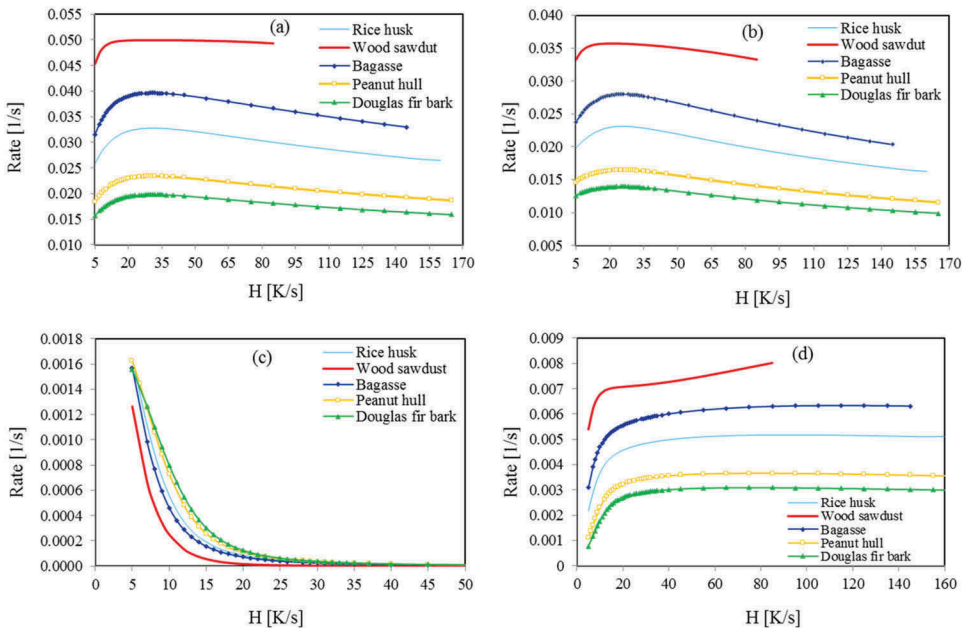


Figure 2. Pyrolysis rate of virgin biomass (a) and rate of volatile/gases 1 (b), char 1 (c), and volatile 2/char 2 (d) vs. heating rate under non-isothermal conditions.

heating rate (Babu and Chaurasia 2003). So, the virgin biomass needs more time to reach the same final concentration, and hence the biomass consumption rate decreases.

It has also been observed that for each of the biomass douglas fir bark, peanut hull, bagasse, wood sawdust, and rice husk, the maximum pyrolysis rate occurs at the same heating rate value, i.e., at $H = 31$ K/s, although at this optimum heating rate the maximum pyrolysis rate for each biomass is different. At optimum conditions, the fastest pyrolysis rate is for wood sawdust ($n_1 = 1.0$) at 0.0499 s^{-1} followed by bagasse and rice husk at 0.03962 and 0.032769 s^{-1} , respectively. The lowest curve in Figure 2a is for douglas fir bark ($n_1 = 8.914$) which thermally degraded at the rate of 0.0197945 s^{-1} at the optimum

heating rate. The simulated rate of volatile/gases 1 and char 1 is shown in Figure 2b,c,, respectively. It can be observed that at higher heating rates, the rate of both species decreases attributed to the fact that the secondary reactions are dominant at higher heating rate which is clear from Figure 2d that shows the effect of heating rate on the rate of volatile 2/char 2.

A comparison of the simulated concentration profiles of primary and secondary species for different biomass at the optimum heating rate of 31 K/s is shown in Figure 3. It is clear from the figure that the concentration of each biomass decreases with time, but the final concentration achieved is different for each biomass. In the case of wood sawdust, the final concentration of virgin biomass is reduced even below 0.0013. For bagasse and rice husk, the final concentration values do not fall below 0.2 showing that about 80% of biomass is utilized at optimum heating rate conditions. The final concentration values for peanut hull and douglas fir bark are 0.5321 and 0.6041, respectively. This indicates that at optimum heating rate, although the pyrolysis rate of biomass is maximum, only about 47% of initial biomass is thermally destroyed for peanut hull and about 40% for douglas fir bark. This suggests that for complete thermal utilization of virgin biomass a compromise has to be made between pyrolysis rate and other operating parameters of a pyrolyzer or gasification system.

Table 2 gives a comparison of the simulated optimum parameters for pyrolysis of wood sawdust under non-isothermal conditions with the data already reported in the literature. The difference in some parameter values with the reported literature is due to the different methodologies adopted and different termination criteria selected for simulation. Babu's (Babu and Chaurasia 2003) optimization results are based on the minimization of pyrolysis time and final concentration of initial biomass equal to 0.03 as termination criteria. In the present study, the optimum parameters are based on the maximization of pyrolysis rate of virgin biomass with a simulation time of 20 s. A summary of the optimum parameters found in this study under non-isothermal conditions for wood sawdust, bagasse, peanut hull, douglas fir bark, and rice husk is provided in Table 3.

Isothermal conditions

The solution of kinetic model Equations (1–5) for wood sawdust ($n_1 = 1$) under isothermal conditions at the temperature 1023 and 873 K is shown in Figure 4. The simulation results are

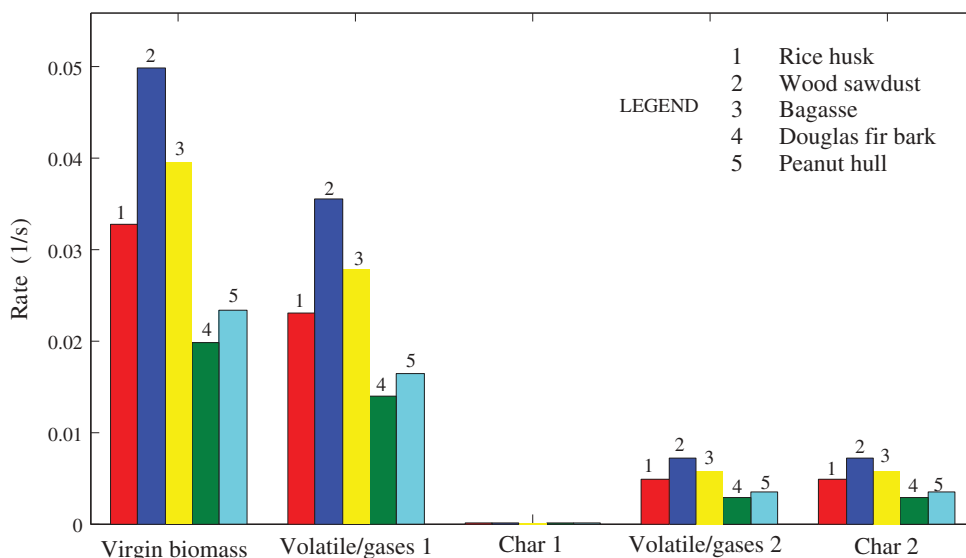


Figure 3. Simulated concentration distribution during biomass pyrolysis under non-isothermal conditions at an optimum heating rate of 31 K/s.

Table 2. Comparison of the predicted optimum parameters for pyrolysis under non-isothermal conditions for wood sawdust with already reported data.

| Optimum parameter | Present study | Babu's results (Babu and Chaurasia 2003) |
|---|---------------------------------|--|
| Decay order | $n_1 = 1, n_2 = 1.5, n_3 = 1.5$ | $n_1 = 1, n_2 = 1.5, n_3 = 1.5$ |
| Heating rate H (K/s) | 31 | 51 |
| Final T (K) | 1320 | 1259.03 |
| Final pyrolysis time (s) | 20 | 9.53 |
| Pyrolysis rate of virgin biomass (s^{-1}) | 0.049938 | 0.101784 ^a |
| Final C_B (-) | 0.001238 | 0.030004 |
| Final C_{V1} (-) | 0.712. | 0.685557 |
| Final C_{C1} (-) | 0.0000661 | 0.000699 |
| Final C_{V2} (-) | 0.14335 | 0.141870 |
| Final C_{C2} (-) | 0.14335 | 0.141870 |

^a Not reported; calculated based on the final concentration value and time.

Table 3. Optimum parameter values for pyrolysis of different biomass under non-isothermal conditions.

| Optimum parameter | Wood sawdust | Bagasse | Peanut hull | Douglas fir bark | Rice husk |
|---|--------------|---------|-------------|------------------|-----------|
| Heating rate H (K/s) | 31.00000 | 31.0000 | 31.00000 | 31.00000 | 31.00000 |
| Final T (K) | 1320.000 | 1320.00 | 1320.000 | 1320.000 | 1320.000 |
| Final pyrolysis time (s) | 20.00000 | 20.0000 | 20.00000 | 20.00000 | 20.00000 |
| Pyrolysis rate of virgin biomass (s^{-1}) | 0.049938 | 0.03962 | 0.023392 | 0.019794 | 0.032769 |
| Final C_B (-) | 0.001238 | 0.20781 | 0.532170 | 0.604110 | 0.344620 |
| Final C_{V1} (-) | 0.712000 | 0.55892 | 0.328440 | 0.277970 | 0.460400 |
| Final C_{C1} (-) | 0.000066 | 0.00054 | 0.000644 | 0.000695 | 0.000537 |
| Final C_{V2} (-) | 0.143350 | 0.11636 | 0.069373 | 0.058608 | 0.097218 |
| Final C_{C2} (-) | 0.143350 | 0.11636 | 0.069373 | 0.058608 | 0.097218 |
| r_{V1} (s^{-1}) | 0.035600 | 0.02788 | 0.016422 | 0.013899 | 0.023020 |
| r_{C1} (s^{-1}) | 0.000003 | 0.00002 | 0.000032 | 0.000034 | 0.000026 |
| r_{V2} (s^{-1}) | 0.007168 | 0.00586 | 0.003469 | 0.002930 | 0.004861 |
| r_{C2} (s^{-1}) | 0.0071680 | 0.00586 | 0.003469 | 0.002930 | 0.004861 |

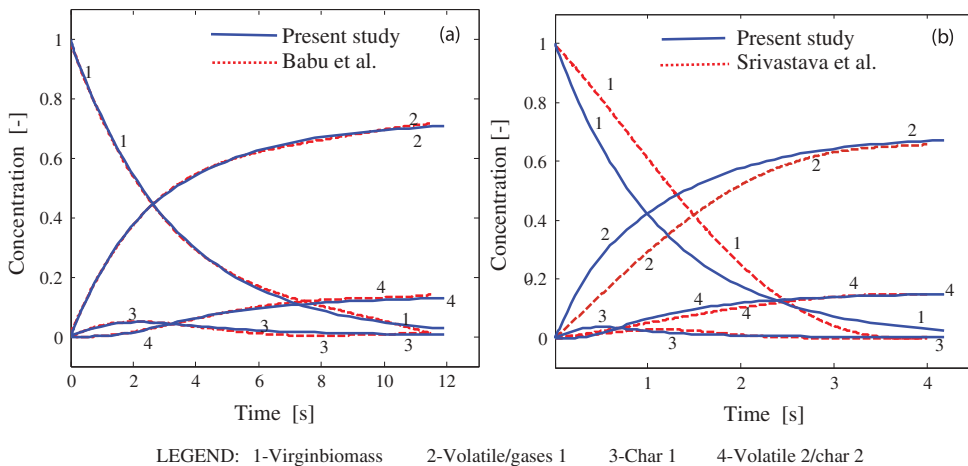


Figure 4. Simulated concentration distributions for wood sawdust under isothermal conditions at $T = 873$ K (a) and $T = 1023$ K (b).

found to have the same qualitative trends as already reported (Babu and Chaurasia 2003; Gao and Li. 2008). Figure 5a shows the variation of pyrolysis rate with temperature for different biomass when simulated under isothermal conditions. It has been observed that the pyrolysis rate increases with temperature, but this trend is observed up to a certain value of temperature; after that the pyrolysis rate decreases with increasing temperature providing an optimum value of temperature at which the pyrolysis rate of virgin biomass is maximum. It has been observed in the present study that for

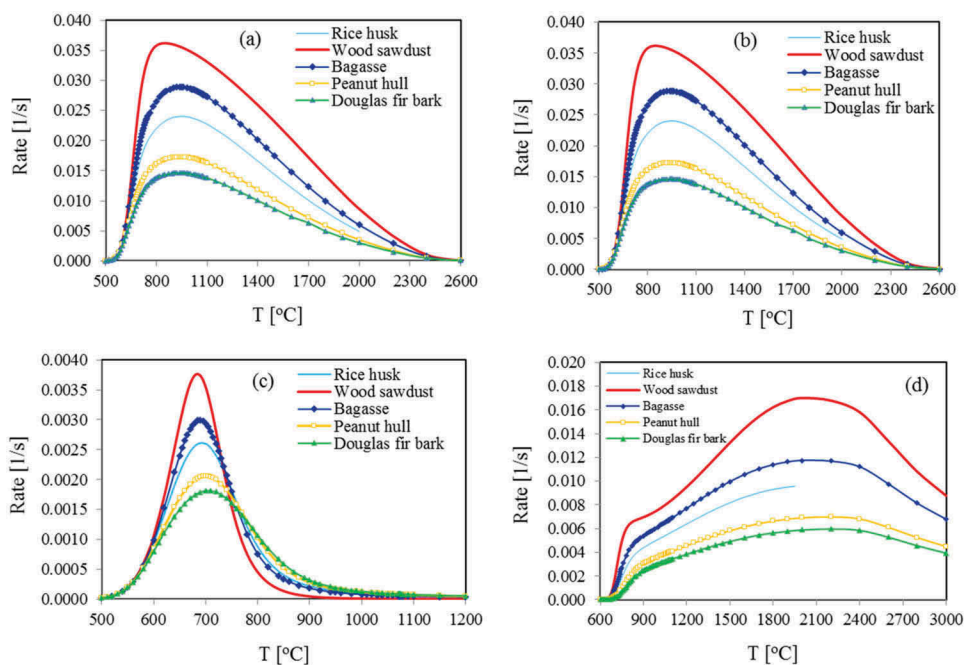


Figure 5. Pyrolysis rate of virgin biomass (a) and rate of volatile/gases 1 (b), char 1 (c), and volatile 2/char 2 (d) vs. temperature under isothermal conditions.

each of the biomass douglas fir bark, peanut hull, bagasse, wood sawdust, and rice husk, the maximum pyrolysis rate occurs at the same temperature value, i.e., at $T = 1071$ K, although at this optimum temperature the maximum pyrolysis rate for each biomass is different. At optimum temperature, the fastest pyrolysis rate is achieved for wood sawdust ($n_1 = 1.0$) at 0.0499922 s^{-1} followed by bagasse and rice husk at 0.041175 and 0.0342910 s^{-1} , respectively. The lowest curve in the Figure 5a is for douglas fir bark which thermally degraded at the rate of 0.02079 s^{-1} at optimum temperature. Figure 5b and 5c shows the simulated results for the rate of volatile/gases 1 and char 1, respectively, as a function of temperature under isothermal conditions. In lower temperature range, the rate of these two species increases with temperature, but at higher temperature values, the reverse is true. This suggests that as the temperature increases, the secondary reactions dominate and the rate of formation of volatiles 2 and chars 2 increases which can also be observed from the simulated results of Figure 5d.

A comparison of the simulated concentration distribution for different biomass at an optimum temperature of 1071 K has been presented in Figure 6. In the case of wood sawdust, almost all of the initial biomass has been consumed in the given simulation time. It is clear from the final concentration values of bagasse and rice husk (0.1765 and 0.3141 , respectively) that about 87% for bagasse and 69% of virgin biomass in case of rice husk has been consumed at optimum temperature during pyrolysis under isothermal conditions. But for peanut hull and douglas fir bark, the optimum temperature is obtained when only about 50% of the initial biomass has been converted into volatiles and chars (final concentration values 0.5086 and 0.5841 , respectively).

Table 4 gives a comparison of simulated optimum parameters for pyrolysis of wood sawdust under isothermal conditions with the data already reported in the literature (Babu and Chaurasia 2003). The difference in the values of some parameters with the reported literature is due to the different methodologies adopted and different termination criteria for simulation as explained earlier. Further, a summary of the optimum parameters found in this study under isothermal

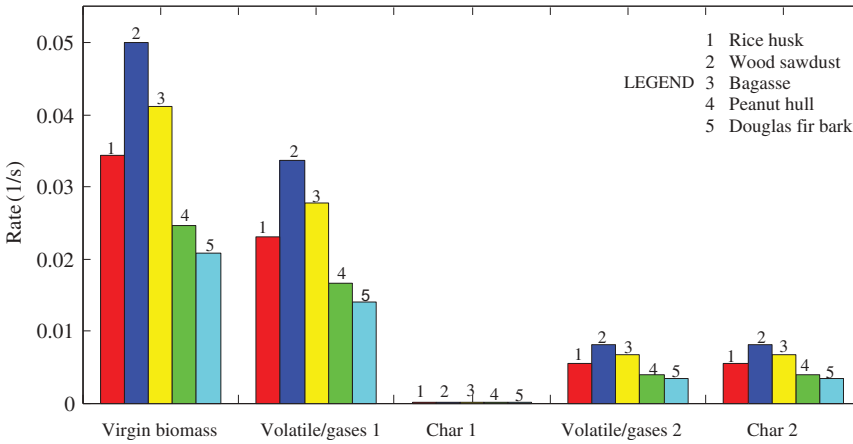


Figure 6. Simulated concentration distribution during biomass pyrolysis under isothermal conditions at optimum temperature of $T = 1071$ K.

Table 4. Comparison of the optimum parameters during pyrolysis under isothermal conditions for wood sawdust with those reported in the literature.

| Optimum parameter | Present study | Babu's results (Babu and Chaurasia 2003) |
|---|---------------------------------|--|
| Decay order | $n_1 = 1, n_2 = 1.5, n_3 = 1.5$ | $n_1 = 1, n_2 = 1.5, n_3 = 1.5$ |
| Temperature (K) | 1071.000 | 1066.000 |
| Final pyrolysis time (s) | 20.00000 | 7.987000 |
| Pyrolysis rate of virgin biomass (s^{-1}) | 0.049990 | 0.12144 ^a |
| Final C_B (-) | 0.000154 | 0.030008 |
| Final C_{V1} (-) | 0.672710 | 0.656206 |
| Final C_{C1} (-) | 0.000090 | 0.001900 |
| Final C_{V2} (-) | 0.163520 | 0.155943 |
| Final C_{C2} (-) | 0.163520 | 0.155943 |

^aNot reported; calculated based on the final concentration value and time.

conditions for wood sawdust, bagasse, peanut hull, douglas fir bark, and rice husk is provided in Table 5.

Conclusions

Due to the promising nature of biomass pyrolysis, kinetic modeling and simulation have been performed to optimize the different operating parameters like temperature, heating rate, pyrolysis rate of virgin biomass as well as rate of primary and secondary volatiles and char for various

Table 5. Optimum parameter values for pyrolysis of different biomass under isothermal conditions.

| Optimum parameters | Wood sawdust | Bagasse | Peanut hull | Douglas fir bark | Rice husk |
|---|--------------|----------|-------------|------------------|-----------|
| Optimum temperature T (K) | 1071.0000 | 1071.000 | 1071.000 | 1071.000 | 1071.0000 |
| Final pyrolysis time (s) | 20.000000 | 20.00000 | 20.00000 | 20.00000 | 20.000000 |
| Pyrolysis rate of virgin biomass (s^{-1}) | 0.0499922 | 0.041175 | 0.024570 | 0.020795 | 0.0342910 |
| Final C_B (-) | 0.0001540 | 0.176510 | 0.508610 | 0.584100 | 0.3141800 |
| Final C_{V1} (-) | 0.6727100 | 0.555060 | 0.332160 | 0.281510 | 0.4626800 |
| Final C_{C1} (-) | 0.0000902 | 0.001078 | 0.001592 | 0.001720 | 0.0013090 |
| Final C_{V2} (-) | 0.1635200 | 0.133680 | 0.078800 | 0.066337 | 0.1109200 |
| Final C_{C2} (-) | 0.1635200 | 0.133680 | 0.078800 | 0.066337 | 0.1109200 |
| r_{V1} (s^{-1}) | 0.0336355 | 0.027753 | 0.016608 | 0.014076 | 0.0231340 |
| r_{C1} (s^{-1}) | 0.0000045 | 0.000053 | 0.000079 | 0.000086 | 0.0000654 |
| r_{V2} (s^{-1}) | 0.0081760 | 0.006684 | 0.003941 | 0.003317 | 0.0055460 |
| r_{C2} (s^{-1}) | 0.0081760 | 0.006684 | 0.003941 | 0.003317 | 0.0055460 |

lignocellulosic materials such as douglas fir bark, bagasse, rice husk, peanut hull, and wood sawdust. Optimization of these parameters has been performed on the basis of maximization of pyrolysis rate of virgin biomass. It has been found that maximum pyrolysis rate for different biomass occurs at the same heating rate and temperature under non-isothermal and isothermal conditions, respectively, which proves that these two quantities are independent of reaction order of virgin biomass. But the value of optimum pyrolysis rate is different for each biomass attributed to the different final concentration attained in given simulation time. In both cases, the fastest optimum pyrolysis rate is found for wood sawdust with minimum reaction order ($n_1 = 1.0$) followed by bagasse and rice husk, whereas the slowest optimum pyrolysis is found for douglas fir bark with maximum reaction order ($n_1 = 8.914$). Although at optimum conditions each biomass suffers a maximum pyrolysis rate, any biomass does not give complete thermal utilization except wood sawdust which attains a final concentration of 0.000154 and 0.001238 under non-isothermal and isothermal conditions, respectively. In both cases, the secondary rate of char and volatiles dominates at higher heating rate and temperature. The simulated results of biomass pyrolysis might be integrated with the combustion and/or reduction zone in a biomass gasifier to simulate the overall performance of a gasifier.

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References

- Akhtar, J., and N. S. Amin. 2012. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renewable and Sustainable Energy Reviews* 16 (7):5101–09. doi:10.1016/j.rser.2012.05.033.
- Babu, B. V., and A. S. Chaurasia. 2003. Modeling, simulation and estimation of optimum parameters in pyrolysis of biomass. *Energy Conversion and Management* 44 (13):2135–58. doi:10.1016/S0196-8904(02)00237-6.
- Channiwala, S. A., and P. P. Parikh. 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* 81 (8):1051–63. doi:10.1016/S0016-2361(01)00131-4.
- Demirbas, A. 2006. Sustainable biomass production. *Energy Sources, Part A* 28 (10):955–64. doi:10.1080/00908310600718866.
- Demirbas, A., A. Sahin-Demirbas, and A. Hilal Demirbas. 2004. Global energy sources, energy usage, and future developments. *Energy Sources* 26 (3):191–204. doi:10.1080/00908310490256518.
- Ding, Y., O. A. Ezekoye, J. Zhang, C. Wang, and S. Lu. 2018. The effect of chemical reaction kinetic parameters on the bench-scale pyrolysis of lignocellulosic biomass. *Fuel* 232:147–53. doi:10.1016/j.fuel.2018.05.140.
- Gao, N., and A. Li. 2008. Modeling and simulation of combined pyrolysis and reduction zone for a downdraft biomass gasifier. *Energy Conversion and Management* 49 (12):3483–90. doi:10.1016/j.enconman.2008.08.002.
- Gao, W., M. R. Farahani, M. Rezaei, A. Q. Baig, M. K. Jamil, M. Imran, and R. Rezaee-Manesh. 2017. Kinetic modeling of biomass gasification in a micro fluidized bed. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 39 (7):643–48. doi:10.1080/15567036.2016.1236302.
- Georgiou, A., H. Polatidis, and D. Haralambopoulos. 2012. Wind energy resource assessment and development: Decision analysis for site evaluation and application. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 34 (19):1759–67. doi:10.1080/15567036.2011.559521.
- Hashimoto, K., I. Hasegawa, J. Hayashi, and K. Mae. 2011. Correlations of kinetic parameters in biomass pyrolysis with solid residue yield and lignin content. *Fuel* 90 (1):104–12. doi:10.1016/j.fuel.2010.08.023.
- Hu, S., A. Jess, and M. Xu. 2007. Kinetic study of Chinese biomass slow pyrolysis: Comparison of different kinetic models. *Fuel* 86 (17–18):2778–88. doi:10.1016/j.fuel.2007.02.031.
- Koufopoulos, C. A., N. Papayannakos, G. Maschio, and A. Lucchesi. 1991. Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects. *The Canadian Journal of Chemical Engineering* 69 (4):907–15. doi:10.1002/cjce.v69:4.
- Limayem, A., and S. C. Ricke. 2012. Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects. *Progress in Energy and Combustion Science* 38 (4):449–67. doi:10.1016/j.pecs.2012.03.002.
- Mahmood, H., M. Moniruzzaman, T. Iqbal, and S. Yusup. 2017. Effect of ionic liquids pretreatment on thermal degradation kinetics of agro-industrial waste reinforced thermoplastic starch composites. *Journal of Molecular Liquids* 247:164–70. doi:10.1016/j.molliq.2017.09.106.

- Mahmood, H., M. Moniruzzaman, S. Yusup, and H. M. Akil. 2016a. Pretreatment of oil palm biomass with ionic liquids: A new approach for fabrication of green composite board. *Journal of Cleaner Production* 126:677–85. doi:10.1016/j.jclepro.2016.02.138.
- Mahmood, H., M. Moniruzzaman, S. Yusup, M. I. Khan, and M. J. Khan. 2016b. Kinetic modeling and optimization of biomass pyrolysis for bio-oil production. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 38 (14):2065–71. doi:10.1080/15567036.2015.1007404.
- Ozbay, N., A. E. Pütün, and E. Pütün. 2006. Bio-oil production from rapid pyrolysis of cottonseed cake: Product yields and compositions. *International Journal of Energy Research* 30 (7):501–10. doi:10.1002/er.1165.
- Parikh, J., S. A. Channiwala, and G. K. Ghosal. 2007. A correlation for calculating elemental composition from proximate analysis of biomass materials. *Fuel* 86 (12–13):1710–19. doi:10.1016/j.fuel.2006.12.029.
- Pütün, A. E., N. Özbay, E. A. Varol, B. B. Uzun, and F. Ateş. 2007. Rapid and slow pyrolysis of pistachio shell: Effect of pyrolysis conditions on the product yields and characterization of the liquid product. *International Journal of Energy Research* 31 (5):506–14. doi:10.1002/er.1263.
- Sheeba, K. N., J. Sarat Chandra Babu, and S. Jaisankar. 2010. The reaction kinetics for coir pith pyrolysis in thermogravimetric analyzer. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 32 (19):1837–50. doi:10.1080/15567030902789007.
- Srivastava, V. K., and R. K. Jalan. 1994. Predictions of concentration in the pyrolysis of biomass materials—I. *Energy Conversion and Management* 35 (12):1031–40. doi:10.1016/0196-8904(94)90007-8.
- Srivastava, V. K., and R. K. Jalan. 1996. Prediction of concentration in the pyrolysis of biomass material—II. *Energy Conversion and Management* 37 (4):473–83. doi:10.1016/0196-8904(95)00200-6.
- Wang, Z., D. Shen, C. Wu, and S. Gu. 2018. Thermal behavior and kinetics of co-pyrolysis of cellulose and polyethylene with the addition of transition metals. *Energy Conversion and Management* 172:32–38. doi:10.1016/j.enconman.2018.07.010.
- Yang, H., R. Yan, H. Chen, C. Zheng, D. H. Lee, and D. T. Liang. 2006. In-depth investigation of biomass pyrolysis based on three major components: Hemicellulose, cellulose and lignin. *Energy & Fuels* 20 (1):388–93. doi:10.1021/ef0580117.
- Yiin, C. L., S. Yusup, A. T. Quitain, Y. Uemura, M. Sasaki, and T. Kida. 2018. Thermogravimetric analysis and kinetic modeling of low-transition-temperature mixtures pretreated oil palm empty fruit bunch for possible maximum yield of pyrolysis oil. *Bioresource Technology* 255:189–97. doi:10.1016/j.biortech.2018.01.132.
- Yörgun, S., S. Şensöz, and Ö. M. Koçkar. 2001. Flash pyrolysis of sunflower oil cake for production of liquid fuels. *Journal of Analytical and Applied Pyrolysis* 60 (1):1–12. doi:10.1016/S0165-2370(00)00102-9.
- Zhang, S., Y. Yan, T. Li, and Z. Ren. 2009. Lumping kinetic model for hydrotreating of bio-oil from the fast pyrolysis of biomass. *Energy Sources, Part A* 31 (8):639–45. doi:10.1080/15567030701750523.