EFFECT OF TAR DECOMPOSITION ON GAS GENERATION DURING PYROLYSIS IN PACKED BED OF WOODY BIOMASS

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Abstract

In this report, the effect of tar decomposition on gas generation during pyrolysis in a packed bed of woody biomass was studied experimentally and numerically. The setting temperature of the furnace, T_S, was changed from 673 K to 1073 K. The diameter of the biomass particles, D_P, was changed from 0.34 mm to 1.13 mm. The heating rate of the furnace was 400 K /hr. From the experimental results, the mass flow rate of generated gas reached a maximum at a certain time $t = t_{max}$ for $T_S > 773$ K due to the secondary decomposition of tar. The t_{max} became longer as the diameter of the biomass decreased. The reasons for this finding are as follows. The thermal diffusivity of nitrogen is greater than that of biomass. The porosity in the packed bed for small particles is less than that for large particles. So the gas temperature in the bed decreased as the particles became smaller. Therefore, the t_{max} got longer for smaller particles. The calculated gas flow rate with the effects of temperature distribution and tar decomposition during pyrolysis in the packed bed mostly agreed with the results of the experimental model. Furthermore, in order to understand the chemical reactions during pyrolysis, it is necessary to include not only gas phase reactions but also fluid flow in the numerical model.

Keywords: pyrolysis, tar decomposition, heat transfer, numerical simulation

1. Introduction

As Japan has many mountains with steep slopes, it is difficult to transport felled trees. Therefore, the development of a high-quality, compact gasifier that can cope with variations both in the amount of biomass collected and in energy demand, is necessary. Furthermore, in order to ensure that the system is used in the most efficient manner, it is necessary to increase our understanding of the reaction mechanisms involved in both the decomposition of biomass and heat transfer in the packed bed of biomass.

Woody biomass decomposes to char and gas when a middle heating value is applied and tar during pyrolysis. There are many chemical reaction models of pyrolysis [1]. Heat transfer, including the chemical reactions occurring during pyrolysis, was investigated by Koufopanos et al. [2] and Won et al. [3]. The rough mechanism of the heat transfer could be predicted by numerical simulation [4]. However, most reports assumed that the volume did not change during pyrolysis and there have been no reports on how the thermal conduction in the bed changes with the effect of the volume reduction.

In our previous reports [5, 6, 7, 8], the numerical simulation of the unsteady thermal conduction without the chemical reaction was conducted and compared with the experimental model. The yield of the solid component could be reproduced by analysis using the model by Miller et al. [9] even if the heating rate and the lignin content were changed [5]. The volume in the packed bed of the biomass subjected to pyrolysis can be estimated using the model by Miller et al. [9] and the dependence of gas volume in the bed on the temperature can also be estimated [5]. Furthermore, heat transfer and chemical reactions during the pyrolysis in the packed bed of biomass were investigated experimentally and numerically taking into account the porosity change in the packed bed [8]. The results indicated that the gas generation rate could be partly reproduced by the numerical simulation because the calculation model did not take into account secondary tar decomposition [8].

In this report, the gas generation rate during pyrolysis in the packed bed of biomass was investigated experimentally and numerically taking into account tar decomposition.

2. Experimental Apparatus and Procedure

Figure 1 shows the experimental apparatus for measuring the heat transfer and chemical reaction during pyrolysis [5, 6, 7, 8].

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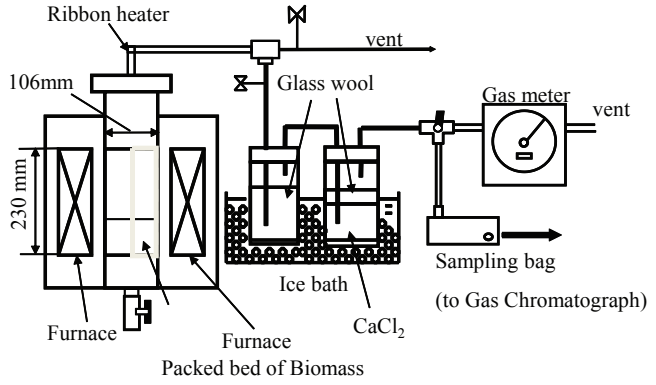

Figure 1. Experimental apparatus for measuring heat transfer and chemical reaction during pyrolysis.

The rig consisted of a nitrogen gas supply, a tubular reactor, cold traps for tar and water, a gas-sampling bag, and a gas flow meter. The diameter and height of the tubular reactor were 106 mm and 230 mm, respectively. The furnace had a maximum output of 1.5 kW, and the wall temperature of the reactor could be set to temperatures up to about 800 °C. The cold traps, which were situated in an ice bath, were two 500-mL Erlenmeyer flasks filled with glass wool and solid $CaCl_2$. During pyrolysis, tar and water were adsorbed by the traps, and the gas generated in the reaction flowed through the traps and filled the sampling bag (GL Science Co., Ltd.) for measurement of the gas component. The gas flow rate was measured using a wet-type gas meter (Shinagawa Co., Ltd., W-NK-2B). An O_2 monitor was placed at the exit of the reactor. Before the experiment, air in the reactor was replaced by nitrogen gas, which was allowed to flow into the reactor until the concentration of O_2 at the exit was less than 1%, after which time the nitrogen gas supply was stopped. Woody biomass particles of W_0 [g] were introduced into the tube reactor, and the wall of the reactor was heated to 800 °C by the electric furnace at a heating rate of 400 K/h. The height of the packed bed of biomass was about 90 mm. In order to maintain the height, the initial weights of biomass were changed for every particle size. The temperature of the reactor wall was then maintained at the setting temperature for about 60 min. Three samples with different particle sizes (D_P = 0.34, 0.78 and 1.1 mm) were used, and for each sample, two pyrolysis experiments were conducted: in the first, the temperature profile of the packed bed of biomass, the flow of gas generated, and the material balance were measured; and in the second, the components of the generated gas were analyzed. The carbide material remaining in the reactor is defined as char. Samples of the gas generated in the reaction were collected in the sampling bag every 20 min and analyzed quantitatively by gas chromatography (GL Science Co., Ltd., GC323) to determine the concentrations of H_2, CH_4, CO and CO_2. Experimental conditions are listed in Table 1.

Table 1. Experimental conditions

Table 1 Experimental conditions

		Run A	Run B	Run C
Average Particle diameter [mm]	D_P	0.38	0.78	1.13
Initial weight of packed bed [g]	W_0	183	100	82
Initial height of packed bed [mm]	z_S	90	90	90
Initial porosity of packed bed [-]	ε_0	0.847	0.917	0.932
Setting temperature [K]	T_S	1073	673, 773, 873, 973, 1073	1073
Operation time [min]	t	180	180	180

3. Numerical Simulation

3.1 Thermal conduction without the heat of the chemical reaction

The tubular reactor can be divided into two zones as shown in Figure 2; the upper zone is filled with nitrogen gas, while the lower zone is filled with the packed bed of biomass.

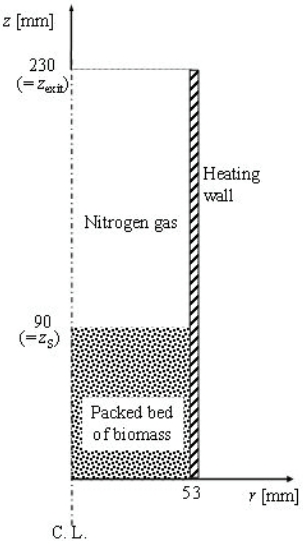

Figure 2. Calculation domain in the tubular reactor.

If we ignore the process of convective heat transfer and the heat source of the chemical reaction, the energy equations for the gas phase and solid phase are as follows:.

(For gas phase)

$$\frac{\partial \varepsilon \rho_G C_{P,G} T_G}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(\varepsilon \lambda_G r \frac{\partial T_G}{\partial r}\right) + \frac{\partial}{\partial z}\left(\varepsilon \lambda_G \frac{\partial T_G}{\partial z}\right) + h_B a_B \left(T_B - T_G\right) \quad (1)$$

(For solid phase)

$$\frac{\partial\{(1-\varepsilon)\rho_B C_B T_B\}}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left((1-\varepsilon)\lambda_B r\frac{\partial T_B}{\partial r}\right) + \frac{\partial}{\partial z}\left((1-\varepsilon)\lambda_B\frac{\partial T_B}{\partial z}\right) - h_B a_B\left(T_B - T_G\right) \quad (2)$$

The initial and boundary conditions are given by the following equations:

ii) $t = 0$

$$T_G = T_0 \quad (3)$$

$$T_B = T_0 \quad (4)$$

ii) $t > 0$

(For gas phase)

$$\frac{\partial T_G}{\partial r} = 0 \ \ at\ r = 0 \quad (5)$$

$$T_G = T_W(t,z) \ \ at\ r = R \quad (6)$$

$$\frac{\partial T_G}{\partial z} = 0 \ \ at\ z = 0 \quad (7)$$

$$\frac{\partial T_G}{\partial z} = 0 \ \ at\ z = z_{exit} \quad (8)$$

(For solid phase)

$$\frac{\partial T_B}{\partial r} = 0 \ \ at\ r = 0 \quad (9)$$

$$T_B = T_W(t,z) \ \ at\ r = R \quad (10)$$

$$\frac{\partial T_B}{\partial z} = 0 \ \ at\ z = 0 \quad (11)$$

$$(1-\varepsilon)\lambda_B\frac{\partial T_B}{\partial z} = h_p(T_B - T_S) + e\sigma\left(T_W^4 - T_B^4\right) \ \ at\ z = z_S \quad (12)$$

The governing equations and the boundary conditions were discretized over a control volume using the finite difference method. The temperature profile in the packed bed and the temperature at the top of the packed bed are solved by the Successive Over Relaxation (SOR) method and the Newton-Raphson method, respectively. The dependence of the temperature on all physical properties was described in our previous report [8]. The dependence of grid numbers on the heat transfer was investigated using 6 sets of grid numbers (number of grids for r-component, number of grids for z-component) = (5, 22), (10, 44), (20, 87), (30,131), (40,174) and (53,230). The set of grid numbers (30, 131) was applied because the time course of the average temperature for (30, 131) was less than 1% of that for (53, 230).

3.2 Chemical reactions during pyrolysis of biomass

There are many models for pyrolysis of biomass. In this study, the chemical reaction model, which was reported by Miller et al. [9], was used because the model agreed well with the experimental results for char formation in our previous work [5]. Figure 3 shows our previous reaction model with secondary decomposition of tar [10].

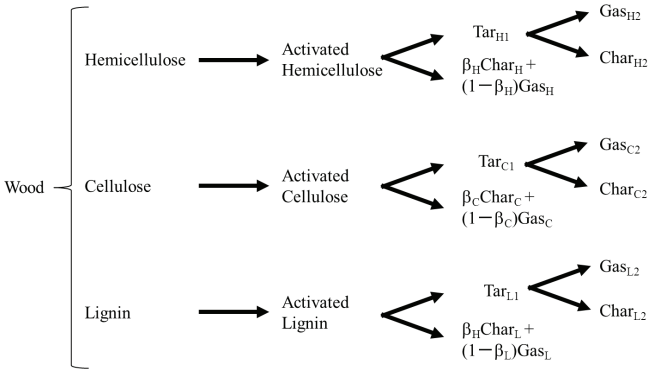

Figure 3. Chemical reactions during pyrolysis with the effect of tar decomposition. $\beta_H = 0.6$, $\beta_C = 0.35$ and $\beta_L = 0.75$

In the scheme in Fig. 3, the selectivities of char/(char + gas) from activated hemicellulose, activated cellulose and activated lignin are assumed to be constant, and are denoted as β_H, β_C and β_L, respectively. The model shows that hemicellulose, cellulose and lignin decompose parallel to gas, tar and char. Reaction rates and mass balance for all species were listed in our previous report [10]. These chemical reactions were assumed to occur only in the packed bed. The yields of solid component, tar component, gas component and the generation rate of the gas for every control volume were calculated by the Runge-Kutta method. Initial mass fraction of hemicellulose, cellulose and lignin in the Pseudotsuga menziesii [11] was assumed to be 0.24, 0.47 and 0.29, respectively.

3.3 Calculation model

In order to investigate the dependence of temperature distribution in the packed bed on the gas generation rate during pyrolysis, heat balance and mass balance for all components were solved

simultaneously. Furthermore, the effect of tar decomposition on the gas generation was investigated. The flow chart of the calculation model was shown in our previous report [8]. As the calculated results for temperature distribution in the packed bed are the same as those in our previous report [8], the results for gas generation rate are only discussed in the present paper.

4. Results and Discussion

Figure 4 shows the dependence of the generated gas flow rate during pyrolysis on the setting temperature, T_S. Plots and lines show the experimental and calculated results, respectively. The average particle size of biomass is about 0.78 mm.

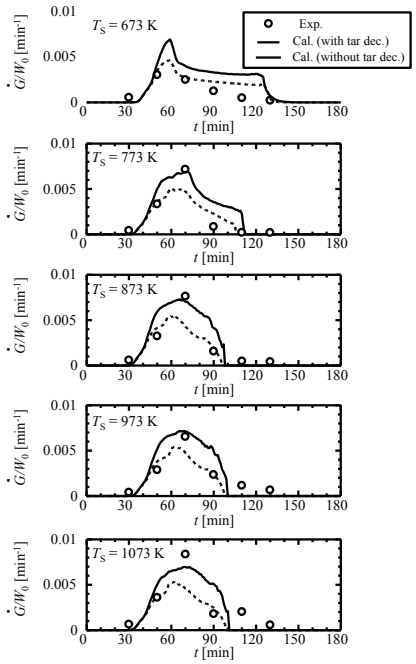

Figure 4 Time course of generated gas flow rate during pyrolysis for the effect of setting temperature T_S. (D_P = 0.78 mm)

The vertical axis shows the gas flow rate per initial weight of the biomass, W_0 = 100 g. For T_S = 673 K, the gas was generated at t = 30 min and had a maximum value at t = 50 min. Although the average gas temperature in the packed bed was almost 430 K at t = 50 min, the gas generated mainly at the top surface due to the temperature distribution. At t > 50 min, the generated gas flow rate decreased over time. For T_S = 773 K, the gas flow rate had a maximum value at t = 70 min and T_G = 650 K. The range of the temperature suggests that the gas was generated mainly by the secondary decomposition of tar rather than the decomposition of lignin. For T_S > 873 K, the time course of the gas flow rate did not change compared to that for TS = 773 K. The experimental values could be reproduced by calculated values without tar decomposition except for the maximum gas flow rate at t = 70 min. In contrast, the calculated results with tar decomposition agreed well with the experimental results until 90 min. In this calculation model, it was assumed that all chemical reactions occurred in the packed bed. However, the generated gas and tar pass through the gas phase zone above the packed bed in the tubular reactor high temperature channel except for the packed bed and then tar decomposition also occurs in the gas phase of the tubular reactor above the packed bed. Therefore, the experimental gas flow rate for t > 90 min and T_S > 873 K could not be reproduced even if the tar decomposition in the packed bed was taken into account.

Figure 5 shows the dependence of heat transfer and chemical reaction on the particle size, *Dp*. Plots and lines show the experimental and calculated results, respectively.

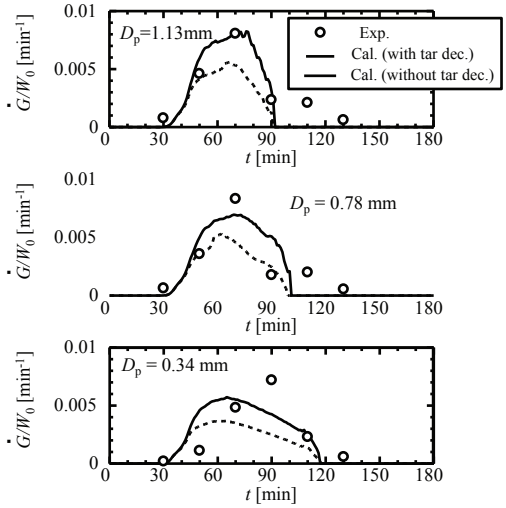

Figure 5 Time course of generated gas flow rate during pyrolysis for the effect of particle size D_P. (*Ts* = 1073 K)

The setting temperature is 1073 K. The vertical axis shows the gas flow rate per initial weight of the biomass, W_0. There was no difference between the experimental results for *Dp* = 0.78 mm and 1.13 mm. However, the start time of gas generation for *Dp* = 0.38 mm became later than that for *Dp* = 0.78 mm and 1.13 mm. The heat flux for the gas phase in the packed bed depends not only on the thermal conductivity and the gradient of temperature, but also the porosity. The smaller the particles, the less porosity they have. Therefore, the start of gas generation for smaller particles became later than that for larger particles due to the decrement of the gas temperature. For *Dp* = 1.13 mm, the calculated results with tar decomposition agreed with the experimental results until 90 min. However, at t > 90 min, the calculated results could not reproduce

the experimental results due to tar decomposition at the gas phase zone above the packed bed in the tubular reactor. If the particle size became smaller, the difference between the calculated results and the experimental results became more significant.

In future work, numerical simulation that takes into consideration not only the tar decomposition in the gas phase zone above the packed bed in the tubular reactor but also the fluid flow in the reactor is expected.

5. Conclusions

The effect of tar decomposition on gas generation during pyrolysis in a packed bed of woody biomass was studied experimentally and numerically. The setting temperature of the furnace, *Ts*, was changed from 673 K to 1073 K. The diameter of biomass particles, *Dp*, was changed from 0.34 mm to 1.13 mm. The heating rate of the furnace was 400 K /hr. Our conclusions are as follows:

1) From the experimental results, the mass flow rate of generated gas has a maximum at a certain time t = t_{max} for *Ts* > 773 K due to the secondary decomposition of tar. The t_{max} became longer as the diameter of biomass decreased. The reasons for this finding are as follows. The thermal diffusivity of nitrogen is greater than that of biomass. The porosity in the packed bed for small particles is less than that for large particles. So the gas temperature in the bed became lower as the particles became smaller. Therefore, the t_{max} got longer for smaller particles.

2) The calculated gas flow rate with the effects of temperature distribution and tar decomposition during pyrolysis in the packed bed mostly agreed with the experimental model. Furthermore, in order to understand chemical reactions during pyrolysis, it is necessary to include not only gas phase reactions but also fluid flow in the numerical model.

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Nomenclature

a_B:	Surface area of the biomass particle per unit volume in the packed bed	[m^2/m^3-packed bed]
C_B:	Heat capacity of biomass	[J/(kg K)]
$C_{P,G}$:	Heat capacity of gas	[J/(kg K)]
D_p	Particle size of biomass	[mm]
e:	Emissivity of biomass (= 0.95)	[-]
$\dot{G}$	Generated gas flow rate	[kg/s]
h_B:	Heat transfer coefficient between biomass and gas	[$W/(m^2 K)$]
r:	Radial position in the reactor	[m]
R:	Radius of the reactor (= 0.053 m)	[m]
T_0:	Initial temperature	[K]
T_B:	Temperature of biomass	[K]
T_G:	Temperature in the gas phase	[K]
T_S:	Temperature at the setting point (r = 53 mm, z =115 mm)	[K]
T_W (t, z):	Temperature at the wall of the reactor at t = t and z = z	[K]
t:	Operation time	[s]
W_0:	Initial weight of biomass in the packed bed	[kg]
z:	Axial position in the reactor	[m]
z_{exit}:	Outlet of the reactor (= 0.23 m)	[m]
z_S:	Axial position at the surface of the packed bed (= 0.09 m)	[m]

Greek symbol

ε:	Porosity	[-]
λ_B:	Thermal conductivity of biomass	[W/(m K)]
λ_G:	Thermal conductivity of gas	[W/(m K)]
ρ_B:	Density of biomass (=1500 kg/m^3)	[kg/m^3]

ρ_G:	Density of gas	[kg/m^3]
σ:	Stefan-Boltzman constant (=5.669x10^{-8} W/(m^{2}K^4))	[W/(m^2 K^4)]

Subscript in chemical component

C	Cellulose
H	Hemicellulose
L	Lignin

References

[1] Okumura Y, Modeling of Pyrolysis and Gasification Reactions of Many Types of Biomass. Journal of Japanese Institute of Energy 2011; 90 (2); 122-131.

[2] Koufopanos C P , Maschio A N G and Lucchesi A, Modelling of the Pyrolysis of Biomass Particles. Studies on Kinetics, Thermal and Heat Transfer Effects. Candian Journal of Chemical Engineering 1991; 69: 907-915.

[3] Won C P, Arvind A and Howard R B, Experimental and Theoretical Investigation of Heat and Mass Transfer Processes during Wood Pyrolysis. Combustion and Flame 2010; 157: 481-494.

[4] Di Blasi C, Modeling Chemical and Physical Processes of Wood and Biomass Pyrolysis. Progress in Energy and Combustion Science 2008; 34; 47-90.

[5] Tanoue K, Yamasaki K, Nishimura T, Taniguchi M and Sasauchi K, A Relationship between the Formation Rate of Solid Component and Volume Reduction of Packed Bed of Woody Biomass Particles during Pyrolysis. Journal of the Japan Institute of Energy 2011; 90(-11): 1031-1037.

[6] Tanoue K, Hinauchi T, Thaung Oo, Nishimura T, Taniguchi M and Sasauchi K, Modeling of Heterogeneous Chemical Reactions Caused in Pyrolysis of Biomass Particles. Advanced Powder Technology 2007; 18(-6): 825-840.

[7] Tanoue K, Widya W, Yamasaki K, Kawanaka T, Yoshida A, Nishimura T, Taniguchi M, Sasauchi K, Numerical Simulation of the Thermal Conduction of Packed Bed of Woody Biomass Particles Accompanying Volume Reduction Induced by Pyrolysis. Journal of the Japan Institute of Energy 2010; 89 (10); 948-954.

[8] Tanoue K, Suetomi T, Nishimura T, Taniguchi M and Sasauchi K, Thermal Conduction and Gas Generation Undergoing Pyrolysis in the Packed Bed of Woody Biomass. Journal of the Japan Institute of Energy 2012; 91 (10); 976-984.

[9] Miller R S, Bellan J A, Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicelluloseand Liqnin Kinetics, Combustion Science and Technology. 1997;126:97-137.

[10] Tanoue K, Uemura Y, Nishimura T, Taniguchi M, Sasauchi K, Numerical Simulation of Heat Transfer and Heterogeneous Chemical Reactions in a Biomass Particle during Pyrolysis. International Journal of Biomass and Renewables 2012; 1 (2); 39-47.

[11] Ayhan D, Calculation of Higher Heating Values of Biomass Fuels. Fuel 1997; 76(-5): 431-434.