

Pyrolysis of Shrinking Cylindrical Biomass Pellet

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Abstract

In the present study, impact of shrinkage on pyrolysis of biomass particles is studied employing a kinetic model coupled with heat transfer model using a practically significant kinetic scheme consisting of physically measurable parameters. The numerical model is used to examine the impact of shrinkage on temperature profile and pyrolysis conversion time considering cylindrical geometry. Finite difference pure implicit scheme utilizing TDMA is employed for solving heat transfer model equation. Runge-Kutta 4th order method is used for chemical kinetics model equations. Simulations are carried out for radius ranging from 0.0000125 m to 0.025 m, temperature ranging from 303 K to 1100 K and shrinkage factors ranging from 0.0 to 1.0. The results obtained in the present study are in excellent agreement with many experimental studies, much better than the agreement with the earlier models reported in the literature. The impact of shrinkage reflects on pyrolysis in several ways. The temperature profile of the particle changes due to increased density and decreased distance across the pyrolysis region. The magnitude of the temperature gradient is more for shrinking particle as compared to non-shrinking particle. Shrinkage affects the pyrolysis time in thermally thick regime. Pyrolysis conversion process is fast for shrinking particle as compared to non-shrinking particle.

Introduction

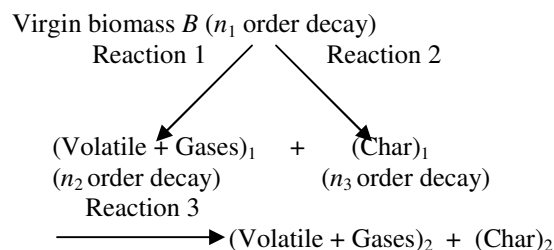
Biomass has either been processed to increase its energy content or burned directly in furnaces. The processes such as pyrolysis, gasification, anaerobic digestion and alcohol production, have been widely applied to biomass in order to increase its energy content. Energy produced from biomass or

its conversion products represent an important part among today's energy sources. Pyrolysis is one of the promising routes for the production of charcoal, medium heating value gases and condensable organic components.

Several researchers have developed models for pyrolysis of biomass [1-6]. Many of these models do not include the impact of shrinkage on the pyrolysis process. It is based on the assumption that the total volume of the particle does not change during thermal degradation. On the other hand, experiments conducted for large biomass particles [7-8] have shown significant shrinkage of the char layer as the pyrolysis front propagates through the solid. The shrinking of the solid particle affects the pyrolysis in several ways. The medium properties (porosity, permeability, density, mass diffusivity, specific heat capacity and thermal conductivity), the volume occupied by the volatiles (gas and tar), the volume occupied by the solid (wood and char), and consequently the total volume of the particle also change continuously. As a result of the chemical restructuring during pyrolysis, the density of the char increases. The temperature profile of the particle changes due to increased density and decreased distance across the pyrolysis region. The product yield is also affected by the thinner and hotter char layer.

The effects of particle size, orders of reaction, heat of reaction, density, shrinkage, thermal and thermodynamic properties have already been discussed by the present authors in their earlier studies [9-21]. In the present study, the impact of shrinkage on temperature profile and pyrolysis conversion time is examined considering cylindrical geometry.

Kinetic scheme and model equations



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The pyrolysis reactions can be described by means of kinetic scheme as proposed by Koufopoulos *et al* [6] as shown above. The dimensionless forms of kinetic equations for the mechanism shown above considering shrinkage are as follows:

$$\frac{\partial(\bar{C}_B \bar{V})}{\partial t} = -(k_1 + k_2) \bar{C}_B^{n_1} \bar{V} \quad (1)$$

$$\frac{\partial(\bar{C}_{G1} \bar{V}_g)}{\partial t} = k_1 \bar{C}_B^{n_1} \bar{V} - k_3 \bar{C}_{G1}^{n_2} \bar{V}_g \bar{C}_{C1}^{n_3} \bar{V} \quad (2)$$

$$\frac{\partial(\bar{C}_{C1} \bar{V})}{\partial t} = k_2 \bar{C}_B^{n_1} \bar{V} - k_3 \bar{C}_{G1}^{n_2} \bar{V}_g \bar{C}_{C1}^{n_3} \bar{V} \quad (3)$$

$$\frac{\partial(\bar{C}_{G2} \bar{V}_g)}{\partial t} = k_3 \bar{C}_{G1}^{n_2} \bar{V}_g \bar{C}_{C1}^{n_3} \bar{V} \quad (4)$$

$$\frac{\partial(\bar{C}_{C2} \bar{V})}{\partial t} = k_3 \bar{C}_{G1}^{n_2} \bar{V}_g \bar{C}_{C1}^{n_3} \bar{V} \quad (5)$$

The equation for heat transfer along with initial and boundary conditions in dimensionless forms are as follows:

$$\frac{\partial \theta}{\partial \tau} = \frac{b-1}{x} \frac{\partial \theta}{\partial x} + \frac{\partial^2 \theta}{\partial x^2} + \frac{Q'' R^2 k_1}{\alpha} \quad (6)$$

$$\tau = 0, \bar{C}_{G1} = \bar{C}_{C1} = \bar{C}_{G2} = \bar{C}_{C2} = 0 \quad (7)$$

$$\bar{C}_B = 1, \bar{V} = 1, \bar{V}_g = 0.5, \theta(x, 0) = 1$$

$$\tau > 0; \quad x = 0, \quad \frac{\partial \theta}{\partial x} = 0 \quad (8)$$

$$\tau > 0; \quad x = 1, \quad \frac{\partial \theta}{\partial x} = -\theta H \quad (9)$$

Equations describing the time evolution for V_S , V_g and V are as follows:

$$\frac{V_S}{V_{S0}} = \frac{M_B}{M_{B0}} + \frac{\alpha}{M_{B0}} M_C \quad (10)$$

$$V_g = V_{g0} + \beta (V_{S0} - V_S) \quad (11)$$

$$V_{g0} = \eta V_{gi} + (1 - \eta) V_{gf} \quad (12)$$

$$V_{gf} = \gamma V_{gi} \quad (13)$$

$$V = V_g + V_S \quad (14)$$

Koufopoulos *et al.* [6] correlation:

$$h = 0.322 (k/l) Pr^{1/3} Re^{0.5} \quad (15)$$

Other relations:

$$\varepsilon'' = V_g / V, \quad \eta = M_B / M_{B0} \quad (16)-(17)$$

The equations (1)-(5) are solved by Runge-Kutta fourth order method. The equation (6) is solved by finite difference method using pure implicit scheme using initial and boundary

conditions as given by equations (7)-(9). The values of various parameters employed and the used in the present study are taken from Babu and Chaurasia [11, 15]. The notations used in the above equations have the same meaning as given by Babu and Chaurasia [11, 15].

Results and discussion

Models' validation and comparison

Fig. 1 shows the temperature profile as a function of time at the centre (i.e. $x=0$) of the cylindrical pellet of radius 0.003 m for final temperature of 780 K. This was compared with profiles obtained by Jalan and Srivastava model [5], Babu and Chaurasia model results without shrinkage [11] and the experimental data obtained by Pyle and Zaror [22]. It was found that the present model result with shrinkage was in excellent agreement with the experimental data better than the

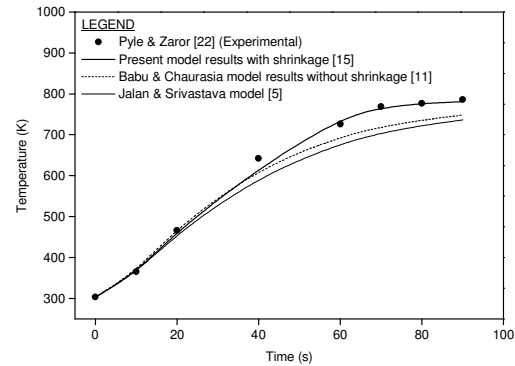


Fig. 1: Temperature profile as a function of time at the centre of the cylindrical pellet ($R=0.003$ m, $T_0=303$ K, $T_f=780$ K, $x=0$).

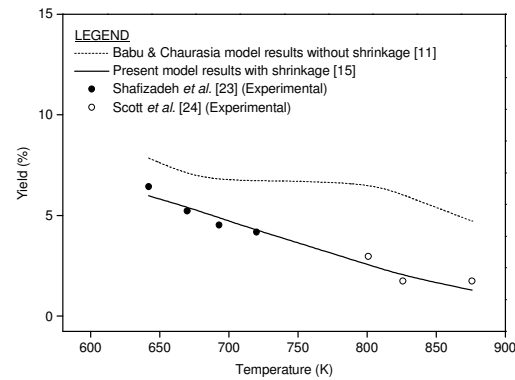


Fig. 2: Average char yield as a function of temperature for particle half-thickness of 0.000125 m.

agreement with the Jalan and Srivastava model [5] and Babu and Chaurasia model [11]. The experimental data have been replotted together with the simulation results, obtained for particle half-thickness of 0.000125 m (thermally thin regime) as shown in Fig. 2. Since in both experiments very thin particles (powder) by Shafizadeh *et al.* [23] and particle sizes of about 100 μm by Scott *et al.* [24] are used, it can be guessed that intraparticle resistance to heat transfer is negligible. As shown, the inclusion of shrinkage significantly improves the modeling results.

Simulation results

(i) Effect of temperature profile

Fig. 3 shows the temperature profile during pyrolysis of a thermally thin cylindrical particle of radius 0.0003 m exposed to a final temperature of 800 K. The temperature at the centre and the surface of the particle is found to be uniform. As expected, there is a very little difference in between the case in which shrinkage is considered and the case in which shrinkage is not considered. In this case there is no char insulating the unreacted core. As a consequence, the shrinkage has a minor impact on pyrolysis time and product yield. The pyrolysis time for both the cases is found to be 9.6 s. In the pyrolysis of thermally thin particle, the resistance to heat transfer within the particle is small compared to the external heat transfer. Thus, there is little residence time in the particle, and the secondary pyrolysis reactions have a little impact on the product yield.

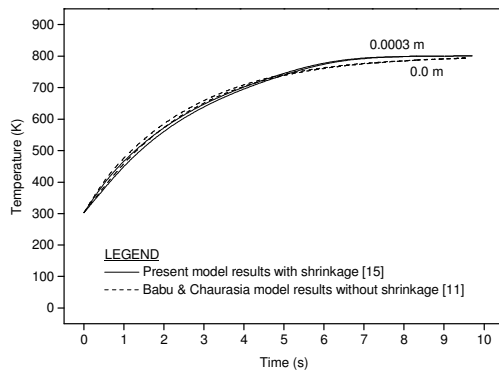


Fig. 3. Temperature profile as a function of time with cylindrical pellet at the centre and the surface of the particle ($R=0.0003$ m, $T_0=303$ K, $T_f=800$ K).

Fig. 4 shows the temperature profile as a function of time for a particle of radius 0.025 m

exposed to a final temperature of 1000 K for different radial positions. The temperature of the shrinking particle (present model results [15]) is more than non-shrinking particle [11] at any radial position. The increase in temperature is less near the centre of the particle than at the surface of the particle. There is >50 K variation between shrinking and non-shrinking particle at the surface. As the char layer begins to develop, the shrinking char layer allows more rapid internal heat transfer. The increase in the rate of internal heat transfer increases the interior temperature of the particle. The higher temperature values within the shrinking particle increase the rate of primary pyrolysis reactions thus reducing the time for completion of pyrolysis.

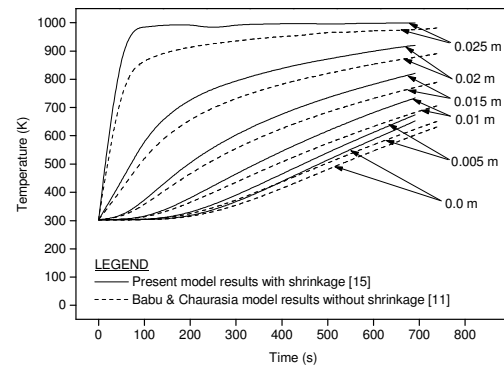


Fig. 4. Temperature profile as a function of time with cylindrical pellet for different radial positions ($R=0.025$ m, $T_0=303$ K, $T_f=1000$ K).

(ii) Effect of pyrolysis time

Figs. 5 and 6 summarize the impact of shrinkage on the pyrolysis time. The effects of shrinkage increase with particle size and the final temperature. The thicker char layer is formed for larger particle sizes. The internal resistance to heat transfer for the unreacted core reduces as a result of shrinkage by reducing the insulating affect of the char. This increases the importance of the char layer and hence the importance of shrinkage. As shown in Fig. 5, shrinkage does not have a significant affect on pyrolysis time, as the particle radius is small (0.0005 m). The pyrolysis time decreases as the temperature is increased. There is very less difference (< 1 s) in the pyrolysis time between the shrinking and the non-shrinking particle. As the particle radius increases to 0.025 m, the impact of shrinkage on pyrolysis time is observed as shown in Fig. 6. As the shrinkage reduces the insulating affect of the char, the pyrolysis time reduces by more than 50 s for

all the external temperatures as compared to the non-shrinking particle.

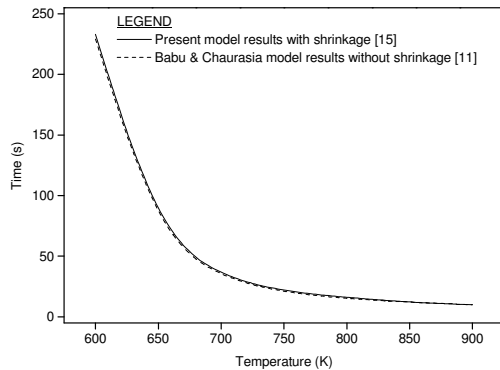


Fig. 5. Pyrolysis times as a function of temperature with cylindrical pellet ($R=0.0005$ m, $T_0=303$ K).

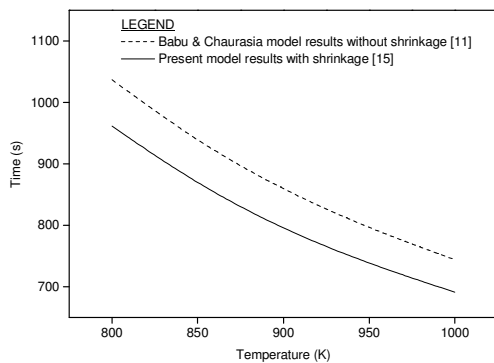


Fig. 6. Pyrolysis times as a function of temperature with cylindrical pellet ($R=0.025$ m, $T_0=303$ K).

Conclusion

It is found that shrinkage has negligible affect on pyrolysis in the thermally thin regime. However, shrinkage affects both the pyrolysis time and the yield of pyrolysis products in thermally thick regime. The higher heat transfer rates of the shrinking particle reduce the pyrolysis time. The model was used to examine the impact of shrinkage, to gain an understanding of how it can affect the pyrolysis process, and to understand what pyrolysis or combustion conditions must be considered. This can provide an improved qualitative understanding of pyrolysis and guide further research into modeling biomass pyrolysis and combustion. The results discussed above have a lot of practical importance and physical significance in industrial pyrolysis applications.

The results are also important and useful for design of biomass gasifiers, reactors, etc.

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Nomenclature

b	geometry factor (slab=1, cylinder=2, sphere=3)
B	virgin biomass
G_1	(gases and volatiles) ₁
C_1	(char) ₁
G_2	(gases and volatiles) ₂
C_2	(char) ₂
C_B	concentration of B , kg m ⁻³
C_{G1}	concentration of G_1 , kg m ⁻³
C_{C1}	concentration of C_1 , kg m ⁻³
C_{G2}	concentration of G_2 , kg m ⁻³
C_{C2}	concentration of C_2 , kg m ⁻³
h	convective heat transfer coefficient, W m ⁻² K ⁻¹
H	modified Biot number
k	thermal conductivity, W m ⁻¹ K ⁻¹
k_1, k_2, k_3	rate constants, s ⁻¹

l	axial length of cylinder, m
n_1, n_2, n_3	orders of reactions
r	radial distance, m
R	radius for cylinder and sphere; half thickness for slab, m
R_c	universal gas constant, J mol ⁻¹
t	time, s
T	temperature, K
V	total particle volume, sum of the volume occupied by pores and by the solid phase, m ³
V_g	volume occupied by the pores, m ³
V_s	solid-phase (wood and char) volume, m ³
V_{s0}	initial effective solid volume, m ³
x	dimensionless radial distance
X	conversion of biomass

Greek letters

ΔH	heat of reaction, J kg ⁻¹
$\Delta \tau$	axial grid length
Δx	radial grid distance
ρ	density, kg m ⁻³
α	thermal diffusivity, m ² s ⁻¹
τ	dimensionless time
θ	normalized temperature
ε	emissivity coefficient
ε''	void fraction of particle
σ	Stefan Boltzmann constant, W m ⁻² K ⁻⁴
η	reaction progress variable
α'	shrinkage factor
β'	shrinkage factor
γ'	shrinkage factor