

HEAT TRANSFER BEHAVIOUR OF A WHEAT STRAW PELLET UNDERGOING PYROLYSIS

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ABSTRACT

Pyrolysis is widely used to convert biomass to liquid biofuel. It is also an interesting technology at an industrial scale, which is a motivation to seek an increase in process efficiency. The pyrolysis of large biomass particles differs from the pyrolysis of fine particles because they do not heat and decompose homogeneously. In this work, experimental data for the pyrolysis of a wheat straw pellet and a single particle model are presented. Furthermore, the key parameters controlling the internal temperature distribution are discussed.

Keywords: biomass pyrolysis, wheat straw pellet, single particle model

1. INTRODUCTION

The environmental impact derived from the use of fossil fuels and their limited supply, prompts a need for clean and renewable energy technologies. Biomass is organic material derived in its major part from plants and, if sustainably harvested, is a readily available resource. The use of biomass for energy has already proved its value, but at an industrial level it is still in an efficiency improvement phase.

Pyrolysis is a thermo-chemical technology that can be applied to biomass to obtain a range of products of interest. Pyrolysis consists of heating the biomass feedstock in the absence of oxygen in order to obtain solid, gas and liquid products, whose distribution depends on the operating conditions. The desired products are char, gas and tar, also called bio-oil. The resulting bio-oil yield and composition depends on the

pyrolysis operating conditions like the temperature and the biomass chemical composition [1].

Kinetic models assuming a thermally thin regime are usually used to describe biomass pyrolysis, in small particles, the internal temperature gradient is negligible and the particle is considered to heat up homogeneously, and as a result the pyrolysis reactions also happen homogeneously across the particle. The homogeneous temperature assumption is not applicable to large particles, because apart from the reaction kinetics, the internal transport processes also play an important role. The two main transport processes are the transport of heat and the transport of mass.

The study of thermally thick biomass particles is mainly focused on understanding the internal transport processes that affect the bio-oil composition. For an increasing size of biomass particle, up to a size of around 1.5 mm, there is a decrease of bio-oil yield, favouring the light bio-oil volatiles over the high molecular weight volatiles. This decrease in the volatile yield is attributed to the slower heating rates that larger particles experience, and not by heterogeneous or homogeneous reactions of the resulting products [2].

Single particle models (SPM) study the temperature gradients of the particle, its shrinkage [3] and breakage [4] during pyrolysis. Different particle shapes and sizes have been considered [5], as well as the particle microstructure [6]. The SPM has unknown parameters that are difficult to derive from the experiments, and their values are usually assumed; i.e. the heat capacity, thermal conductivity and heat transfer coefficients. The most sensitive parameters, at least at low-temperature pyrolysis, are the enthalpy of

formation of char and tar, the heat transfer coefficient, thermal conductivity of the biomass and the rate of char formation [7].

In this work, to study the pyrolysis of large biomass particles, wheat straw pellets have been pyrolysed at different temperature conditions to obtain experimental data about the internal temperature distribution. To understand better the thermal processes that take place inside the particle and at the surface, a single particle model has been employed to predict the particle thermal behaviour. Our objective is to further develop the fundamental knowledge on biomass pyrolysis of large biomass particles, specially focusing on the internal heat transfer mechanisms.

2. MATERIAL AND METHODS

Cylindrically shaped wheat straw pellets with a diameter of 7 mm and a length of approximately 10 mm (Fig 1) were used in this study; their chemical properties are summarized in Table 1. The pellets have a bulk density of approximately 780 kg m^{-3} .



Fig 1 Wheat straw pellet

Table 1 Physical and chemical characterization of wheat straw pellets from Agripellets Ltd., in 'as received' basis.

Proximate analysis (%)					Ultimate analysis (%)				
Moisture	Ash	VM	FC	C	H	O	N	S	Cl
9.3	6.7	67.8	16.2	41	4.76	37.4	0.64	0.14	0.11

The pellets were dried overnight at 105°C and kept in a desiccator cabinet until use. The single particle reactor used in this work consists of a quartz tube reactor, with an inner diameter of 0.0443 m, inserted in an electrically heated ceramic furnace. A more detailed description and schematic of the device can be found elsewhere [8], [9].

Nitrogen gas was flowed into the furnace at a rate of 220 L h^{-1} for all runs, and the generated pyrolysis gases were entrained with the nitrogen flow and vented. The pellet was placed in the sample holder and in the insertion tube. The insertion tube was then introduced into the reactor, leaving the reactor sealed to the surroundings. The sample was left in the insertion tube for while until the nitrogen flow swept away all the oxygen to ensure the pyrolysis conditions. When the pellet is in the insertion tube, its temperature rises a bit due to being so close to the reactor core, but its temperature is still below pyrolysis levels. The pellet is then introduced into the reactor, placed at the centre of the furnace, where it is pyrolysed.

To measure the mass loss in pyrolysis conditions, the samples were removed from the reactor at different times and rapidly cooled down with nitrogen flow at ambient temperature. The internal temperature was measured continuously, using thermocouples inserted at 2 and 5 mm from an end of the pellet (see Fig 1).

3. MODEL

The model describes a single particle, in the shape of a cylinder, that heats due to its higher temperature surroundings. The thermal mechanisms considered in this model are thermal convection and radiation from the surroundings to the surface of the particle, thermal conduction through the particle, and also an internal heat source that is the heat released from the pyrolysis reactions.

The decomposition of the wheat straw was assumed to follow the reaction mechanism proposed by Lanzetta et al. [10]. This is a one-component, multi-step and first-order reaction mechanism, and consists of four reactions: wheat straw decomposes into volatiles ($r1$) and activated wheat ($r2$); the activated wheat then reacts further to form more volatiles ($r3$) and char ($r4$). In our model, the solid phase consists of the raw biomass, the intermediate solid product, and the resulting char; the gas phase contribution to the temperature has been considered not significant and therefore neglected. The gas/volatiles phase would become interesting when the objective of the model is to predict the bio-oil species generated.

The heat of reaction ΔH_r for $r1$ is 50 kJ kg^{-1} , for $r2$ is 0 kJ kg^{-1} and for $r3$ and $r4$ is -100 kJ kg^{-1} . Other values might also be consistent with the experimental data, in this case, the values have been chosen according to the trends presented in Park et al. [4] in which there is an endothermic initial tar formation and an exothermic char formation. The heat zero from the intermediate formation and the heat release from the secondary volatiles formation might be similar to other proposed models, but in this case, they obey to fitting purposes.

The specific particle density of wheat straw has been previously measured to be around 1.1 g cm^{-3} [11] and 9.83 g cm^{-3} [12]; in this paper we used a mean value of 1 g cm^{-3} to estimate the initial particle porosity ε_0 .

3.1 MATHEMATICAL DESCRIPTION

This SPM, comprises a mass balance for the solids, and an energy balance with respect to the solids. The mass balance for the solid phase depends on the extents of reaction of all the reactions r involving the solid species i

$$\frac{\partial \rho_s}{\partial t} = \sum_i \sum_r v_{r,i} \frac{\partial \xi_r}{\partial t}$$

where ρ_s is the bulk density of the solid, $v_{r,i}$ represents the stoichiometric value of the species i in the reaction r , and the extent of reaction ξ_r is calculated with a first order rate law involving the Arrhenius equation,

$$\frac{\partial \xi_r}{\partial t} = k_r \rho_s \quad \text{and} \quad k_r = A_r e^{\frac{-E_r}{RT}}$$

where λ is the effective thermal conductivity, A_r and E_r are the pre-exponential factor and the activation energy of the reaction r , and R is the gas constant. The following equation takes into account the heat transferred by thermal conductivity and the heat released from the exothermic decomposition reactions.

$$(\rho_s C_{p,s}) \frac{\partial T}{\partial t} - \nabla \cdot (\lambda \nabla T) = - \sum_r \Delta H_r \frac{\partial \xi_r}{\partial t}$$

where $C_{p,s}$ refers to the joint heat capacity of the solids; the heat capacity of the wheat straw and the intermediate wheat straw is given by $C_{p,B}$, and the heat capacity of the char by $C_{p,C}$ (see Table 2). The heat flux at the surface depends on the heat transfer by convection and by thermal radiation. The boundary condition applied on the surface of the particle is

$$-\lambda \hat{n} \cdot \nabla T = h_r (T - T_\infty) + \sigma e (T^4 - T_\infty^4)$$

where $-\hat{n}$ is an outwardly pointing unit vector normal to the particle surface, h_r is the heat transfer coefficient (estimated using the Churchill-Bernstein correlation [13]), e is emissivity, σ is the Stefan-Boltzman constant, and T_∞ is the surrounding reactor temperature.

The parameters used in this model can be found in Table 2. The heat capacity of the solid phase depends on the temperature; the heat capacity of the wheat straw and the activated wheat straw is represented by $C_{p,B}$, and the heat capacity of the char by $C_{p,C}$. The porosity of the particle ε depends on how the density of the solids change, the density of the wheat straw and the

activated wheat straw is represented collectively by ρ_B , and the density of the char by ρ_C . In a porous particle, the effective thermal conductivity λ includes thermal conduction and porous thermal radiation. In this case to

Table 2 Thermophysical properties used in the SPM.

Parameter	Value	Ref.
e	0.9	
$C_{p,B}$ ($\text{J kg}^{-1} \text{K}^{-1}$)	$2300 - 1150 e^{-0.0055T}$	[18]
$C_{p,C}$ ($\text{J kg}^{-1} \text{K}^{-1}$)	$1430 + 0.355T - 7.32107T^2$	[18]
ε_0	0.22	
ε	$1 - (1 - \varepsilon_0) \frac{\rho_B + \rho_C}{\rho_{B,0}}$	[16]
λ ($\text{W m}^{-1} \text{K}^{-1}$)	$\lambda_{conduction} + \lambda_{radiation}$	[18]
	$\lambda_{conduction} = \varepsilon \lambda_V + (1 - \varepsilon) \left[\frac{\rho_B}{\rho_{B,0}} \lambda_B + \left(1 - \frac{\rho_B}{\rho_{B,0}} \right) \lambda_C \right]$	[18]
	$\lambda_V = 0.026; \lambda_B = 0.11; \lambda_C = 0.071$	[18]
	$\lambda_{radiation} = \frac{13.5\sigma T^3 d_{pore}}{e}; \quad d_{pore} = 3.2 \cdot 10^{-6} \text{ m}$	[16]

estimate the porous thermal radiation a fixed pore diameter d_{pore} has been assumed.

The equations are solved numerically using the finite element method on a 3D cylindrical mesh, implemented with the FeniCs open-source software [14]. The mesh consists of 25663 tetrahedral elements with 4831 vertices. The basis functions are Lagrange polynomials of first order.

4. RESULTS AND DISCUSSION

Figure 2 shows how the temperature at the center of the particle increases with time for different reactor temperatures. The dotted lines are experimental data from multiple repeated runs at the same reactor conditions; slight differences are an indication of the reproducibility of the experiments, possibly due to the natural variability of the composition and size wheat straw pellets, variations in the placement of the particle, etc. The center temperature of pyrolysis at 400°C shows a small peak or shoulder just before it stabilizes to the reactor temperature. The same peak has been observed at reactor temperatures between 400 and 550°C [4]. When this happens, the rate of heat release is higher than the rate of heat transfer. It is believed to be caused

by exothermic reactions happening just before all the devolatilization reactions finish, that is why it is associated with the decomposition of a solid intermediate [4]. Also, the exothermic reaction causing the peak might be related to char formation, which is favored at low heating rates [15]. After the peak, the particle temperature equilibrates with the reactor temperature [16]. The calculated curve has not been able to predict the temperature peak for the reactor temperature of 400°C; to achieve this, for the current values of heat capacity and thermal conductivity, a more exothermic heat of reaction for r_3 and r_4 is needed, but in that case, the heat released would be too high for the reactor temperatures of 500°C and 600°C.

The temperature for pyrolysis at 600°C is slightly higher than the reactor temperature; at high temperatures, there might be further exothermic reactions causing the overheating of the particle, and those reactions might be related to the dense volatile released, transforming further into light volatiles.

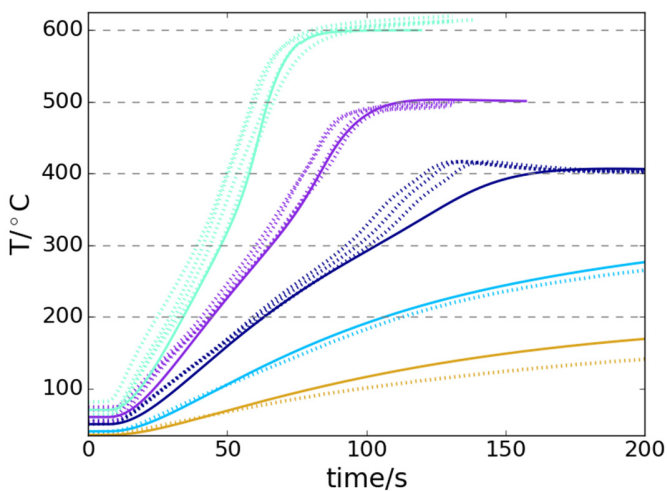


Fig 2 Pellet center temperature for a reactor temperature of 200°C (yellow), 300°C (light blue), 400°C (dark blue), 500°C (purple), and 600°C (green). The solid lines are simulations, and the dotted lines are experimental data.

For the curves at 200°C and 300°C where the reaction still does not take place, with the right combination of thermal conductivity and heat capacity, we should be able to reproduce the temperature profile. Other factors like the particle density might also affect the temperature profile. From Fig 2, it can be seen that the simulation for 200°C does not match the experimental curves, but it does for 300°C. In this case, the density parameter has been measured, but for the

heat capacity and the thermal conductivity, correlations have been taken from the literature. The correlations available, might already entail a certain degree of error because they have been calculated from given sets of experimental data that are not necessarily representative for all biomass types and all temperature ranges.

Figure 3 shows the overall mass loss with time. The higher the reactor temperature, the quicker the decomposition happens, despite they end up having a similar amount of char of 30% of the initial mass, it is slightly higher for a lower reactor temperature. The reported char yields for reactor temperatures between 365 and 606°C are 31 and 17% respectively [4]. For a reactor temperature of 500°C, the main decomposition

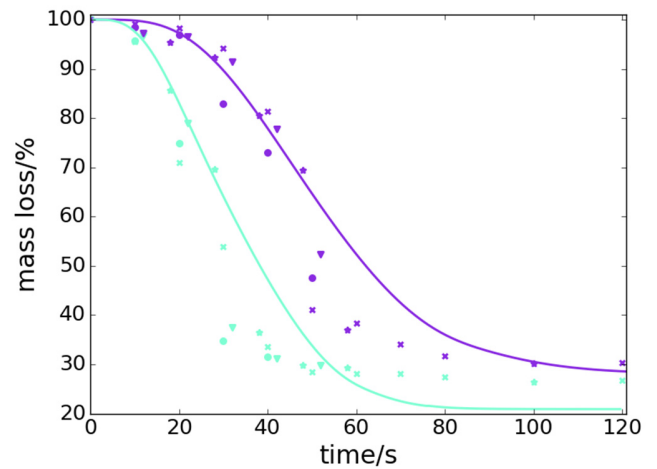


Fig 3 Pellet overall mass loss for a reactor temperature of 500°C (purple) and 600°C (green). The symbols are experimental and the solid line calculated.

happens between 30 and 60 s, for a reactor temperature of 600°C the main decomposition takes place between 20 and 50 s.

Figure 4 shows how the internal temperature of the pellet changes with time at two experimental positions, one at the center and the other at 2 mm from the surface, for each position, multiple runs were performed in order to obtain reliable experimental results; it also includes the predicted temperature at the same positions. The experimental temperature nearer the surface increases steeply from the beginning, reaching the reactor temperature earlier than the temperature at the center. The center temperature starts increasing after a delayed period of time, in which the heat travels from the surface to the center. In the experimental data reported by Haseli et al. [16] the same trend can be observed.

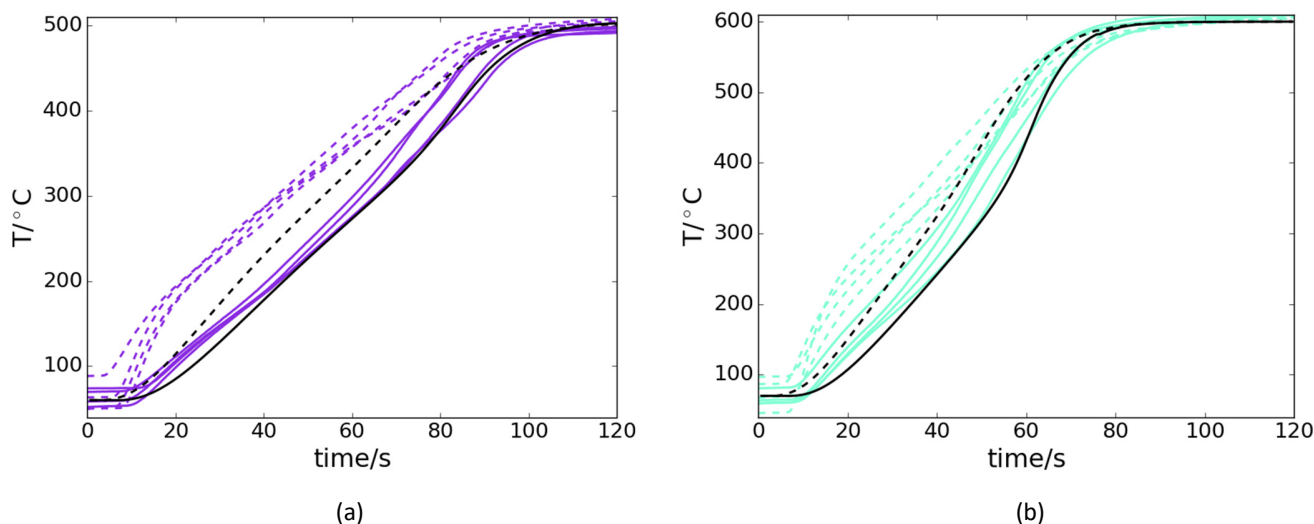


Fig 4 Pellet center temperature and internal temperature at 2 mm from the surface for a reactor temperature of 500°C (a) and 600°C (b). The colored line is experimental and the black line is calculated. The colored solid line is the temperature at the center, and the dashed colored line is the temperature at 2 mm from the surface.

For the curve at 2 mm and a reactor temperature of 500°C, a clear first shoulder appears shortly before the 20 s, and for the reactor temperature of 600°C, the shoulder appears at about 20 s, but perhaps a bit less visible due to the overlap with a steeper temperature gradient. It would seem that at that point that the particle starts reacting and releasing heat, however, the kinetics used in this work do not show reactive activity below 300°C, which is consistent with the typical pyrolysis temperature ranges; one possibility is that during the insertion of the thermocouples, the surface of the pellet was damaged, and at 2 mm depth, there was still influence of heat convection and thermal radiation from the surroundings.

5. CONCLUSIONS

The internal temperature gradient of a biomass particle undertaking pyrolysis depends mainly on the temperature of the solid phase. The key parameters controlling how the heat is transferred before the decomposition starts are the thermal conductivity and the heat capacity. During decomposition, the heat of reaction becomes the parameter more relevant in defining the internal temperature gradient. Further work on this topic should include the study of other critical parameters that affects the resulting bio-oil composition, like the residence time of the volatiles in the particle.

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