FLASH PYROLYSIS KINETICS OF PINE WOOD

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Abstract

The kinetics of sawdust pyrolysis in the temperature range from 300 to 600 °C has been measured. A thermogravimetric analyser was applied for the temperature range from 300 to 450 °C while for measurements in the temperature range from 450 to 600 °C, an entrained flow reactor has been used. The kinetic expression that describes the mass loss of sawdust due to pyrolysis is assumed to be of a single first-order in the unconverted wood. The first-order rate constant obtained from measurements in both the thermogravimetric analyser and the entrained flow reactor can be described by an Arrhenius equation with $k_0 = 1.4 \times 10^{10}$ kg.kg^{-1}.s^{-1} and $E_a = 150$ KJ.mol^{-1}.

1. INTRODUCTION

Biomass waste materials can be used as a fuel as such, or after conversion processes like pyrolysis or gasification. A direct application is co-firing in existing combustion systems, meant to reduce the amount of waste material while using the heat of combustion of the feedstock. Because biomass contains less sulphur compared to coal, a reduction in the sulphur oxide production can be achieved in a coal fired furnace. Less limestone is then required to bind the sulphur components by which the amount of waste materials produced in the combustion process will be lower. The co-firing of biomass also reduces the CO_2 emission because biomass is an integrated part of the natural carbon cycle.

Any description of the combustion or gasification of biomass starts with a description of the pyrolysis process of a single biomass particle. Pyrolysis of sawdust is extensively studied; a survey of previous work is given in a review by Antal [1]. Biomass particles like wood dust have pores with a diameter of 5 μm and porosity of approximately 50%. A hot isothermal particle will have a uniform production of pyrolysis vapours throughout the particle volume. The

highest pressure occurs in the centre of the biomass particle; it decreases towards the particle surface. Pyrolysis vapours leave the particle due to diffusion and a pressure gradient built-up inside the particle. For the small and open sawdust particles, pyrolysis vapours can leave the particle instantaneously and the decomposition kinetics itself are determining the rate of the process.

2. KINETIC MODEL

In absence of any heat or mass transfer limitation, the decomposition of wood is usually described by a single first-order model for weight loss of the reacting aggregate. Because the rate of reaction must be zero when the wood has been converted completely, the driving force for wood pyrolysis must be equal to the total aggregate weight minus the final char weight:

$$\frac{\partial W}{\partial t} = -k_1 (W - W_c^\infty) \tag{1}$$

The mass conversion of wood follows from the experimentally observed weight change:

$$\zeta_p = (W_0 - W) / (W_0 - W_c^\infty) \tag{2}$$

The assumption of a first-order wood decomposition only holds if the mass of the reacting aggregate keeps the same reactivity throughout the entire pyrolysis process. In other words, the first-order rate constant k_1 should be independent of the changing chemical structure of the reacting aggregate at any instant in the pyrolysis process. The reaction path model, proposed by Shafizadeh et al. [2], suggests that all chemical decomposition reactions are of first order. It can be represented schematically as:

with $k_1 = k_g + k_t + k_c$

The solution of equation (1) combined with equation (2) yields:

$$\zeta_p = 1 - e^{-k_1 t} \tag{3}$$

A wood conversion of 63% corresponds to:

$$k_1 t_1 = 1 \tag{4}$$

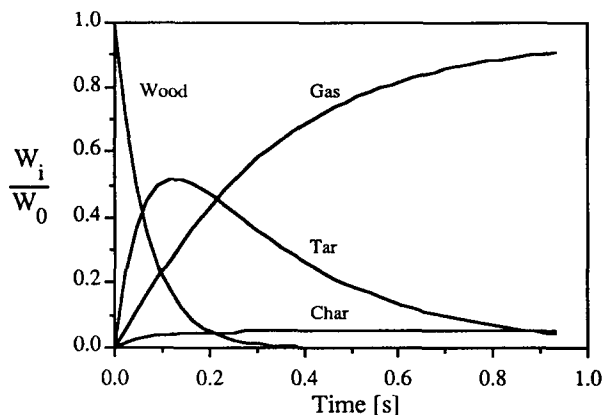A typical result of the kinetic model is presented in figure 1.

Figure 1. The weight fraction W_i/W_0 of each product as a function of the time. Intermediate products remain at reactor conditions. Typical kinetic constants which have been used in this simulation are $k_g = 2.2$, $k_t = 12$, $k_c = 0.8$ and $k_2 = 3.4$ s^{-1}, evaluated at 873 K.

3. EQUIPMENT AND EXPERIMENTAL PROCEDURES

Pine wood sawdust was hammer-milled and screened to particle diameters varying between 100 and 212 µm. This sieve fraction was used in all TGA or drop tube experiments. Micro-photographs revealed that the sawdust particles belonging to the sieve fraction of 100-212 µm had a cylindrical shape with an average diameter of 90 µm, and an average length of 320 µm. Before every experiment, the sawdust was dried for 12 hours at a temperature of 105 °C. The elemental composition of pine wood derived from analyses can be formulated as $C_{12}H_{20}O_9$.

Thermogravimetric analyser
A Setaram TG 85-1000 thermogravimetric analyser has been used to measure the weight change of a decomposing wood sample as a function of time. After attaching the sample holder to the TGA, a hot tube furnace was positioned quickly around the sample. At the relatively high TGA temperature of 380°C it has been checked whether the rate of heat transfer to the sample holder could disturb the kinetic measurements. This was done by varying the sample weight (1 to 7 mg), the average wood particle diameter (20 to 300 µm) and the material of the sample holder (quartz or copper foil). Neither of these factors had an effect on the observed wood decomposition rate. Consequently it was concluded that possible heat transfer limitations could be excluded.

Drop tube reactor

The drop tube reactor consists of a vertically positioned 20 mm inner diameter stainless steel tube of which the length could be varied from 0.3 to 1.2 meter. After entering the tube through a water-cooled inlet device, the sawdust was transported by nitrogen gas towards the drop tube exit. At the tube exit, the nitrogen carrier gas flow was mixed with a cold equimolar nitrogen flow to achieve a rapid thermal quench of the product gas·flow. Partly converted solids were collected in a pot which was positioned below the drop tube. The chemical conversion of the sawdust was determined by the weight measurement of the solid product.

Product composition measurements for ultimate tar yield conditions

The product composition as a function of the temperature has been measured in a modified version of the drop tube reactor, (tube length of 0.25 m). In the top of the drop tube a steel-wire plug was inserted which collected all reacting particles. This steel wire plug covered the tube cross sectional area completely and was positioned 0.05 m below the sawdust entrance. Vapours flowing through the wire plug reached the exit of the tube in less than 40 ms and were immediately quenched after leaving the tube. At a temperature of 600°C, no significant degradation of the produced vapours could be measured for vapour residence times smaller then 100 ms, and a constant tar yield was obtained under these conditions. The non-condensible fraction of the produced vapours is called "gas", while the condensible product is called "tar". For the conditions of these measurements the quantity of liquid products is maximal (ultimate tar yield).

4. RESULTS

Results of the product composition measurements are presented in figure 2. In most experiments, the total weight of the collected products was approximately 90% of the initial weight of wood. The deviation from a full weight recoverage is due to weight losses in the collection system.
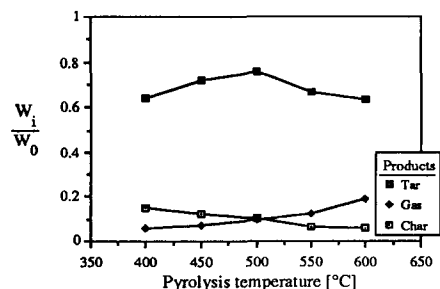

Figure 2. The measured weight fractions of the products as a function of the pyrolysis temperature. Tar vapours and gases are thermally quenched within 40 ms.

Because of the rapid removal of the pyrolysis vapours, secondary tar cracking reactions are suppressed. From the measurements presented in figure 2, the rate constants of the reaction path model can be evaluated. The formulation used in equation (5) takes an incomplete collection efficiency of the pyrolysis products into account.

$$\frac{W_i}{W_g + W_t + W_c} = \frac{k_i}{k_g + k_t + k_c} \qquad i = g, t, c. \qquad (5)$$

The particle conversion in the TGA and the drop tube reactor has been calculated with equation (2). Figure 3 shows direct results of typical TGA experiments at three different temperatures. Results of the drop tube experiments are presented in a similar diagram (Fig. 4), now containing discrete data points plus the corresponding best-fit lines. These lines are obtained by introducing the proper value of k_1 into equation (3).
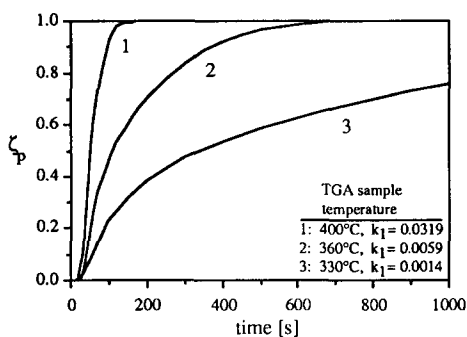

Figure 3. Mass conversion ζ_p of saw-
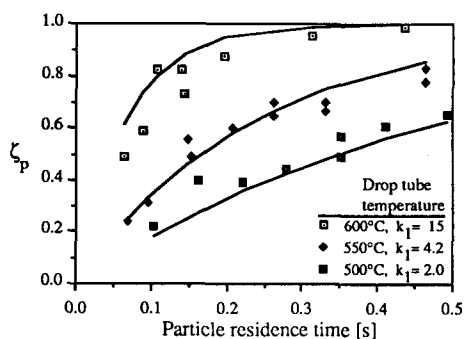dust as a function of time, measured
in the thermogravimetric analyser.

Figure 4. Measured mass conver-
sion ζ_p of sawdust as a function of
the residence time in the drop tube
reactor.

True kinetics of the sawdust decomposition can only be measured if no thermal gradients inside the particle occur, which corresponds to a small value for the particle Biot number. In addition, external heat transfer limitations should not limit the pyrolysis process which corresponds to a large value of the pyrolysis number Py', see [3].

$$Bi = \frac{\alpha \, r_p}{\lambda_p} \ll 1 \qquad \text{and} \qquad Py' = \frac{\alpha}{k_1 \, \rho_p \, C_p \, r_p} \gg 1 \qquad (6, 7)$$

During the time the reacting particle travels through the drop tube, its temperature should not deviate too much from the gas phase temperature. The

temperature difference between a particle and the gas phase bulk can be estimated from the heat balance applied to a single particle.

$$k_1 \rho_w \Delta H_r = \alpha \frac{A_p}{V_p} (T_g - T_p) \qquad (8)$$

Calculations showed that conditions (6, 7) are satisfied. With respect to relation (8) it can be estimated that the error in the prediction of k_1 is less than 30% if the endothermic heat of reaction ΔH_r is smaller than 500 KJ/kg, a value reported in reference [4].

The first-order rate constant of the reaction path model was derived from maximizing the correlation between the experimental data and the reaction path model prediction by fitting the k_1 value. Results of this method are given in figure 5.
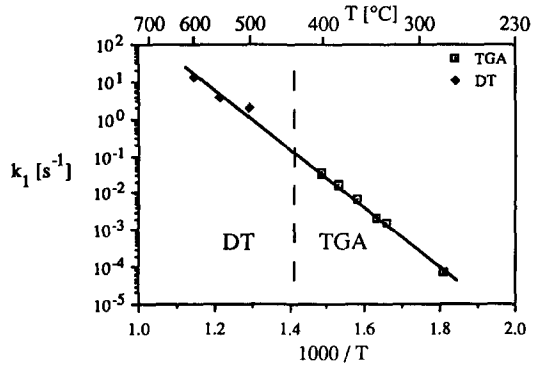
Figure 5.   Values of the first-order wood decomposition rate constant at different temperatures, measured in a thermogravimetric analyser and a drop tube reactor.

The observed temperature dependence for first-order rate constant of the wood decomposition could be described by an Arrhenius type of relation:

$$k_1 = 1.4 \ 10^{10} \ e^{-\frac{150\,000}{R\,T}} \qquad 573 \ K < T < 873 \ K \qquad (9)$$

5. CONCLUSIONS

Below a temperature of 400 °C the kinetics of wood decomposition can be succesfully measured in a TGA . Above 500 °C a drop tube should be applied. From the combined results of such measurements an Arrhenius relationship between the first-order rate constant and the temperature has been established. The parameters of the Arrhenius equation (9) are: $k_0 = 1.4 \ 10^{10} \ s^{-1}$ and $E_a = 150 \ KJ.mol^{-1}$. From measurements of the ultimate gas, tar and char yields it is possible to evaluate the various rate constants of the reaction path model.

6. NOTATION

A	Surface	$[m^2]$
Bi	Particle Biot number	[-]
C	Heat capacity	$[J\ kg^{-1}\ K^{-1}]$
E_a	Reaction activation energy	$[J\ mol^{-1}]$
ΔH_r	Heat of reaction	$[J\ kg^{-1}]$
k_1	first-order rate constant of the primary wood decomposition reaction	$[kg\ kg^{-1}\ s^{-1}]$
k_2	first-order rate constant of the secondary tar cracking reaction	$[kg\ kg^{-1}\ s^{-1}]$
Py'	Particle pyrolysis number	[-]
r	Particle radius	[m]
R	Universal gas constant	$[J\ mol^{-1}\ K^{-1}]$
t	Time	[s]
t_1	Real time required for 63% wood conversion	[s]
T	Temperature	[K]
V	Volume	$[m^3]$
W	Weight	[N]

Greek symbols

				Subscripts	
α	External heat transfer coefficient	$[W\ m^{-2}\ K^{-1}]$		c	char
λ	Thermal conductivity	$[W\ m^{-1}\ K^{-1}]$		g	gas
ρ	Density	$[kg\ m^{-3}]$		p	particle
ζ_p	Mass conversion of the sawdust particles	[-]		t	tar
				w	wood
				0	initial
				*	ultimate

7. REFERENCES

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3. Pyle, D.L. and Zaror, C.A. Heat transfer and kinetics in the low temperature pyrolysis of solids. Chem.Eng.Sci., 39, 147, (1984).
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Discussion

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Question: J.E. Hustad

Biomass can have different compositions of cellulose, hemi-cellulose and lignin. Your model represents a very simple description of the wood structure, visually only cellulose. Do you have plans to incorporate a more complex structure suitable for several biomass fuels?

Answer

The material used in the experimental investigations was pine-wood sawdust which displayed a first-order behaviour in weight change, in correspondence with the results from the random chain dissociation model. The model can be extended to contain other features, but this must be based on well-defined parameters.