PYROLYSIS OF CELLULOSE PARTICLES IN A FLUIDIZED BED

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Spherical particles made of cellulose powder were pyrolyzed in a 4.3 cm i.d. fluidized bed over a temperature range of 350 to 550°C in a stream of nitrogen gas with the primary aim of producing tar and levoglucosan in the tar.

Higher yields of tar and levoglucosan were achieved under operating conditions in which the cellulose particles tended not to sink into the bed, and secondary decomposition of tar was reduced accordingly. The highest yields of tar and levoglucosan respectively at 400°C were 63% and 32% of the original weight of cellulose. These values are much higher than those reported in previous studies of fluidized beds and fixed-bed reactors in atmospheres of inert gases. The variation with time of the concentration of gas containing carbon dioxide and carbon monoxide could be simulated satisfactorily by a kinetic model in which secondary decomposition of the tar was taken into account.

Introduction

Saccharification of cellulosic materials such as wood waste has been achieved by processes using either enzymatic or acid hydrolysis.

Recently, new methodology involving a pyrolysis process has been investigated.[12-14] In pyrolysis reactions of cellulosic materials below 500°C, gasification reactions proceed slowly, and the primary product is tar. The major product present in the tar is an anhydro sugar, levoglucosan (1,6-anhydro-β-D-glucopyranose), which can be converted to glucose under much milder conditions than those used in the saccharification of wood. The tar can also be used as an intermediate in the production of synthetic resins[2] or itaconic acid.[9]

Shafizadeh et al.[12,13] showed that vacuum pyrolysis of cellulose powder provided more tar (and levoglucosan) than did the corresponding pyrolysis under nitrogen. Their reasoning about this result was as follows. Under vacuum, tars readily escape from the heated reaction zone before secondary decomposition can occur, whereas pyrolysis conducted in nitrogen at atmospheric pressure limits the volatilization and removal of tars, thus increasing decomposition.

However, vacuum pyrolysis appears not to be feasible from the economical standpoint, and fluidized-bed processes have been studied as a potential means for pyrolysis of cellulosic materials. Miura et al.[7] and Gray et al.[4] pyrolyzed wood waste

in fluidized beds; the yield of levoglucosan was not mentioned in either report. Hopkins et al.[5] studied the radiant flash pyrolysis of Avicel cellulose powder in a spouted-bed reactor and obtained a high tar and levoglucosan yield comparable to the results obtained by Shafizadeh et al.[13] They attributed the high tar and levoglucosan yields to the quenching of pyrolysis products by a steam flow used in spouting the bed, and also to high particle-heating rates. Funazukuri et al.[3] reported that pyrolysis of cellulose in a microfluidized bed gave an 8% yield of levoglucosan based on cellulose, and concluded that levoglucosan was not a primary product under flash pyrolysis conditions.

In this work, the yields of pyrolysis products, i.e., tar, levoglucosan in the tar, gas and char from cellulose were investigated in a fluidized bed of glass beads under an atmosphere of nitrogen gas. The effects of operating conditions such as fluidizing gas velocity and size of fluidized particles were examined. The variation of gas concentration with time was analyzed by a kinetic model.

1. Experimental Apparatus and Procedure

Figure 1 shows the experimental apparatus, in which a cylindrical column of 4.3 cm diameter constructed of stainless steel type 310 was used as a reactor. The experimental conditions, including the properties of fluidized particles, are listed in **Table 1**. The static bed height was varied from 0.3 to 1.5 D_T. Nitrogen, used as a fluidizing gas, was dispersed with a perforated plate with 0.9% fractional open area and a fixed bed of stainless steel balls of 5 mm depth. The temperature
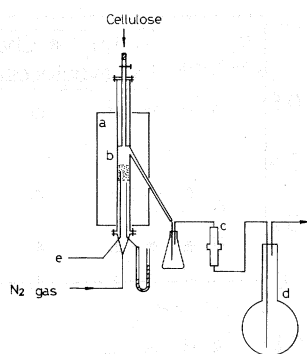
Fig. 1. Experimental apparatus
(a) Tube furnace; (b) Fluidized bed; (c) Filter (d) Buffer tank;
(e) Temperature controller

Table 1. Experimental conditions for the pyrolysis of cellulose

		Glass beads		
		Size	d_p	u_{mf}
Temperature range	350–550°C			(at 400°C)
Bed diameter, D_T	4.3 cm			
Static bed height	$(0.3–1.5)D_T$	[mesh]	[mm]	[cm/s]
Fluidizing gas	nitrogen	170–325	0.062	0.6
$u_g - u_{mf}$	up to 8 cm/s	100–170	0.11	1.4
Diameter of cellu-		60–100	0.19	2.8
lose particles	7.5 mm	35– 60	0.32	7.3
		24– 32	0.59	17.5

range examined was from 350 to 550°C. The spherical samples were prepared from cellulose powder (Toyo Roshi, 100–200 mesh) by adding distilled water, manually shaping into spheres 7.5 mm in diameter and drying at 105°C for more than 2 h. The sample cellulose spheres were fed into the top of the reactor at a rate of about 0.1 g/min, the total amount of cellulose being 4 g.

To measure the rate of pyrolysis reaction, a single cellulose particle was kept in the reactor for a set period of time, then cooled in a nitrogen gas chamber at room temperature, and weighed.

The products of the pyrolysis reaction were grouped into three components: tar, gases and char. The gases were sampled at the outlet of a buffer tank set to reduce fluctuations of gas concentration, and were then analyzed with a gas chromatograph. The tar was emitted as white aerosol particles, which condensed on the inner walls of the tubing or were trapped in a filter of glass wool, from which they were recovered by washing with methanol. After the methanol was evaporated, the weight of tar was measured. A part of the product tar was analyzed for levoglucosan using gas-liquid chromatography after adding methyl-β-D-glucoside as the internal standard and acetylating the mixture.[6] The yield of char was determined by weighing particles of char remaining in the reactor
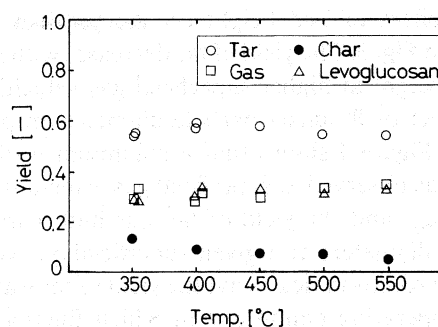

Fig. 2. Effect of temperature on yields of products ($u_g = 8$ cm/s; fluidized particle size = 60–100 mesh)

Table 2. Yields of gases (Experimental conditions are the same as in Fig. 2)

Temp. [°C]	CO	CO_2	H_2O	Total gas yield
	[mol/kg-cellulose]			[kg/kg-cellulose]
350	0.281	1.15	12.9	0.291
400	0.575	1.29	11.5	0.280
450	0.936	1.32	11.3	0.288
500	1.87	1.77	12.1	0.348
550	2.80	1.69	10.9	0.350

after the reaction.

2. Results and Discussion

2.1 Pyrolysis of cellulose spherical particles

1) Effect of temperature and static bed height on products yields **Figure 2** shows the effect of temperature on the yields of the products, where the yields indicate weight fraction of products based on the initial amount of cellulose (on a dry basis). The yield of gas was calculated from the sum of the fractions of components, mainly consisting of carbon dioxide, carbon monoxide and water. The material balance over the yields of gas, tar and char closed to higher than 95%. The yields of each component of the gas are listed in **Table 2**. The molar ratio of carbon dioxide to carbon monoxide was about 2 to 1 at 400°C, and the yields of carbon dioxide and carbon monoxide were similar to those reported by Funazukuri et al.[3] The fluidized bed of 60–100 mesh glass beads gave maximum yields of 59% tar containing 32% levoglucosan, both yields being based on the initial amount of cellulose at 400°C; hereafter, the effects of the operating conditions will be explained for the results obtained at this optimum temperature. Although this value of levoglucosan is lower than the 39% yield obtained in the vacuum process reported by Shafizadeh et al.,[12,13] it is comparable to the 31% yield of a flash pyrolysis in a spouted bed,[5] and is much higher than the 17% yield obtained in a tube furnace under nitrogen atmosphere,[12,13] in a microfluidized bed (8% at 400°C)[3] and in the vacuum process by Miura et al. (22% at 500°C).[8]

The effect of bed height on the product yield is shown in **Fig. 3**. The yield of tar decreases with increase in bed height at higher superficial gas velocities.

2) Effect of fluidized particle diameter on products yields   **Figure 4** shows that a maximum in the yield of tar was observed at superficial gas velocities slightly above u_{mf}, and the yield of tar was higher for larger particle diameters at a given superficial gas velocity.

These results indicate that the yield of tar was higher under operating conditions in which fluctuations at the top of the bed were less. This corresponds to the fact that the sample particles were pyrolyzed while they were floating at the top of the bed. Also, the less the fluctuations, the less were the chances of the samples sinking into the bed, so the tar forming at the top could escape to the freeboard without undergoing secondary pyrolysis.

The effect of the size of the fluidized particle on the yield of tar and gas is shown in **Fig. 5**. The yield of tar was proportional to $d_p^{0.23}$ for $d_p < 0.3$ mm and constant for $d_p \geq 0.3$ mm. The yield of gas conversely decreased in proportion to $d_p^{-0.21}$. After the reaction, char particles were in most cases seen floating at the top of the bed because of their low density. However, when the diameter of the fluidized glass beads was small ($d_p = 0.062$ mm), some of the char particles were found at the bottom of the bed, covered with beads glued with the tar. In this case, the tar could be decomposed severely underneath the bed surface by the secondary decomposition reaction. This is another reason for the reduction in tar yield, in addition to sinking of the sample particles by the fluctuations. **Figure 6** shows the yields of tar and gas modified for the effect of particle size by using the correlations shown in Fig. 5.

3) Relation between carbonaceous gas yield and tar yield   **Figure 7** shows the yield of carbon dioxide plus carbon monoxide under various operating conditions of fluidized particle size, superficial gas velocity and bed height. The lower right points in the graph correspond to the results with less fluctuation of the top of the bed and hence smoother fluidization, whereas the upper left points correspond to those with greater chances of sinking of sample particles owing to fluctuations at the top of the bed and/or caking of fluidized particles. The trend that an increase in the yield of carbon dioxide plus carbon monoxide corresponds to a reduction in the yield of tar means that the tar was decomposed via secondary pyrolysis reactions to gases and char.[1] This was further confirmed by the fact that the color of the fluidized particles after the reaction was white for the lower right points, while it was blackish for the upper left ones. When the cellulose spheres were immersed in the bed, the tar produced inside the bed would be decomposed and a thin layer of char would deposit
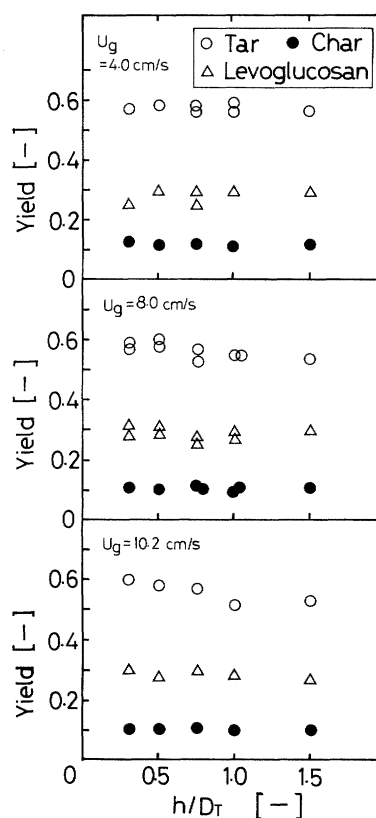

Fig. 3. Effect of static bed height on yields of products (400°C; fluidized particle size = 60-100 mesh)
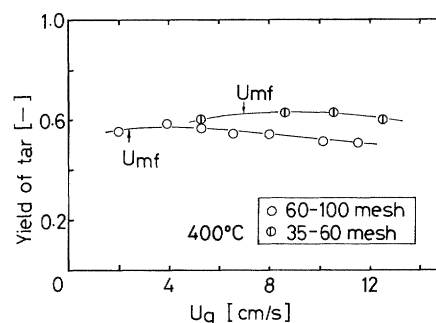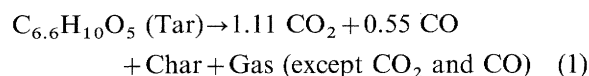

Fig. 4. Effect of superficial gas velocity on tar yield

on the surface of the fluidized particles. If the molar ratio of carbon dioxide and monoxide is assumed to be 2 : 1 at 400°C as shown in Table 2 and the elemental composition of tar (**Table 3**) is taken into account, the hypothetical stoichiometric balance for the secondary decomposition of tar can be determined from the slope of the empirical straight line in Fig. 7 and written as follows:

$$C_{6.6}H_{10}O_5 \ (Tar) \rightarrow 1.11 \ CO_2 + 0.55 \ CO$$
$$+ Char + Gas \ (except \ CO_2 \ and \ CO) \quad (1)$$

It is concluded that to maximize the yield of tar, operating conditions which would cause immersion of feed materials in the bed must be avoided. In light of this, the way by which the raw materials are fed
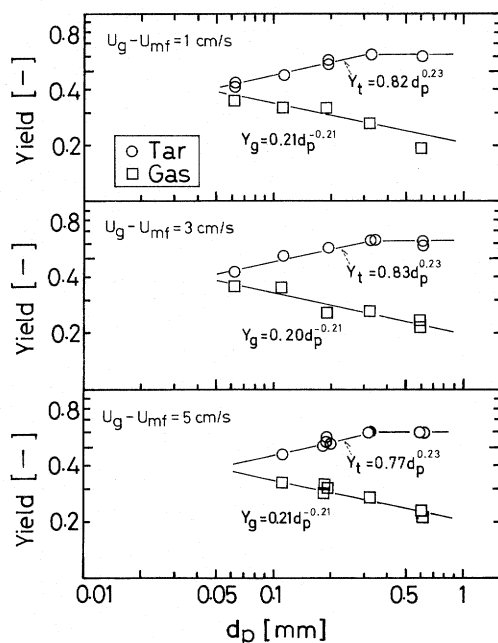
Fig. 5. Yields of tar and gas as functions of fluidized particle diameter (400°C; d_p: [mm])
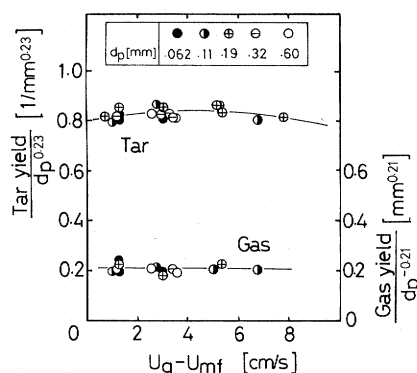

Fig. 6. Yields of tar and gas as functions of $u_g - u_{mf}$ (400°C; tar yield was modified for $d_p < 0.3$ mm as shown in the text)
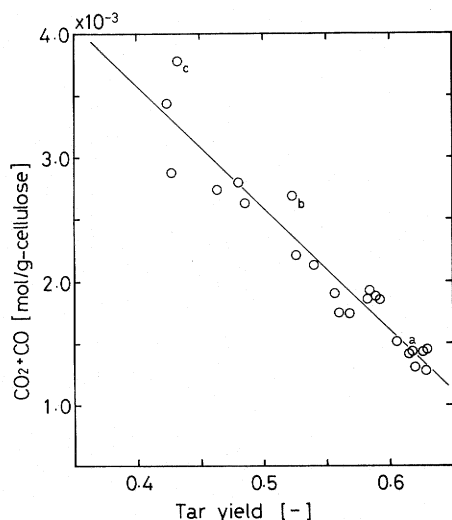

Fig. 7. Yield of $CO_2 + CO$ as a function of tar yield (400°C; particle size: point a = 0.32 mm; point b = 0.11 mm; point c = 0.062 mm)
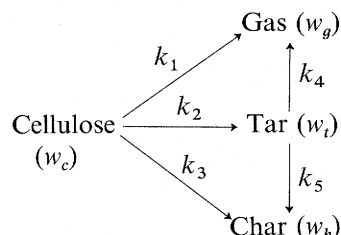
Table 3. Elemental compositions of tar

Temp. [°C]	C [%]	H [%]	(O) [%]
350	47.4	5.9	46.7
400	47.0	5.8	47.2
450	47.2	5.9	46.8
500	47.3	6.0	46.8
550	46.7	6.0	47.3

through the immersed tip of the pipe often used in previous works[3,4] might be inappropriate to obtaining tars as desired products.

2.2 Reaction rate of pyrolysis of cellulose particles

1) Kinetic model of the pyrolysis of cellulose The pyrolysis reaction was analyzed by the mechanism reported in previous studies[11,16] in which the secondary decomposition of tar was taken into account.

If each primary and secondary reaction is assumed to be first-order, the rate of change of each component in the reactor and the buffer tank is given for discrete sample particles as follows:

$$-dw_c/dt = (k_1 + k_1 + k_3)w_c \qquad (2)$$

$$dw_t/dt = k_2 w_c - (k_4 + k_5)w_t - u_g S_R w_t/V_R \qquad (3)$$

$$dw_g/dt = k_1 w_c + k_4 w_t - u_g S_R w_g/V_R \qquad (4)$$

$$dw_h/dt = k_3 w_c + k_5 w_t \qquad (5)$$

$$dW_{gT}/dt = u_g S_R w_g/V_R - (u_g S_R W_{gT}/V_T)(T_T/T_R) \qquad (6)$$

Eqs. (2) to (6) can be solved analytically (see **Appendix**). If it is assumed that secondary decomposition of tar occurs only outside the sample particle, and this then consists of unreacted cellulose and char formed by the primary decompositon of cellulose, the weight of the particle (w) is given by combining the analytical solutions of Eqs. (2) and (5) as

$$(w - w_\infty)/(w_{c0} - w_\infty) = \exp\{-(k_1 + k_2 + k_3)t\} \qquad (7)$$

2) Estimation of the kinetic parameters The variations in weight of single spherical samples with time are shown in **Fig. 8**. The data fitted Eq. (7) except for the initial time lag necessary for the samples to reach the reaction temperature, and the values of $k_1 + k_2 + k_3$ ($= \alpha$), determined from the slope of the straight lines, were correlated by the following
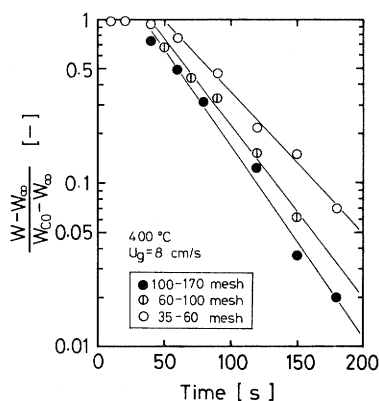
Fig. 8. Variation of weight of single cellulose particles with time

Fig. 9. Rate constant α as a function of superficial gas velocity (400°C)

empirical formula as shown in **Fig. 9**:

$$\alpha = 1.67 \times 10^{-2}\{(u_g - u_{mf})/u_{mf}\}^{0.23} \quad [\text{s}^{-1}] \quad (8)$$

The reason why the rate constant α is expressed as a function of the superficial gas velocity is related to the rate processes involved in the pyrolysis of sample particles. The relative contribution of the rate processes in the pyrolysis, namely the intrinsic pyrolysis reaction, heat conduction and external heat transfer, can be estimated by the following three nondimensional parameters[10]: $P_y = \lambda/k\rho C_p R^2$, $P'_y = h_t/k\rho C_p R$ and $Bi = h_t R/\lambda$, where k, the intrinsic reaction rate constant, is determined as a limiting value of α when the size of the sample particle is sufficiently small. The magnitude of the above three parameters is on the order of 1 at 400°C, which means that the relative importance of the three rate processes is almost equal to one another. Thus, the constant α in Eq. (8) is expressed as a function of superficial gas velocity because the external heat transfer rate, one of the three processes, is a function of the gas velocity.[15]

The values of k_1, k_2 and k_3 were estimated on the basis of the result by Shafizadeh *et al.*[13] in a vacuum pyrolysis process, which is deemed to have involved the least secondary decomposition of tar. Based on the 77% yield of tar and 5% yield of char in their report, the three rate constants were determined respectively as $k_1 = 0.77\alpha$, $k_2 = 0.18\alpha$ and $k_3 = 0.05\alpha$. The parameters k_4 and k_5, which refer to those of secondary decomposition, were estimated from the overall mass balance by use of the values of tar and gas yields at steady state. When the reaction time is sufficiently long, the values of $k_{4\text{exp}}$ and $k_{5\text{exp}}$ are given by substituting the experimental values of tar and gas yields into Eqs. (A-6) and (A-7) respectively. On the other hand, the values of yield of tar and gas are estimated by use of the correlations shown in Fig. 5, and the calculated values of $k_{4\text{cal}}$ and $k_{5\text{cal}}$ can be obtained by substituting the calculated yield values of
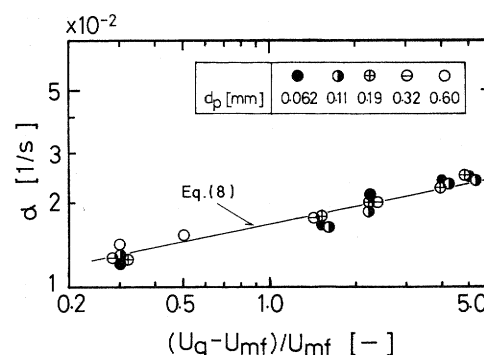
gas and tar into Eqs. (A-6) and (A-7). The comparison of experimental and estimated values of the secondary decomposition parameters agreed well for both parameters k_4 and k_5 as shown in **Fig. 10**.

3) Simulation of the concentration response of carbonaceous gas Substituting the five parameters $k_1 \sim k_5$ into Eq. (A-1) gives the concentration response of the gas component at the outlet of the buffer tank. Among the three components of the outlet gas, *viz.* carbon dioxide, carbon monoxide and water, the water partially condensed on the wall of the tubing and the shape of the overall response curve was affected. Therefore, only the concentration of carbon dioxide plus carbon monoxide (carbonaceous gas) was compared with the calculated response curve, which was obtained by multiplying the value from Eq. (A-1) by an empirical ratio[*] of the carbonaceous gas. **Figure 11** shows the variations of the carbonaceous gas with time, where the dotted lines indicate the calculated response; Figures 11(a), (b) and (c) correspond respectively to points a, b and c in Fig. 7. The calculated concentration response of gas agreed well with the data under various experimental conditions with various degrees of secondary decomposition of tar.

Conclusions

It has been shown that tar and levoglucosan in the tar can be produced effectively by the fluidized bed, ensuring high yields comparable to those in a vacuum pyrolysis process. The yields of carbonaceous gases (CO_2 plus CO) increased as the yield of tar decreased due to secondary decomposition. To maximize the yield of tar, cellulose particles must be processed under operating conditions in which the particles tend not to sink into the bed, because if the sample materials

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[*] The ratio of the weight of carbon dioxide plus monoxide to that of the total gas, c_g, is given by the following empirical equation as a function of the tar yield

$$c_g = -0.75 Y_t + 0.68 \quad [-]$$

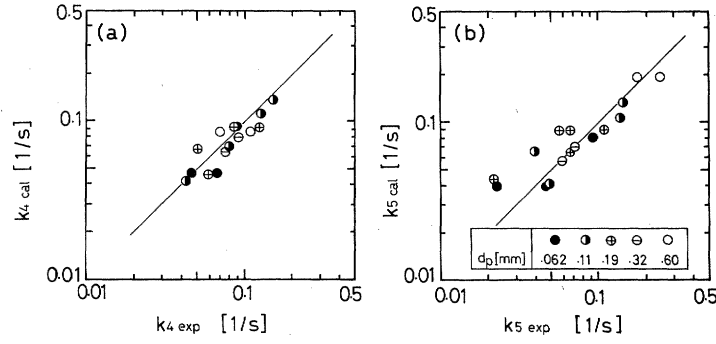which was obtained from the data shown in Fig. 7.

Fig. 10. (a) Comparison of calculated and experimental values of parameter k_4 (400°C)
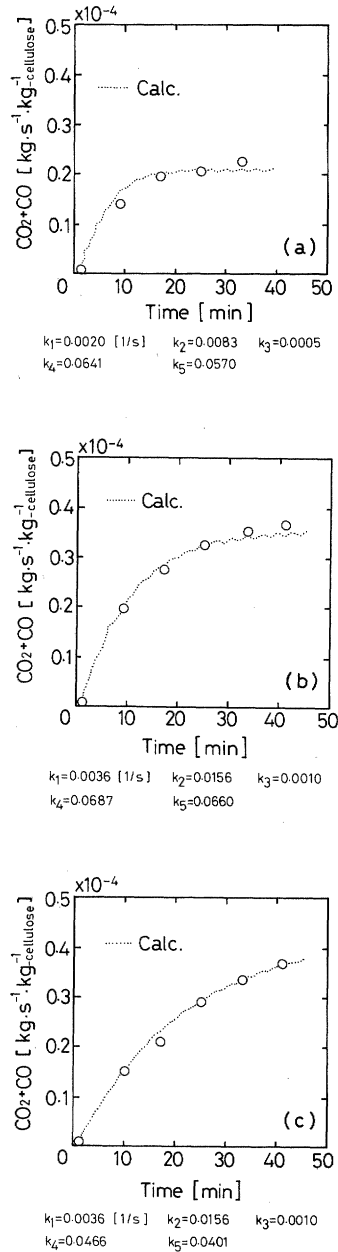
(b) Comparison for parameter k_5 (400°C)

$k_1 = 0.0020$ [1/s] $k_2 = 0.0083$ $k_3 = 0.0005$
$k_4 = 0.0641$ $k_5 = 0.0570$

$k_1 = 0.0036$ [1/s] $k_2 = 0.0156$ $k_3 = 0.0010$
$k_4 = 0.0687$ $k_5 = 0.0660$

$k_1 = 0.0036$ [1/s] $k_2 = 0.0156$ $k_3 = 0.0010$
$k_4 = 0.0466$ $k_5 = 0.0401$

Fig. 11. Concentration response of carbonaceous gas (400°C; $h/D_T = 1$) (a) $d_p = 0.32$ mm, $u_g - u_{mf} = 1.1$ cm/s; (b) $d_p = 0.11$ mm, $u_g - u_{mf} = 2.7$ cm/s; (c) $d_p = 0.062$ mm, $u_g - u_{mf} = 1.8$ cm/s

are pyrolyzed while underneath the bed surface the tar produced will be severely reduced by secondary decomposition. The variations of carbonaceous gas with time can be simulated satisfactorily by using the model that incorporates the effect of secondary decomposition of tar.

Appendix

The flow rate of gas component at the outlet of the buffer tank can be given by analytically solving simultaneous ordinary differential equations, *i.e.* Eqs. (2) to (6) in the text:

$$\frac{R_g}{w_{c0}} = \left[\frac{1}{\kappa - \sigma} \left\{ \frac{\kappa(k_1 - k_4\beta)}{\alpha - \kappa} + \frac{\kappa k_4 \beta}{k_4 + k_5} \right\} \{\exp(-\sigma t) - \exp(-\kappa t)\} \right.$$

$$+ \frac{\kappa(k_1 - k_4\beta)}{(\sigma - \alpha)(\alpha - \kappa)} \{\exp(-\sigma t) - \exp(-\alpha t)\}$$

$$\left. + \frac{\kappa k_4 \beta}{(k_4 + k_5)(k_4 + k_5 + \kappa - \sigma)} \{\exp(-(k_4 + k_5 + \kappa)t) - \exp(-\sigma t)\} \right] \sigma$$

$$(A-1)$$

where

$$\alpha = k_1 + k_2 + k_3$$
$$\beta = k_2 / \{\alpha - (k_4 + k_5 + \kappa)\}$$
$$\kappa = u_g S_R / V_R$$
$$\sigma = (u_g S_R / V_T)(T_T / T_R)$$

The solution for the total amount of tar is

$$\frac{M_t}{w_{c0}} = \kappa\beta \left\{ \frac{1 - \exp(-(k_4 + k_5 + \kappa)t)}{k_4 + k_5 + \kappa} - \frac{1 - \exp(-\alpha t)}{\alpha} \right\} \qquad (A-2)$$

The total amount of generated gas is given by

$$\frac{M_g}{w_{c0}} = \kappa \left\{ \frac{k_1 - k_4\beta}{\alpha - \kappa} \left(\frac{1 - \exp(-\kappa t)}{\kappa} - \frac{1 - \exp(-\alpha t)}{\alpha} \right) \right.$$

$$\left. + \frac{k_4\beta}{k_4 + k_5} \left(\frac{1 - \exp(-\kappa t)}{\kappa} - \frac{1 - \exp(-(k_4 + k_5 + \kappa)t)}{k_4 + k_5 + \kappa} \right) \right\} \qquad (A-3)$$

Equations (A-1) to (A-3) are obtained for a discrete particle. To compare the calculated values with the experimental results for a group of particles, it is necessary to integrate the discrete values of the above equations.

The yield of tar can be equated with the limiting value of Eq. (A-2) at long reaction time ($t \to \infty$); then

$$Y_t = \kappa k_2 / \{\alpha(k_4 + k_5 + \kappa)\} \qquad (A-4)$$

Similarly, the yield of gas can be given by Eq. (A-3) as

$$Y_g = \{k_1(k_4 + k_5 + \kappa) + k_2 k_4\} / \{\alpha(k_4 + k_5 + \kappa)\} \qquad (A-5)$$

Solving Eqs. (A-4) and (A-5) for k_4, k_5 gives

$$k_4 = \kappa(Y_g\alpha - k_1)/(Y_t\alpha) \qquad \text{(A-6)}$$

$$k_5 = \kappa\{k_1 + k_2 - \alpha(Y_t + Y_g)\}/(Y_t\alpha) \qquad \text{(A-7)}$$

Acknowledgement

Nomenclature

C_p	= specific heat	[J/(kg·K)]
d_p	= mean diameter of glass beads	[mm]
D_T	= bed diameter	[cm]
h	= static bed height	[cm]
h_t	= heat transfer coefficient	[W/(m²·K)]
k	= intrinsic reaction rate constant	[s⁻¹]
k_1, k_2, k_3, k_4, k_5	= reaction rate constant	[s⁻¹]
M_g	= total weight of gas generated	[kg]
M_t	= total weight of tar	[kg]
R	= radius of cellulose particle	[m]
R_g	= flow rate of gas component at outlet of the buffer tank	[kg/s]
S_R	= cross-sectional area of the reactor	[cm²]
t	= time	[s]
T_R	= temperature of the reactor	[K]
T_T	= temperature of the buffer tank	[K]
u_g	= superficial gas velocity	[cm/s]
u_{mf}	= minimum fluidization velocity	[cm/s]
V_R	= volume of the reactor	[cm³]
V_T	= volume of the buffer tank	[cm³]
w	= weight of particle	[kg]
w_∞	= weight of particle at $t=\infty$	[kg]
w_c	= weight of cellulose	[kg]
w_{c0}	= initial weight of cellulose	[kg]
w_g	= weight of gas in the reactor	[kg]
W_{gT}	= weight of gas in the buffer tank	[kg]
w_t	= weight of tar in the reactor	[kg]
Y_g	= weight fraction yield of gas	[—]
Y_t	= weight fraction yield of tar	[—]
α	= reaction rate constant $=k_1+k_2+k_3$	[s⁻¹]
λ	= thermal conductivity	[W/(m·K)]
ρ	= bulk density of cellulose particle	[kg/m³]

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