Numerical simulations on the effect of potassium on the biomass fast pyrolysis in fluidized bed reactor

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HIGHLIGHTS

- CFD model developed for fast pyrolysis of cellulose with potassium.
- Effect of potassium on the products yield and composition has been studied and analyzed.
- Effect of reactor temperature has been analyzed.
- Effect of unstable flow on the products yield has been studied.

ABSTRACT

In this study, the effect of potassium on the cellulose fast pyrolysis in a fluidized bed reactor has been studied using Computational Fluid Dynamics (CFD). A multiphase pyrolysis model of cellulose has been implemented by integrating the hydrodynamics of the fluidized bed with an adjusted cellulose pyrolysis mechanism that accounts for the effect of potassium. The model has been validated with the reported experimental data. The simulation results show that potassium concentration and reactor temperature have a significant effect on the yield and component of cellulose pyrolysis products. The product yields fluctuate is caused by the unstable flow in the fluidized bed. The result shows that the increased potassium concentration in the cellulose causes a significant increase of the gas and char yields and reduction in the bio-oil. Also, the dramatic composition variations in bio-oil and gas were observed due to the inhibition of fragmentation, and the depolymerization reaction of activated cellulose, and the catalysis of the depolymerization reaction of cellulose. It is also found that the increase in reactor temperature greatly enhances the endothermic pyrolysis reaction, which leads to the significant changes in the yield and composition of cellulose pyrolysis products.

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1. Introduction

Fast pyrolysis is one of the most promising technologies for producing bio-oil, gas and char from biomass [1–3]. Fluidized bed reactor is widely used in biomass fast pyrolysis, as they have good temperature control and high heat transfer rates [3,4]. The thermochemical conversion of biomass in fluidized beds has been extensively investigated using both experimental and numerical methods in the literature [5–8].

Biomass usually contains considerable amounts of alkali and alkaline earth metallic species (AAEMs) such as sodium, potassium, calcium, etc. Many studies have reported that AAEMs play an important role in biomass pyrolysis reactions [9–15]. Shimada et al. [9] studied the effect of AAEMs on cellulose pyrolysis and found that potassium chloride and sodium chloride caused a reduced levoglucosan yield and increased the yield of water, carbon monoxide, and char. Patwardhan et al. [10] found that potassium chloride and sodium chloride led to a significant increase in the yield of low molecular weight species, while there was a severe reduction of the levoglucosan yield. Rutkowski [11] investigated the effects of potassium carbonate on cellulose pyrolysis. The results indicate that potassium carbonate influenced the decomposition temperature of cellulose and the composition of a pyrolysis product significantly. Hu et al. [12] investigated the effects of inherent AAEMs on biomass pyrolysis. The results indicate that inherent AAEMs can enhance the production of carbon dioxide.
and hydrogen, and the decomposition of levoglucosan significantly.

Computational Fluid Dynamics (CFD) has been widely used for modeling of the hydrodynamics, heat transfer and chemical reactions inside the fluidized bed, and various CFD models for biomass pyrolysis process in fluidized bed have been developed that can be categorized into Euler–Lagrangian and Euler–Euler models. The Euler–Euler model could simulate the biomass pyrolysis in a fluidized bed reactor effectively. It includes the space-time evolution of pyrolysis products in a fluidized bed, the interaction between the sand, biomass and gases, and the effects of operating conditions on the yield and composition of pyrolysis products [16–23]. The Euler–Lagrangian model could simulate the pyrolysis of discrete biomass particle in a fluidized bed reactor accurately, but it needs huge computational cost [24–27].

There are several experimental studies on the effect of potassium on the cellulose fast pyrolysis. However, a numerical study has not been conducted and published so far. In this work, a model of cellulose fast pyrolysis in a fluidized bed based on the Eulerian framework has been developed. The spatial-temporal evolutions of products from cellulose fast pyrolysis in a fluidized bed are studied using CFD. The effects of potassium concentration and reactor temperature on the composition and yield of cellulose fast pyrolysis products are intensively investigated.

2. Model description

The sketch of the numerically simulated 300 g/h fluidized bed reactor of Aston University is shown in Fig. 1, and the specifications of the computational domain can be seen in Table 1 [28]. 2-D simulations are performed in the present work. The fluidization gas is preheated pure nitrogen, which flows from the bottom of the reactor of Aston University is shown in Fig. 1, and the specifications of the computational domain can be seen in Table 1 [28].

![Fig. 1. Schematic diagram of the 2-D fluidized bed reactor.](image)

<table>
<thead>
<tr>
<th>Reactor height, H</th>
<th>257 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor width, W</td>
<td>41 mm</td>
</tr>
<tr>
<td>Biomass inlet diameter, a</td>
<td>14 mm</td>
</tr>
<tr>
<td>Biomass inlet height, b</td>
<td>16 mm</td>
</tr>
<tr>
<td>Product outlet diameter, c</td>
<td>7 mm</td>
</tr>
<tr>
<td>Product outlet height, h</td>
<td>244 mm</td>
</tr>
</tbody>
</table>

Table 1 Specifications of the computational domain [28].

Euler–Euler multiphase model, and the cellulose pyrolysis reactions are simulated using a detailed chemical kinetic model. These models were solved using the CFD software ANSYS Fluent 15.0.

3.1. Multiphase flow governing equations

There are three phases in the fluidized bed reactor, i.e., gas phase, biomass particles and sand. The gas phase includes nitrogen as a fluidization gas and gas products from biomass fast pyrolysis. The biomass particle includes unreacted cellulose, activated cellulose which is an intermediate product of cellulose pyrolysis and char produced from biomass pyrolysis. In the Euler–Euler multiphase model, all the three phases are treated as interpenetrating continua. The gas phase is the primary phase and the solid phases, i.e., biomass particles and sand, are considered as secondary phases.

3.1.1. Gas phase

The continuity equation for the gas phase is

\[
\frac{\partial}{\partial t} (\varphi_g \rho_g) + \nabla \cdot (\varphi_g \rho_g \vec{v}_g) = \dot{m}_g
\]

where \( \vec{v}_g \) and \( \rho_g \) are the velocity and density of gas, respectively, \( \dot{m}_g \) is the mass transfer between phases and \( \varphi_g \) is the gas volume fraction [29].

The species transport equation is

\[
\frac{\partial}{\partial t} (\varphi_g \rho_g Y_k) + \nabla \cdot (\varphi_g \rho_g \vec{v}_g Y_k) = \sum_{m=1}^{M} \dot{m}_{m,g,k}
\]

where \( Y_k \) is the mass fraction of \( k \)th species, \( \dot{m}_{m,g,k} \) is the net mass exchange between the gas phase component \( k \) and the solid phase \( m \), and \( M \) is the total number of solid phases [29].

The conservation of momentum for the gas phase is

\[
\frac{\partial}{\partial t} (\varphi_g \rho_g \vec{v}_g) + \nabla \cdot (\varphi_g \rho_g \vec{v}_g \vec{v}_g) = -\varphi_g \nabla p + \varphi_g \rho_g \vec{g} + \nabla \cdot \vec{t}_g
\]

\[
+ \sum_{m=1}^{M} [K_{res} (\vec{v}_{in} - \vec{v}_k) + m_{res} \vec{v}_{in}]
\]

where \( p \) is the pressure, \( \vec{g} \) is the acceleration of gravity, \( \vec{t}_g \) is the gas phase stress-strain tensor, and \( K_{res} \) is the interphase momentum exchange coefficient between \( m \)th solid phase and gas phase.

Gas-solid exchange coefficient is given by Gidaspow [30]. Although Gidaspow drag model does not work well in the free-board region of fluidized bed reactor, according to the previous studies reported in the literature [8,18], this model is suitable for simulating the biomass pyrolysis in the bubbling fluidized bed. The model equations are

when \( \varphi_g > 0.8 \), the exchange coefficient \( K_{gs} \) is

\[
K_{gs} = \frac{3}{4} C_D \frac{\varphi_g \rho_g |\vec{v}_g - \vec{v}_k|}{d_i} \varphi_g^{-2.65}
\]

where

\[
C_D = \frac{24}{\varphi_g Re_i} \left[ 1 + 0.15 (\varphi_g Re_i)^{0.87} \right]
\]
when $x_g \leq 0.8$.

$$K_{sg} = 150 \frac{z_g(1 - x_g)H_{sg}}{x_g d^2_s} + 1.75 \rho_s z_g |\tilde{v}_g - \tilde{v}_q|$$

(6)

The energy conservation equation for gas phase is

$$\frac{\partial}{\partial t}(x_g \rho_g \tilde{h}_g) + \nabla \cdot (x_g \rho_g \tilde{v}_g \tilde{h}_g) + \frac{\partial}{\partial t} \tilde{h}_g + \nabla \cdot \tilde{q}_g + \Delta H_g = \sum_{m=1}^M \tilde{h}_{sm} \rho_{sm} (T_g - T_s)$$

(7)

where $\tilde{q}_g$ is the heat flux, $\Delta H_g$ is the heat of the chemical reaction in the gas phase, and $h_{sm}$ is the volumetric heat exchange between the gas phase and $m$th solid phase which is given by Gunn [31]

$$h_{sm} = 5k_{sm} x_s N_{u_s} d_s^2$$

(8)

$$N_{u_s} = (7 - 10x_g + 5x_g^2)(1 + 0.7 E_0^{1/3} P)^{1/3} + (1.33 - 2.4x_g + 1.2x_g^2) R_0^{1/3} P^{1/3}$$

(9)

The gas phase stress-strain tensor $\tilde{t}_g$ in Eqs. (3) and (7) is defined as

$$\tilde{t}_g = \frac{\partial}{\partial t} x_g \rho_g \tilde{v}_g + \nabla \cdot (x_g \rho_g \tilde{v}_g \tilde{h}_g)$$

(10)

where $\mu_g$ denotes the molecular viscosity of gas phase, while $\lambda_g$ denotes the bulk viscosity of gas phase.

3.1.2. Solid phase

The continuity equation for solid phase $m$ is

$$\frac{\partial}{\partial t} (x_m \rho_m \tilde{u}_m) + \nabla \cdot (x_m \rho_m \tilde{u}_m \tilde{v}_m) = \tilde{m}_m$$

(11)

where $\tilde{u}_m$ is the velocity of solid phase $m$, and $\tilde{m}_m$ is the mass transfer from the $m$th solid phase to gas phase.

The conservation of momentum for the $m$th solid phase is

$$\frac{\partial}{\partial t} (x_m \rho_m \tilde{u}_m \tilde{v}_m) + \nabla \cdot (x_m \rho_m \tilde{u}_m \tilde{v}_m \tilde{h}_m) = -x_m \nabla p + x_m \rho_{sm} \tilde{g} + \nabla \cdot \tilde{t}_m + \sum_{n=1}^N (K_{mn} (\tilde{v}_n - \tilde{v}_m))$$

(12)

where $K_{mn}$ is the momentum exchange coefficient between $m$th and $n$th gas phase or solid phase.

The energy conservation equation for solid phase $m$ is

$$\frac{\partial}{\partial t} (x_m \rho_m \tilde{h}_m) + \nabla \cdot (x_m \rho_m \tilde{u}_m \tilde{h}_m)$$

$$= x_m \frac{\partial}{\partial t} \tilde{u}_m + \tilde{m}_m \nabla \cdot \tilde{u}_m + \Delta H_m + h_{sm} \rho_{sm} (T_m - T_g)$$

(13)

where $\tilde{q}_m$ is the heat flux; $\Delta H_m$ is the heat of reaction in the $m$th solid phase.

The solid phase stress-strain tensor $\tilde{t}_m$, in Eqs. (12) and (13) is defined as

$$\tilde{t}_m = -P_m \tilde{I} + x_m \rho_{sm} (\nabla \tilde{v}_m + \nabla \tilde{v}_m^T) + x_m \tilde{\sigma}_m (\frac{2}{3} \tilde{\mu}_m) \nabla \cdot \tilde{v}_m \tilde{I}$$

(14)

where $\mu_{sm}$ denotes the solid shear viscosity of solid phase which is given by (15), while $\lambda_m$ denotes bulk viscosity of solid phase which is given by (16) and $P_m$ is the solid phase pressure given by (17).

$$\mu_m = \mu_{m, col} + \mu_{m, kin} + \mu_{m, fr}$$

(15)

where $\mu_{m, col}$, $\mu_{m, kin}$, and $\mu_{m, fr}$ are the collisional viscosity, the kinetic viscosity, and the frictional viscosity, respectively.

$$\lambda_m = \frac{4}{3} x_m \rho_{m} d_m g_{0, sm} (1 + e_{m, sm}) \left(\frac{\theta_m}{P_c}\right)^{1/2}$$

(16)

where $e_{m, sm}$ is the coefficient of restitution for particle collisions, $g_{0, sm}$ is the radial distribution function, and $\theta_m$ is the granular temperature.

$$P_m = x_m \rho_m \tilde{m}_m + 2 \rho_m (1 + e_{m, sm}) x_m^2 g_{0, sm} \tilde{h}_m \theta_m$$

(17)

The granular temperature for the $m$th solids phase $\theta_m$ is proportional to the kinetic energy of the particles random motion. The formal expression is

$$\theta_m = \frac{1}{3} u_{m,j} \tilde{a}_{m,j}$$

(18)

where $u_{m,j}$ represents the $j$th component of the fluctuating solids velocity.

The transport equation derived from kinetic theory is

$$\frac{3}{2} \frac{\partial}{\partial t} (x_m \rho_m \tilde{t}_m) + \frac{\nabla}{\nabla} \cdot (x_m \rho_m \tilde{u}_m \tilde{t}_m)$$

$$= -(P_m \tilde{I} + \tilde{\sigma}_m) \nabla \tilde{v}_m + \lambda_m \nabla \cdot (g_{0, sm} \nabla \tilde{h}_m) - \gamma_{m, sm} + \rho \tilde{h}_m$$

(19)

where $\gamma_{m, sm}$ represents the diffusion coefficient, while $\rho \tilde{h}_m$ denotes the colloidal dissipation of energy and $\rho \tilde{h}_m$ denotes the energy exchange between the $m$th gas or solid phase and the $m$th solid phase.

3.2. Cellulose pyrolysis model

The reaction mechanisms of the cellulose pyrolysis with and without potassium used in this work are developed by Ranzi et al. [32] and Trendewicz et al. [33], respectively. The latter is a modified version of the cellulose pyrolysis mechanism developed by Ranzi et al. [32], in order to include the effect of potassium on cellulose pyrolysis reactions. As shown in Table 2, four reactions were included in the pyrolysis mechanism: the depolymerization reaction of cellulose (R1), the fragmentation reaction of activated cellulose (R2), the depolymerization reaction of activated cellulose (R3), and the dehydration reaction of cellulose (R4-1 or R4-2).

All reactions were modeled using an Arrhenius expression:

$$k = A \exp[-E/RT]$$

(20)

The kinetic parameters for cellulose pyrolysis, as the functions of potassium concentration, are summarized in Tables 3 and 4.

As the fragmentation and depolymerization reactions of activated cellulose (CELLA) were inhibited and the depolymerization reaction of cellulose was catalyzed by potassium, the activation energies of reactions R2 and R3 increased with increasing potassium concentration. However, the activation energy of reaction R4-2 decreased. In this work, the temperature and concentration

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction mechanism of cellulose with and without potassium [32,33].</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>CELL → CELLA</td>
</tr>
<tr>
<td>R2</td>
<td>CELLA → 0.8HAA + 0.2GLYX + 0.1 CH-HCOC + 0.25HMFU + 0.3C1H2O + 0.21CO2 + 0.1H2 + 0.4CH4O + 0.16CD + 0.02CD2H4 + 0.02H2COOH + 0.01H2O</td>
</tr>
<tr>
<td>R3</td>
<td>CELLA → LVG</td>
</tr>
<tr>
<td>R4-1</td>
<td>CELL → 6char + 5H2O</td>
</tr>
<tr>
<td>R4-2</td>
<td>CELL → 3char + H2O + 2CO + CO2 + 4H2</td>
</tr>
</tbody>
</table>

* a The dehydration reaction of pure cellulose.
* b The dehydration reaction of cellulose with potassium.
gradients, and diffusion inside the particle were neglected as the biomass particles are very small.

3.3. Solution methodology

The fluidized bed is initially closed-packed up to 69.37 mm with the sand volume fraction of 0.618. The diameter of sand is 0.55 mm, and its initial temperature is same as the inlet fluidization gas temperature. All initial phase velocities are set to be zero. The velocity inlet and mass flow inlet boundary conditions are used as the gas and biomass inlets, respectively. One atmospheric pressure boundary condition is used at the outlet of the fluidized bed. No-slip boundary and adiabatic walls are applied for all the walls. The k–ε turbulence model is used to model the effect of turbulence. The physical properties of particle phases are given in Table 5.

The simulations were conducted for a real reaction time of around 40–50 s, according to the solution convergence histories. The time-averaged yields of cellulose fast pyrolysis products were obtained from the last 10 s of the simulation. A time step size of $10^{-4}$ s and 50 iterations per time step were used.

4. Results and discussion

In this study, CFD simulations were conducted under five different potassium concentration and three different reactor temperature conditions to investigate the effects of potassium concentration and reactor temperature on the yield and the composition of cellulose fast pyrolysis products.

4.1. Hydrodynamics and fast pyrolysis in the fluidized bed reactor

Levoglucosan (LVG) is one of the main products of cellulose pyrolysis. The temporal-spatial evolutions of the gas phase flow velocity along with a LVG mass fraction of the pure cellulose pyrol-

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Kinetic parameters of pure cellulose pyrolysis [33].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>Activation energy (kJ/mol)</td>
</tr>
<tr>
<td>R1</td>
<td>188.4</td>
</tr>
<tr>
<td>R2</td>
<td>121.4</td>
</tr>
<tr>
<td>R3</td>
<td>41.9</td>
</tr>
<tr>
<td>R4-1</td>
<td>129.8</td>
</tr>
</tbody>
</table>

Table 4 Kinetic parameters of cellulose pyrolysis with potassium [32,33].

| Reaction | Activation energy (kJ/mol) | Pre-exponent (1/s) |
|---|---|
| R1 | 188.4 | $4.0 \times 10^{13}$ |
| R2 | $100.16x^{0.0168}$ | $3.78 \times 10^{9}$ |
| R3 | $118.99x^{0.056}$ | $2.61 \times 10^{7}$ |
| R4-2 | $124.52x^{0.03}$ | $2.00 \times 10^{5}$ |

$x$ is mass fraction of potassium in cellulose.

Table 5 Physical properties of solid phases.

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>Density (kg/m$^3$)</th>
<th>Thermal conductivity W/(m K)</th>
<th>Specific heat capacity (kJ/kg K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.55</td>
<td>2650</td>
<td>0.35</td>
</tr>
<tr>
<td>Biomass</td>
<td>0.6</td>
<td>780</td>
<td>0.418</td>
</tr>
</tbody>
</table>

Fig. 2. Temporal-spatial evolutions of the LVG mass fraction and gas flow velocity ($K = 0.0$ wt.%, $T_0 = 480$ °C, solid lines: the gas velocity that higher than 0.744 m/s, dashed lines: the gas velocity that lower than 0.744 m/s).
ysis at $T_0 = 480$ °C are shown in Fig. 2. The contours and lines in the figure represent LVG mass fraction and gas phase flow velocity, respectively. The velocity that higher than 0.744 m/s is indicated using solid lines, and the dashed lines indicate the velocity that lower than 0.744 m/s. It can be seen that a high concentration region of the LVG occurs in the bed region at $t = 30.5$ s. This region is located within the low-velocity region of the fluidized bed, as LVG is released due to the devolatilization reaction and is not diluted rapidly in this region. However, LVG mass fraction near the outlet of the fluidized bed is low, resulting in a low yield of LVG. At the $t = 30.6$ s and 30.65 s, the high concentration LVG is observed at entrained and flowed downstream. At $t = 30.7$ s, as the high concentration LVG transports to the outlet of the fluidized bed, the LVG yield increases significantly (see Fig. 3(b)). At $t = 30.8$ s, the high concentration LVG near the outlet of the fluidized bed has been flowed out, while the new LVG formed in the fluidized bed has not been transported to the outlet, resulting in a dropped yield of the LVG (see Fig. 3(b)).

The yields of LVG and Hydroxyacetaldehyde (HAA) at the reactor outlet are shown in Fig. 3. LVG and HAA yields increase significantly in the initial stage ($t < 5$ s) of the biomass fast pyrolysis, then following by a drastic fluctuation in the yields. The significant fluctuation in the LVG yield is caused by the unstable flow in the fluidization zone that can affect the flow in the freeboard significantly, as the height of the fluidized bed is small in this work [22].

The ratio of LVG and HAA yields tends to be constant, as shown in Fig. 3(d), indicates that the fast pyrolysis process of cellulose in the fluidized bed reaches a steady state. The weak fluctuation of the yield ratio of LVG and HAA is likely to be dependent on non-uniform pyrolysis reaction temperature in the fluidized bed reactor.

4.2. Effect of potassium concentration on the product distribution of the cellulose fast pyrolysis

First, the simulation was performed to validate the present models. As shown in Table 6, the simulation results are in good agreement with the reported experimental data at 0.1% potassium concentration and temperature of $T_0 = 500$ °C [33]. Further, the effect of potassium concentration on the cellulose fast pyrolysis was studied at reactor temperature $T_0 = 480$ °C. As shown in the same Table, the enhancement of potassium concentration causes a significant reduction of the bio-oil and increase of the gas and char yields. The bio-oil yield decreases from 94.3% in pure cellulose case to 70.4% and 35.1% with 0.05% and 1.0% potassium concentration, respectively. The char yield increases from 2.5% in pure cellulose case to 16.6% and the gas yield increases from 3.3% in pure cellulose case to 48.3% at 1.0% potassium concentration. The effects of potassium concentration on the yields of the bio-oil, char and gas are consistent with the previous results in the literature [9–11,34].
The main components of bio-oil found during cellulose pyrolysis are LVG, HAA, Hydroxymethylfurfural (HMFU), Acetone (C₃H₆O), H₂O, Formaldehyde (CH₂O), Glyoxal, Acetaldehyde (CH₃-HCO) and Formic acid (HCOOH). The composition of various components with respect to potassium concentration is shown in Fig. 4. As shown in Fig. 4(a), LVG mass fraction decreases from 63.8% of the bio-oil in pure cellulose case to 22.1% and 2.5% with 0.05% and 1.0% potassium concentration, respectively. The dramatic decrease of LVG mass fraction due to the inhibition of the depolymerization reaction of CELLA (R3) leads to decrease in LVG formation. The water mass fraction increases from 4.7% of the bio-oil in pure cellulose case to 29.7% at 1.0% potassium concentration. This behavior may be because water is formed through two reactions (R2 and R4) and the catalysis of the depolymerization reaction (R4-2) of cellulose results in the increased yields of water, as shown in Fig. 4(b).

As the potassium concentration increases from 0% to 0.1%, the mass fraction of HAA increases significantly, following by slight variations in the mass fraction of HAA when the potassium concentration further increases. The initial increase of the HAA mass fraction in bio-oil with potassium concentration caused by the inhibition of LVG formation (R3) occurs when competing with the HAA formation reaction (R2). The competition between R1 and R4-2 reactions results in the slight variation of the HAA mass fraction in bio-oil when potassium concentration increases from 0.1% to 1.0%. Moreover, the effects of potassium on the yields of other components in the bio-oil are similar to that of HAA.

The main components of produced non-condensable gas in the pyrolysis of cellulose are CO, CO₂ and H₂. As shown in Fig. 5(a), all of the yields of CO, CO₂ and H₂ increase significantly with increasing potassium concentration. It can be seen in Fig. 5(b) that the CO₂ mass fraction decreases from 66.4% to 42.1%, the CO mass fraction increases from 32.2% to 50.8%, and the H₂ mass fraction increases from 1.5% to 7.1%, respectively, as the potassium concentration increases from 0.0% to 1.0%. These compositions are formed via the R2 and R4 reactions. The CO₂ mass fraction of the gas produced

<table>
<thead>
<tr>
<th>Potassium (wt.%)</th>
<th>Bio-oil (wt.%)</th>
<th>Char (wt.%)</th>
<th>Gas (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>66.4</td>
<td>9.2</td>
<td>24.4</td>
</tr>
<tr>
<td>0.05</td>
<td>68.6</td>
<td>8.3</td>
<td>22.9</td>
</tr>
<tr>
<td>0.1</td>
<td>94.3</td>
<td>2.5</td>
<td>3.3</td>
</tr>
<tr>
<td>0.5</td>
<td>70.4</td>
<td>8.1</td>
<td>21.4</td>
</tr>
<tr>
<td>1.0</td>
<td>61.8</td>
<td>10.2</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>41.5</td>
<td>15.1</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
<td>35.1</td>
<td>16.6</td>
<td>48.3</td>
</tr>
</tbody>
</table>

**Fig. 4.** Effects of the potassium concentration on bio-oil compositions (T₀ = 480 °C).

**Fig. 5.** Effects of the potassium concentration on gas compositions (T₀ = 480 °C, Potassium concentration: 1 – 0.0 wt.% 2 – 0.05 wt.% 3 – 0.1 wt.% 4 – 0.5 wt.% 5 – 1.0 wt.%).
in the R4 reaction is less than that produced in the R2 reaction. The decrease of CO₂ mass fraction and the increase of both CO and H₂ mass fraction with the increased potassium concentration are attributed to the inhibition of the R2 reaction and catalysis of the R4 reaction by the addition of potassium, which results in increases the gas yields significantly, as shown in Fig. 6.

4.3. Effect of reactor temperature on the cellulose fast pyrolysis

The temperature of the fluidized bed reactor is an important parameter that affects the thermochemical reactions. In the present study, the temperature of the fluidized bed reactor was varied by changing the temperature of the preheated fluidization gas. It can be seen in Table 7, as the reactor temperature increases from 430 °C to 515 °C, the yield of gas increases from 2.2% to 4.4% and the yield of char increases from 2.3% to 2.8% whereas the bio-oil yield decreases from 95.5% to 92.8% for the pure cellulose case. These behaviors may be because more tar is cracked to gas and char products at a higher temperature. This trend of product yields agrees with the literature for the pure cellulose [22,35]. However, the trend of the product yields for the cellulose with potassium is reversed when compared with the results of the pure cellulose case. As shown in Table 2, there is a significant difference between the dehydration reaction equations of the pure cellulose and cellulose with potassium (R4-1 and R4-2), i.e., the produced CO₂, CO and H₂ were incorporated in the equation R4-2. The increased reactor temperature promotes the endothermic R2 and R3 reactions, and the R4-2 reaction that forms gas is at a disadvantage in the competition with R2 and R3 reactions, so the gas yield decreases with increasing of the reactor temperature for the pyrolysis of cellulose with potassium.

In Table 8, as the reactor temperature increases from 430 °C to 515 °C, the mass fraction of LVG decreases and the mass fractions of other compositions in the bio-oil increase for the pyrolysis of the pure cellulose. The decrease of the LVG mass fraction is due to the competition of R2 and R3 reactions. For the fast pyrolysis of cellulose with 0.1% potassium, as the reactor temperature increases from 430 °C to 515 °C, the H₂O mass fraction decreases significantly, the mass fractions of LVG and all other bio-oil compositions increase. This is because the R2 and R3 reactions inhibited by potassium have a larger potential to be improved when the reactor temperature increases.

In Table 9, as the reactor temperature increases, the gas compositions of the pure cellulose pyrolysis are constant. This is because all gas compositions are from the same fragmentation reaction of activated cellulose (R2). For the fast pyrolysis of cellulose with

![Fig. 6. Effects of the potassium concentration on sources of gas products (T₀ = 480 °C).](image-url)

<table>
<thead>
<tr>
<th>Potassium (wt.%)</th>
<th>0.0</th>
<th>0.0</th>
<th>0.0</th>
<th>0.1</th>
<th>0.1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₀ (°C)</td>
<td>430</td>
<td>480</td>
<td>515</td>
<td>430</td>
<td>480</td>
<td>515</td>
</tr>
<tr>
<td>Oil (wt.%)</td>
<td>95.5</td>
<td>94.3</td>
<td>92.8</td>
<td>52.1</td>
<td>61.8</td>
<td>69.0</td>
</tr>
<tr>
<td>Char (wt.%)</td>
<td>2.3</td>
<td>2.5</td>
<td>2.8</td>
<td>12.6</td>
<td>10.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Gas (wt.%)</td>
<td>2.2</td>
<td>3.3</td>
<td>4.4</td>
<td>35.4</td>
<td>28.0</td>
<td>22.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T₀ (°C)</th>
<th>430</th>
<th>480</th>
<th>515</th>
<th>430</th>
<th>480</th>
<th>515</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium (wt.%)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>LVG</td>
<td>0.750</td>
<td>0.638</td>
<td>0.518</td>
<td>0.132</td>
<td>0.148</td>
<td>0.160</td>
</tr>
<tr>
<td>HAA</td>
<td>0.080</td>
<td>0.120</td>
<td>0.162</td>
<td>0.262</td>
<td>0.269</td>
<td>0.272</td>
</tr>
<tr>
<td>HMFU</td>
<td>0.053</td>
<td>0.079</td>
<td>0.106</td>
<td>0.172</td>
<td>0.177</td>
<td>0.179</td>
</tr>
<tr>
<td>CH₂H₂O</td>
<td>0.029</td>
<td>0.044</td>
<td>0.059</td>
<td>0.095</td>
<td>0.098</td>
<td>0.099</td>
</tr>
<tr>
<td>CH₂O</td>
<td>0.020</td>
<td>0.030</td>
<td>0.040</td>
<td>0.065</td>
<td>0.067</td>
<td>0.068</td>
</tr>
<tr>
<td>GLYOXAL</td>
<td>0.019</td>
<td>0.029</td>
<td>0.039</td>
<td>0.063</td>
<td>0.065</td>
<td>0.066</td>
</tr>
<tr>
<td>CH₃O</td>
<td>0.007</td>
<td>0.011</td>
<td>0.015</td>
<td>0.024</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>HCOOH</td>
<td>0.002</td>
<td>0.002</td>
<td>0.003</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.040</td>
<td>0.047</td>
<td>0.057</td>
<td>0.182</td>
<td>0.146</td>
<td>0.126</td>
</tr>
</tbody>
</table>
0.1% potassium, the CO₂ mass fraction increases from 43.6% to 46.9%, whereas the CO mass fractions decreases from 49.6% to 47.1%, and the H₂ mass fractions decreases from 6.8% to 6.0%, as the reactor temperature increases from 430 °C to 515 °C. The decrease of CO and H₂ mass fractions and the increase of CO₂ mass fraction are due to the fact that the elevated reactor temperature enhances the R2 and R3 reactions which form more CO₂ than R4 reaction.

5. Conclusions

In this study, the effect of potassium on the biomass fast pyrolysis in the fluidized bed reactor has been investigated using an Euler–Euler CFD model. The effects of potassium concentration and reactor temperature on the yield and component of pyrolysis products were analyzed. The simulation results indicate that the unstable flow in the fluidized bed results in the significant fluctuation in the product yield, and the weak fluctuation of the yield ratio between LVG and HAA is found. It is also observed that as the potassium concentration increases from 0% to 0.1%, the bio-oil yield decreases from 94.3% to 35.1% and the gas yield increases from 3.3% to 48.3%. Further, the addition of potassium leads to the significant change in the compositions of bio-oil and gas due to the inhibitions of decomposition reactions of activated cellulose and the catalysis of the depolymerization reactions of cellulose. For the effect of reactor temperature, the bio-oil yield decreases for the pure cellulose pyrolysis, while it has a reverse trend for the cellulose with potassium when the reactor temperature increases from 430 °C to 515 °C.

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References