1-D Coupled Chemical Reaction and Heat Transfer Models for Biomass Fast Pyrolysis

Presenter: Jianqiu Huang (Tim)
Mentor: Shankar Subramaniam
Department of Mechanical Engineering
Motivation

• To understand the gas-solid heat transfer and chemical reaction in fast pyrolysis of biomass particles
• To develop a realistic or predictive model for gas-solid flow in biomass fast pyrolysis based on literature of Xue et al. (2011)
• To improve the existing models to predict biofuel yield accurately
Introduction

- Sustainable energy generation from renewable sources that minimizes environmental impact such as the potential of biofuels
- Biomass fast pyrolysis is one of the most promising technologies to produce bio-fuel
- Experiments of biomass fast pyrolysis is time-consuming and expensive
- Multiphase computational fluid dynamics (CFD) with chemical reactions is increasingly being used
- Improvement of the CFD models to predict the biofuel yield precisely

A flow diagram of the fluidized-bed pyrolysis reactor system (from Xue et al.)
Biomass Fast Pyrolysis

- Biomass = αCellulose + βHemicellulose + γLignin
- Reaction constant $k_{n,m}$
  \[ k = A \cdot e^{-\frac{E}{RT}} \]
Deterministic Model

\[
\frac{d m_1}{dt} = -k_{1c}m_1, \quad (3)
\]
\[
\frac{d m_2}{dt} = -k_{1h}m_2, \quad (4)
\]
\[
\frac{d m_3}{dt} = -k_{1l}m_3, \quad (5)
\]
\[
\frac{d m_4}{dt} = k_{1c}m_1 - (k_{2c} + k_{3c})m_4, \quad (6)
\]
\[
\frac{d m_5}{dt} = k_{1h}m_2 - (k_{2h} + k_{3h})m_5, \quad (7)
\]
\[
\frac{d m_6}{dt} = k_{1l}m_3 - (k_{2l} + k_{3l})m_6, \quad (8)
\]
\[
\frac{d m_7}{dt} = k_{2c}m_4 + k_{2h}m_5 + k_{2l}m_6 - k_4m_7, \quad (9)
\]
\[
\frac{d m_8}{dt} = (1 - Y_c)k_{3c}m_4 + (1 - Y_h)k_{3h}m_5 + (1 - Y_l)k_{3l}m_6 + k_4m_7
\]
\[
- \left[ \frac{dm_1}{dt} + \frac{dm_2}{dt} + \frac{dm_3}{dt} + \frac{dm_4}{dt} + \frac{dm_5}{dt} + \frac{dm_6}{dt} \right] \rho_b \left( \begin{array}{c}
\frac{dm_9}{dt} - \frac{dm_1}{dt} \\
\frac{dm_9}{dt} - \frac{dm_2}{dt} \\
\frac{dm_9}{dt} - \frac{dm_3}{dt} \\
\frac{dm_9}{dt} - \frac{dm_4}{dt} \\
\frac{dm_9}{dt} - \frac{dm_5}{dt} \\
\frac{dm_9}{dt} - \frac{dm_6}{dt}
\end{array} \right) \rho_b \rho_g, \quad (10)
\]
\[
\frac{d m_9}{dt} = Y_c k_{3c}m_4 + Y_h k_{3h}m_5 + Y_l k_{3l}m_6
\]
\[
+ \left[ \frac{dm_1}{dt} + \frac{dm_2}{dt} + \frac{dm_3}{dt} + \frac{dm_4}{dt} + \frac{dm_5}{dt} + \frac{dm_6}{dt} \right] \rho_b \left( \begin{array}{c}
\frac{dm_9}{dt} - \frac{dm_1}{dt} \\
\frac{dm_9}{dt} - \frac{dm_2}{dt} \\
\frac{dm_9}{dt} - \frac{dm_3}{dt} \\
\frac{dm_9}{dt} - \frac{dm_4}{dt} \\
\frac{dm_9}{dt} - \frac{dm_5}{dt} \\
\frac{dm_9}{dt} - \frac{dm_6}{dt}
\end{array} \right) \rho_b \rho_g, \quad (11)
\]
Deterministic Model

Reaction constants highly depend on temperature

Reaction rate of raw materials VS. Temperature (k1)

Reaction constant vs Temperature for 1st phase
Reaction rate of cellulose is very fast.

Mass decay vs. time for pure cellulose for T=790K

Material components (s) → Active material (s) → Tar vapor (g) → Gas (g)

$k_1$ $k_2$ $k_3$ $k_4$

Char (s) + (1-γ) Gas (g)

Reaction rate of cellulose is very fast.
Chemical Reaction and Heat Transfer Model

Two-way coupling system

Gas mass balance:
\[ \frac{d \rho_g}{dt} = -\frac{1}{\varepsilon_g} \sum_{n=1}^{N} R_{s2,n} \]

Gas species mass balance:
\[ \frac{d X_{g,n}}{dt} = \frac{1}{\rho_g \varepsilon_g} \left( R_{gn} + X_{gn} \sum_{l=1}^{N} R_{s2,l} \right) \]

Solid mass balance:
\[ \frac{d \rho_{s2}}{dt} = \frac{1}{\varepsilon_{s2}} \sum_{n=1}^{N} R_{s2,n} \]

Solid species mass balance:
\[ \frac{d X_{s2,n}}{dt} = \frac{1}{\rho_{s2} \varepsilon_{s2}} \left( R_{s2,n} - X_{s2,n} \sum_{l=1}^{N} R_{s2,l} \right) \]

Heat transfer model:
\[ \varepsilon_g \rho_g C_{pg} \frac{dT_g}{dt} = \gamma_{gm} \left( T_{s2} - T_g \right) - \Delta H_{rg} \]
\[ \varepsilon_{s2} \rho_{s2} C_{ps2} \frac{dT_{s2}}{dt} = -\gamma_{gm} \left( T_{s2} - T_g \right) - \Delta H_{rs2} \]

R is the reaction rate. S2 stands for solid mass, and g stands for gas mass.

All simulations are using the same gas phase velocity since we assume that this is a homogeneous case.

\[ \gamma_{gm} = \int (Nu_m) \]
\[ Nu_m = \int (Re_m) \]
\[ Re_m = \frac{d_{pm} |u_g - u_m| \rho_g}{\mu_g} \]
Results

Temperature Changes of Solid and gas species applied heat transfer model
### Results

Changes of Reaction Rate for all phases

- $R_{s1} = -\rho_{s1} e_{s1} X_{s1,1} k_{1c}$
- $R_{s2} = -\rho_{s2} e_{s2} X_{s2,2} k_{1h}$
- $R_{s3} = -\rho_{s3} e_{s3} X_{s3,3} k_{1l}$
- $R_{s4} = \rho_{s4} e_{s4} X_{s4,1} k_{1c} - \rho_{s4} e_{s4} X_{s4,4} (k_{2c} + k_{3c})$
- $R_{s5} = \rho_{s5} e_{s5} X_{s5,2} k_{1h} - \rho_{s5} e_{s5} X_{s5,5} (k_{2h} + k_{3h})$
- $R_{s6} = \rho_{s6} e_{s6} X_{s6,3} k_{1l} - \rho_{s6} e_{s6} X_{s6,6} (k_{2l} + k_{3l})$
Results

Mass fraction plot for pure cellulose in $1\Delta t$

Changes of mass fraction for all phases

- Cellulose(s) $X_{s21}$
- Active Cellulose(s) $X_{s24}$
- Tar(g) $X_{g7}$
- Total gas: $X_{g8}+X_{g9}$
- Char(s) $X_{s29}$

Non-dimensional time ($t^*k_1c$)

Mass fraction (%)

0 0.2 0.4 0.6 0.8

0 0.2 0.4 0.6 0.8 1 1.2

0 500 1000 1500 2000 2500 3000
Results

Mass fraction plot the reaction is reaching stable
Summary and Future work

- Implementation of first-order chemical kinetics model
  1. Reaction constant changed by 6 orders of magnitude with gas temperature from 400K to 800K
  2. Limitation of this first order chemical model due to the one-way coupling system

- Development of the coupled chemical reaction and heat transfer model
  1. Two-way coupling system with variation of density, temperature, and reaction rate
  2. This model can build a more realistic and predictive model for biofuel yields during fast pyrolysis of biomass

- Future work: Incorporation of probability distribution function (PDF) of temperature with the model to obtain uncertainty for final biofuel yields
Questions?
Changes of mass fraction for all phases

- Cellulose(s) Xs21
- Semicellulose(s) Xs22
- Lignin(s) Xs23
- Active Cellulose(s) Xs24
- Active Semicellulose(s) Xs25
- Active Lignin(s) Xs26
- Tar(g) Xg7
- Total gas: Xg8+Xg9
- Char(s) Xs29

Mass fraction plot for Bagasse in $1\Delta t$
Mass decay vs. time

Non-dimensional Time (t*k1c)

Mass change

Mass decay plot for Bagasse in $1\Delta t$
Applied Heat Transfer Model

Gas energy:
\[ \varepsilon_g \rho_g c_{pg} \left( \frac{\partial T_g}{\partial t} + \vec{v}_g \cdot \nabla T_g \right) = -\nabla \cdot \vec{q}_g + \sum_{m=1}^{M} \gamma_{gm}(T_{sm} - T_g) \]
Solid energy:
\[ \varepsilon_{sm} \rho_{sm} c_{psm} \left( \frac{\partial T_{sm}}{\partial t} + \vec{v}_{sm} \cdot \nabla T_{sm} \right) = -\nabla \cdot \vec{q}_{sm} - \sum_{m=1}^{M} \gamma_{gm}(T_{sm} - T_g) \]

Gas energy balance:  Solid energy balance:
\[ \frac{dT_g}{dt} = -\frac{\Delta H_{rg}}{\rho_g \varepsilon_g c_{pg}} \]
\[ \frac{dT_{s2}}{dt} = -\frac{\Delta H_{rs2}}{\rho_{s2} \varepsilon_{s2} c_{ps2}} \]
\[ \varepsilon_g \rho_g c_{pg} \frac{dT_g}{dt} = \gamma_{gm}(T_{s2} - T_g) - \Delta H_{rg} \]
\[ \varepsilon_{s2} \rho_{s2} c_{ps2} \frac{dT_{s2}}{dt} = -\gamma_{gm}(T_{s2} - T_g) - \Delta H_{rs2} \]
Testament and Evaluation

- **Mass conservation**

\[
\text{sum}_{\text{specific mass}} = \varepsilon_{\text{gas}} \cdot \rho_{s2} + \varepsilon_{\text{gas}} \cdot \rho_{\text{gas}}
\]

*Summation of specific mass (g+s)*

- **Energy conservation**

\[
\text{sum}_{\text{specific enthalpy}} = \rho_{s2} \cdot C_{p,s2} \cdot T_{s2} \cdot \varepsilon_{s2} + \rho_{\text{gas}} \cdot C_{p,\text{gas}} \cdot T_{\text{gas}} \cdot \varepsilon_{\text{gas}}
\]

*Summation of specific energy*
Summation of specific mass

Summation of specific enthalpy
Introduction

- Major alternative resource of energy supply
- Using bio-wasted to generate bioenergy (recycle)
- Less pollution to the environment
- Economics
- Less dangerous and easier to control
- Raw material for the reaction is common and easy to obtain

Fig. 1. A flow diagram of the fluidized-bed pyrolysis reactor system.