CFD Simulation of Catalytic Upgrading of Pyrolytic Vapours in FCC Riser

Prof Sai Gu,
Centre for Biofuel and Resource Management, Cranfield University
Development of fast pyrolysis based advanced bioenergy technologies for biofuel
Sai Gu, Tony Bridgwater, Karen Wilson

WP1: Zeolite based catalytic fast pyrolysis
Process development of integrated catalytic fast pyrolysis through laboratory scale investigation.

WP2: Two stage catalytic processes with vapour cracking and HDO
Catalyst screening for pre-treatment of pyrolysis vapor;
Design of catalyst (Red mud)
Aqueous phase HDO upgrading of pre-treated bio-oil.

WP3: Computational modelling and reactor development
Development of computational models for an integrated fast pyrolysis for bio-oil production--fast pyrolysis, pyrolytic vapour cracking and hydrodeoxygenation reactors.
Overview: Fast Pyrolysis

- **Conditions:** ~500°C, residence time <2s
- **Products:** (a) Non-condensable gases, (b) liquid, including water, (c) solids, char & ash
- **Status:** Commercial/pre-commercial
- **Quality:** Produced oil not suitable for transportation fuels: high oxygen, acidity and reactivity, needs hydroprocessing for upgrading to acceptable quality

Most common upgrading method: liquid bio-oil from **pyrolysis** followed by **hydrotreating**.

- It can convert only fraction of the carbon in the bio-oil to gasoline and rest as light gases.
- An alternative approach: C-C coupling of small oxygenates (**Catalytic deoxygenation**).
Catalytic upgrading of Pyrolysis Vapour

RISER REACTOR SIMULATION

Structure of H-ZSM-5
Catalytic upgrading of Pyrolysis Vapour(ii): Motivation

- Vapour phase cracking could be first step for bio-oil stabilisation before condensation removal of small oxygenates in the form of H₂O, CO and CO₂ retain carbon and deoxygenate with minimum hydrogen consumption

- Mostly used catalysts are Zeolite and Metal oxide

- Issues related upgrading of pyrolysis vapours over catalyst
  - **lower yield of bio-oil and higher yield of gas and water** - Because a heavy fraction of the oxygen in vapour is removed as CO₂, CO and H₂O
    **Solution**: The pathways involved in the removal of oxygen from the vapour are to be optimised.

- Typical vapor residence time in reactor: **2–3 sec** and longer contact time: excessive coking, deactivation of the catalyst.

- The formation of coke and catalyst deactivation in catalytic pyrolysis – type of catalyst, reactor configuration and process condition.

- Fluidized bed operations are preferred because it produces relatively lesser coke and reduces catalyst deactivation compared with fixed beds.
Goal and Objectives

Goal
• To develop computational models that help to understand and improve the catalytic upgrading of pyrolysis vapours in FCC riser.

Objectives
• To simulate hydrodynamics of pyrolysis vapours and catalyst particles flows in a circulating riser reactor (Davison circulating riser).
• To predict vapour residence and catalyst residence times in a riser for improving contact time of pyrolysis vapour with catalyst.
• To simulate pyrolysis vapour cracking using coupled CFD and lumped (pseudo components model) kinetic approach.
Simplified diagram of a generic FCC unit. Catalyst circulates from the regenerator to the bottom of the riser, where it mixes with feed, flows up the riser into the reactor, and is separated from the products by cyclone separators. Stripping steam removes entrained hydrocarbon vapors, and the catalyst flows back to the regenerator where air is injected to burn off the coke. The cycle then repeats.
The Davison Circulating Riser is the industry standard for FCC pilot development (Grace).
Vapor Phase Upgrading for FCC-type processing: Davison Circulating Reactor (DCR)

- Vapors fed to continuously circulating catalyst for hydrocarbon production with no added hydrogen or preliminary deoxygenation
- Advantage: Continuous coke removal to keep catalyst active
To understand Reaction Pathways: Model compounds

Light oxygenates:
- Acetic acid,
- Acetone,
- Acetaldehyde,

Sugar derived compounds:
- Furfurals

Lignin derived compounds:
- Phenolics

Hydrocarbon fuels
Strategies for Catalytic Upgrading of Bio-oil compounds

Model compound studies have been reported in literature to define favorable chemistry and catalysts in small scale micro-pyrolysis unit.
## Modelling Methods for FCC

<table>
<thead>
<tr>
<th>Modelling approach</th>
<th>Main feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D hydrodynamics + lumped kinetics</td>
<td>Model is simple, easy to solve, but with relatively low accuracy</td>
</tr>
<tr>
<td>1D hydrodynamics + molecular level kinetics</td>
<td>Kinetics is complicated, needs a great deal of instrumental analysis data</td>
</tr>
<tr>
<td>2D empirical hydrodynamics + lumped kinetics</td>
<td>Computational time and precision are acceptable, but quite empirical</td>
</tr>
<tr>
<td><strong>CFD + lumped kinetics</strong></td>
<td><strong>Comprehensive and informative, with high accuracy but long computational period</strong></td>
</tr>
<tr>
<td>CFD + molecular level kinetics</td>
<td>Main feature: Most complicated model to solve, but benefits deep understanding of FCC process</td>
</tr>
</tbody>
</table>
Model Validation

- PSRI experimental research facility in Chicago (Knowlton et al., 1995)
  - Diameter of riser, D: 0.2m
  - Height of riser, h: 14.2m
  - Particle diameter: 76μm
  - Particle density: 1712kg/m^3
  - Air viscosity: 1.8e-05 kg/m^3
  - Air density: 1.2kg/m^3
  - Air inlet velocity: 5.2 m/s
  - Solid mass flux: 489 kg/m^2s
  - Solid inlet velocity: 0.714 m/s
  - Solid inlet volume fraction: 0.4
Fluid–Solid Interphase Drag Model

EMMS and Filtered drag closures for sub-grid structure

- Based on the minimum energy required for suspending and transporting dense particle regions
- Accounts for the effect of heterogeneous structures on drag based on drag index;
- Integrated into the Eulerian multiphase model in order to reach a mesh-independent solution of the subgrid structure,

Filtered drag law derived from small scale (Igci et al., 2008)

\[
K_{sg} = K_{sg,p} (1 + c)
\]

\[
K_{sg,p} = \frac{3}{4} C_D \frac{\alpha_g \alpha_s \rho_s \left| \frac{v_s - v_g}{d_s} \right| \alpha_s^{-2.65}}{\alpha_g}
\]

\[
c = \frac{Fr_f^{-1.6}}{Fr_f^{-1.6} + 0.4} h(\alpha_s)
\]

\[
Fr_f^{-1} = g \Delta f / V_t^2
\]

\[
\Delta_f = 2V_{cell}^{1/3}
\]

\[
K = \frac{150 \varepsilon_s (1 - \varepsilon_p) \rho_s^2 \varepsilon_p}{\varepsilon_p d_p} |v_g - v_s| \quad \varepsilon_s < 0.4
\]

\[
\frac{3}{4} C_D \frac{\rho_g \alpha_s \varepsilon_s |v_g - v_s|}{d_p} \varepsilon_g^{-2.65} H_d \quad \varepsilon_s \geq 0.4
\]

**Scaling function, \( h(\alpha_s) \)**

\[
2.7 \alpha_s^{0.234} \alpha_s < 0.0012
\]

\[
-0.019 \alpha_s^{-0.455} + 0.963, 0.0012 \leq \alpha_s \leq 0.014
\]

\[
0.868 \exp(-0.38 \alpha_s) - 0.17 \exp(-11.2 \alpha_s), 0.25 \leq \alpha_s \leq 0.25
\]

\[
-4.59 \times 10^{-9} \exp(19.75 \alpha_s) + 0.852 \exp(-0.268 \alpha_s), 0.25 \leq 0.455
\]

\[
(\alpha_s - 0.59) (1501 \alpha_s^2 + 2203 \alpha_s^2 - 1054 \alpha_s + 162), 0.455 \leq \alpha_s \leq 0.59
\]

\[
0.059 < \alpha_s \leq 0.65
\]

\[
h(\alpha_s) = \begin{cases} 
2.7 \alpha_s^{0.234} \alpha_s < 0.0012 \\
-0.019 \alpha_s^{-0.455} + 0.963, 0.0012 \leq \alpha_s \leq 0.014 \\
0.868 \exp(-0.38 \alpha_s) - 0.17 \exp(-11.2 \alpha_s), 0.25 \leq \alpha_s \leq 0.25 \\
-4.59 \times 10^{-9} \exp(19.75 \alpha_s) + 0.852 \exp(-0.268 \alpha_s), 0.25 \leq 0.455 \\
(\alpha_s - 0.59) (1501 \alpha_s^2 + 2203 \alpha_s^2 - 1054 \alpha_s + 162), 0.455 \leq \alpha_s \leq 0.59 \\
0.059 < \alpha_s \leq 0.65
\end{cases}
\]
Hydrodynamics of FCC Riser: Model Validation

Pressure drop vs. height of riser

Solid volume fraction vs. radial position
CFD Results (i): Hydrodynamics

- Gas velocity: 0.5 m/s
- Pyrolysis vapour mass fraction = 0.47
- Nitrogen mass fraction = 0.5
- Steam mass fraction = 0.03
- Solid velocity: 0.25 m/s

- Once gas was introduced to the bottom of the riser, the bed began to expand with some particles hitting the top wall and falling down.
- At t=11s particles are started to leave from the bed.
CFD Results (ii): Hydrodynamics

- **Flow pattern in riser:** Core-Annular flow
- **Core:** Upward flow of solid at centre region of riser
- **Annular:** Downward flow at wall region of riser

**Vapour mass fraction profiles**

**Time averaged solid velocity profiles**
Residence time distribution (RTD) in Davison Circulating Riser

- Residence Time Distribution
  - Degree of solid mixing; Closely related to hydrodynamics of gas and solid
  - Reactor performance in terms of conversion and selectivity of chemical reactions

- It is characterised as $E(t)$, is related to the tracer concentration, $C_i$ in each sample, $i$ along the sampling period

- The average residence time of the phases,

**CFD model setup**
- Tracer injected at the inlet for 1 sec;
- Tracer properties are similar to phase properties;
- Flow fields from hydrdyodynamic simulation are used as Initial condition;
- Diffusion coefficient for gas phase is $1\text{e}-08\text{m}^2/\text{s}$ and for solid phase is $1\text{e}-05\text{m}^2/\text{s}$;
- Tracer concentration at outlet is monitored.
Residence time distribution (RTD)

Gas Phase RTD

Solid Phase RTD

Conditions

<table>
<thead>
<tr>
<th>Vapour phase</th>
<th>Solid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas velocity: 0.5m/s</td>
<td>4.6sec</td>
</tr>
<tr>
<td>Solid velocity: 0.25m/s</td>
<td></td>
</tr>
<tr>
<td>Gas velocity: 1.0m/s</td>
<td>3.28sec</td>
</tr>
<tr>
<td>Solid velocity: 0.25m/s</td>
<td></td>
</tr>
</tbody>
</table>
Reaction pathways, kinetics of Pyrolysis Vapour upgrading

Proposed reaction pathways for conversion of bio-oil through HZM-5 catalyst (Adjaye and Bakhshi, 1995)

Lumped Models

<table>
<thead>
<tr>
<th>Lumped Compounds</th>
<th>Model compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous fraction</td>
<td>steam</td>
</tr>
<tr>
<td>Coke</td>
<td>Carbon-solid</td>
</tr>
<tr>
<td>Gas</td>
<td>CO2</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>Benzene</td>
</tr>
<tr>
<td>Residue</td>
<td>N-Heptane</td>
</tr>
</tbody>
</table>

Kinetic parameters at 410°C (Adjaye and Bakhshi, 1995)

<table>
<thead>
<tr>
<th>Rate of a reaction (k)</th>
<th>Activation Energy, E (kJ/mol)</th>
<th>Reaction Order</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>79</td>
<td>1.4</td>
<td>0.6e-05</td>
</tr>
<tr>
<td>k₂</td>
<td>61</td>
<td>1.2</td>
<td>7.5e-05</td>
</tr>
<tr>
<td>k₃</td>
<td>38</td>
<td>0.8</td>
<td>18e-05</td>
</tr>
<tr>
<td>k₄</td>
<td>3</td>
<td>0.9</td>
<td>80e-05</td>
</tr>
<tr>
<td>k₅</td>
<td>61</td>
<td>0.7</td>
<td>37e-05</td>
</tr>
</tbody>
</table>
Mass fraction of various lumped species during catalytic cracking of vapours

Gas velocity: 0.5 m/s; Solid velocity: 0.25 m/s and temperature: 410°C
Gas: organic volatile mass fraction = 0.32; Nitrogen mass fraction = 0.5; steam mass fraction = 0.03; residue (heavy non-volatile) mass fraction = 0.15
### Kinetic results (ii)

<table>
<thead>
<tr>
<th>Lumped Compounds</th>
<th>Mass fraction from CFD Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>Pyrolysis vapour (volatile)</td>
<td>0.32</td>
</tr>
<tr>
<td>Aqueous fraction</td>
<td>0.03</td>
</tr>
<tr>
<td>Coke</td>
<td>0</td>
</tr>
<tr>
<td>Gas</td>
<td>0</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>0</td>
</tr>
<tr>
<td>Residue (heavy non-volatile)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

- The present kinetic models predict the lower value for aqueous fraction and gaseous mass fraction.
- A kinetic model needs to be improved.
Conclusions and Continue Research works (i)

- Hydrodynamics of pyrolytic vapours–catalyst flows in a pilot-scale FCC riser (DCR) using CFD simulation was studied.

- Hydrodynamics models were validated with literature data (PSRI system). The filtered sub-grid based drag law is better prediction for hydrodynamic parameters in comparison with EMMS model.

- Using converged hydrodynamics simulation results, RTD of vapour and solid phases in DCR was performed.

- Effects on RTD will be further investigated including Smaller feedstock inlet area; catalyst inlet flow rate; fluidizing N₂/steam; different Feedstock (heavy petroleum vapours)
Conclusions and Continue Research works (ii)

• Multiphase flow CFD model along with 5 lumped pseudo components based kinetic model for vapour upgrading was attempted in this study.

• The present kinetic system predicts the lower value for all pseudo component species. The research will further be investigated in kinetic model development to improve the predictions.

• In future, first principle based microkinetic model will be developed for vapour phase upgrading.

• This study can help to design a reactor for pyrolysis vapour upgrading experimental investigation.
Acknowledgement

EPSRC project (EP/K036548/1): Development of fast pyrolysis based advanced biofuel technologies.

THANK YOU