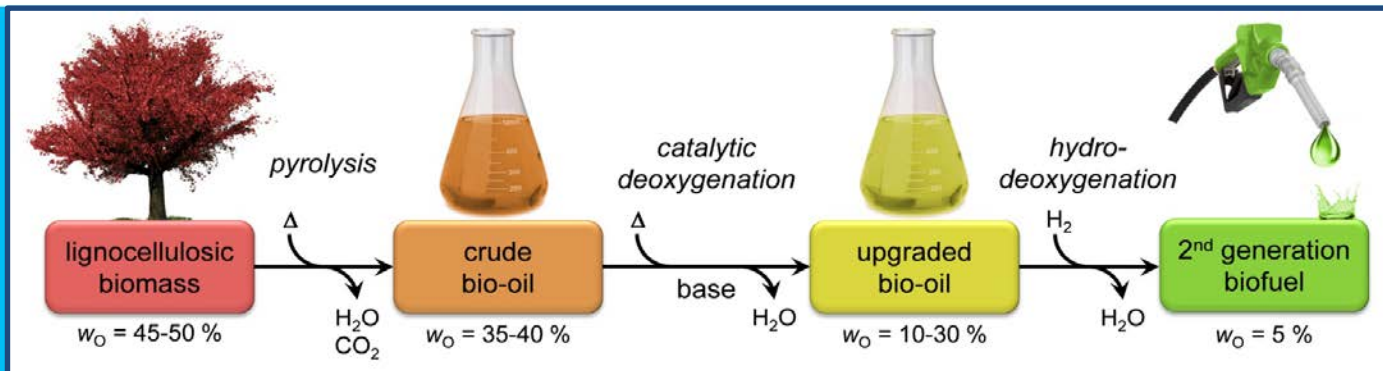# CFD Simulation of Catalytic Upgrading of Pyrolytic Vapours in FCC Riser

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SUPERGEN Bioenergy Challenge Project

Development of fast pyrolysis based advanced bioenergy technologies for biofuel

Sai Gu, Tony Bridgwater, Karen Wilson

WP1: Zeolite based catalytic fast pyrolysis

WP2: Two stage catalytic processes with vapour cracking and HDO

WP3: Computational modelling and reactor development

**Process development of integrated catalytic fast pyrolysis through laboratory scale investigation.**

Catalyst screening for pre-treatment of pyrolysis vapor;
Design of catalyst (Red mud)
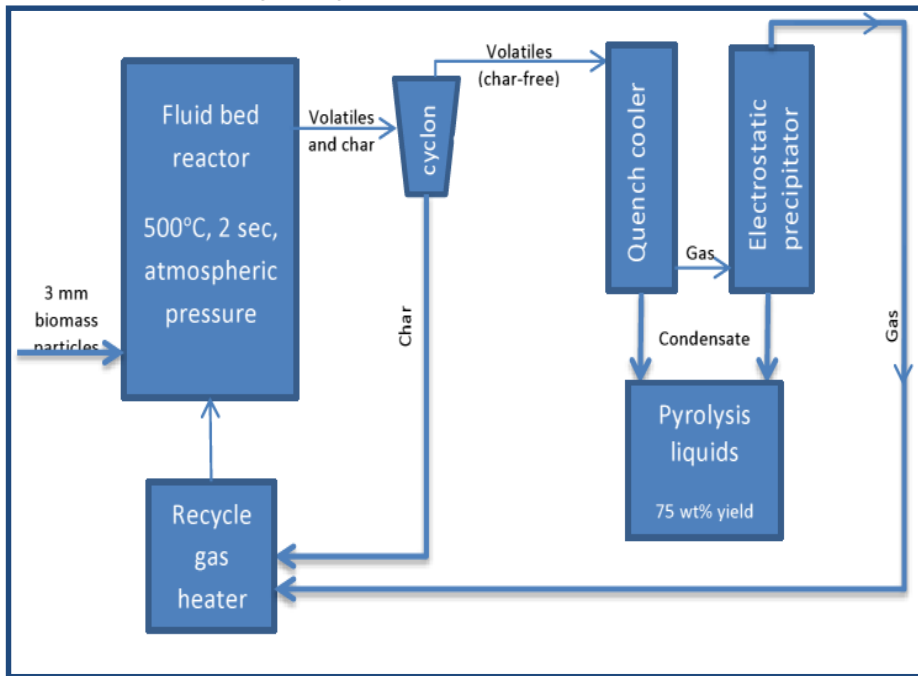**Aqueous phase HDO upgrading of pre-treated bio-oil.**

Development of computational models for an integrated fast pyrolysis for bio-oil production–fast pyrolysis, pyrolytic vapour cracking and hydrodeoxygenation reactors.

Cranfield UNIVERSITY

Aston University
Birmingham

Overview: Fast Pyrolysis

Biomass
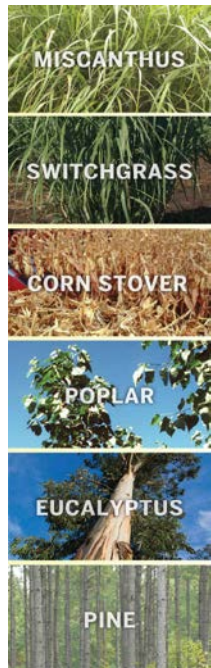
Pyrolysis

- **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
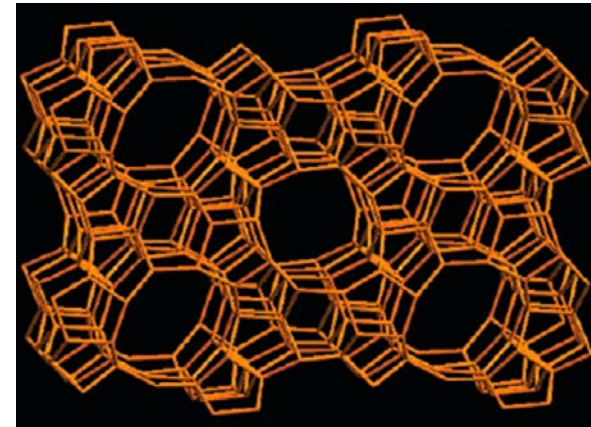
- Most common upgrading method : liquid bio-oil from pyrolysis followed by hydrotreating.
- It can convert only fraction of the carbon in the bio-oil to gasoline and rest as light gases.
- An alternative approach: C-C coupling of small oxygenates (Catalytic deoxygenation).

Catalytic upgrading of Pyrolysis Vapour(i)

RISER REACTOR SIMULATION
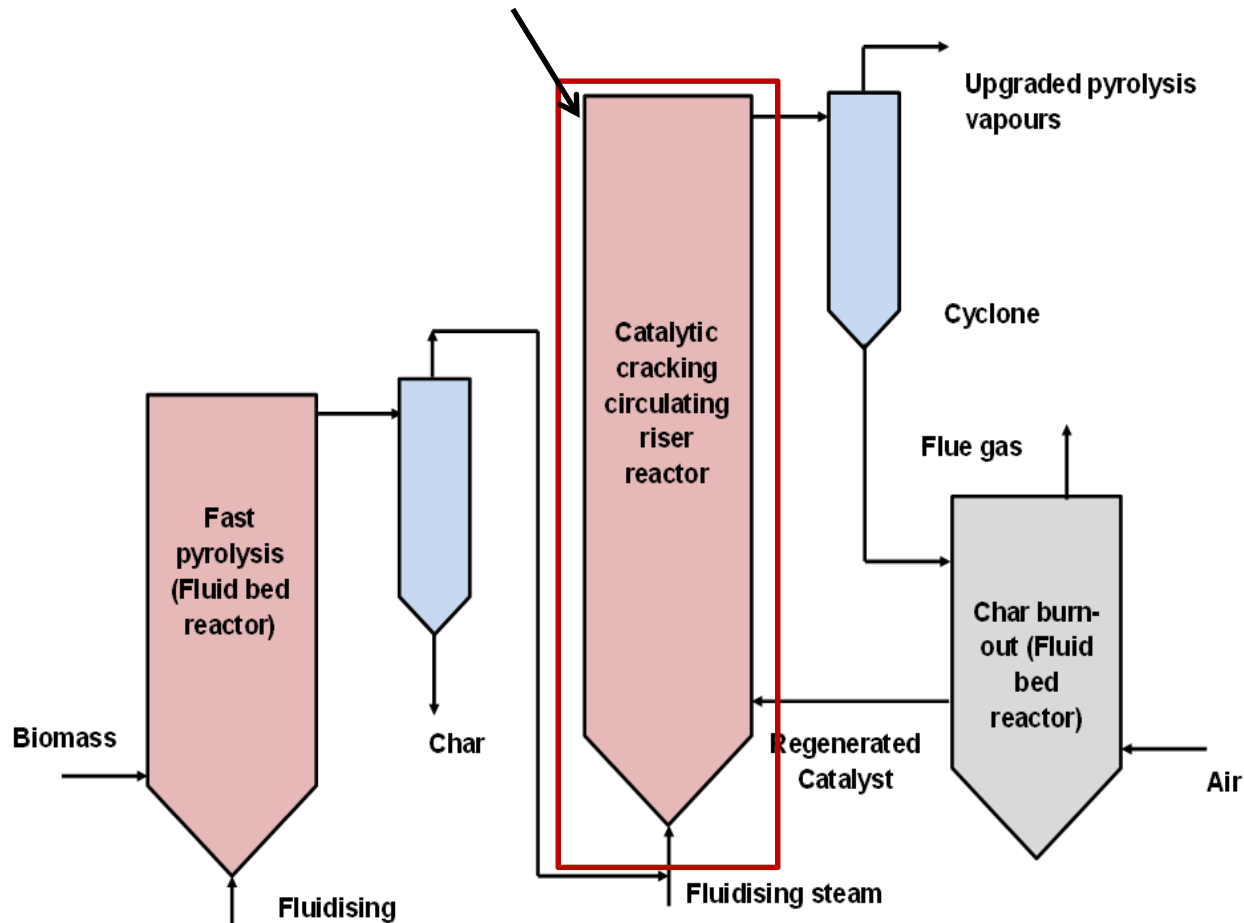
Structure of H-ZSM-5

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 H_2O, CO and CO_2
  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 CO_2, CO and H_2O
    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 FCC Unit Diagram
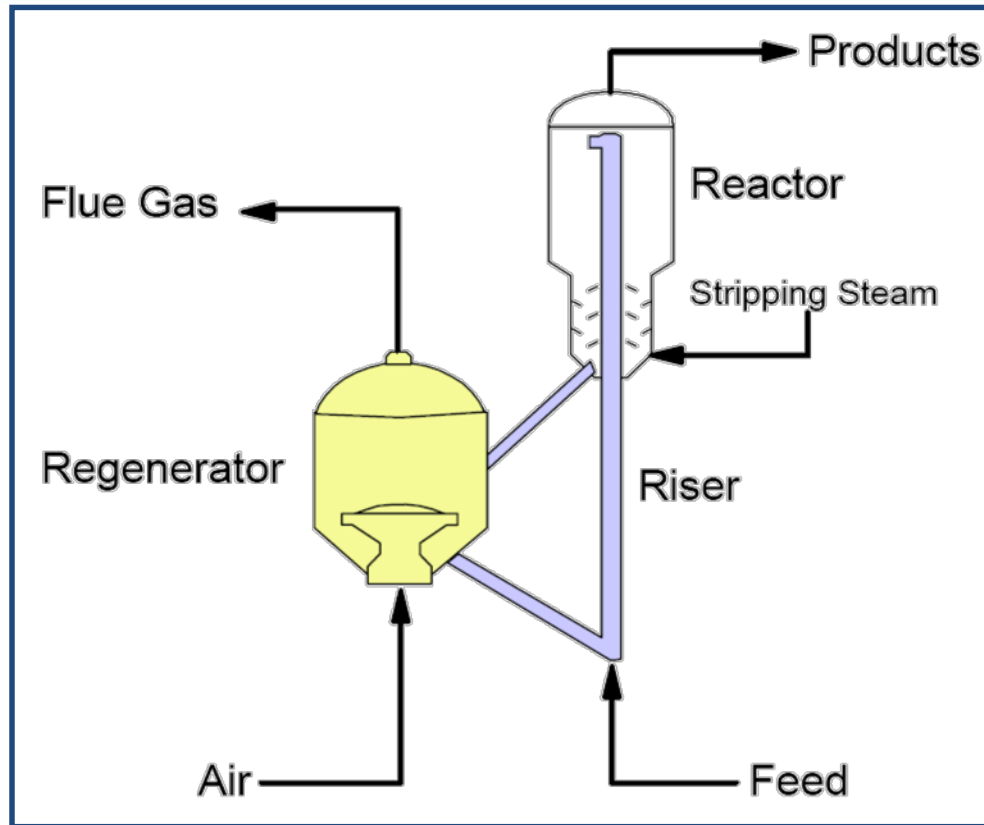
Simplified diagram of a generic FCC unit. Catalyst circulates from the regenerator to the bottom of the riser, where it mixes with feed, flows up the riser into the reactor, and is separated from the products by cyclone separators. Stripping steam removes entrained hydrocarbon vapors, and the catalyst flows back to the regenerator where air is injected to burn off the coke. The cycle then repeats.

Davison Circulating Riser
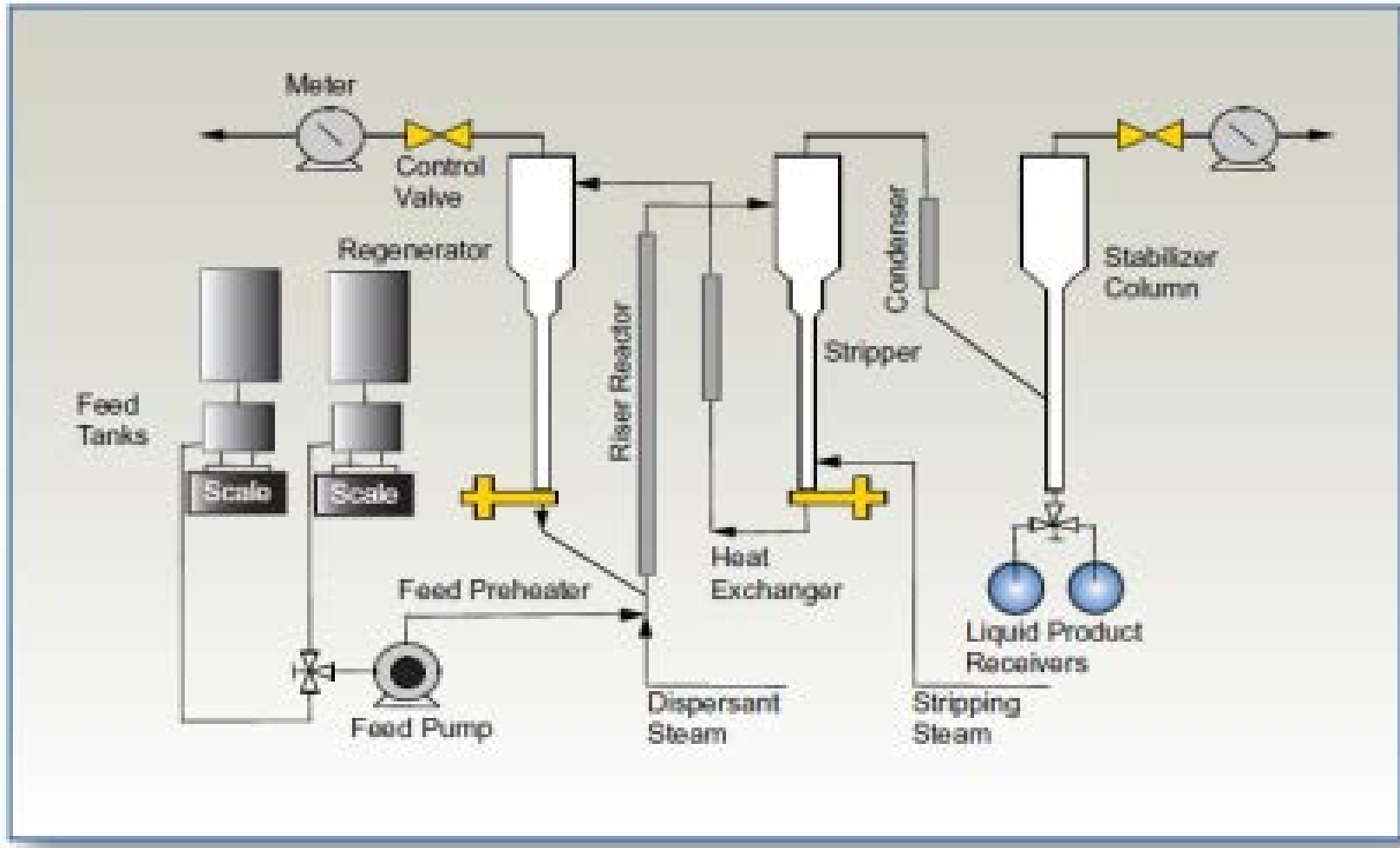
The Davison Circulating Riser is the industry standard for FCC pilot development (Grace)

# Davison Circulating Riser for Pyrolysis Vapour Upgrading

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
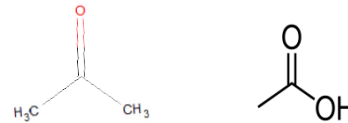- Advantage: Continuous coke removal to keep catalyst active

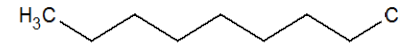**DCR Pilot unit (NREL collaboration with Grace)**

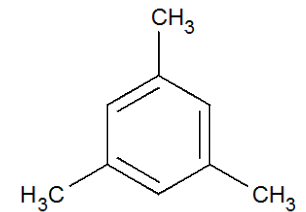# To understand Reaction Pathways: Model compounds
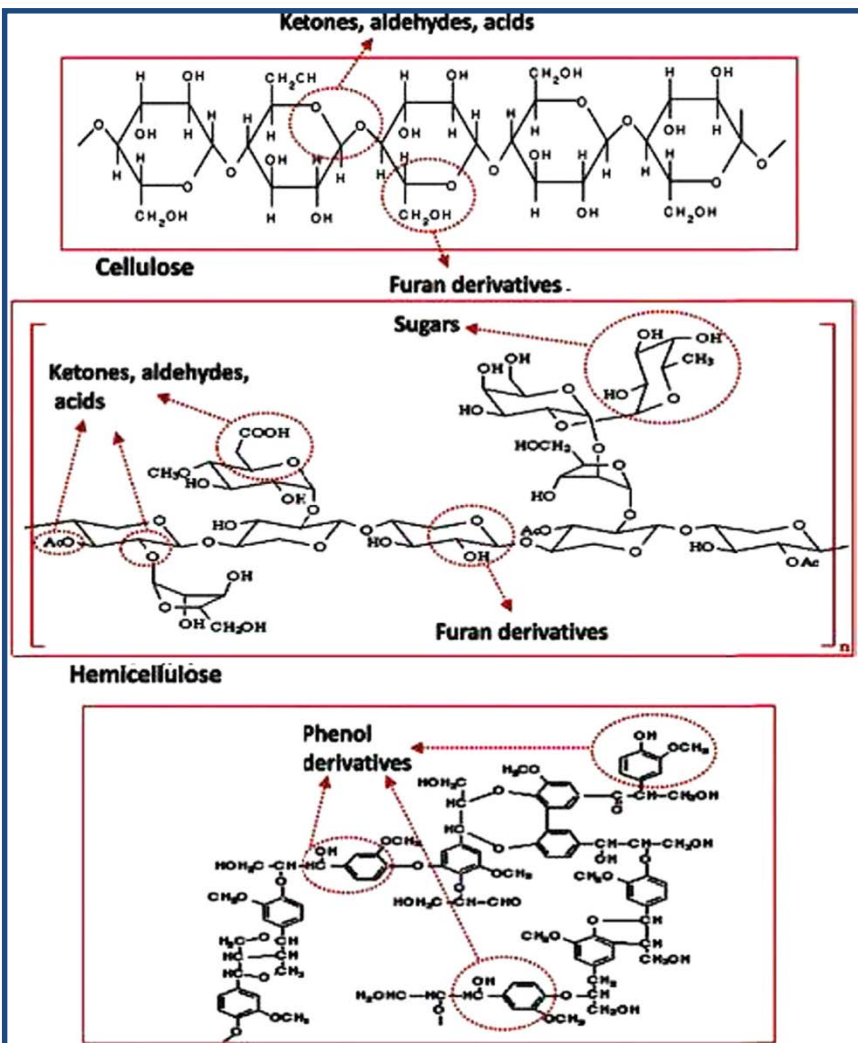
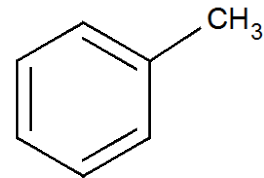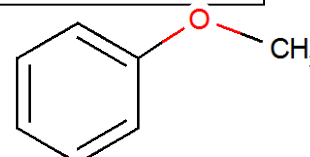Light oxygenates: Acetic acid, Acetone, Acetaldehyde,

Sugar derived compounds: Furfurals

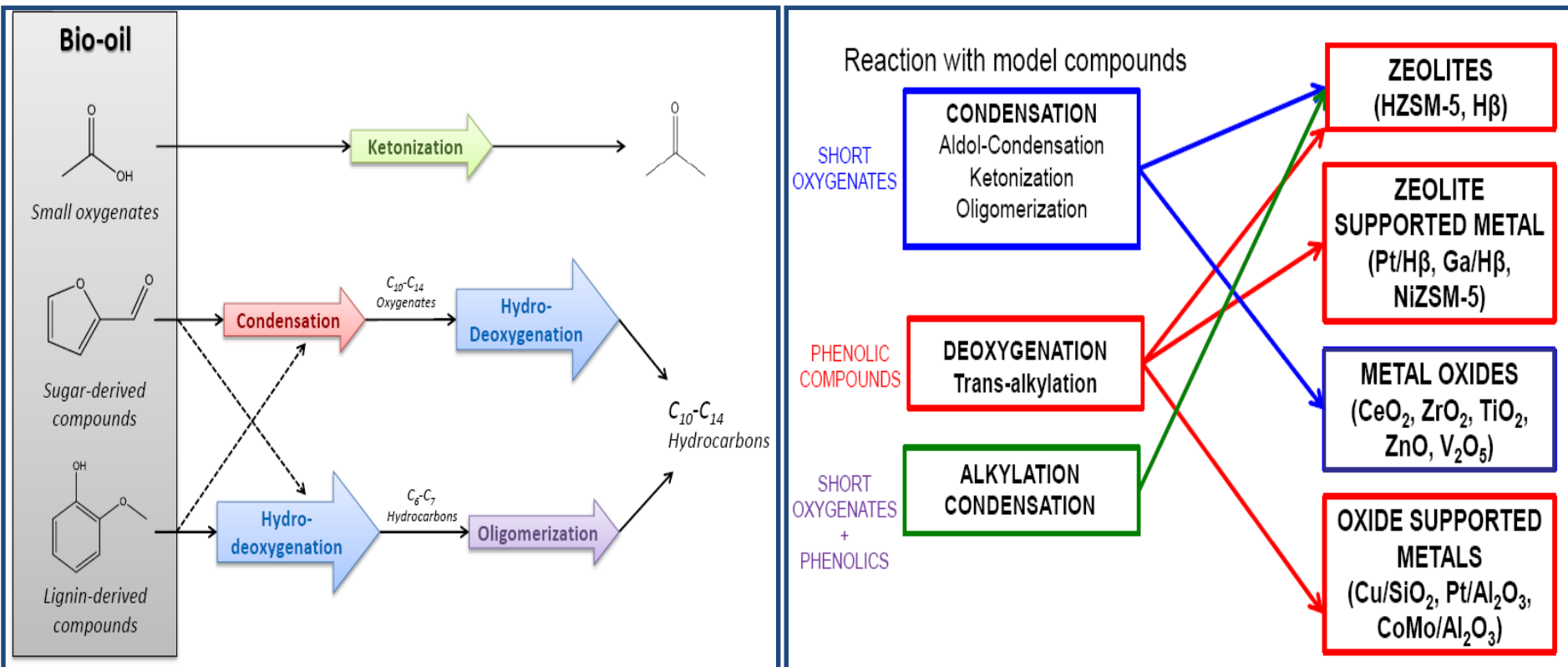Lignin derived compounds: Phenolics

Hydrocarbon fuels

Strategies for Catalytic Upgrading of Bio-oil compounds

Chemistry

Catalysts

Model compound studies have been reported in literature to define favorable chemistry and catalysts in small scale micro-pyrolysis unit

Modelling Methods for FCC

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

Model Validation

- PSRI experimental research facility in Chicogo (Knowlton et a., 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^{2}s

  - Solid inlet velocity: 0.714 m/s

  - Solid inlet volume fraction : 0.4
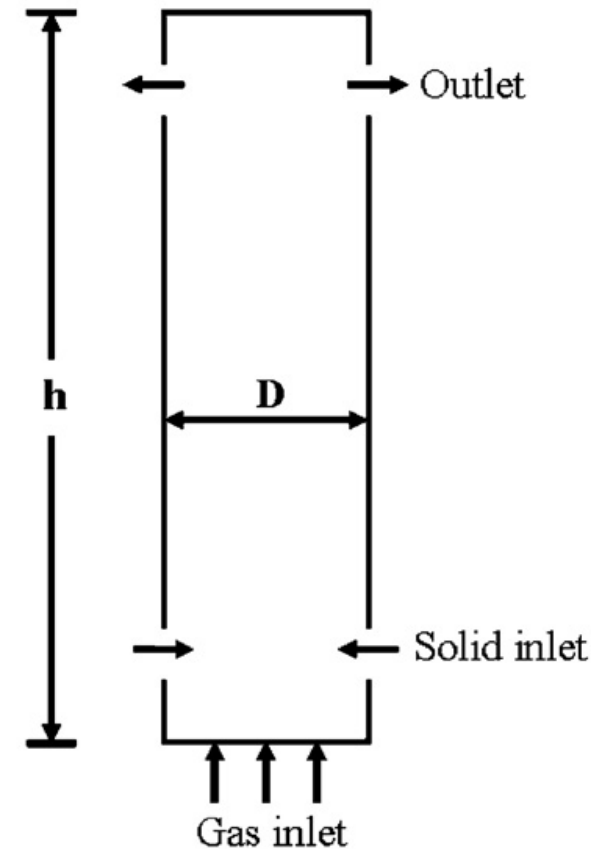
Geometry description

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,

EMMS drag

$$\beta = \begin{cases} 150\dfrac{\varepsilon_s(1-\varepsilon_g)\mu_g}{\varepsilon_g d_p^2} + 1.75\dfrac{\rho_g}{d_p}\varepsilon_s|\mathbf{v}_g - \mathbf{v}_s| & \varepsilon_g < 0.4 \\[2ex] \dfrac{3}{4}C_D\dfrac{\rho_g\varepsilon_g\varepsilon_s|\mathbf{v}_g - \mathbf{v}_s|}{d_p}\varepsilon_g^{-2.65}H_d & \varepsilon_g \geq 0.4 \end{cases}$$

Wen-Yu correlation   Drag index

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

$$K_{sg} = K_{sg,p}(1+c)$$

$$K_{sg,p} = \frac{3}{4}C_D\frac{\alpha_s\alpha_g\rho_g|\vec{v}_s - \vec{v}_g|}{d_s}\alpha_g^{-2.65}$$

$$C_D = \frac{24}{\alpha_g Re_s}\left[1 + 0.15\left(\alpha_g Re_s\right)^{0.687}\right]$$

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

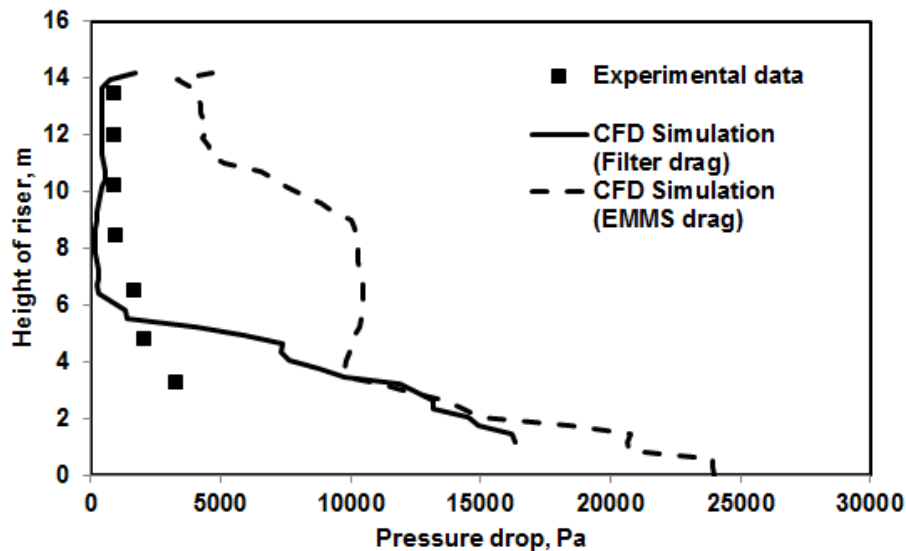$$Fr_f^{-1} = g\Delta_f/v_t^2$$

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

Scaling function, $h(\alpha_s)$

$$h(\alpha_s) = \begin{cases} 2.7\alpha_s^{0.234}, \alpha_s < 0.0012 \\ -0.019\alpha_s^{-0.455} + 0.963, 0.0012 \leq \alpha_s < 0.014 \\ 0.868\exp(-0.38\alpha_s) - 0.17\exp(-11.2\alpha_s), 0.25 \leq \alpha_s < 0.25 \\ -4.59\times10^{-5}\exp(19.75\alpha_s) + 0.852\exp(-0.268\alpha_s), 0.25 \leq 0.455 \\ (\alpha_s - 0.59)\left(-1501\alpha_s^3 + 2203\alpha_s^2 - 1054\alpha_s + 162\right), 0.455 \leq \alpha_s \leq 0.59 \\ 0, 0.59 < \alpha_s \leq 0.65 \end{cases}$$
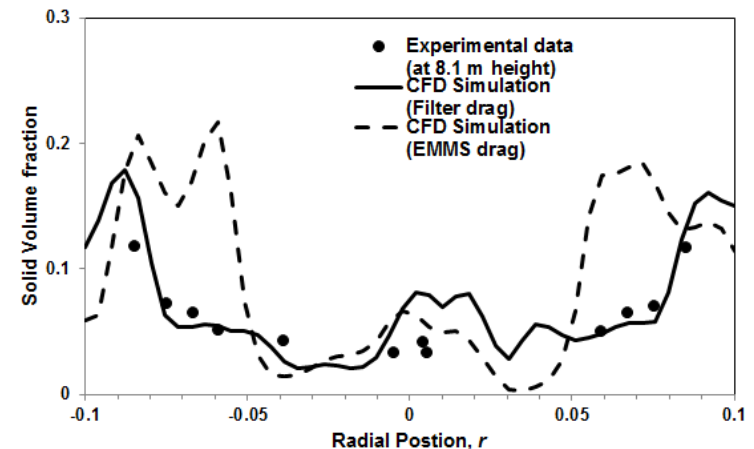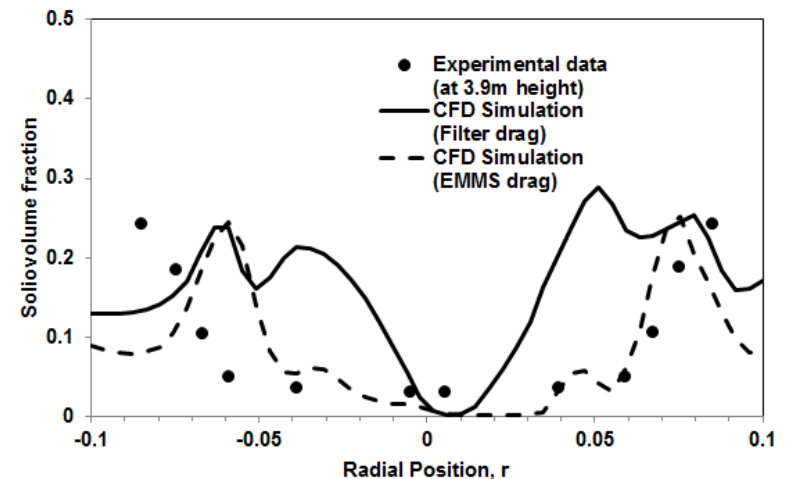
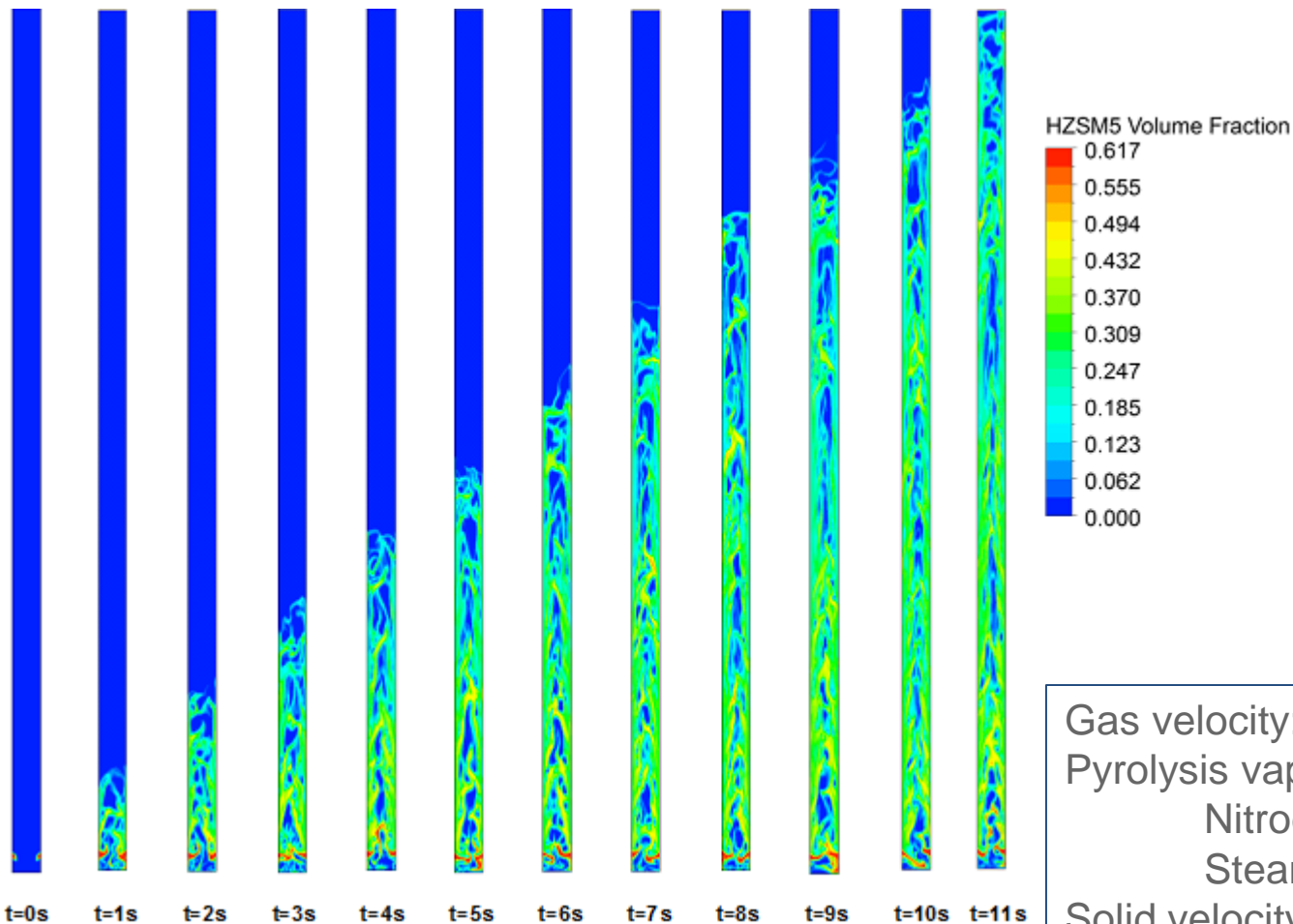| Formulae ($H_D = a(Re_s+b)^c$, $0.001 \leq Re_s \leq 1000$)	Range ($\varepsilon_{mf} \leq \varepsilon_g \leq 1$)
$\begin{cases} a = 0.12621 + 0.51327\exp\left(-0.5\left(\frac{\varepsilon_g - 0.51738}{0.05325}\right)^2\right) \\ c = 0 \end{cases}$	$0.4 < \varepsilon_g \leq 0.51228$
$\begin{cases} a = 0.06022 + \frac{0.64769}{1 + (\varepsilon_g/0.54069)^{38.95086}} \\ b = 1.26148 - \frac{1.25109}{(1 + \exp(-(\varepsilon_g - 0.49842)/0.00835))}\left(1 - \frac{1}{(1 + \exp(-(\varepsilon_g - 0.68685)/0.03593))}\right) \\ c = 0.27698 - \frac{0.298}{1 + (\varepsilon_g/0.55363)^{29.78427}} \end{cases}$	$0.51228 < \varepsilon_g \leq 0.60826$
$\begin{cases} a = 1/\left(15.09342 - 13.31486\varepsilon_g^{6.02771}\right) \\ b = -52.05197 + 346.18273\varepsilon_g - 914.53136\varepsilon_g^2 + 1202.33087\varepsilon_g^3 - 786.52213\varepsilon_g^4 + 204.82611\varepsilon_g^5 \\ c = 1/\left(3.51503 + 3.1596\varepsilon_g^{4.34314}\right) \end{cases}$	$0.60826 < \varepsilon_g \leq 0.9904$
$\begin{cases} a = 0.52193 + \frac{0.8812}{1 + \exp(-(\varepsilon_g - 0.99662)/0.00112)}\left(1 - \frac{1}{1 + \exp(-(\varepsilon_g - 0.99752)/0.00006)}\right) \\ b = 0.47595 - \frac{0.22085}{1 + (\varepsilon_g/0.99594)^{2170.31695}} \\ c = 0.13788 - 0.07951\exp\left(-0.5\left(\frac{\varepsilon_g - 0.99841}{0.00142}\right)^2\right) \end{cases}$	$0.9904 < \varepsilon_g < 0.9997$
$a = 1, c = 0$	$0.9997 \leq \varepsilon_g \leq 1$

Hydrodynamics of FCC Riser: Model Validation

Pressure drop vs. height of riser

Solid volume fraction vs. radial position

CFD Results (i): Hydrodynamics

HZSM5 Volume Fraction

0.617	
0.555	
0.494	
0.432	
0.370	
0.309	
0.247	
0.185	
0.123	
0.062	
0.000	

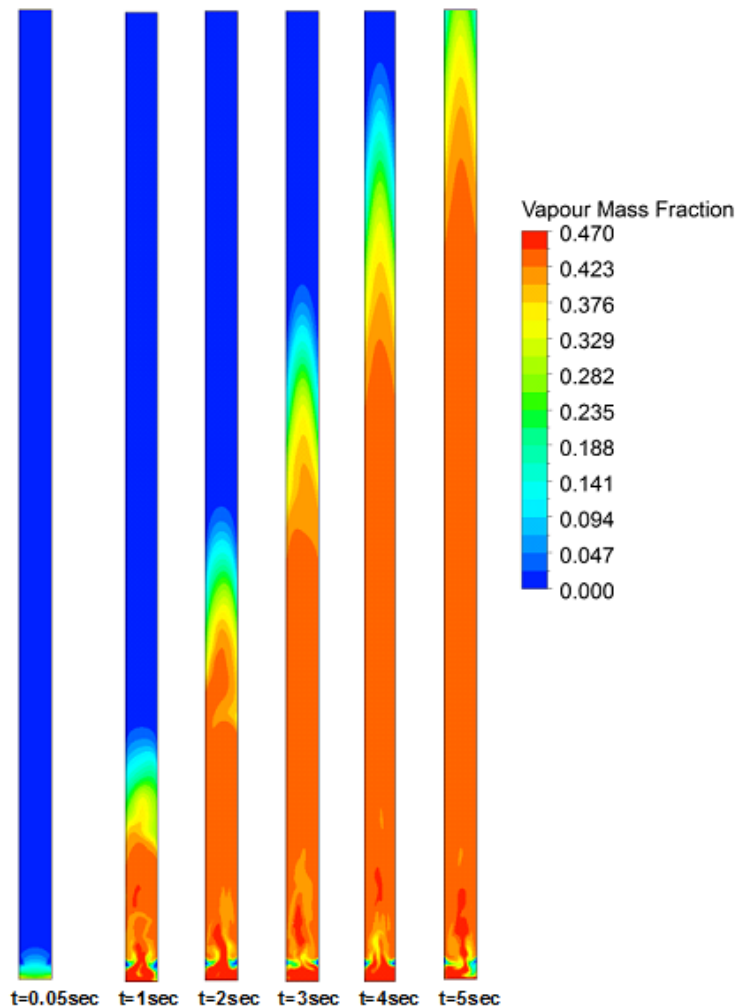t=0s t=1s t=2s t=3s t=4s t=5s t=6s t=7s t=8s t=9s t=10s t=11s

- 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.
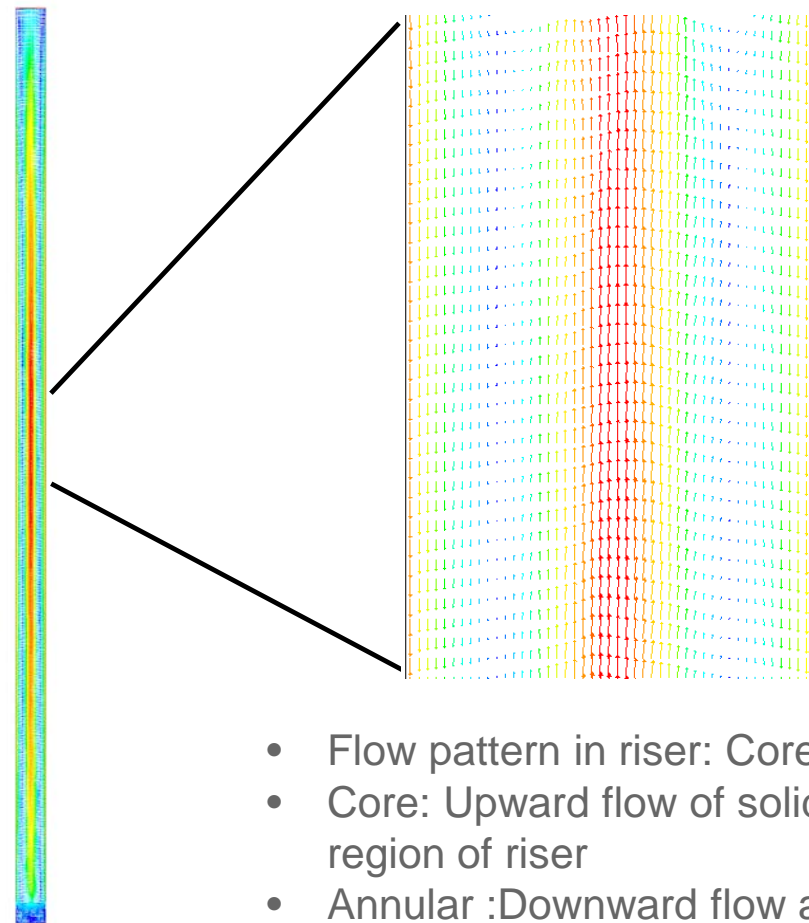- At t=11s particles are started to leave from the bed.

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

CFD Results (ii): Hydrodynamics

Vapour mass fraction profiles

Time averaged solid velocity profiles

Vapour Mass Fraction

| 0.470 |
| 0.423 |
| 0.376 |
| 0.329 |
| 0.282 |
| 0.235 |
| 0.188 |
| 0.141 |
| 0.094 |
| 0.047 |
| 0.000 |

t=0.05sec   t=1sec   t=2sec   t=3sec   t=4sec   t=5sec

- 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

# 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 hydrdyodynmic simulation are used as Initial condition;
- Diffusion coefficient for gas phase is 1e-08m^2/s and for solid phase is 1e-05m^2/s;
- Tracer concentration at outlet is monitored.

Residence time distribution (RTD)

Gas Phase RTD
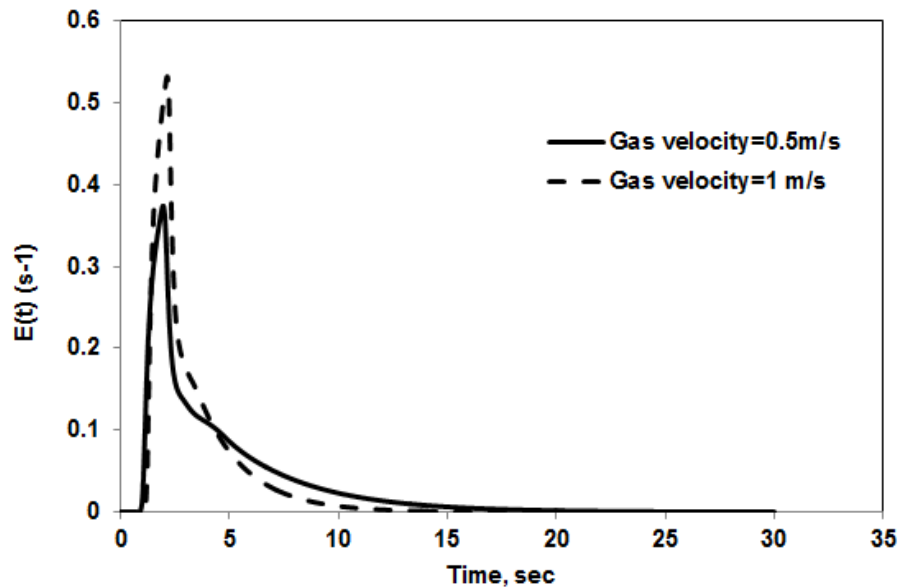
Solid Phase RTD
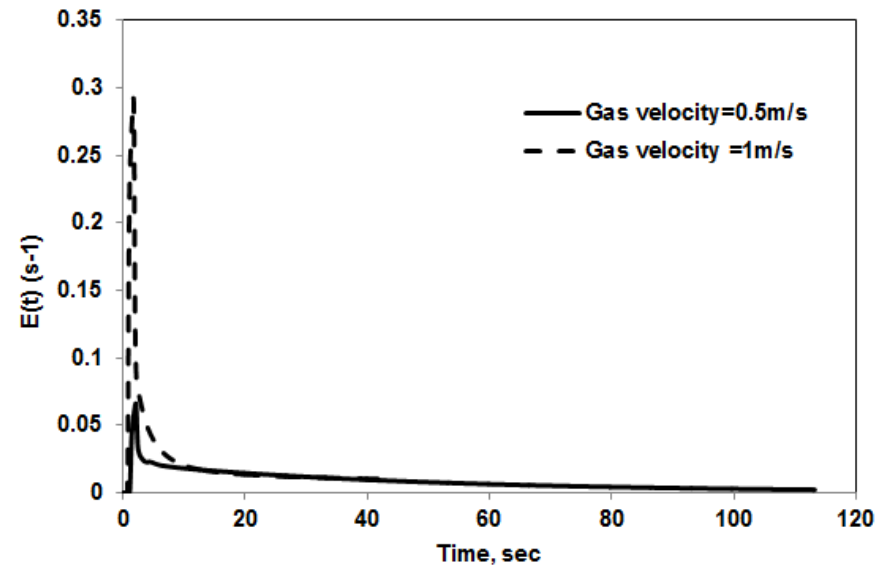
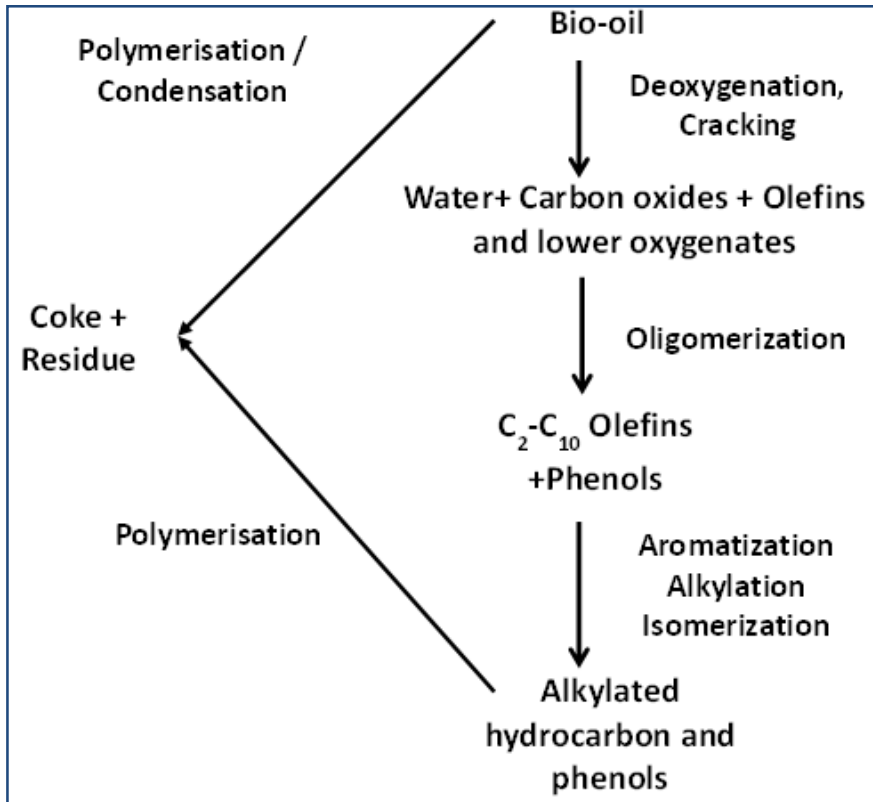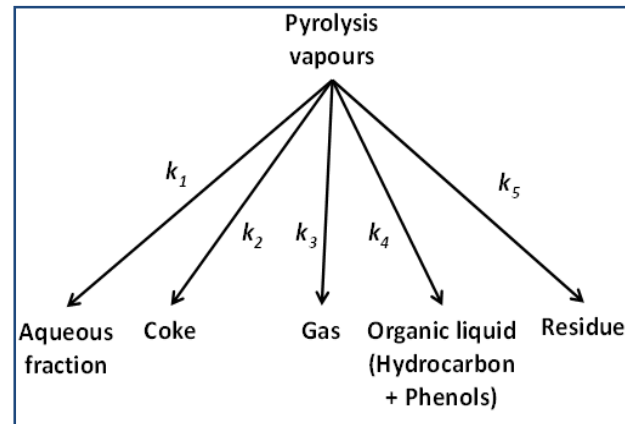| Conditions	RTD	
	Vapour phase	Solid phase
Gas velocity: 0.5m/s Solid velocity: 0.25m/s	4.6sec	36sec
Gas velocity: 1.0m/s Solid velocity: 0.25m/s	3.28sec	11.9sec

Reaction pathways, kinetics of Pyrolysis Vapour upgrading

Lumped Models

Lumped Compounds	Model compound
Aqueous fraction	steam
Coke	Carbon-solid
Gas	CO2
Hydrocarbon	Benzene
Residue	N-Heptane

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

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

Rate of a reaction (k)	Activation Energy, E (kJ/ mol)	Reaction Order	Rate Constant
k_1	79	1.4	0.6e-05
k_2	61	1.2	7.5e-05
k_3	38	0.8	18e-05
k_4	3	0.9	80e-05
k_5	61	0.7	37e-05

Mass fraction of various lumped species during catalytic cracking of vapours
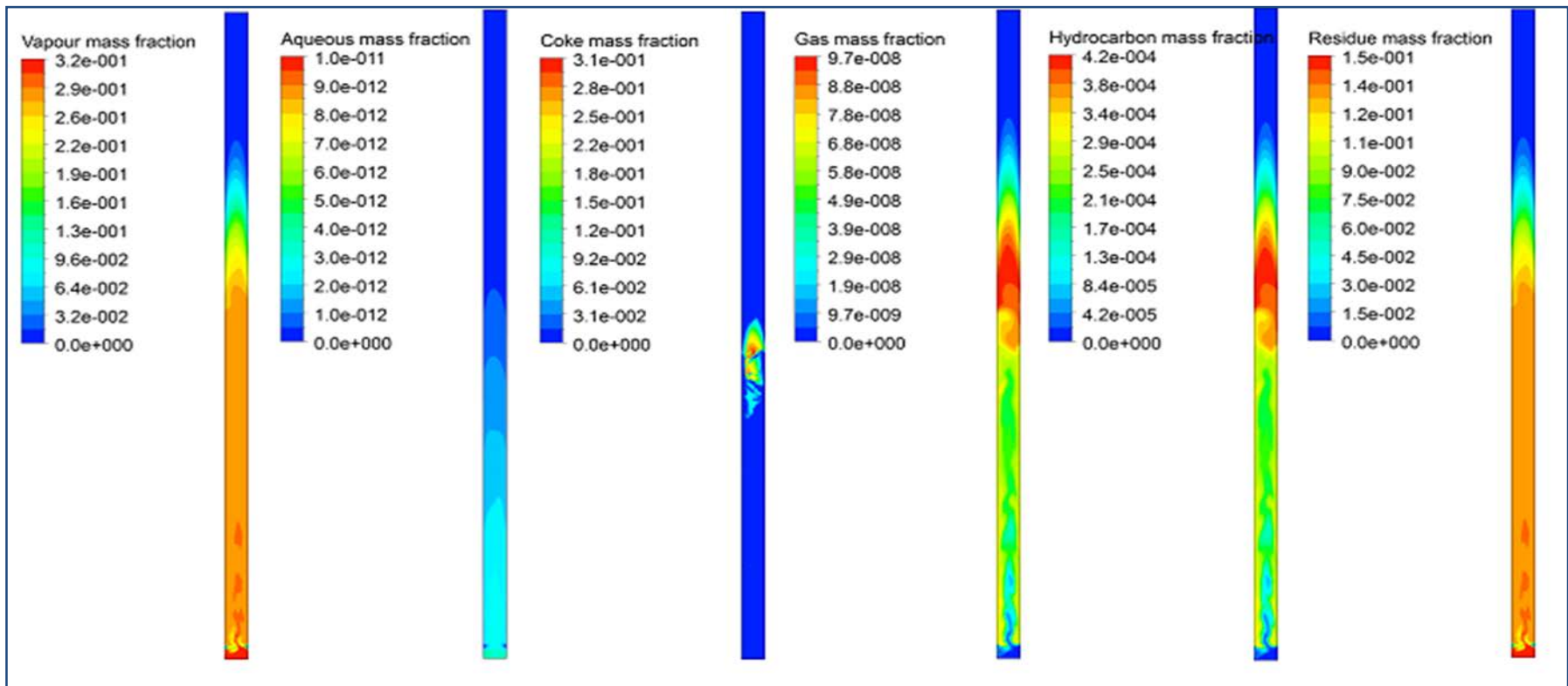
Gas velocity: 0.5 m/s; Solid velocity: 0.25 m/s and temperature : 410°C
Gas : organic volatile mass fraction = 0.32; Nitrogen mass fraction= 0.5; steam mass
    fraction=0.03; residue (heavy non-volatile) mass fraction:0.15

Kinetic results (ii)

Lumped Compounds	Mass fraction from CFD Simulation	
	Before	After
Pyrolysis vapour (volatile)	0.32	0.24
Aqueous fraction	0.03	1.3e-012
Coke	0	0.016
Gas	0	5.8e-008
Hydrocarbon	0	0.00025
Residue (heavy non-volatile)	0.15	0.11

- 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 N_2/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

THANK YOU