Modelling & experimental validation of biomass-steam gasification in bubbling fluidized bed reactor

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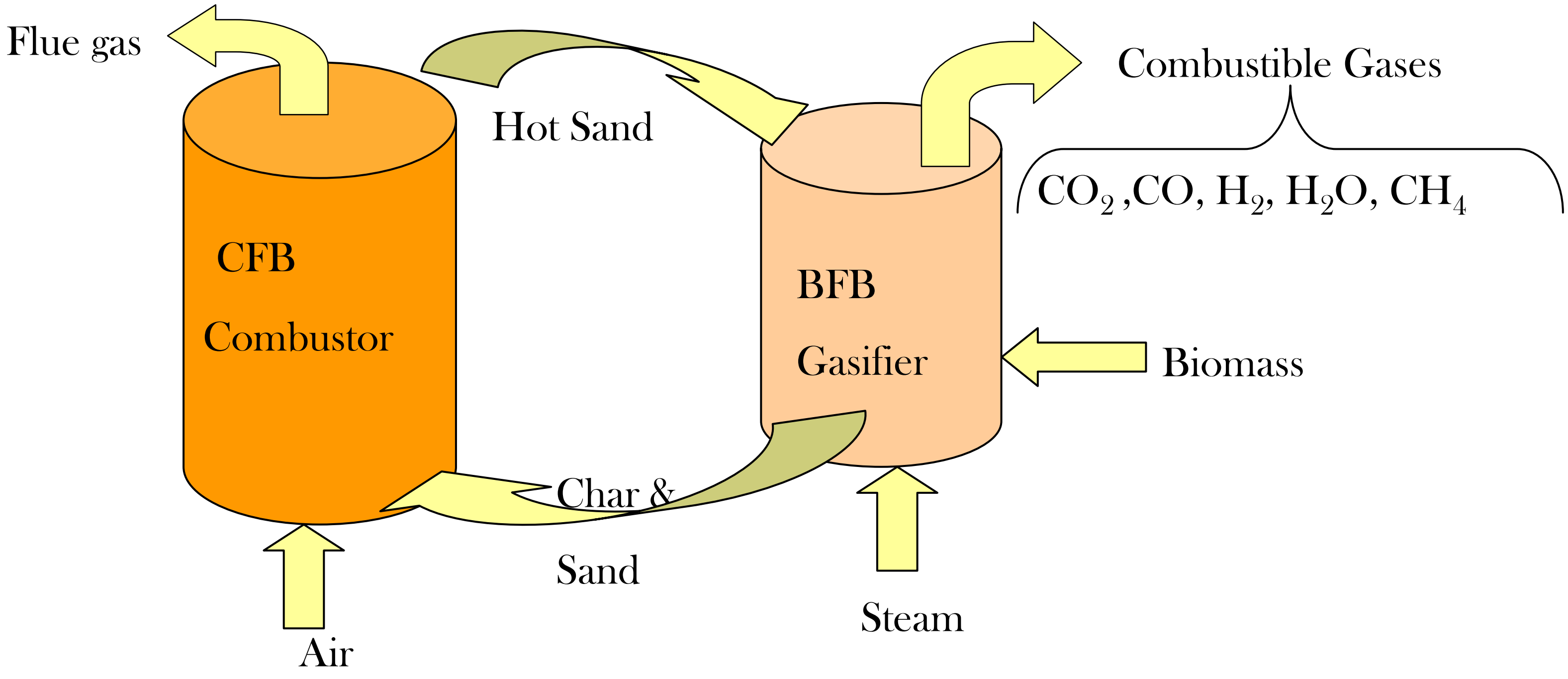
Objective:

- To develop a mathematical model to simulate the gas composition of biomass gasification in the bubbling fluidised gasifier.
  - Unsteady state non isothermal model based on reaction kinetics of produced combustible gases.
- Investigation of the effects of operating parameters such as temperature and steam to biomass ratio on the gas compositions.
- Validate the model with experimental data

Fluidised Bed- Gasification Technology with Steam as Gasification Agent



Biomass - *Pinus radiata*

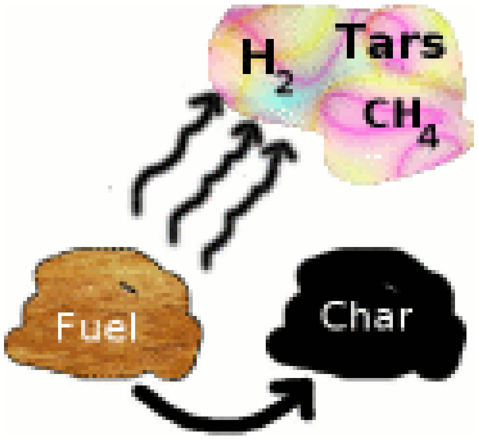
Ultimate Analysis	Wt % dry basis
C	48.28
H	7.31
O	43.88
N	0.03

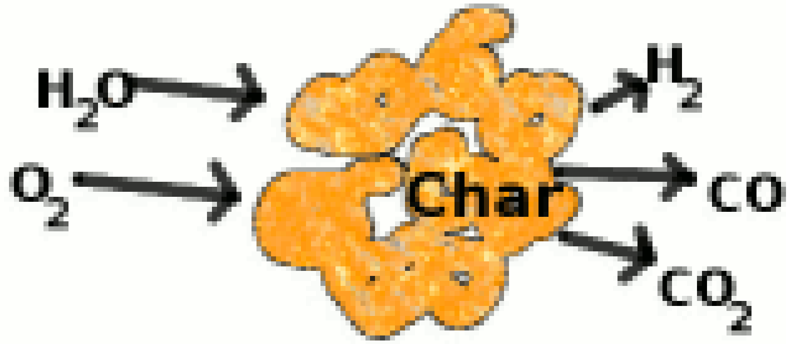
Gasifier at UoC

- Leads a programme on 'Wood IGCC' for wood industry.
- Has built a 100 kWth laboratory-scale Fast Internal Circulating Fluidised Bed (FICFB) Gasifier for tests and evaluation of radiata pine residues.
- Developing producer gas cleaning technologies.
- Biofuels projects (Pyrolysis, Fischer-Tropsch process).

Biomass gasification

- There are two stages of physical and chemical changes in the biomass gasification:
  - Decomposition of the biomass under high temperature. This is a similar process to biomass fast pyrolysis.
  - Secondary reactions involving the evolved volatiles.
  - Char reaction with gasification agent.





Instantaneous Overall Pyrolysis Reactions

$$N_{wood}CH_{1.44}O_{0.66} + N_{moist}H_2O \xrightarrow{\text{Heat at very high Temp}} N_{CO}CO + N_{CO_2}CO_2 + N_{H_2O}H_2O + N_{H_2}H_2 + N_{CH_4}CH_4 + N_{C_2H_4}C_2H_4 + N_{tar}Tar + N_{char}Char$$

For reaction above (fast pyrolysis in fluidized bed) a product distribution, instead of a “typical” kinetic equation, was defined by Gonza´lez-Saiz, in his PhD Thesis “Advances in biomass gasification in fluidized bed”, with the same type of biomass as the one considered in our research (small pine wood chips) and in a fluidized bed working under similar experimental conditions (Sadaka et al., 2002)

y_i = Function (Temperature) i corresponds to volatile gases & tar and char can be used as initial condition

Secondary Reactions Involved in the evolved volatiles and Gasification of char reactions

Reactions		Equilibrium temperature[K]	ΔG^o [J/mol]	ΔH^o [J/mol]
Steam Gasification	$C + H_2O \overset{K_1}{\Leftrightarrow} CO + H_2$	~948	-164.21	124978
	$C + 2H_2O \overset{K_5}{\Leftrightarrow} CO_2 + 2H_2$	~903	42.75	63065
Bouduard Reaction	$C + CO_2 \overset{K_4}{\Leftrightarrow} 2CO$	~973	251.87	187667
Steam Methane Reforming Reaction	$CH_4 + H_2O \overset{K_6}{\Leftrightarrow} CO + 3H_2$	~ 893	-111.52	157224
Water gas - shift Reaction	$CO + H_2O \overset{K_2}{\Leftrightarrow} CO_2 + H_2$	~1098	-119.37	-63988
Methanation Reaction	$C + 2H_2 \overset{K_3}{\Leftrightarrow} CH_4$	~ 820	70.47	-32621

Hydrodynamic model of Fluidization

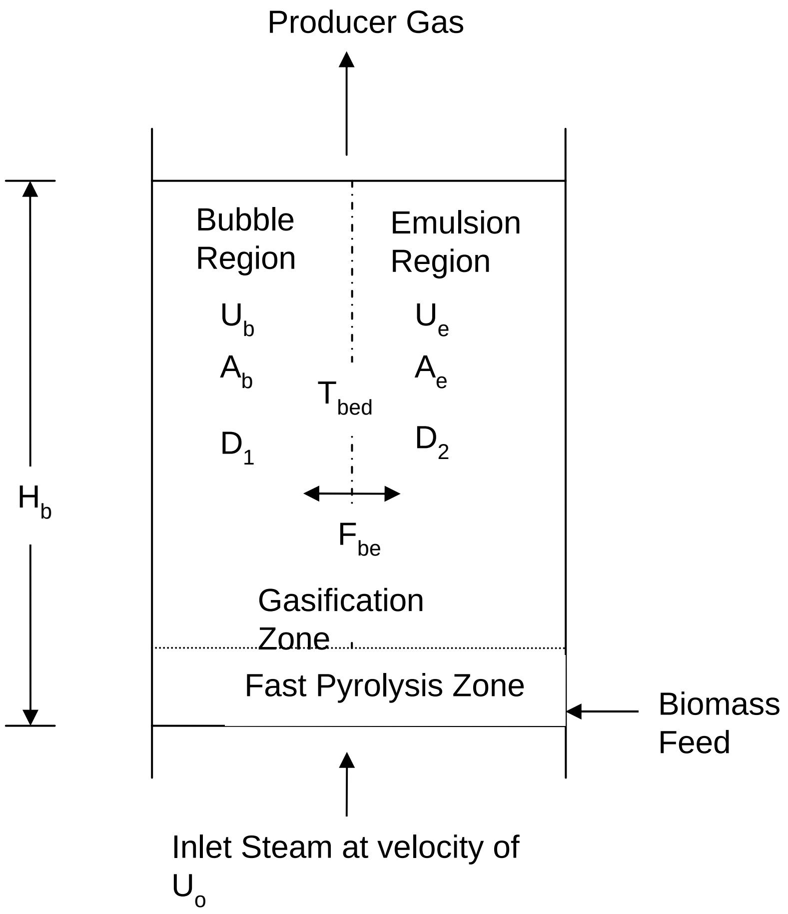


Fig.1 Two phase model for fluidised bed gasifier.

- Mixing & distribution of solids & fluid – "Emulsion Region"
- Formation of motion of bubbles through the bed – "Bubble Region"
- Interphase mass transfer of particles and gases between the regions F_{be}
- Emulsion phase – plug flow and all reactions occurs in this region
- Bubble phase – no solids, only water gas reaction and methane reforming reaction occurs.

Mass Balance

$$\begin{pmatrix}\text{Accumulation}\\ \text{of species (i)}\end{pmatrix} = \underset{\text{convection}}{\begin{pmatrix}\text{rate of i in -}\\ \text{rate of i out}\end{pmatrix}} + \begin{pmatrix}\text{rate of i out by}\\ \text{exchange with}\\ \text{the emulsion}\\ \text{phase}\end{pmatrix} - \begin{pmatrix}\text{rate of production}\\ \text{of i by chemical}\\ \text{reaction}\end{pmatrix}$$

Bubble phase Mass balance

$$\frac{\partial C_{ib}}{\partial t} = -U_b \underbrace{\frac{\partial C_{ib}}{\partial x} + D_{ib}\frac{\partial^2 C_{ib}}{\partial x^2}}_{\text{\{rate of i in– rate of i out \} convection}} - \underbrace{F_{be}\left(C_{ib} - C_{ie}\right)}_{\text{rate of i out by exchange with the emulsion phase}} + R_{ib}$$

Accumulation of
species (i)

Chemical
Reaction term

Emulsion phase Mass balance

{Conc. of i_{th} species [Kgmol/m³]}

{Emulsion phase gas velocity [m/s]}

{Diffusion co-efficient of Component i [m²/s]}

{Gas Exchange Coefficient b/n Bubble & emulsion phase [1/s]}

$$\frac{\partial C_{ie}}{\partial t} = -\frac{U_e}{\varepsilon_{mf}}\frac{\partial C_{ib}}{\partial x} + D_{ie}\frac{\partial^2 C_{ie}}{\partial x^2} + \frac{F_{be}A_b}{\varepsilon_{mf}A_e}\left(C_{ib} - C_{ie}\right) + R_{ie}$$

Accumulation of species (i)

{rate of i in– rate of i out } convection

rate of i into the emulsion phase by exchange with bubble phase

Chemical Reaction term involved in emulsion phase

+ rate of production of species by devolatilization of feed

Energy Balance

(Rate of heat accumulation in the emulsion phase) =

(heat in by gas flow in the emulsion phase) - (heat out by gas flow in the emulsion phase) + (Net heat exchange b/n the bubble & Emulsion phase) +/-

(heat generated by reactions in the emulsion phase) + (Heat input by bed material in) - (Heat removed by bed material char out)

* Similarly for the bubble phase except all the terms applies except the last two terms

Bubble phase Energy balance

Sensible heat [kJ/kmol]

Heat interchange coefficient b/n bubble & emulsion phase [kW/m^{3}K]

$$\frac{\partial C_{ib}C_{pb}T_b}{\partial t} = \frac{\partial}{\partial x}\sum\left(U_b C_{ib}\Delta H_{ib}\right) + \delta_b H_{be}\left(T_e - T_b\right) + \delta_b R_{ib}\Delta H_r$$

Rate of heat accumulation in the bubble phase

heat in by gas flow in the emulsion phase - heat out by gas flow in the emulsion phase

Net heat exchange b/n the bubble & Emulsion phase

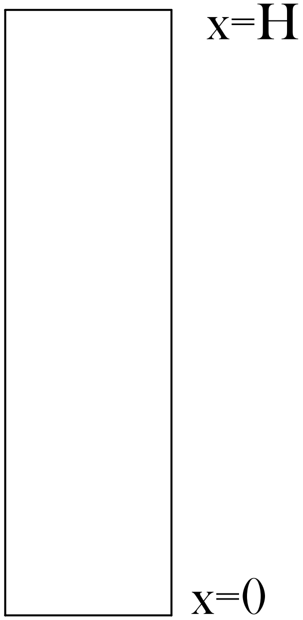
heat generated by reactions in the emulsion phase

Emulsion phase Energy balance

$$\frac{\partial C_{ie}C_{pe}T_e}{\partial t} = \frac{\partial}{\partial x}\sum\left(U_e C_{ie}\Delta H_{ie}\right) + \left(1-\delta\right)H_{be}\left(T_b - T_e\right)$$

$$+\left(1-\delta\right)R_{ie}\Delta H_r + \underbrace{\frac{\partial \dot{m}_{sand} C_{psand} T}{\partial x}}_{\left(\text{Heat input by bed material in}\right) - \left(\text{Heat removed by bed material char out}\right)}$$

Boundary Conditions



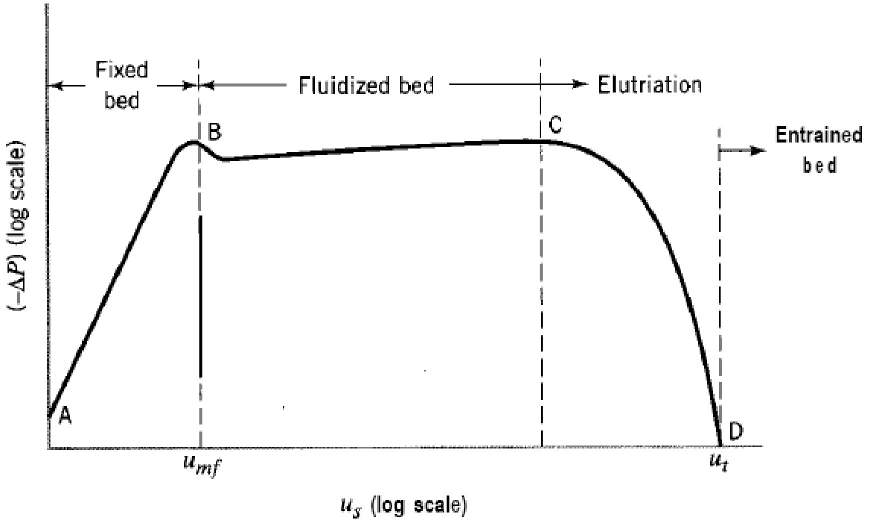
$$\frac{\partial C_{ib}}{\partial x} = 0 \quad \frac{\partial C_{ie}}{\partial x} = 0 \quad \frac{\partial T_b}{\partial x} = 0 \quad \frac{\partial T_e}{\partial x} = 0$$

;

$$C_{ib} - \frac{D_1}{U_b}\frac{\partial C_{ib}}{\partial x} = C_{i0} \quad ; \quad C_{ie} - \frac{D_2}{U_e}\frac{\partial C_{ie}}{\partial x} = C_{i0}$$

$$T_b = T_e = T_{in}$$

Hydrodynamics of Fluidized Bed



- At minimum Fluidization, bed starts lifting.

- At this point the frictional upward lift force just exceeds the gravitational force.

Gravitational force :

$$(-\Delta P)_{mf} A_c = gW = g\rho_{B,app}V = g(\rho_p - \rho_f)(1-\varepsilon_{mf})L_{mf} A_c$$

Pressure drop given by

Ergun's Correlation of fixed bed

$$(-\Delta P)_{mf} = 1.75\frac{(1-\varepsilon_{mf})}{\varepsilon_{mf}^3}\frac{u_{mf}^2\rho_f L_{mf}}{d_p'} + 150\frac{(1-\varepsilon_{mf})^2}{\varepsilon_{mf}^3}\frac{\mu_f u_{mf} L_{mf}}{d_p'^2}$$

$$u_{mf}^2 + \frac{150(1-\varepsilon_{mf})\mu_f}{1.75\rho_f d_p'}u_{mf} - \frac{g(\rho_p - \rho_f)\varepsilon_{mf}^3 d_p'}{1.75\rho_f} = 0$$

Hydrodynamics of Fluidized Bed (Continues…)

Some variables involved in the model are closely interrelated through hydrodynamics derived from (Mori and Wen, 1975) and (Davidson et al., 1985)

Bubble diameter:

$$D_b = D_{bM} - \left(D_{bM} - D_{b0}\right)\exp\left(-0.3x/D\right)$$

Maximum Bubble diameter:

$$D_{bM} = 1.64\left[A\left(U_0 - U_{mf}\right)\right]^{0.4}$$

Initial bubble diameter:

$$D_{b0} = 0.871\left[A\left(U_0 - U_{mf}\right)/N\right]^{0.4}$$

Bubble velocity:

$$U_b = U_0 - U_{mf} + 0.711\left(gD_b\right)^{0.5}$$

Volume fraction of bubble:

$$DEL = \left(U_0 - U_{mf}\right)/U_b$$

Emulsion velocity:

$$Ue = U_{mf}/\left(1 - DEL\right)$$

Gas exchange co efficient

b/n bubble & emulsion phase [1/s]

$$F_{be} = 0.11/D_b$$

Operating Conditions

- Arrhenius reaction type is used
- Temperature : 760 Deg C
- Feed rate : 20 kg/hr
- Steam/Biomass: 0.3
- Initial volatiles after instant fast pyrolysis

$C_{H2,0}$= 0.0051 kmol/m^3 (29.81 mol %)
$C_{CO,0}$ = 0.0067 kmol/m^3 (39.2 mol %)
$C_{CO2,0}$= 0.0023 kmol/m^3 (13.62 mol%)
$C_{CH4,0}$= 0.0021 kmol/m^3 (12.2 mol %)

- Initial concentration of steam ,

$C_{H2O,0}$= 0.0015 kmol/m^3

- Mass of Tar formed during Initial pyrolysis =1.41 kg
- Mass of char formed during Initial pyrolysis =2.99 kg

Experiment Results from published literature data

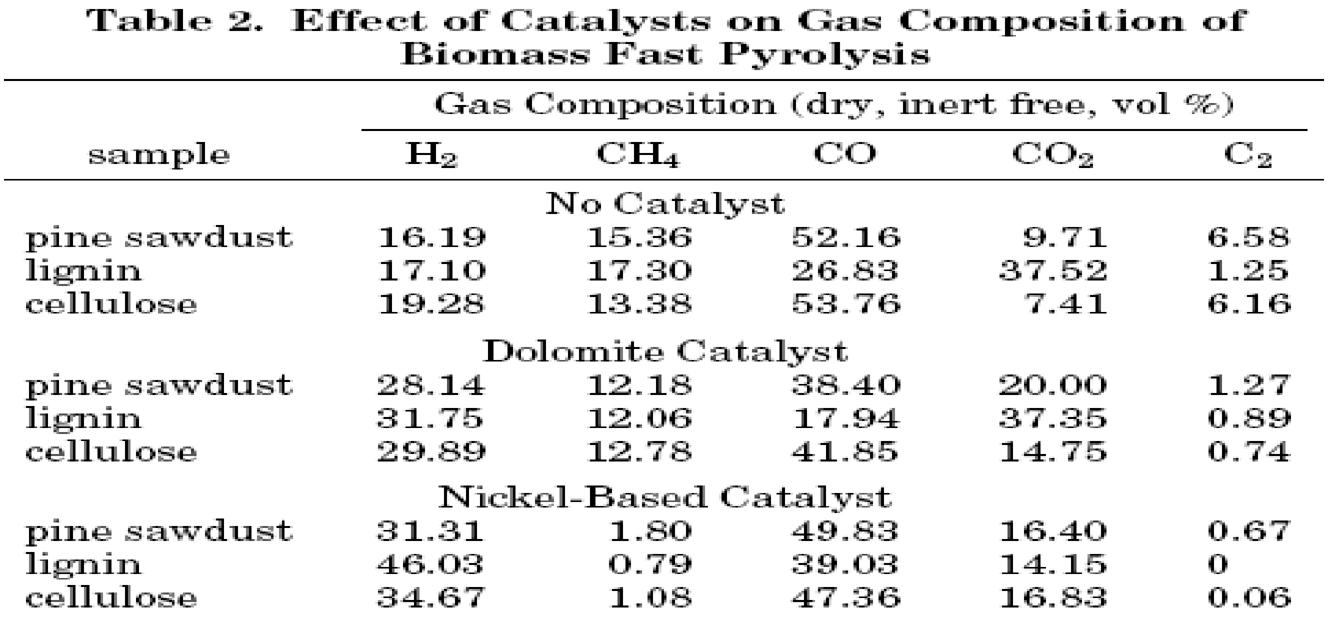
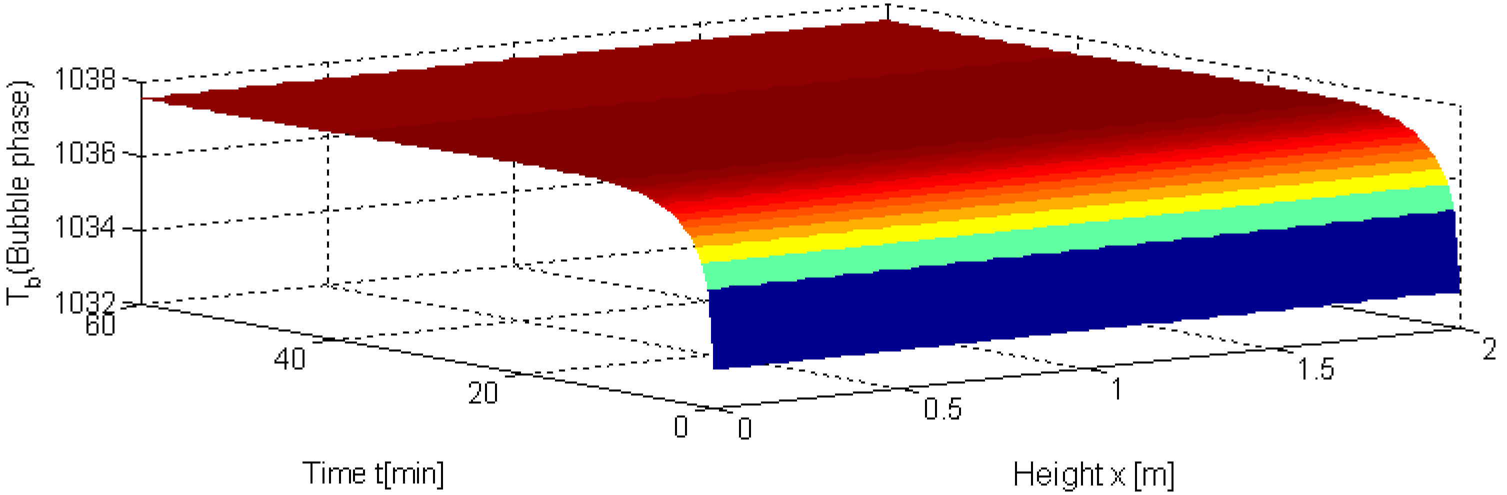


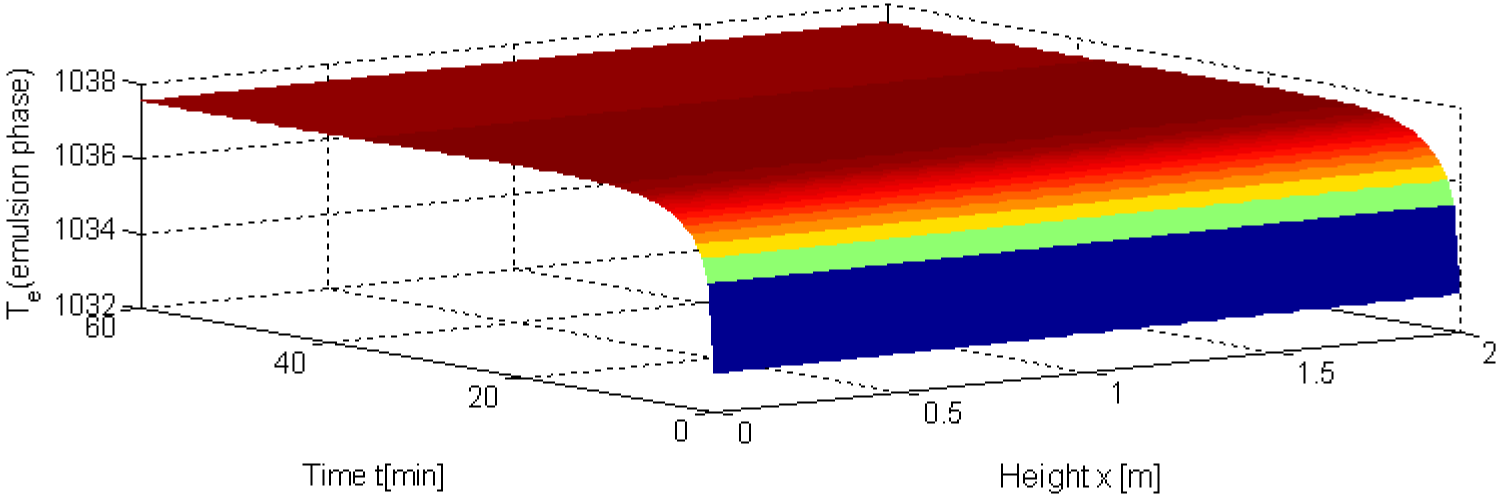
Table 2. Effect of Catalysts on Gas Composition of Biomass Fast Pyrolysis

	Gas Composition (dry, inert free, vol %)				
sample	H_2	CH_4	CO	CO_2	C_2
		No Catalyst			
pine sawdust	16.19	15.36	52.16	9.71	6.58
lignin	17.10	17.30	26.83	37.52	1.25
cellulose	19.28	13.38	53.76	7.41	6.16
		Dolomite Catalyst			
pine sawdust	28.14	12.18	38.40	20.00	1.27
lignin	31.75	12.06	17.94	37.35	0.89
cellulose	29.89	12.78	41.85	14.75	0.74
		Nickel-Based Catalyst			
pine sawdust	31.31	1.80	49.83	16.40	0.67
lignin	46.03	0.79	39.03	14.15	0
cellulose	34.67	1.08	47.36	16.83	0.06

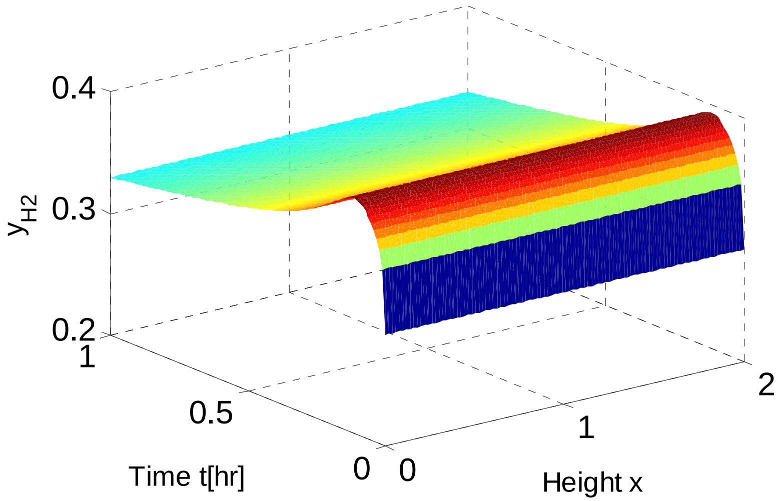
(Lv, Chang et al. 2004)

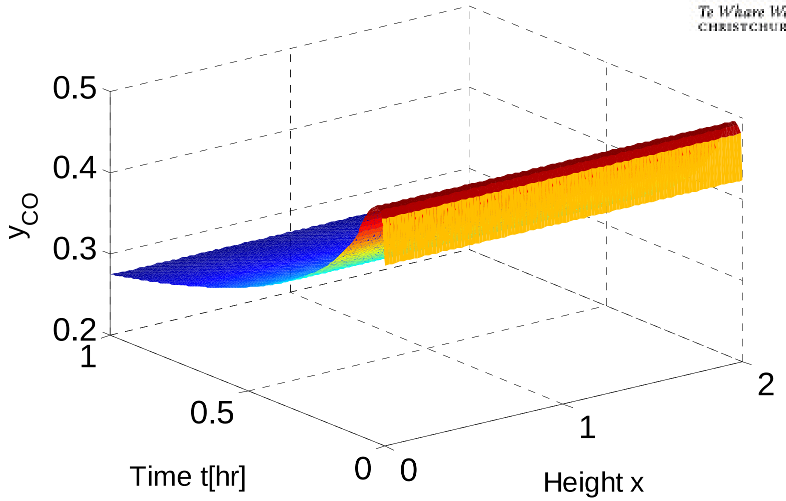
Simulation results

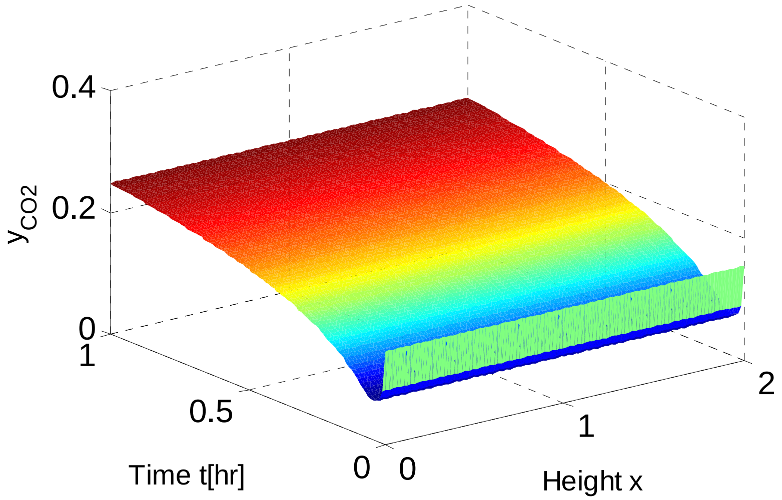


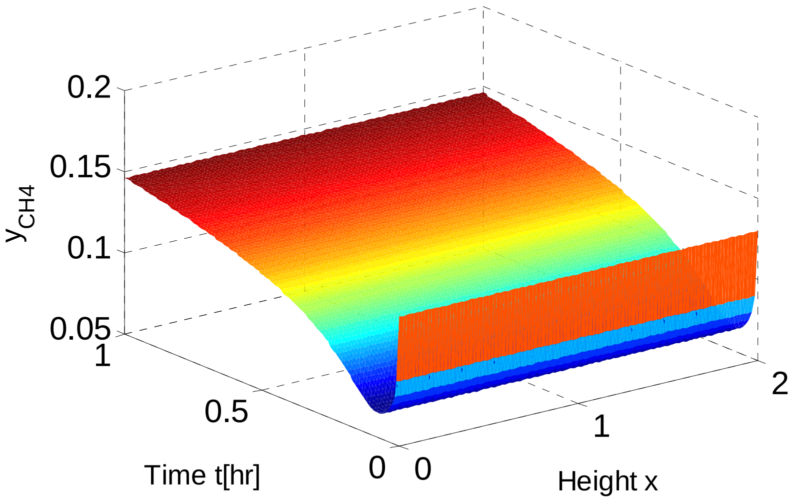


Simulation results









Experiment Results from published literature data

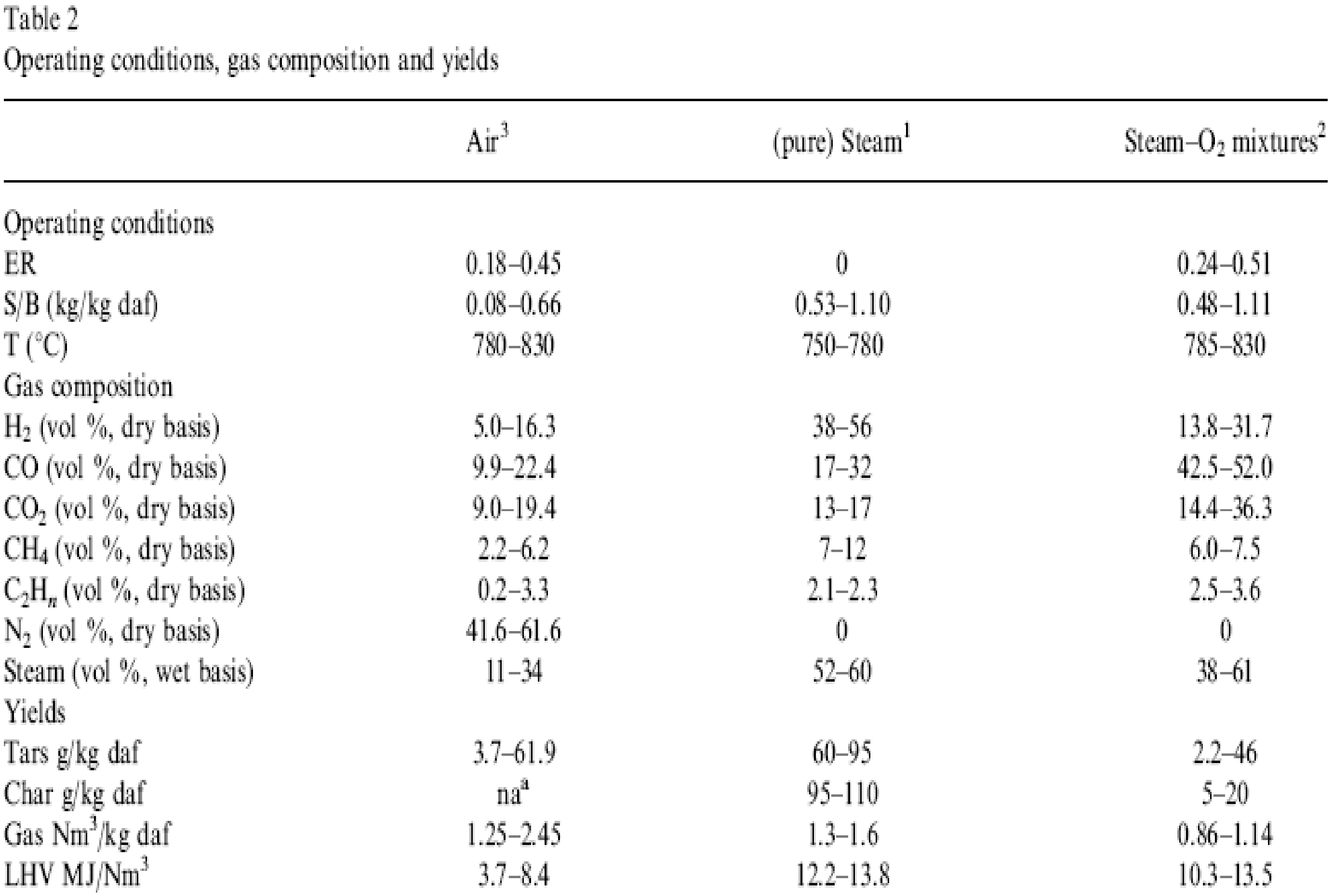
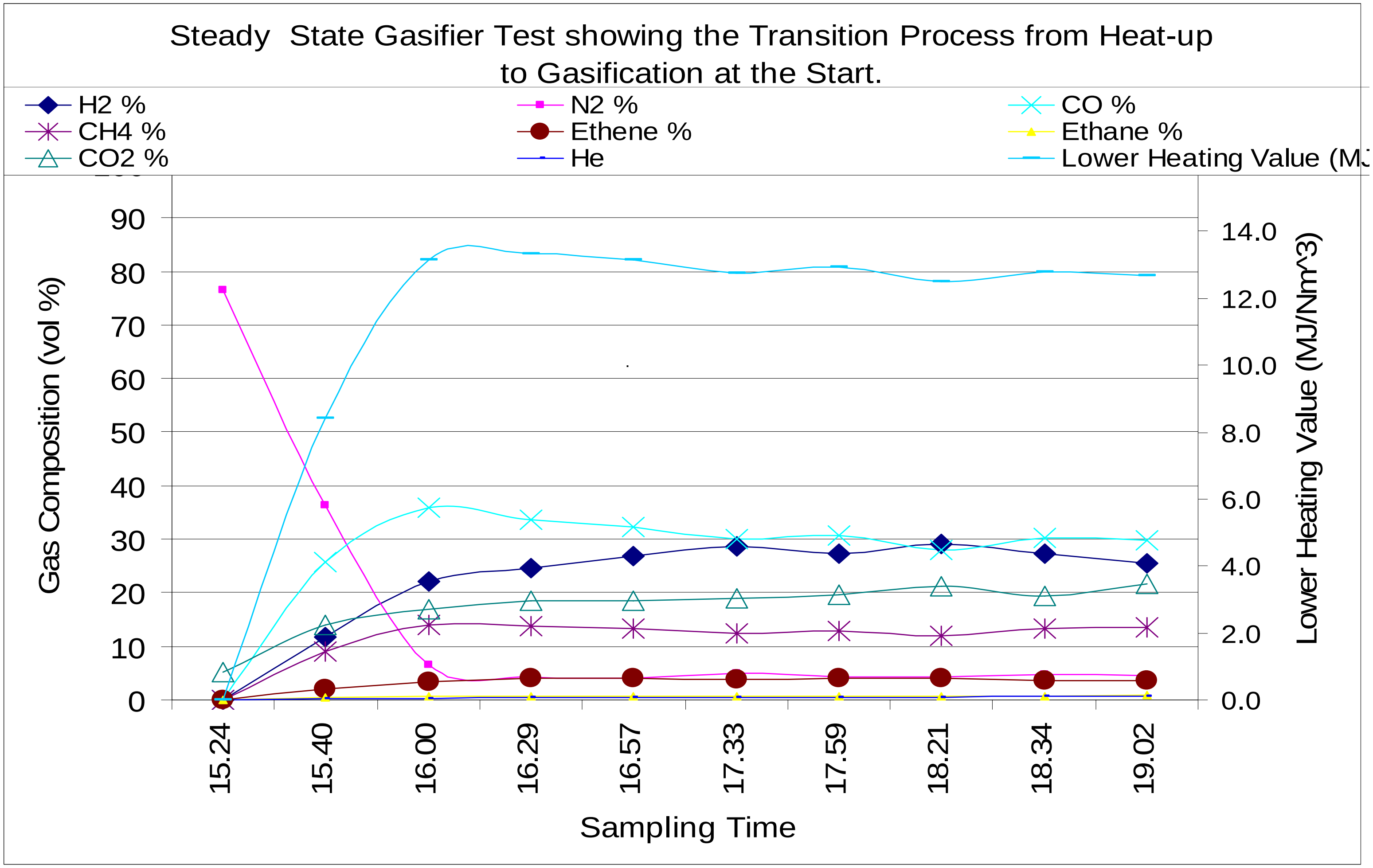


Table 2
Operating conditions, gas composition and yields

	Air[3]	(pure) Steam[1]	Steam–O_2 mixtures[2]
Operating conditions			
ER	0.18–0.45	0	0.24–0.51
S/B (kg/kg daf)	0.08–0.66	0.53–1.10	0.48–1.11
T (°C)	780–830	750–780	785–830
Gas composition			
H_2 (vol %, dry basis)	5.0–16.3	38–56	13.8–31.7
CO (vol %, dry basis)	9.9–22.4	17–32	42.5–52.0
CO_2 (vol %, dry basis)	9.0–19.4	13–17	14.4–36.3
CH_4 (vol %, dry basis)	2.2–6.2	7–12	6.0–7.5
C_2H_n (vol %, dry basis)	0.2–3.3	2.1–2.3	2.5–3.6
N_2 (vol %, dry basis)	41.6–61.6	0	0
Steam (vol %, wet basis)	11–34	52–60	38–61
Yields			
Tars g/kg daf	3.7–61.9	60–95	2.2–46
Char g/kg daf	na[a]	95–110	5–20
Gas Nm^3/kg daf	1.25–2.45	1.3–1.6	0.86–1.14
LHV MJ/Nm^3	3.7–8.4	12.2–13.8	10.3–13.5

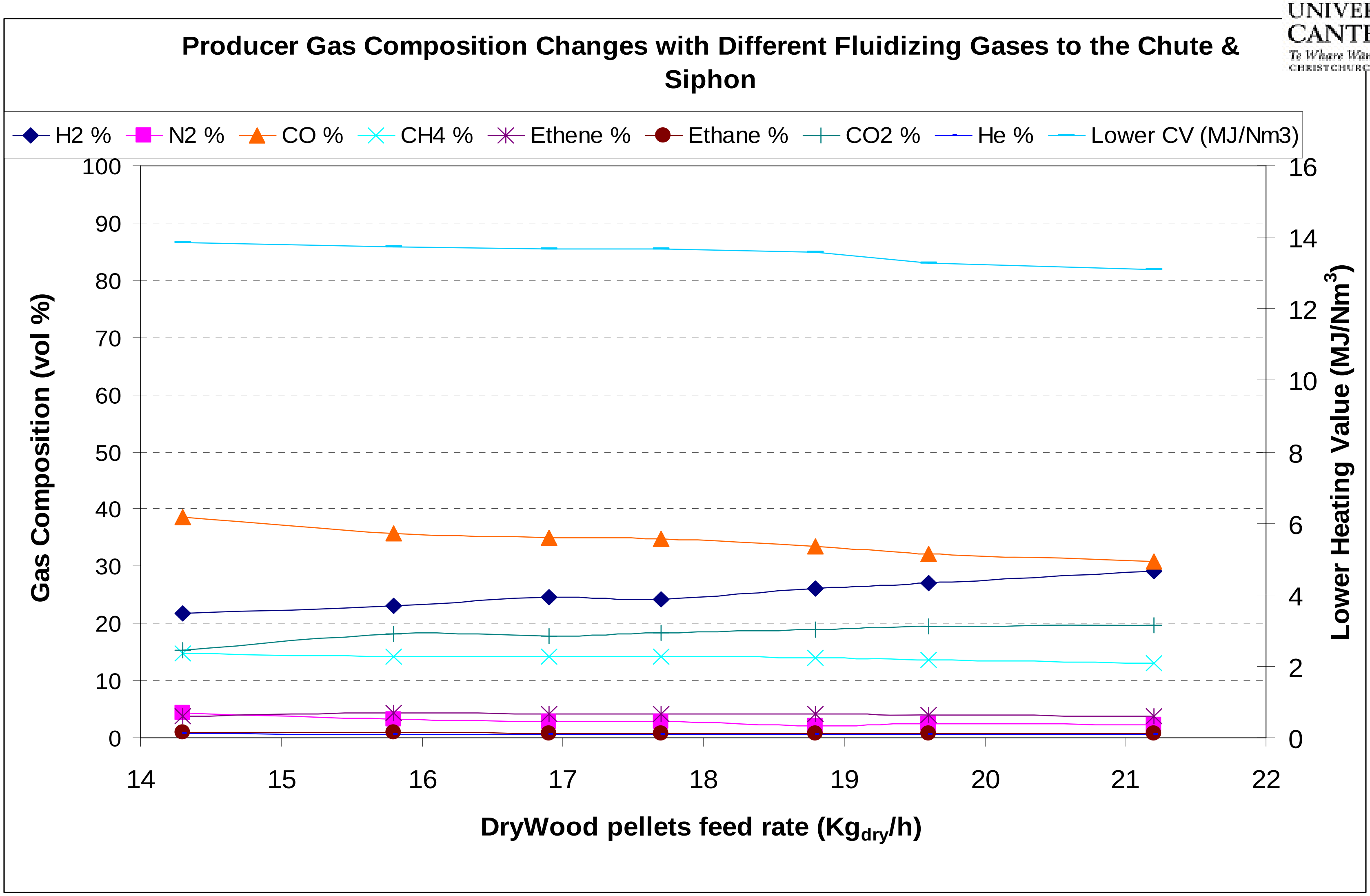
(Gil et al., 1999)

Experimental results from the dual fluidized bed gasifier,UoC

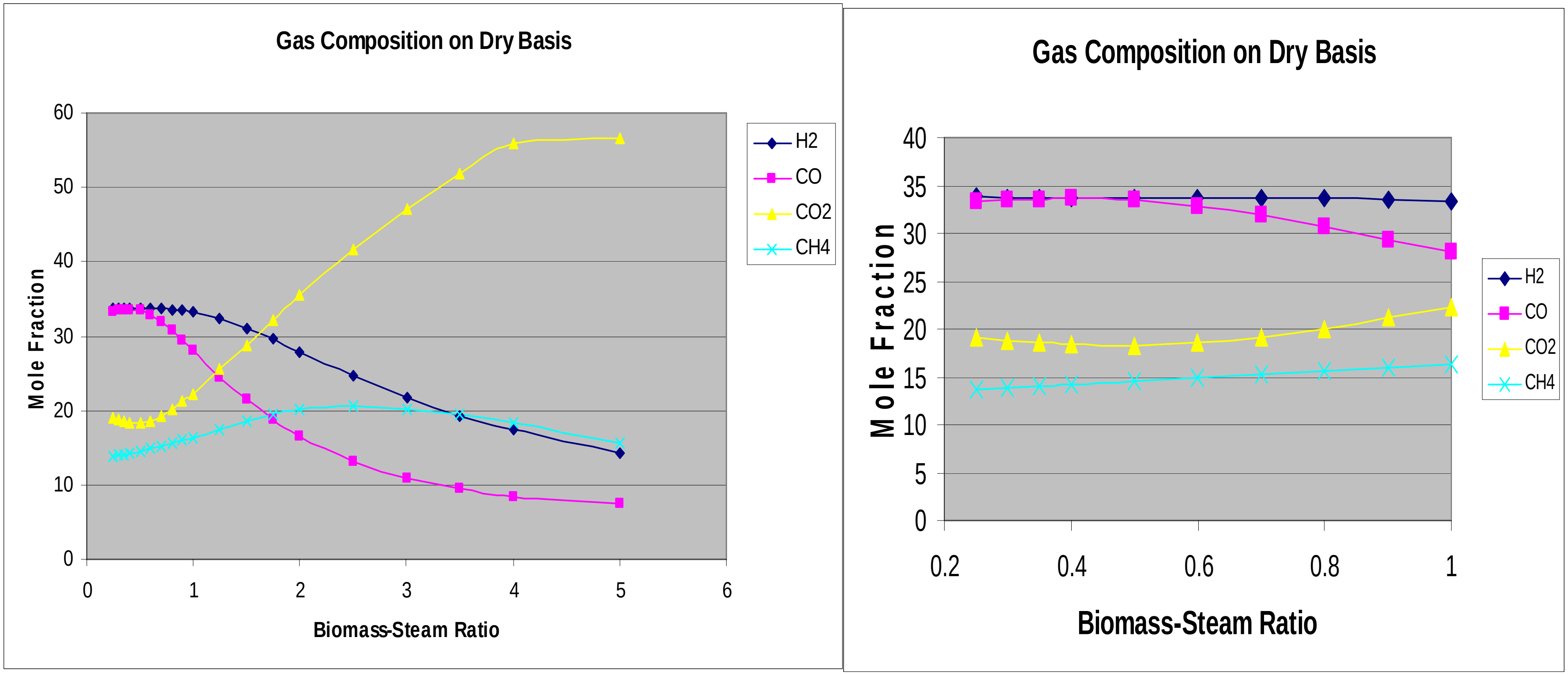


Gasifier run on 03 March 08. Bed material: Sand (12.5kg)

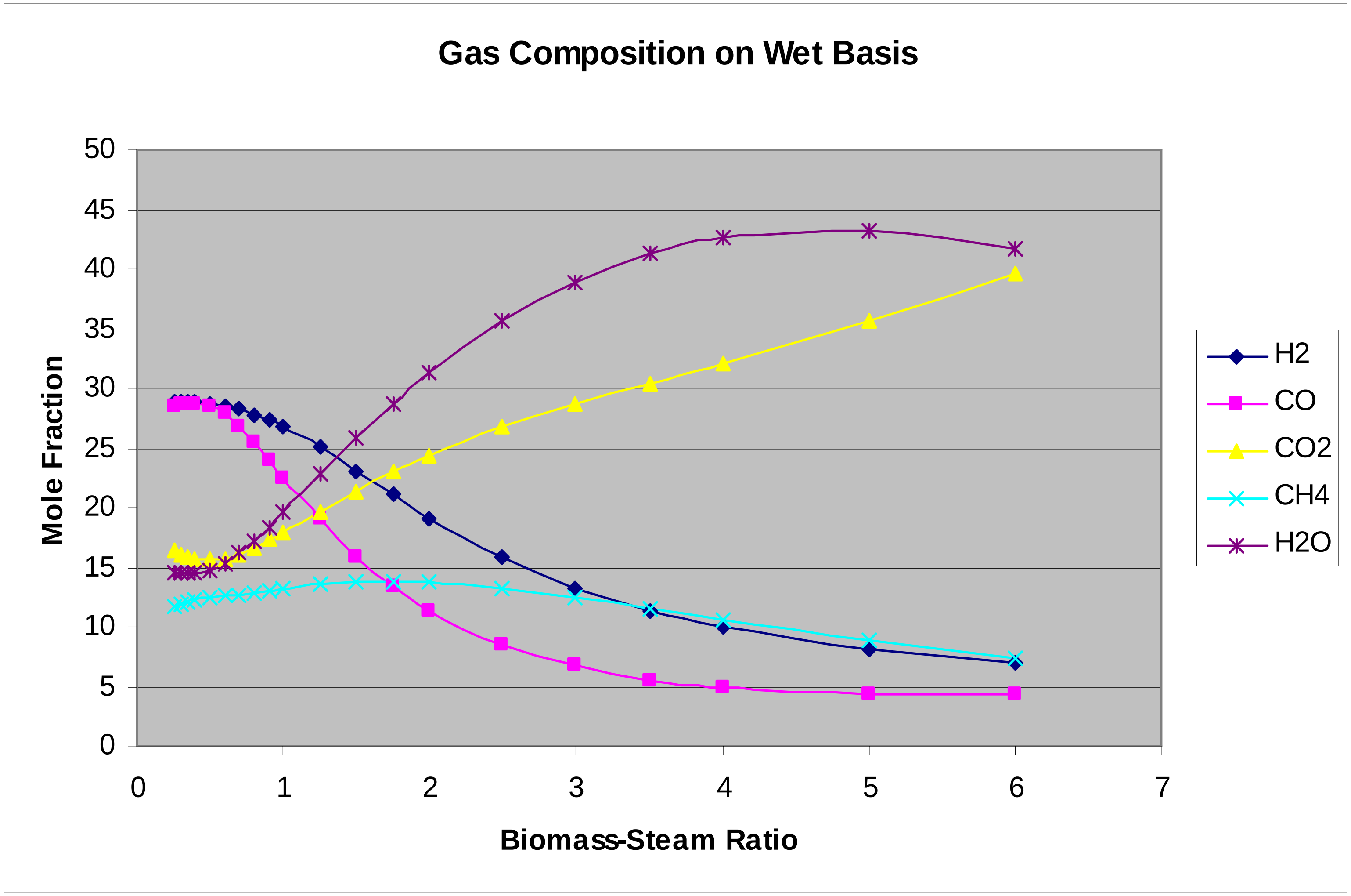
Wood feed rate: 20 kg/hr ; Steam : 6 kg/hr ; S/B=0.3; Bed Temperature: 750 Deg C



Gasifier run: Bed material: Sand (12.5kg); Wood feed rate: 14.2 - 21.25 kg/hr; Steam : 6 kg/hr ; S/B=0.28-0.45; avg bed temperature: 800 Deg C



Effect of Steam to Biomass Ratio when pine is gratified at 800 Deg C


Gas Composition on Wet Basis
Mole Fraction
50
45
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
Biomass-Steam Ratio
H2
CO
CO2
CH4
H2O

Experiment Results from published literature data

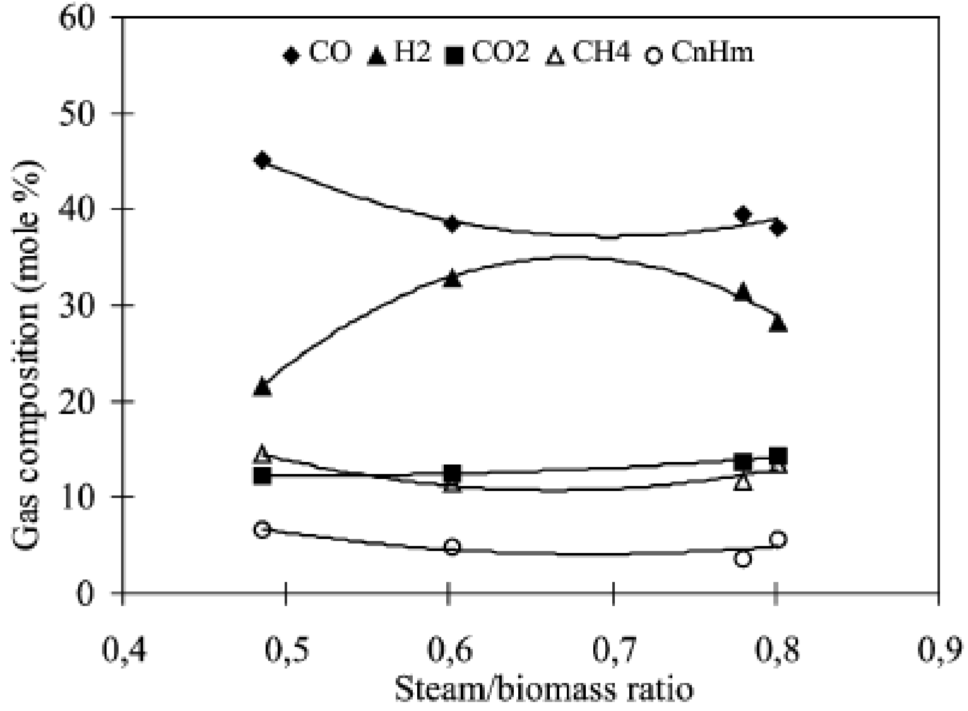


Fig. 7. Effect of steam/biomass ratio (w/w) on gas composition when pine was gasified at 800 °C.

(Franco et al., 2003)

Effects of Temperature and Steam to Biomass Ratio

- Effects of Increase in Temperature
  1. H_2 and CO increased
  2. CO_2 and CH_4 decreased

- Effects of Increase in Steam to Biomass ratio.
  1. CO_2 increased
  2. CO and H_2 decreased
  3. CH_4 insignificant change (remains unchanged)

Extension of the work

- Reaction kinetics of tar and higher hydrocarbon can be included.

- Parameters such as D1 and D2 are the axial dispersion co-efficient for the bubble to emulsion and Emulsion to bubble phase. The values are taken such as D1 constitutes to plug flow and D2 to mixed flow.

- It is recommended to use the diffusion co-efficient of the individual gas components. Finding the appropriate values for the dispersion co-efficient for individual gas components involved in the reactions between the phases, would improve the results.

- Both particle and gas phase void fractions are assumed to be constants. Hence continuity equation along with the momentum equation can be incorporated to the non isothermal reaction kinetics model to evaluate the changes in the void fraction along the length of the gasifier.

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Thank You!

Any Questions???