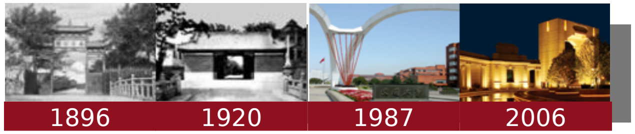

Chemical looping gasification of biomass with Fe_2O_3/CaO : Oxygen carrier activity and process optimization study

Qiang Hu[1], Ye Shen[1,2], Jia Wei Chew[3], Tianshu Ge[4], Chi-Hwa Wang[1,2]*

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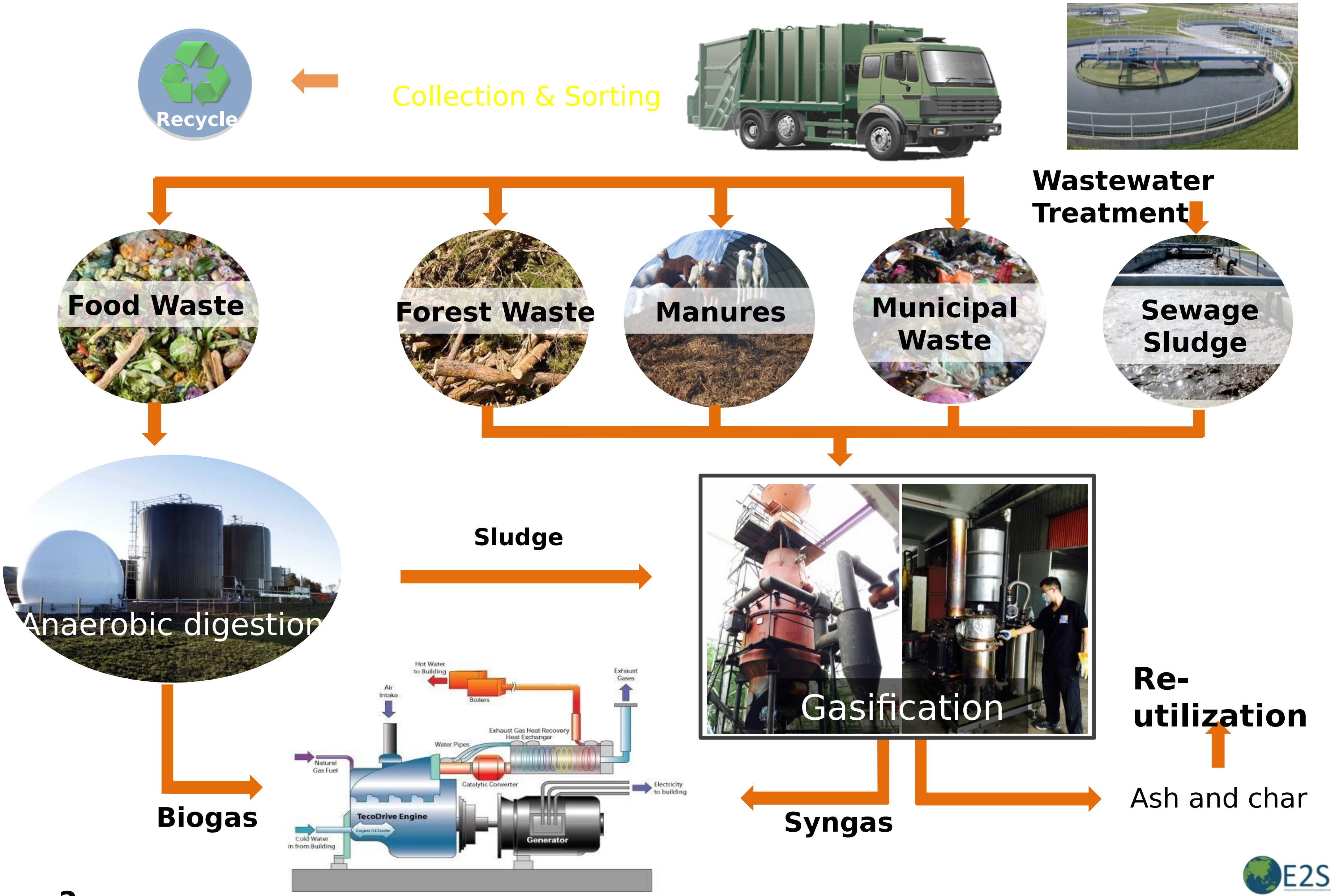
Solid Waste Management Concepts: Waste-to-Energy



Recycle

Collection & Sorting

Wastewater Treatment

Food Waste

Forest Waste

Manures

Municipal Waste

Sewage Sludge

Anaerobic digestion

Sludge

Gasification

Re-utilization

Biogas

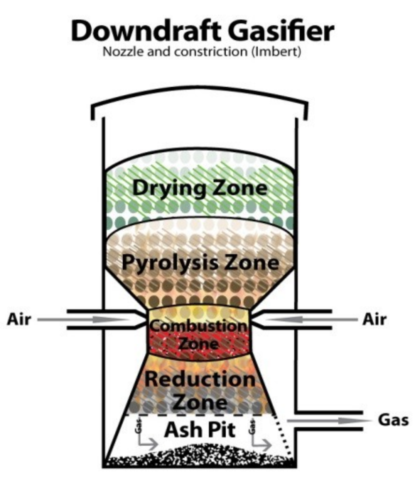
Syngas

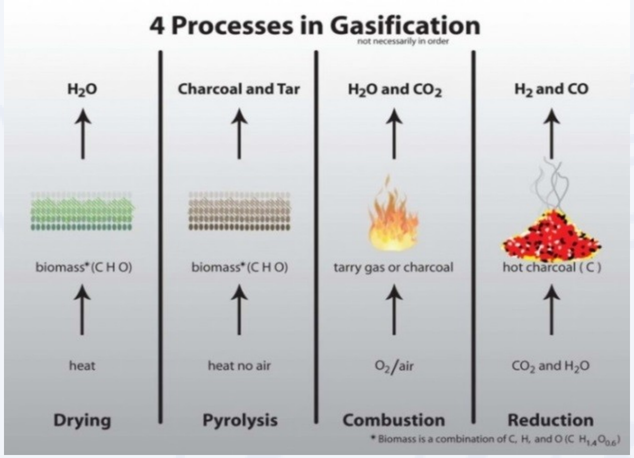
Ash and char

Power Generator

Experimental studies: co-gasification of biomass and solid wastes in a fixed-bed downdraft gasifier.

- 1kg biomass produces about 2 m³ of syngas or 0.75 kWh electricity
- Consumption rate of biomass is about 10 kg/h.

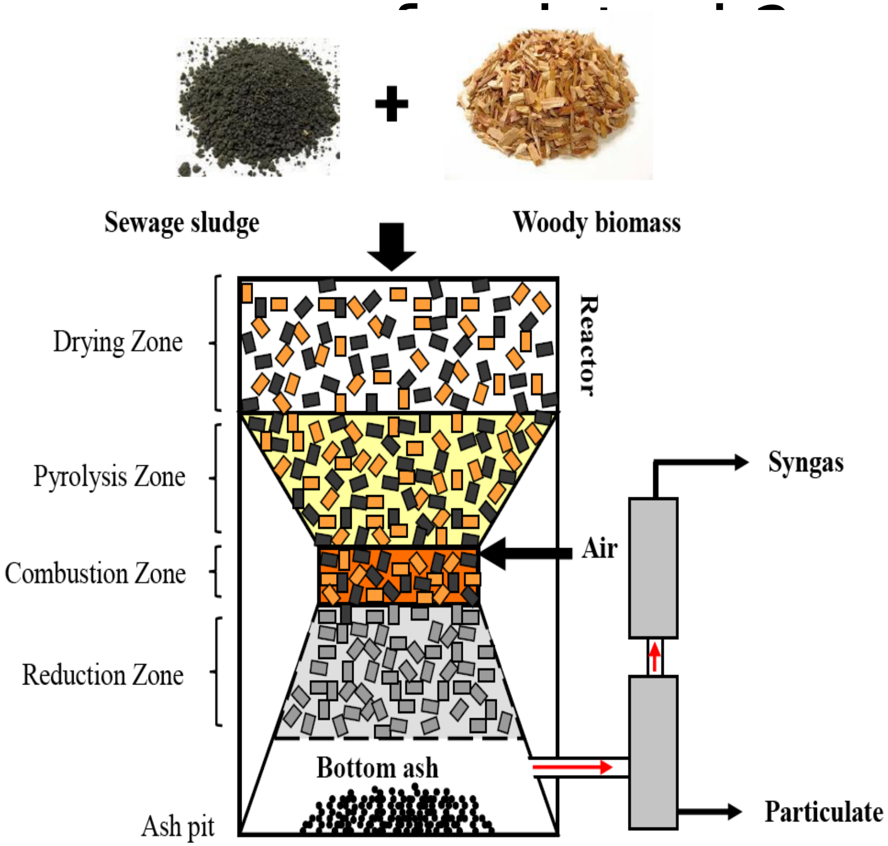




Z. Ong, Y. Cheng, T. Maneerung, Z.Yao, Y. Dai, Y.W. Tong, C.H. Wang," Co-gasification of woody biomass and sewage sludge in a fixed bed downdraft gasifier", ***AIChE Journal*** 61 (2015) 2508-2521.

Co-gasification of **woody biomass** and **sewage sludge**

Sewage sludge as



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Sewage Sludge

- Sewage sludge is unavoidable product from wastewater treatment plant.

- Amount of sewage sludge will increase due to the economic development and increasing populations.

Sewage sludge has less than 10% of Recycling Rate

- Gasification of sewage sludge is regarded as the potential technology, due to the advantages of converting the sludge into combustible gas products

Woody Biomass and sewage sludge as feedstock

ximate, elemental analysis, heating value, and ICP analysis of feedstock mate

* Sewage sludge was collected from wastewater treatment plant, Singapore

Feedstock	**Sewage sludge ***	**Wood chips**
Proximate analysis (dry basis, weight %)		
Moisture	5.8-9.4	8.2-8.5
Volatiles	49.8-51.8	67.8-69.2
Fixed carbon	14.3-15.9	16.2-17.5
Ash	22.8-29.7	6.2-6.3
Elemental analysis (ppm)		
Carbon	33.5-36.42	43.3-44.2
Hydrogen	4.2-5.4	5.4-6.1
Oxygen	24.1-31.5	41.6-42.5
Nitrogen	4.9-5.5	0.9-2.1
Sulfur	1.5-1.9	0.5-1.0
High heating value (MJ/kg)	14.4-15.0	17.0-18.2

Element (ppm)	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Ca**
Sewage Sludge	<0.10	<0.10	<0.10	0.20	2.67	<0.10	<0.10	<0.10	-
Wood chips	-	-	-	<0.10	0.09	<0.10	<0.10	<0.10	3.8

Co-gasification of **woody biomass** and **sewage sludge**

Effect of feed stock composition on gas

Feed stocks		Pure wood chips	10% sludge-mixed wood chips	20% sludge-mixed wood chips [a]	33% sludge-mixed wood chips
Gas composition (vol. %)	CO	16.9	15.9	15.6	12.0
	H_2	17.3	17.1	16.8	13.4
	CH_4	1.7	2.0	2.1	1.8
	CO_2	11.9	12.2	12.7	12.5
	O_2	2.3	1.7	1.0	3.4
	Total	50.1	48.9	48.2	43.1
Lower heating value (MJ/Nm^3)		4.7	4.6	4.5	3.6

20-40 vol.% syngas*

[a] Optimum composition of sewage sludge and wood chips for co-gasification

* 70-80 % biomass conversion

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Formation of Agglomerated Ash

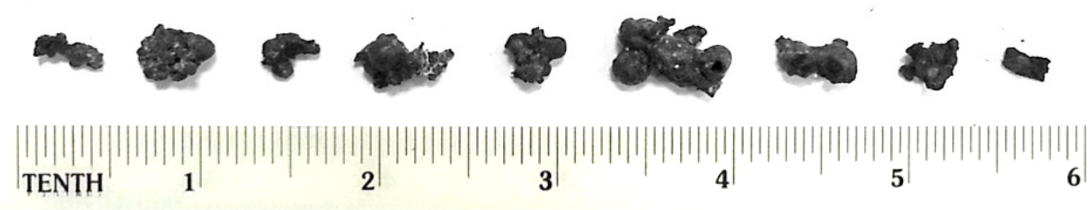
(co-gasification of woody biomass and sewage sludge)

- ❑ Agglomerated ash was found in bottom ash after adding sewage sludge in feedstock
- ❑ Particle size is increased with increasing of sewage sludge content in the feedstock.

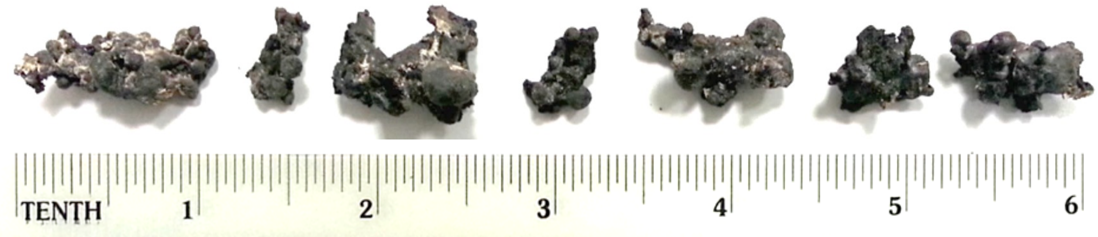
Pure woody biomass

33 wt. % sewage sludge

10 wt. % sewage sludge mixed with 90 wt. % woody biomass



20 wt. % sewage sludge mixed with 80 wt. % woody biomass



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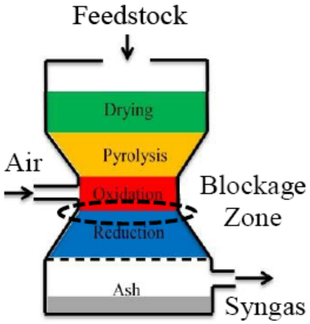
Co-gasification of **woody biomass** and **sewage sludge**

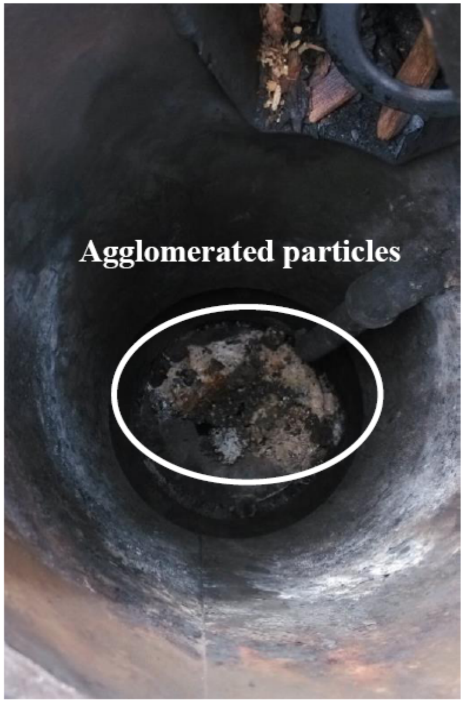
Blockage of gasifier during co-gasification of 33 wt.% sludge-mixed wood

Pure Wood Chips

33 wt. % Sludge

Formation of agglomerated ash during co-gasification of 33 wt. % sludge leads to the blockage of the reactor at the initial stage of reduction zone





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Co-gasification of woody biomass with manure and food waste

Horse Manure

Chicken Manure

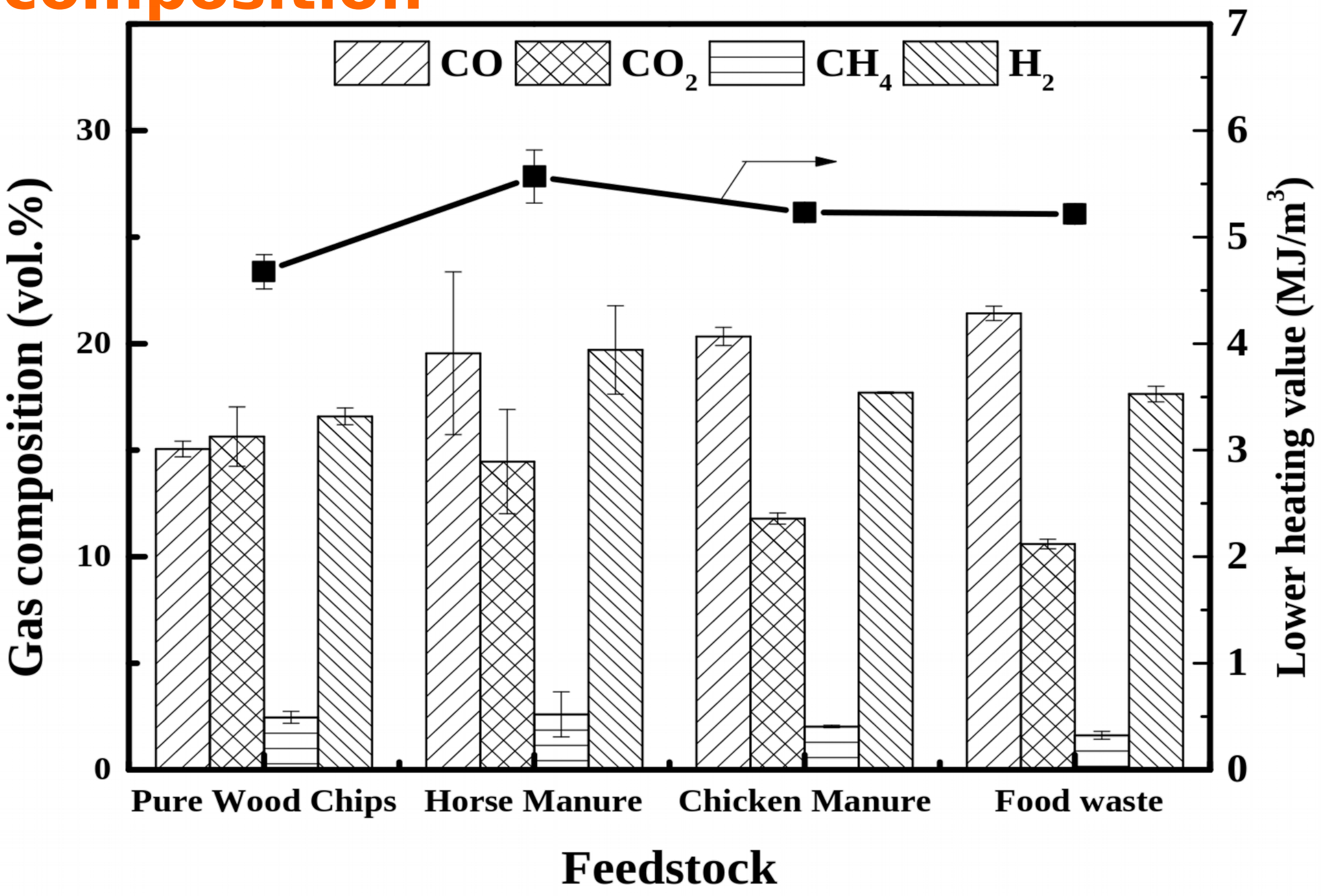
Food Waste

Proximate, elemental analysis and heating value of feeds

Feedstock	Horse manure	Chicken manure	Food waste
Proximate analysis (dried based%)			
Moisture	75.7 (as received)	73.6 (as received)	7.8
Volatile	64.8	61.4	75.2
Fixed Carbon	10.0	10.5	14.5
Ash	25.1	28.1	2.5
Elemental analysis (%)			
Carbon	37.3	28.2	47.71
Hydrogen	5.1	3.5	7.07
Nitrogen	2.0	4.3	2.27
Sulfur	<0.5	0.8	0.55
High Heating Value(MJ/kg	12.8	7.3	20.82

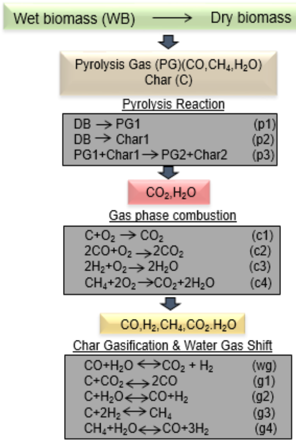
Co-gasification of woody biomass with manure and food waste

Effect of feed stock composition on gas composition



70% of woodchips, 30% of horse manure, chicken manure or food wast

1-D kinetic model and 3-D CFD model



Wet biomass (WB) ⟶ Dry biomass (DB)

Pyrolysis Gas (PG)(CO,CH_4,H_2O)
Char (C)

Pyrolysis Reaction

DB → PG1	(p1)
DB → Char1	(p2)
PG1+Char1 → PG2+Char2	(p3)

CO_2,H_2O

Gas phase combustion

$C+O_2 \rightarrow CO_2$	(c1)
$2CO+O_2 \rightarrow 2CO_2$	(c2)
$2H_2+O_2 \rightarrow 2H_2O$	(c3)
$CH_4+2O_2 \rightarrow CO_2+2H_2O$	(c4)

CO,H_2,CH_4,CO_2,H_2O

Char Gasification & Water Gas Shift

$CO+H_2O \leftrightarrow CO_2 + H_2$	(wg)
$C+CO_2 \leftrightarrow 2CO$	(g1)
$C+H_2O \leftrightarrow CO+H_2$	(g2)
$C+2H_2 \leftrightarrow CH_4$	(g3)
$CH_4+H_2O \leftrightarrow CO+3H_2$	(g4)

1-D chemical reaction kinetics model

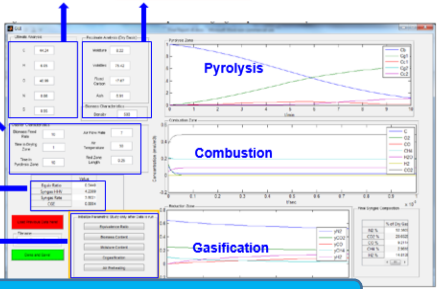
- Fill in biomass ultimate analysis
- Ensure they are in % format

- Fill in biomass proximate analysis
- Ensure they are in % format

- Enter gasifier characteristics

- Equivalence ratio for the run as well as other efficiency measures are also displayed

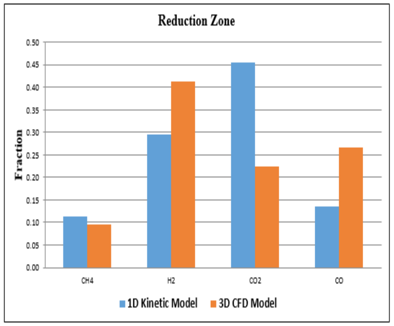
- Display different kinds of results



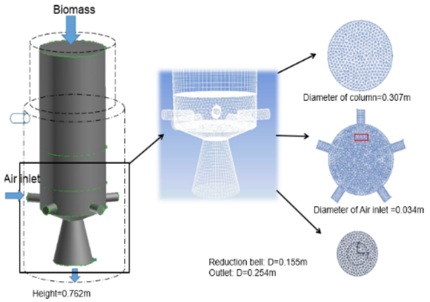
Graphical User Interface (GUI) in Matlab

Downdraft Gasifier Capability of 216 kg biomass /day

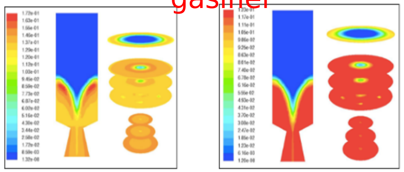
Comparison between 1-D kinetic and 3-D CFD models



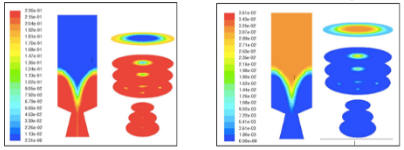
3-D computational fluid dynamic (CFD) model



concentration of various gas components in the gasifier



Mole fraction of CO
Mole fraction of CO_2



Mole fraction of H_2
Mole fraction of O_2

1-D kinetic model

Energy Balance

mass balance

$$n_x(z)Av(z) = n_x(z+\Delta z)Av(z+\Delta z) + R_x A\Delta z \longrightarrow \boxed{\frac{dn_x}{dz} = \frac{1}{v}\left(R_x - n_x\frac{dv}{dz}\right)} \quad \textbf{eq1}$$

energy balance

$$A\left(\sum_x n_x c_x T\right)_{z+\Delta z} - v_z A\left(\sum_x n_x c_x\right)_z = \sum_x r_i \Delta H_i \Delta z - (PAv)$$

$$\Downarrow$$

$$\boxed{\frac{dT}{dz} = \frac{1}{v\sum_x n_x c_x}\left(-\sum_x r_i\Delta H_i - v\frac{dP}{dz} - P\frac{dv}{dz} - \sum_x R_x c_x T\right)} \quad \textbf{eq2}$$

pressure gradience (empirical formula)

$$\boxed{\frac{dP}{dz} = 1183\left(\rho_{gas}\frac{v^2}{\rho_{air}}\right) + 388.19v - 79.896} \quad \textbf{eq3}$$

velocity gradience (by manipulating equation1,2,3)

$$\boxed{\frac{dv}{dz} = \frac{1}{\sum_x n_x c_x + nR}\left[-\sum_x \frac{\sum_x n_x c_x \sum_x R_x}{n} - \frac{\sum_x r_i \Delta H_i}{T} - \frac{dP}{dz}\left(\frac{v}{T} + \frac{v\sum_x n_x c_x}{P}\right) - \sum_x R_x c_x\right]} \quad \textbf{eq4}$$

Graphical User Interface (GUI) in Matlab

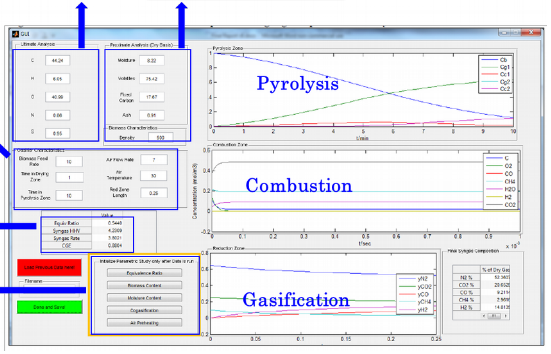
- Fill in biomass ultimate analysis
- Ensure they are in % format

- Fill in biomass proximate analysis
- Ensure they are in % format

- Enter gasifier characteristics

- Equivalence ratio for the run as well as other efficiency measures are also displayed

- Display different kinds of results



GUI

Ultimate Analysis
C 44.24
H 6.05
O 40.99
N 0.86
S 0.95

Proximate Analysis (Dry Basis)
Moisture 8.22
Volatiles 75.42
Fixed Carbon 17.67
Ash 6.91

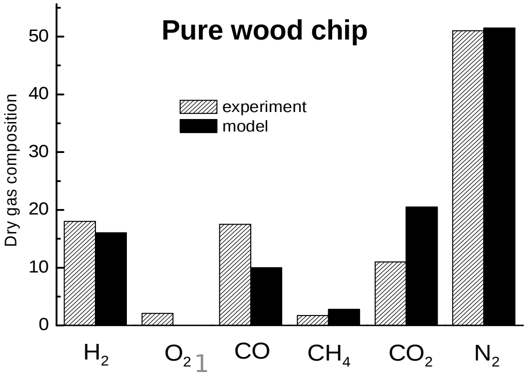
Biomass Characteristics
Density 500

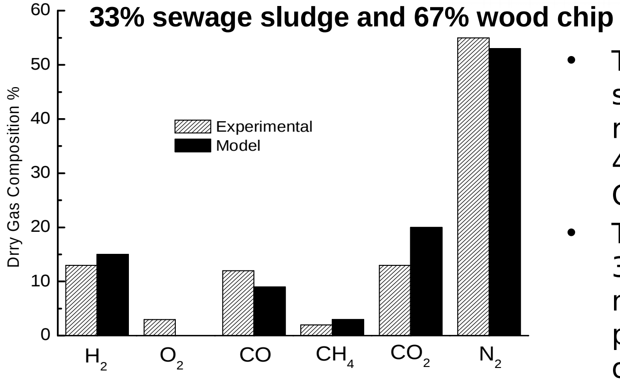
Gasifier Characteristics
Biomass Feed Rate 10
Time in Drying Zone 1
Time in Pyrolysis Zone 10
Air Flow Rate 7
Air Temperature 30
Red Zone Length 0.25

	Value
Equiv Ratio	0.5440
Syngas HHV	4.2309
Syngas Rate	3.8021
CGE	0.8004

Final Syngas Composition

	% of Dry Gas
N2 %	52.3607
CO2 %	20.6520
CO %	9.2114
CH4 %	2.9016
H2 %	14.8135



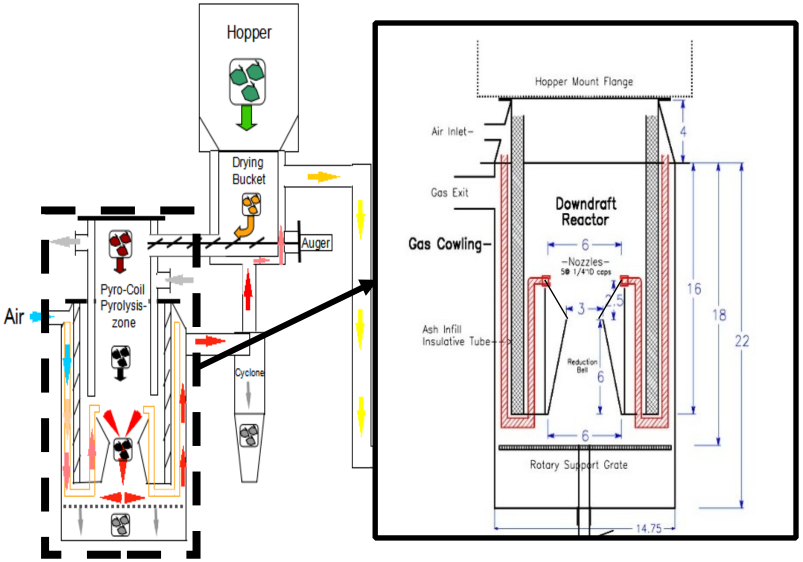


- The model does quite well in predicting syngas compositions of wood chips , registering differences of only around 2% to 4%, a more significant over-prediction of CO_2 and under-prediction of CO .
- The predictions for the co-gasification of a 33% sewage sludge and 67% wood chips mixture are quite accurate, with the largest percentage difference coming from the over-prediction of CO_2 of 6.57%.

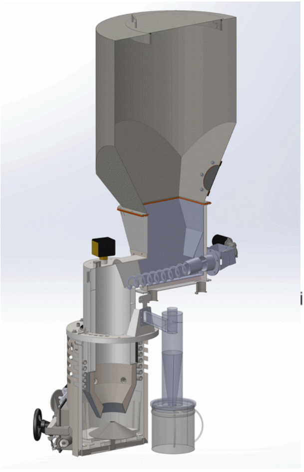
Z. Ong, YP Cheng, T. Maneerung, Z. Yao, Y. Dai, Y.W. Tong, C.H. Wang, “Co-gasification of woody biomass and sewage sludge in a fixed-bed downdraft gasifier”, AIChE Journal, 61, 2508-2521 (2015).

3-D CFD model

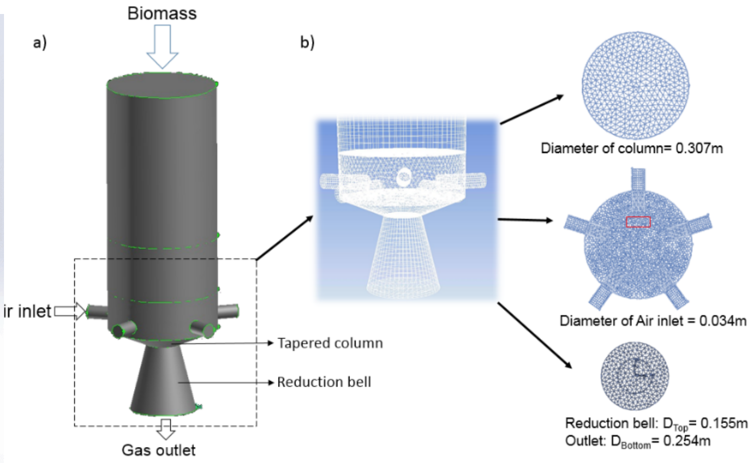
Schematic Diagram of downdraft gasifier



Cross section of gasification unit



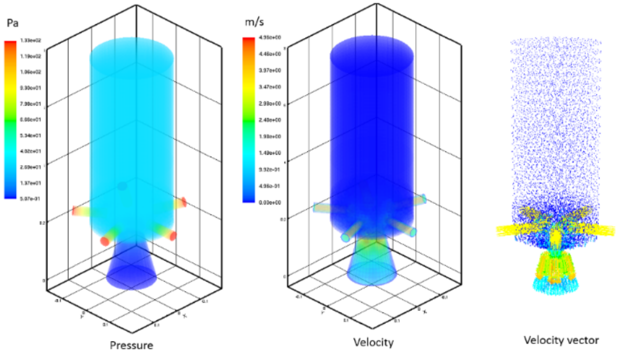
Geometry and mesh



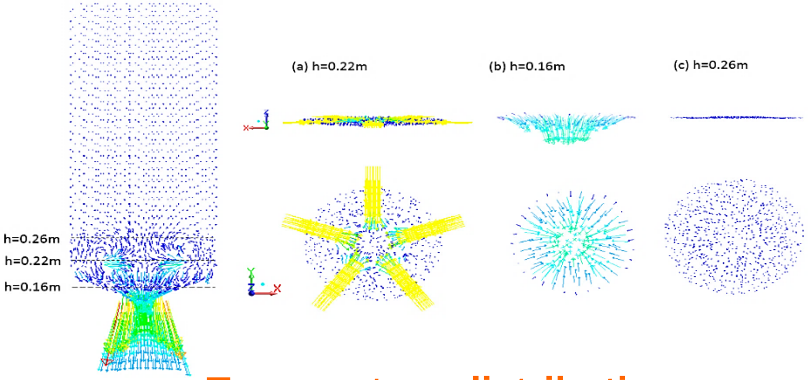
W.C. Yan, Y. Shen, S. You, S.H. Sim, Z.H. Luo, Y.W. Tong, C.H. Wang, "Model-Based Downdraft Biomass Gasifier Operation and Design for Synthetic Gas Production", J. Cleaner Production, 178, 476-493 (2018).

3-D CFD model

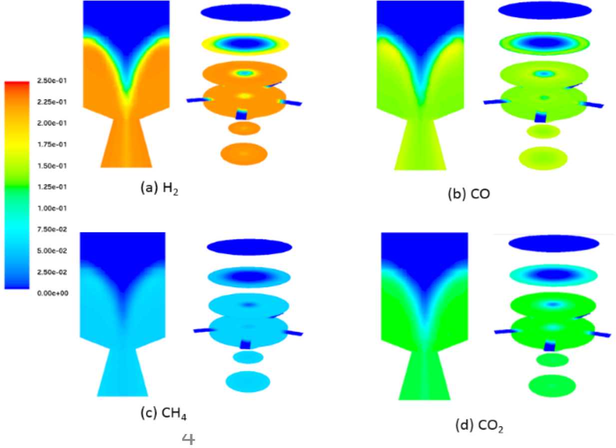
Flow field distributions



Pressure Velocity Velocity vector



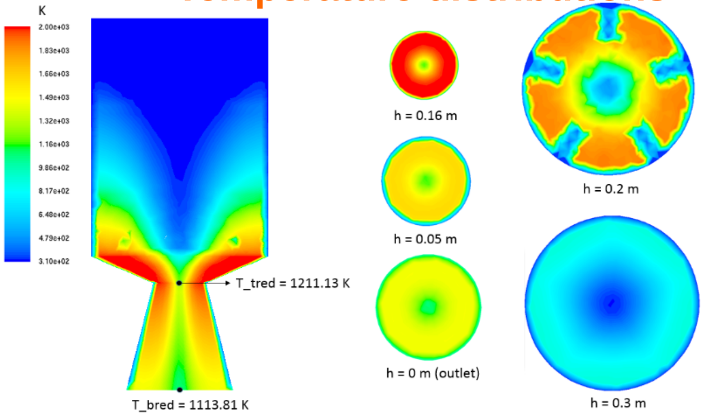
Gas composition distributions



(a) H_2 (b) CO

(c) CH_4 (d) CO_2

Temperature distributions



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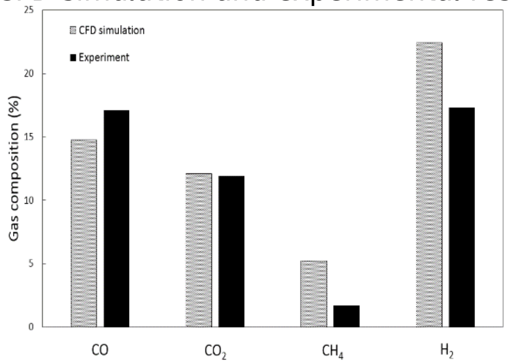
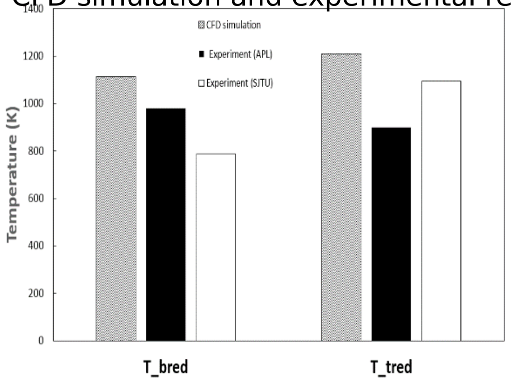
3-D CFD model

Comparison of gas composition between CFD simulation and experimental results.

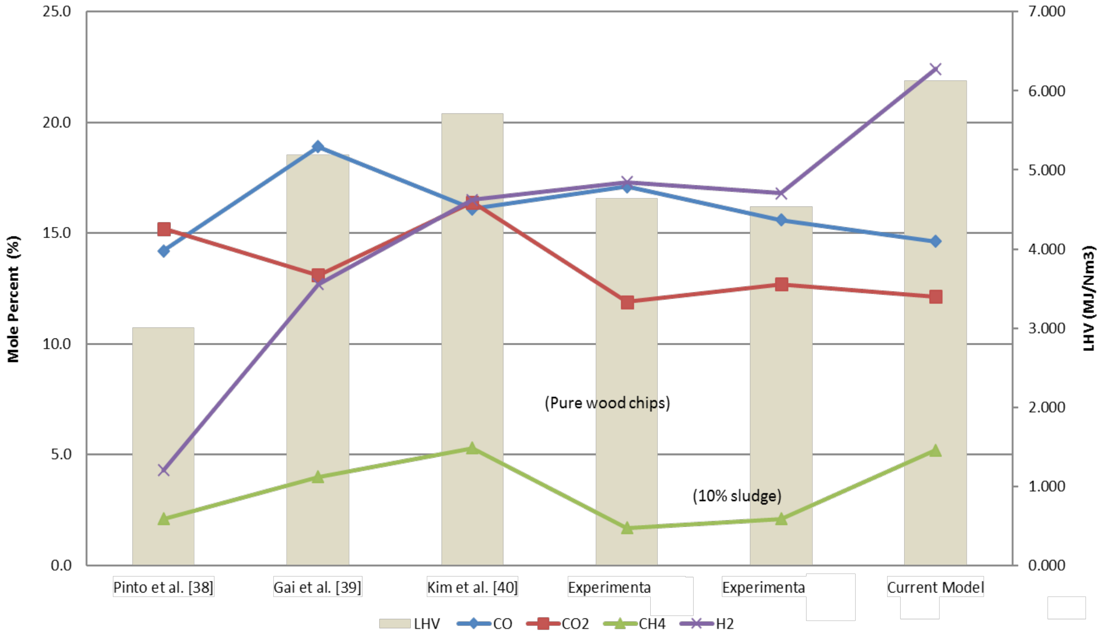


Comparison of temperature profile between CFD simulation and experimental results.



T_bred: Temperature at bottom of reduction bell
T_tred: Temperature at top of reduction bell

Comparison of both experimental and simulation data with others

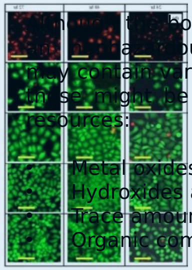


References:
[38] Pinto F.et al., *Energy Fuel 22*, pp. 2314-2325, 2008;
[39] Gai C. et al., *Int. J. Hydrogen Energy 37*, pp. 4935-4944, 2012.;
[40]Kim Y.D. et al., *Appl. Energy 112*, pp. 414-420, 2013.

Z. Ong, YP Cheng, T. Maneerung, Z. Yao, Y. Dai, Y.W. Tong, C.H. Wang, “Co-gasification of woody biomass and sewage
sludge in a fixed-bed downdraft gasifier”, AIChE Journal, 61, 2508-2521 (2015).

Re-utilization of solid residues from gasification and incineration

Solid Residues



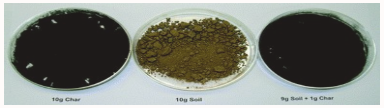
Although the bottom ash is classified as an non-hazardous waste, bottom ash may contain various harmful compounds these might be leached out into water resources:

- Metal oxides
- Hydroxides and alkali salts
- Trace amounts of heavy metals
- Organic compounds

Bottom ash is one of the harmful inorganic residues arising from gasification process. In view of economic and environmental implications, the proper disposal and utilization of bottom ash with emphasis on finding new applications is necessary.

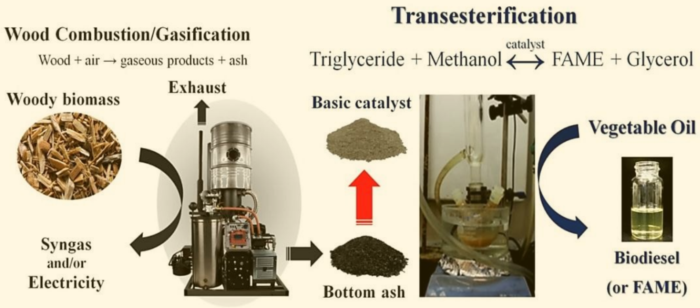
Char/ash for agricultural applications

Char is a carbon-rich substance, which can be further mixed with soil and used as a Biochar



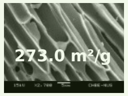
Bottom ash as a source of catalytic materials

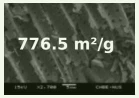
CaO catalyst was successfully developed from gasification bottom ash and has high activity towards transesterification for biodiesel production.

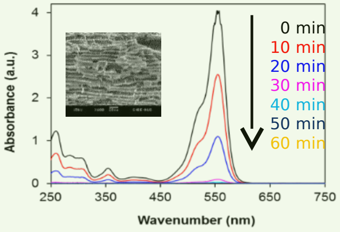


Char as a source of activated carbon

Activated carbon was successfully developed from char and was effectively used for dye removal.

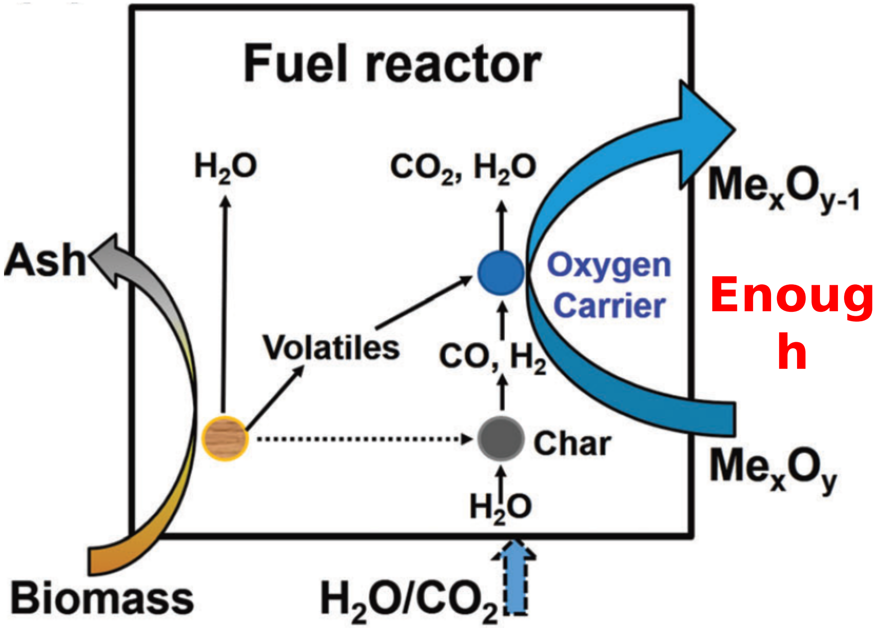


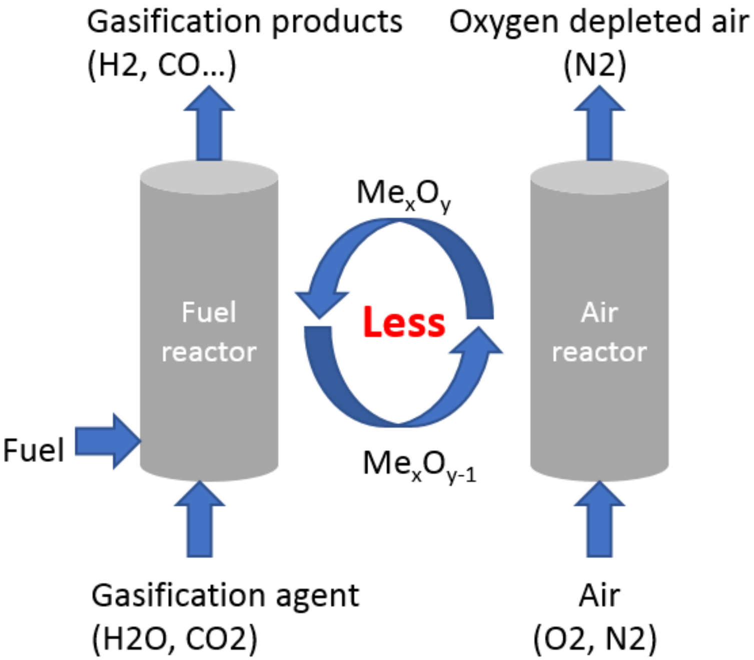




◄ Dye removal using AC developed from char

Chemical looping process





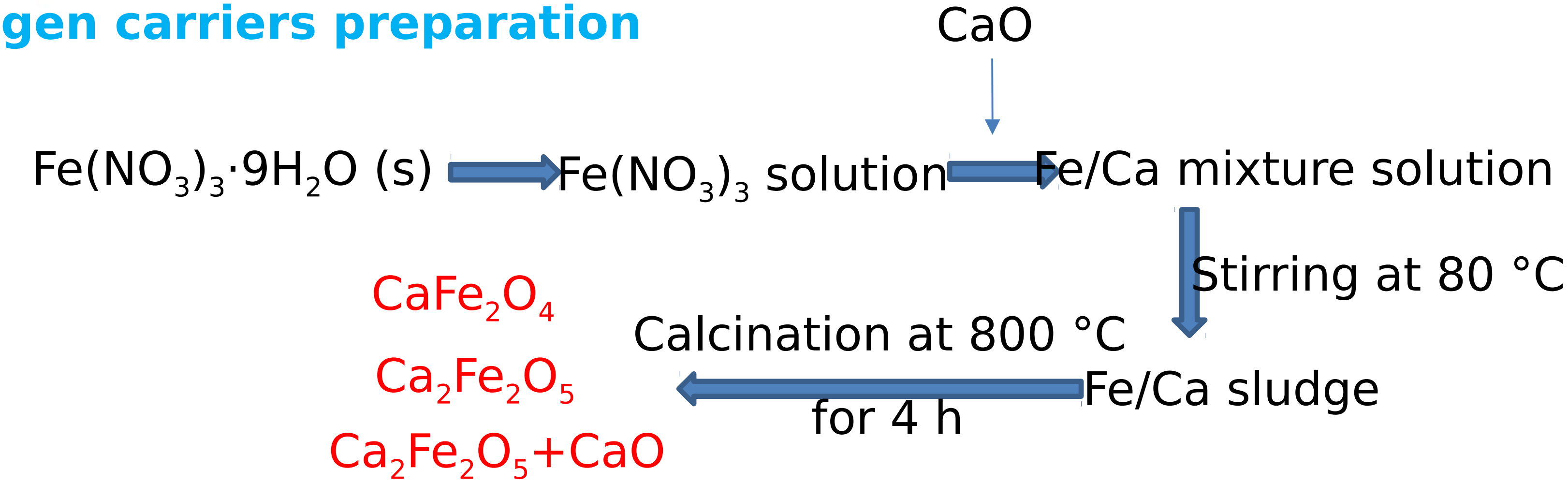
hemical looping combustion VS Chemical looping gasificat

- ➢ Conversion waste to energy
- ➢ Energy saving by OC circulation
- ➢ Promote hydrogen production
- ➢ Less tar generation

Energy & Environmental Science, 2017, 10(9): 1885-1910.
Progress in Energy and Combustion Science, 2018(65):6-66.

Materials and methods

Oxygen carriers preparation



CaO

$Fe(NO_3)_3·9H_2O$ (s) → $Fe(NO_3)_3$ solution → Fe/Ca mixture solution

Stirring at 80 °C

Fe/Ca sludge

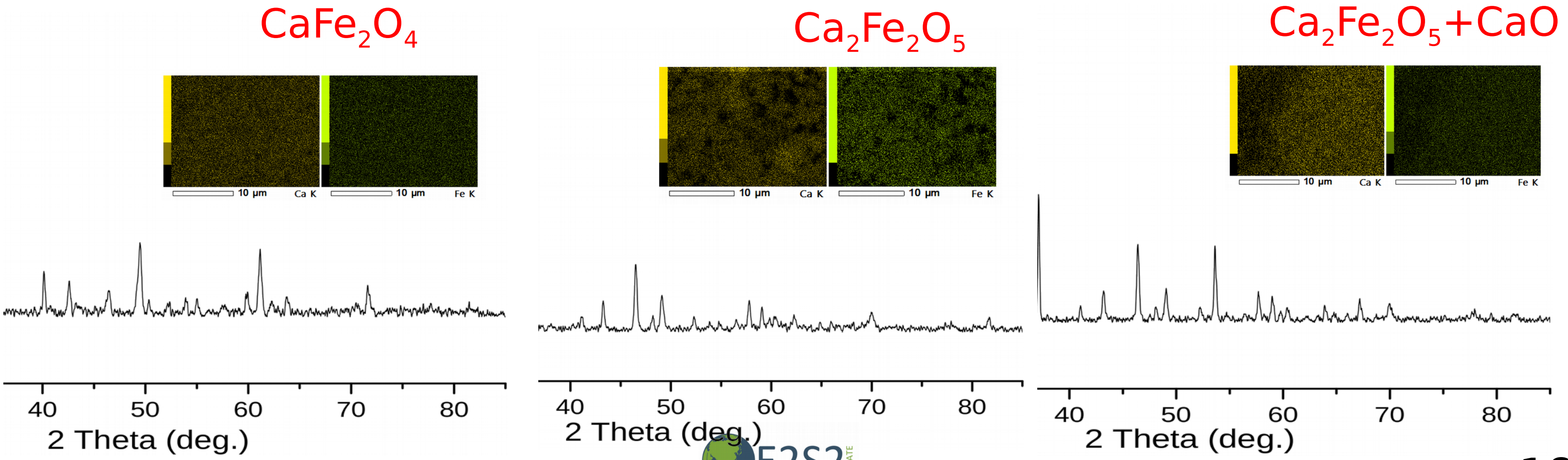
Calcination at 800 °C for 4 h

$CaFe_2O_4$

$Ca_2Fe_2O_5$

$Ca_2Fe_2O_5$+CaO

XRD Results



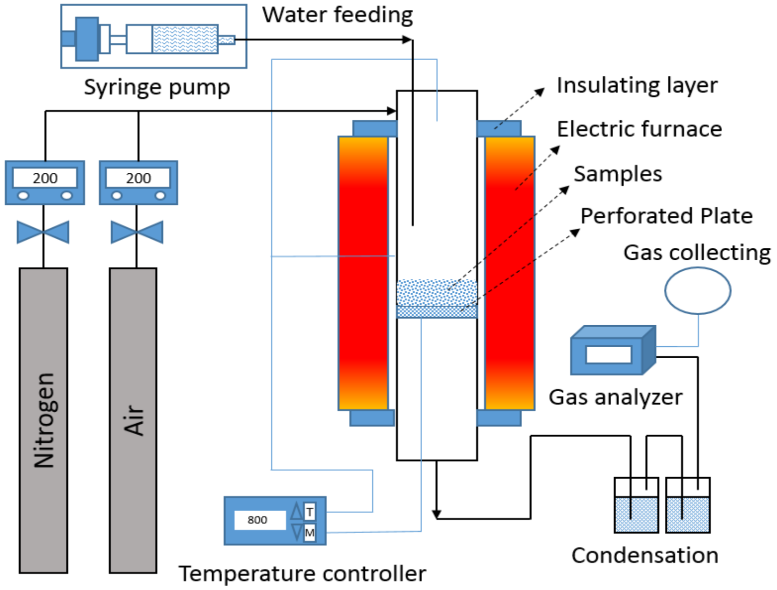
$CaFe_2O_4$

$Ca_2Fe_2O_5$

$Ca_2Fe_2O_5$+CaO

Materials and methods

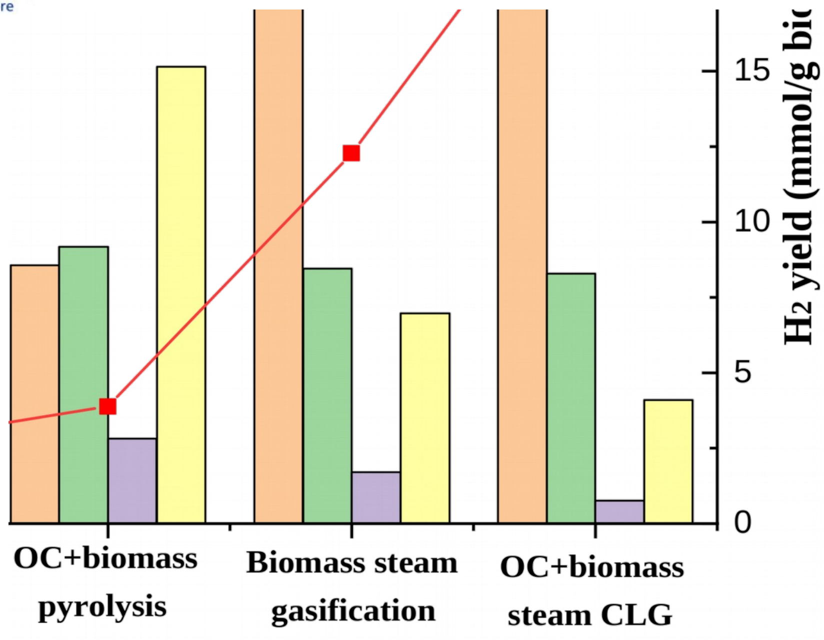
Sample	Properties					
Rice straw	Proximate analysis, dry, wt. %					
	Ash	Volatile		Fixed carbon		
	10.86	76.84		12.30		
	Ultimate analysis, dry, wt. %					
	C	H	N	S	O (by difference)	
	43.08	6.63	0.65	0.21	38.56	
	Ash composition ^{a}, wt. %					
	Si	K	Cl	Mg	Na	O
	44.91	25.72	11.32	0.85	0.41	16.79

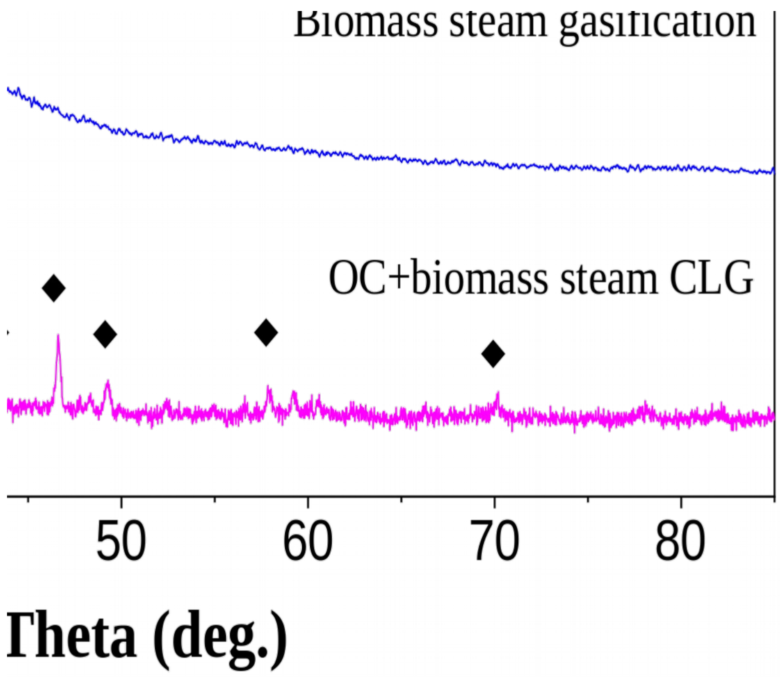


General H_2 concentration:
Air gasification: 10-20%
CO_2 gasification: 15-25%
H_2O gasification: 35-45%

CLG of rice straw with different OCs:
800 °C, 0.1 g/min steam feeding, 30 m

Results 1 – Effect of oxygen carrier





Effect of OC and steam on syngas properties *(Fe:Ca=1:1)*

XRD patterns for solid residues after gasification

- *H_2 yield and heating value of syngas was enhanced by both steam and OC.*
- *The introduction of OC promoted the carbon conversion due to the possible catalytic effect of Ca/Fe.*

One step redox of $Ca_2Fe_2O_5$:

$$Ca_2Fe_2O_5 + 3H_2 \rightarrow 2CaO + 2Fe + 3H_2O$$

$$Ca_2Fe_2O_5 + 3CO \rightarrow 2CaO + 2Fe + 3CO_2$$

$$2CaO + 2Fe + 3H_2O \rightarrow Ca_2Fe_2O_5 + 3H_2$$

Results 1 – Effect of oxygen carrier

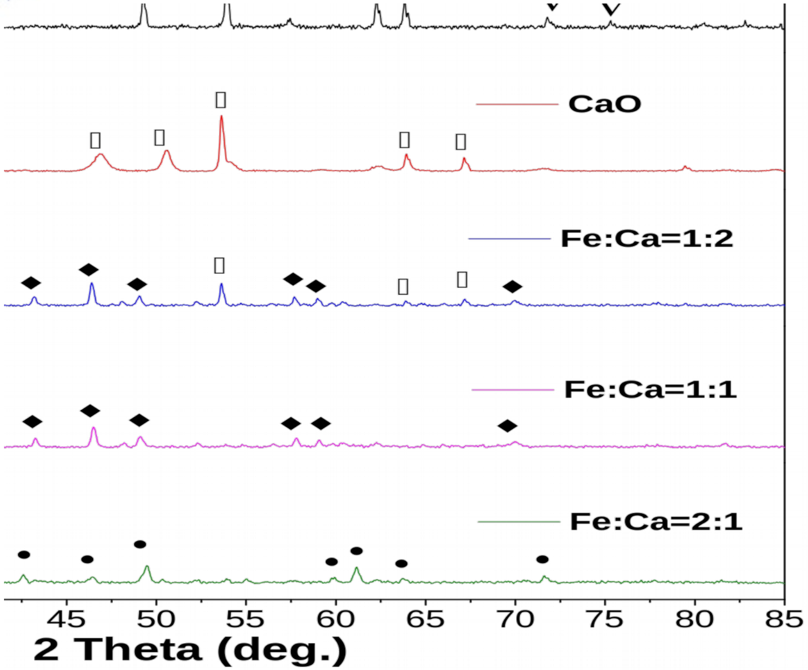
Gas yields under chemical looping gasification with different OCs

	Fe_2O_3	CaO	Fe:Ca=1:2	Fe:Ca=1:1	Fe:Ca=2:1
H2 yield (mmol/g biomass)	20.84	19.94	21.79	23.07	20.42
Carbon yield in syngas (%)	35.70	47.18	42.34	40.95	38.07
Mass balance (%)	93.20	94.55	98.83	96.97	100.13
Syngas heating value (kJ/g biomass)	7.71	8.23	8.22	8.46	7.52
Gas content (%)					
H_2	61.96	54.45	59.29	63.20	60.31
CO_2	23.81	27.32	26.65	23.21	26.85
CH_4	2.00	2.91	2.39	2.11	2.20
CO	12.24	15.32	11.67	11.48	10.64

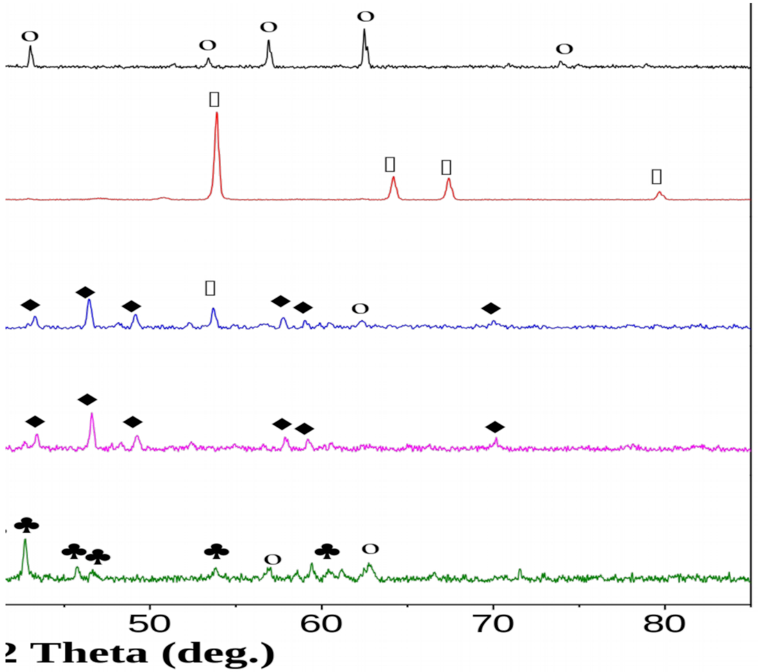
- *Carbon yield in syngas was promoted with more Ca due to the catalytic volatile cracking.*
- *The ratio of 1:1 for Fe:Ca ($Ca_2Fe_2O_5$) is the optimal for hydrogen production and CLG.*

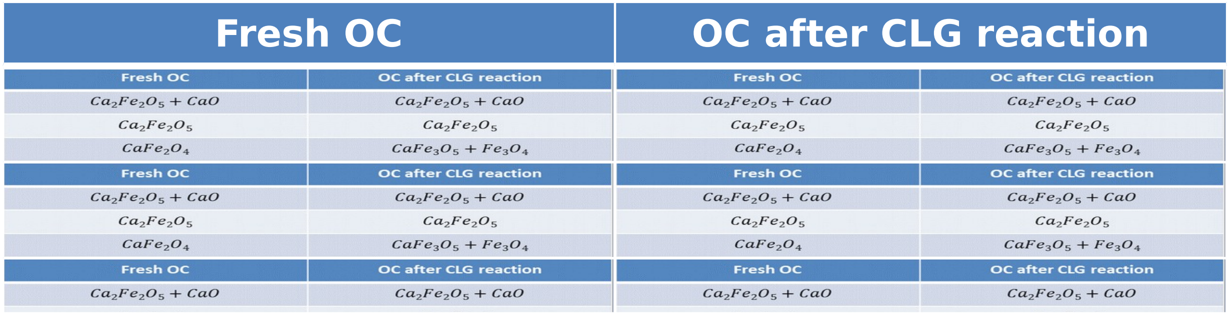
Results 1 – Effect of oxygen carrier

Fresh OCs



Reacted OCs





Fresh OC		OC after CLG reaction	
Fresh OC	OC after CLG reaction	Fresh OC	OC after CLG reaction
$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$
$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$
$CaFe_2O_4$	$CaFe_3O_5 + Fe_3O_4$	$CaFe_2O_4$	$CaFe_3O_5 + Fe_3O_4$
Fresh OC	OC after CLG reaction	Fresh OC	OC after CLG reaction
$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$
$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$	$Ca_2Fe_2O_5$
$CaFe_2O_4$	$CaFe_3O_5 + Fe_3O_4$	$CaFe_2O_4$	$CaFe_3O_5 + Fe_3O_4$
Fresh OC	OC after CLG reaction	Fresh OC	OC after CLG reaction
$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$	$Ca_2Fe_2O_5 + CaO$

Fe:Ca= 1:2

Fe:Ca= 1:1

Fe:Ca=

- *A simple one step reduction and oxidation for $Ca_2Fe_2O_5$ would largely promote H_2 production through the re-oxidation started from Fe^0 by steam, compared with that from FeO and Fe_3O_4*

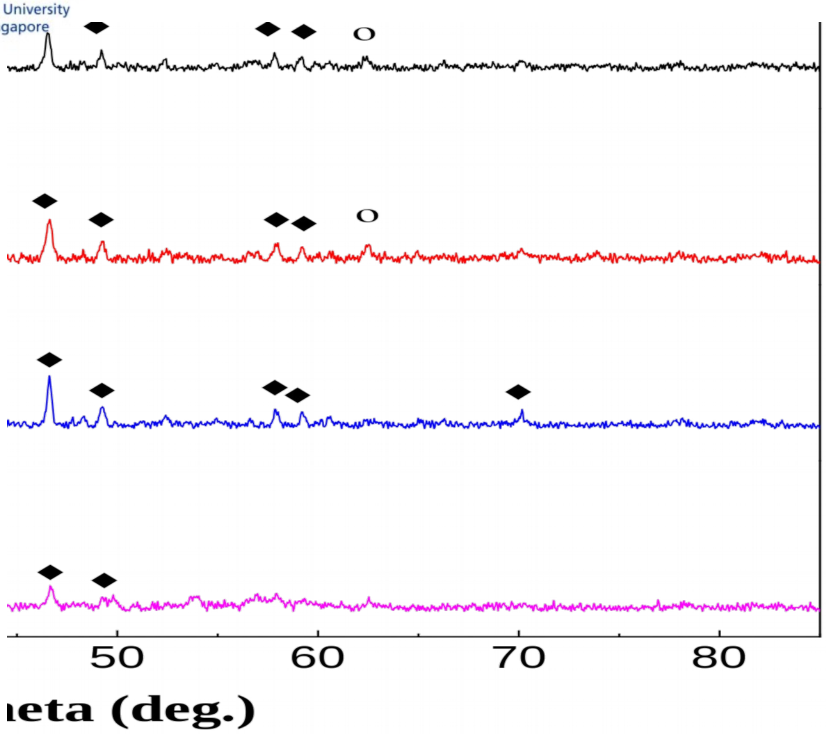
Results 2 – Effect of temperature

Gas yields of chemical looping gasification with Fe:Ca=1:1 under different temperatures

	600 °C	700 °C	800 °C	900 °C
H2 yield (mmol/g biomass)	3.74	8.60	23.07	34.23
Gas yield (%)	20.82	31.88	58.37	83.09
Mass balance (%)	100.76	97.78	96.97	96.92
Syngas heating value (kJ/g biomass)	1.98	3.46	8.46	13.86
Gas content (%)				
H_2	40.66	51.20	63.20	64.10
CO_2	36.85	33.26	23.21	19.70
CH_4	5.83	3.62	2.11	1.74
CO	16.67	11.91	11.48	14.46

- *Hydrogen yield, syngas properties were increased with the increase of gasification temperature.*

Results 2 – Effect of temperature



Less than 700 °C :

$$Ca_2Fe_2O_5 \xrightarrow{CLG} Ca_2Fe_2O_5 + Fe_3O_4$$

Higher than 800 °C :

$$Ca_2Fe_2O_5 \xrightarrow{CLG} Ca_2Fe_2O_5$$

XRD patterns for solid residues after CLG at different temperatures (Ca:Fe=1:1)

- *A temperature of higher than 800 °C was needed for steam chemical looping gasification.*

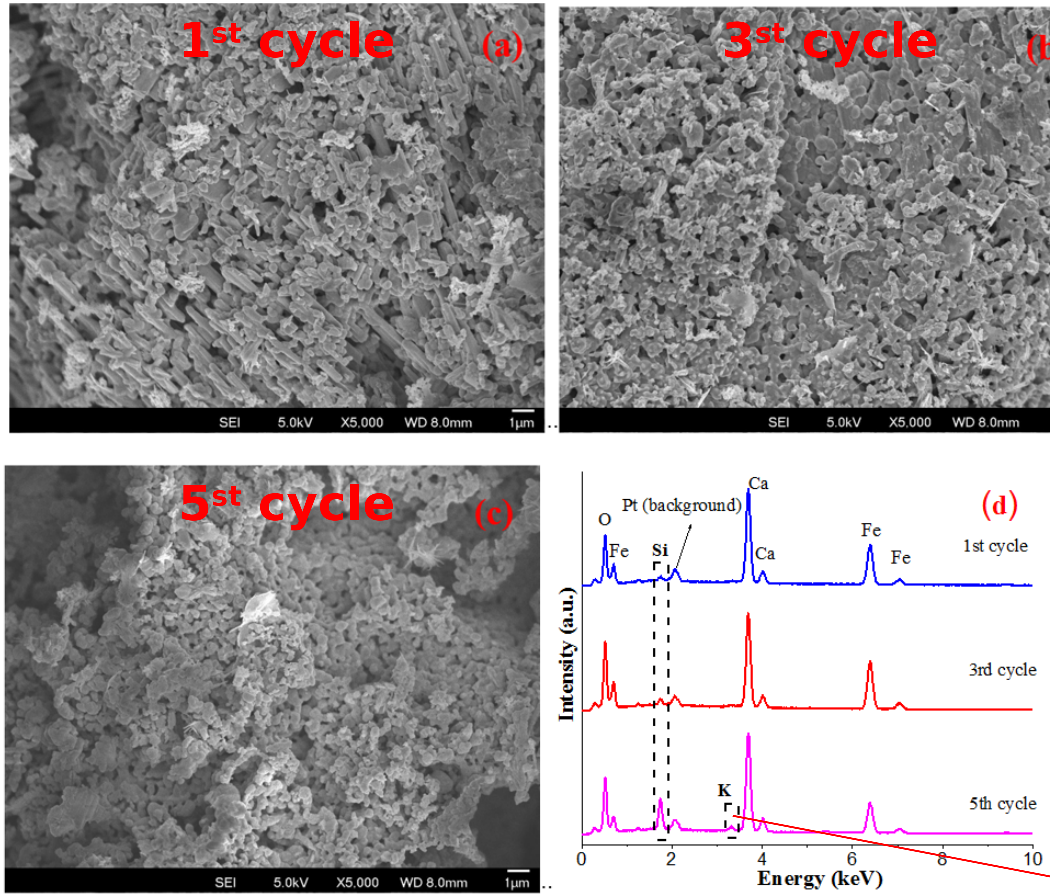
Results 3 – Cycling performance

Gas yields of chemical looping gasification with Fe:Ca=1:1 under different temperatures

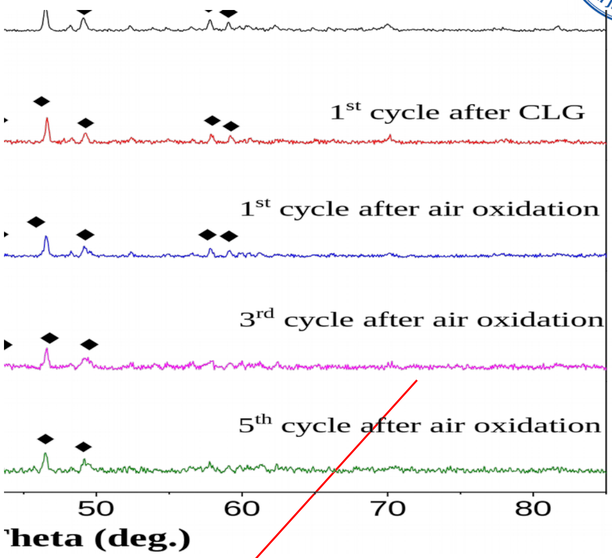
	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
H2 yield (mmol/g biomass)	23.07	20.94	21.14	20.60	18.09
Carbon yield in syngas (%)	40.95	43.02	45.71	45.93	44.32
Gas yield (%)	58.37	58.06	59.79	60.44	56.06
Carbon deposited (%)	12.33	10.47	10.70	8.37	8.60
Gas content (%)					
H_2	63.20	58.91	58.28	57.53	56.18
CO_2	23.21	25.36	25.41	26.56	28.26
CH_4	2.11	3.40	3.59	3.46	4.18
CO	11.48	12.33	12.72	12.46	11.37

- *Hydrogen yield was slightly decreased with the increased cycle times.*
- *The carbon deposited was decreased along with the enhanced CO_2 content and carbon conversion to gas phase.*

Results 3 – Cycling performance



SEM images for Fe:Ca=1:1 ($Ca_2Fe_2O_5$) after several redox



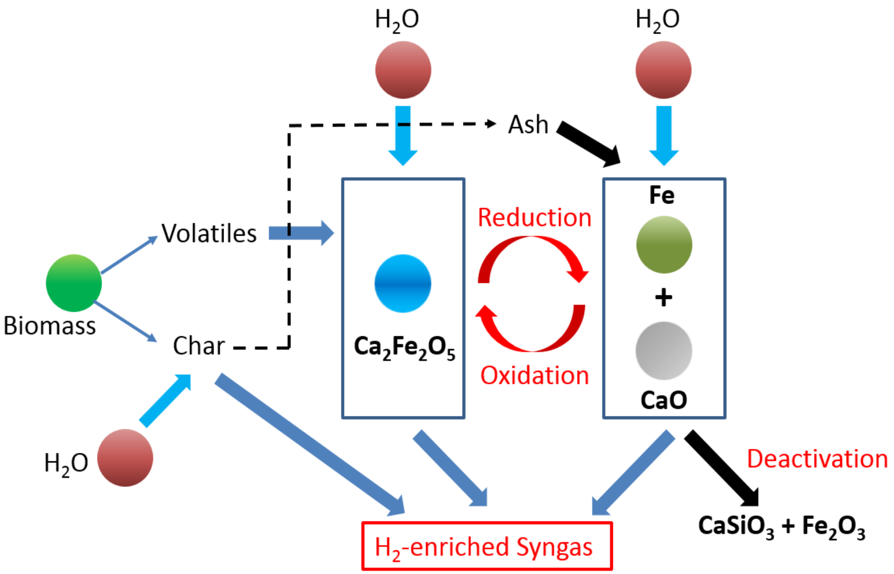
Phase changes of OC for 5 times redox cycles (Ca:Fe=1:1)

$$3rd\ cycle:\ CaO + SiO_2 \xrightarrow{CLG} CaSiO_3$$

K accumulation from ash of bioma

- *The redox cycle of $Ca_2Fe_2O_5$ favours hydrogen production due to an one-step transition ($Fe^{3+} \longrightarrow Fe \longrightarrow Fe^{3+}$).*
- *The combination of CaO with SiO_2 derived from ash of rice straw at high temperature was the reason for reduced hydrogen yield over cycling CLG.*

Conclusions



Schematic of the chemical looping gasification process with $Ca_2Fe_2O_5$ as oxygen carrier

- *The optimized hydrogen yield was 23.07 mmol/g biomass with Fe:Ca=1:1 under the conditions of 800 °C, 0.1 g/min steam.*
- *A temperature of higher than 800 °C was needed to have a completed redox of oxygen carrier.*
- *The redox cycle of $Ca_2Fe_2O_5$ favours hydrogen production due to an one-step transition ($Fe^{3+} \longrightarrow Fe \longrightarrow Fe^{3+}$).*
- *SiO_2 in the ash of biomass may react with Ca in high temperature, and further reduced the cycling performance of $Ca_2Fe_2O_5$.*

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Thank you!

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