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The catalytic effect of inherent and adorbed metals on the pyrolysis and gasification of biomass

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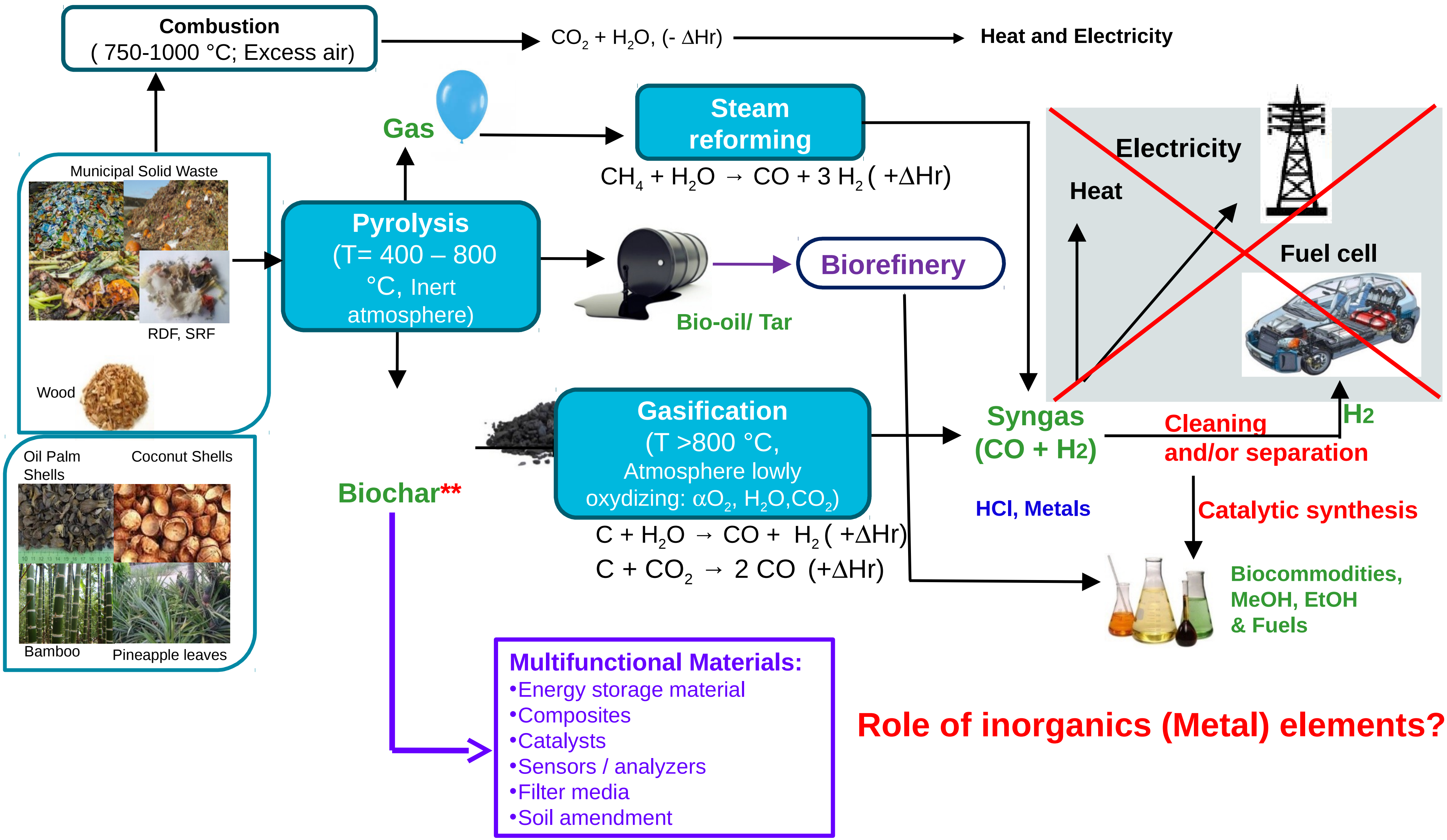
Waste and Biomass to VALUE (Energy and Valuable Materials)



OUTLINE

1. Context
2. Gasification experiments
3. Results and discussion
4. Take to home

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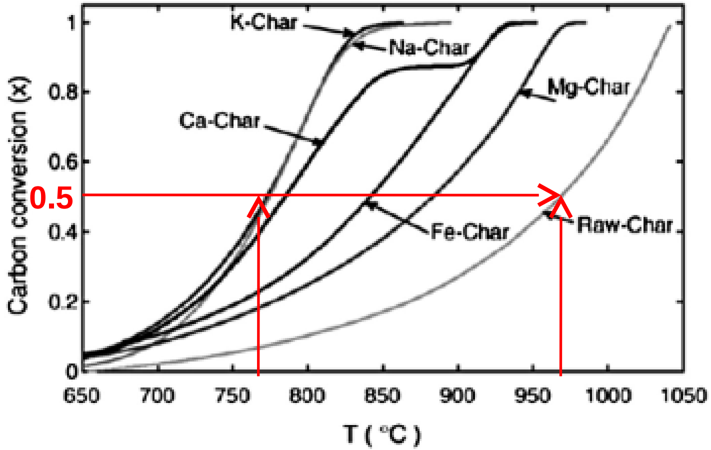
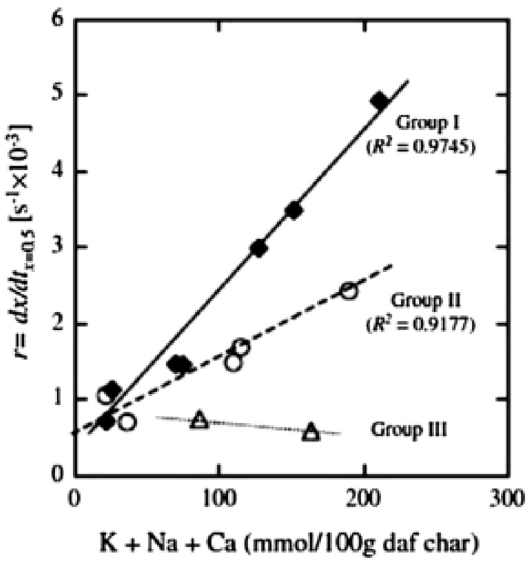
Inorganic elements may impact the rate of gasification reactions

An increase in gasification rate is observed in the presence of Alkali (K, Na) and Alkaline Earth (Ca, Mg, and Fe) [1]

char under 100% CO_2 at 10°C/min [1]





Steam gasification reactivity of 14 biomasses was classified in 3 groups according to their inherent inorganic species [2]

Group I - [K] + [Na] > [Ca]
Group II - [Ca] > [K] + [Na]
} Catalytic effect on gasification

Group III - High [SiO_2] } Inhibit gasification

New classification [3,4] → Biomass Inorganic ratio **K/(Si+P)**

[1] Huang et al. Biotechnol Adv, 2009, 27; [2] Zhang W. Fuel Process Technol, 2010, 91;
[3] Romero M. at al, Fuel, 2019, 235; [4] Dupont C et al, Energy, 2016;

2. Gasification experiments: selection of biomass

Steam gasification experiments of three different Agrowastes

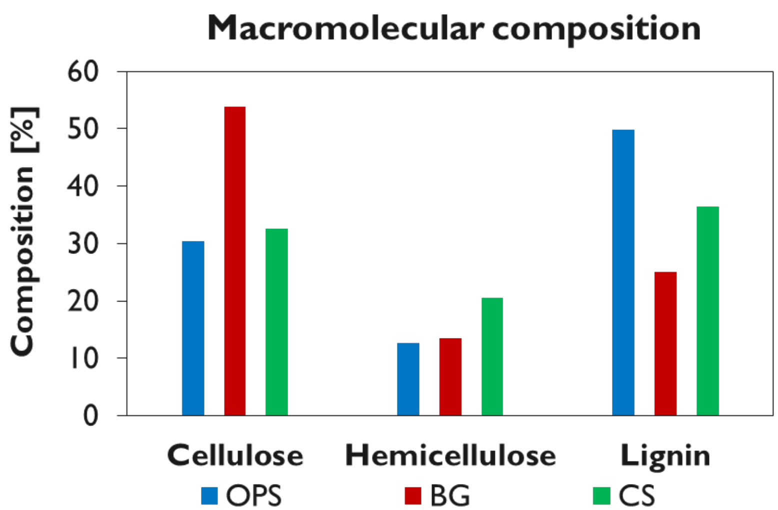
Selected feedstocks for steam gasification process analysis [1,2]

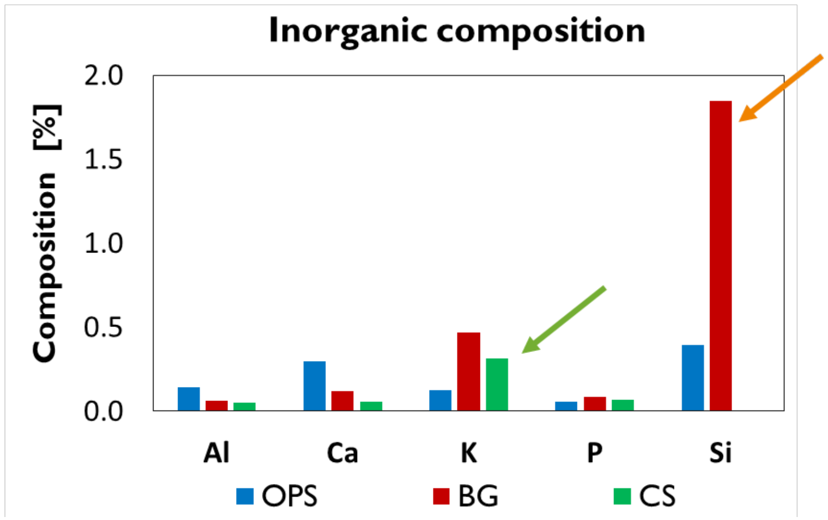
Composition and heating value		OPS Oil Palm Shells	CS Coconut Shells	BG Bambou guadua
Elemental Analysis (wt. % daf)	C	46.7±0.2	46.8 ±0.2	42.7±0.3
	H	6.5±0.1	5.8 ±0.1	5.4±0.1
	O	46.2±0.1	47.1 ±0.1	51.5±0.1
	N	0.6±0.1	0.3 ±0.1	0.4±0.1
	O/C	0.7±0.1	0.7±0.1	0.9±0.1
	H/C	1.7±0.1	1.5±0.1	1.5±0.1
Proximate analysis (wt. %)	Volatile Matter	69.9±0.3	71.4±0.3	68.3±0.2
	Fixed Carbon	19.0±0.3	17.1±0.2	18.1±0.3
	Ash	1.6±0.2	1.3±0.1	5.6±0.4
Heating value (MJ/kg) dry basis.	HHV	19.6±0.3	18.7±0.3	18.1±0.4

[1] Romero M. at al, Fuel, 2019, 235; [2] Romero M. at al, Bioenerg. Res., 2017, 10;

2. Gasification experiments: selection of biomass

Agrowastes



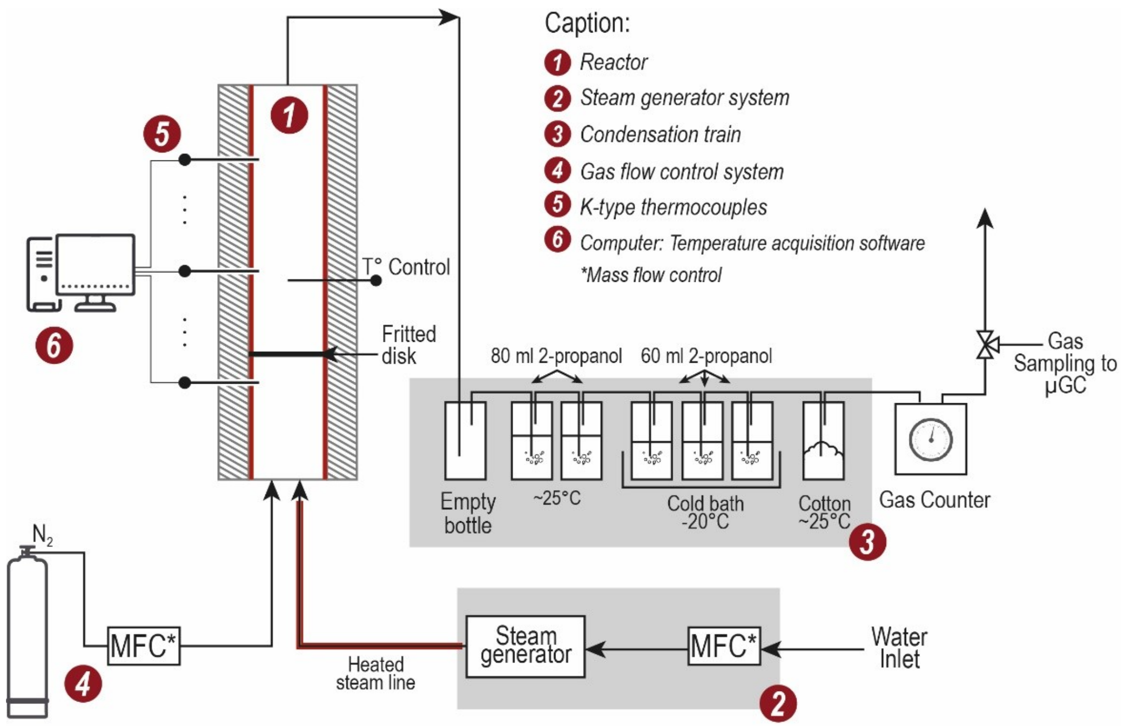


- Oil palm shells (OPS) and Coconut shells (CS) are endocarps with high **lignin** content
- Bamboo guadua (BG) is mainly composed of **cellulose**

- **Si, K** is the most important inorganic constituents of Bamboo guadua (BG)
- **K** is the most important inorganic constituent of Coconut shells (CS)

2. Gasification experiments

Experimental setup



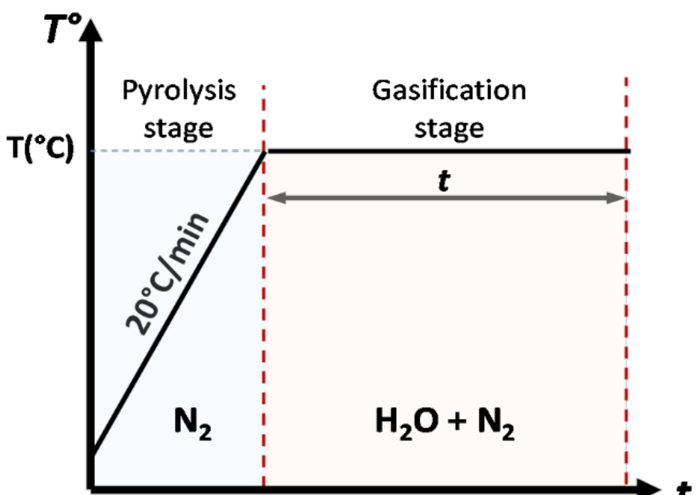
Semi-continuous fluidized bed reactor

H: 60 cm; Φ = 6 cm

Raw biomass: 80 g

Particle size: 2-3 mm

Experimental conditions and protocol



Steam gasification process

Experimental conditions

Temperature	750°C, 850°C
Time	1 hour, 2 hours, 3 hours
Steam fraction	30% vol steam/70%vol N_2
Flow rate	0.7 m^3/h

Measured parameters

- Char yield
- Liquid yield
- Gas yield
- Gas composition

Energy distribution in the gasification products

Biomass composition impacts the product energy distribution:

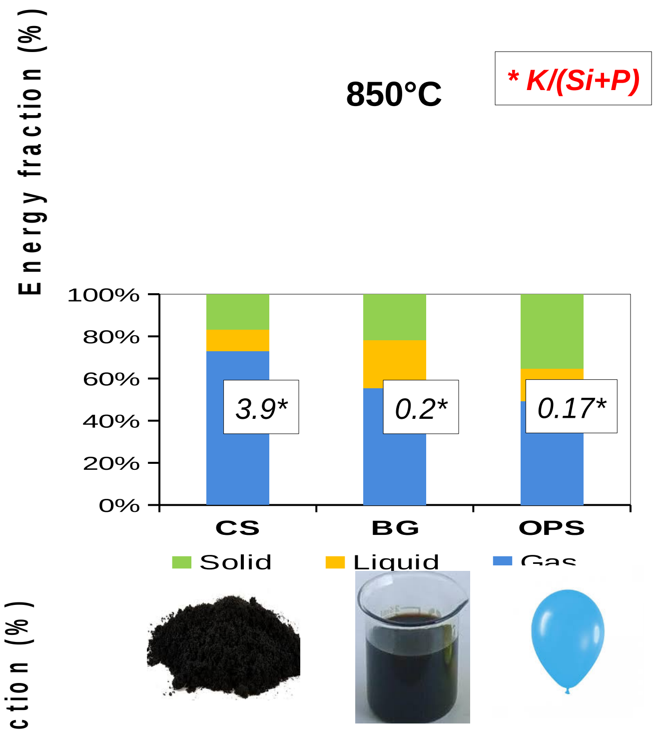
$$Product\ yield\ (\%) = \frac{m_{product}}{m_{biomass} + m_{steam}}\ x\ 100$$

$$E_{products} = E_{solid} + E_{gas} + E_{liquid}$$

$$E_{gas} = m_{gas}\left(h_{gas\ (T_r)} + HHV_{gas}\right)$$

$$E_{liquid} = m_{steam}\left(h_{steam\ (T_r)}\right) + m_{tars}\left(h_{tars\ (T_r)} + HHV_{tars}\right)$$

$$E_{solid} = m_{char}\left(C_{p\ char}T_r + HHV_{char}\right)$$



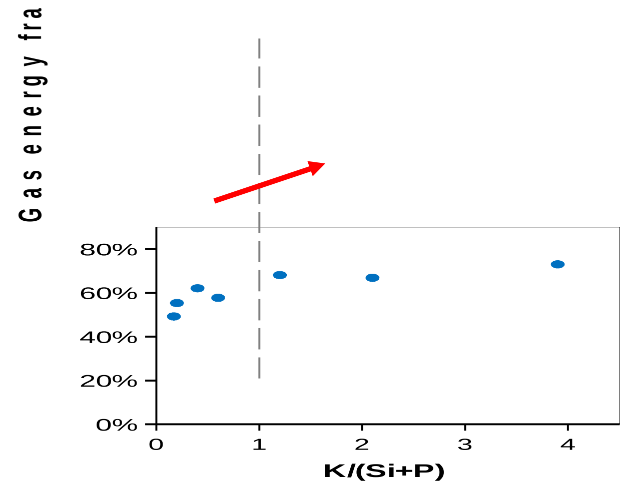
Under the same gasification conditions:

① **K/(Si+P)** > 1

↑ Gas production
Gas energy fraction

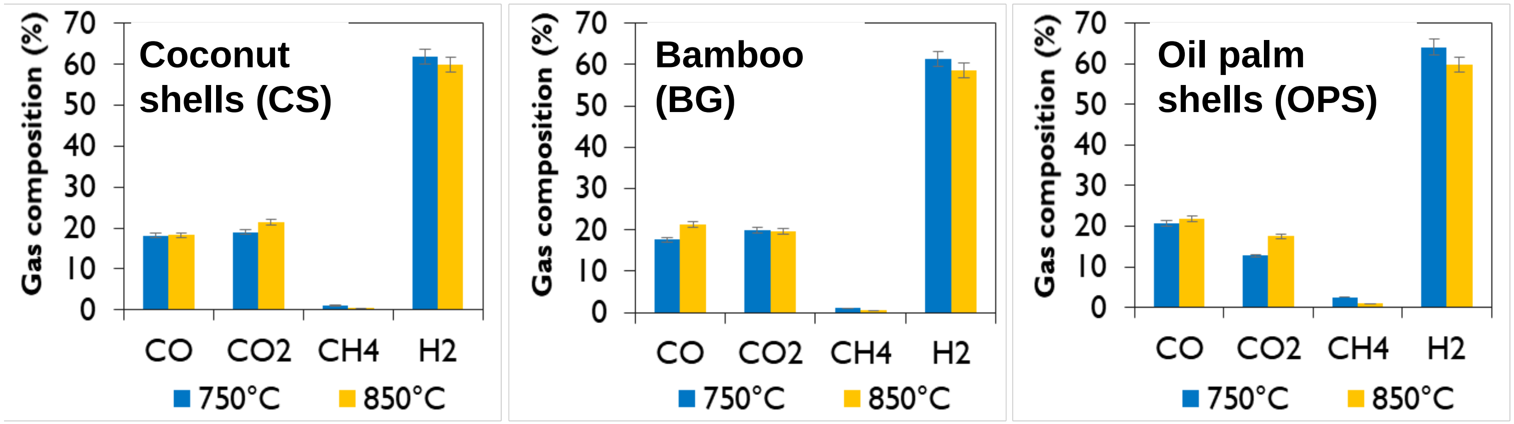
② **K/(Si+P)** < 1

↓ Gas production
Gas energy fraction



K/(Si+P) > 1 are associated with higher gasification reactivities and process efficiencies

Gas composition and heating value



- **Gas H_2/CO: 2.5 – 4.5**
- **Gas HHV: 10-12 MJ/m^3**

Gas suitable for boilers, ICE, and gas turbines[1]

Main gasification reactions

$$C + H_2O \leftrightarrow CO + H_2$$

$$C + CO_2 \leftrightarrow 2CO$$

Other gasification reactions

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$C + 2H_2 \rightarrow CH_4$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Similar gas composition

↓

Possibly related to similar biomass organic composition → **O/C** : 0.7 – 0.9, **H/C** : 1.5 – 1.7

[1] Butterman H. and Castaldi M., Environ. Sci. Technol. 2009

Impact of biomass composition on the gasification behavior

Catalytic impact of AAEM* on gasification reactions → Oxygen transfer mechanism via the metal **M** [1,2]

***AAEM: Alkali and Alkaline Earth Metal**

❖ ***Explaining water gas reaction mechanisms :***

$$C + H_2O \rightarrow CO + H_2$$

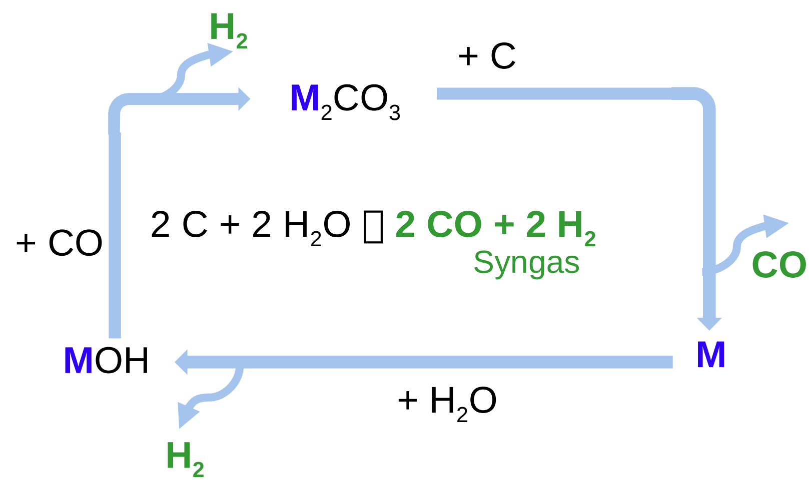
Alkali metals (K, Na)

$$M_2CO_3 + 2C \rightarrow 2M + 3CO$$
$$2M + 2H_2O \rightarrow 2MOH + H_2$$
$$2MOH + CO \rightarrow M_2CO_3 + H_2$$

Alkaline earth metals (Ca, Mg)

$$MCO_3 + 2C \rightarrow M + 3CO$$
$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$
$$M(OH)_2 + CO \rightarrow MCO_3 + H_2$$

Metal (M) loop oxygen transfer



❖ ***Explaining Boudouard reaction mechanism:***

$$C + CO_2 \rightarrow CO$$

Alkali metals

$$M_2CO_3 + 2C \rightarrow 2M + 3CO$$
$$2M + CO_2 \rightarrow M_2O + CO$$
$$M_2O + CO_2 \rightarrow M_2CO_3$$

Alkaline earth metals

$$MCO_3 + 2C \rightarrow M + 3CO$$
$$M + CO_2 \rightarrow MO + CO$$
$$MO + CO_2 \rightarrow MCO_3$$

[1] Di Blasi, Progress in energy and combustion science, 2009 ; [2] Nzihou et al, Energy, 2013

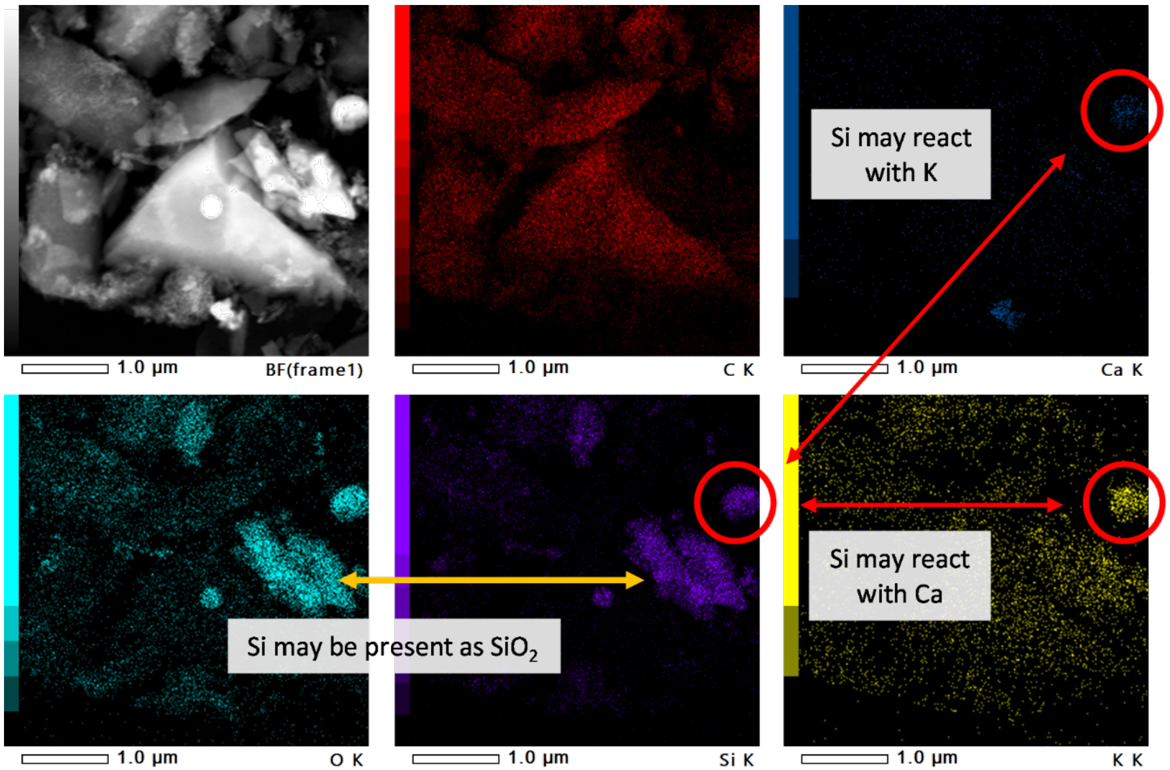
Impact of biomass composition on the gasification behavior

AAEM* Catalytic effect inhibition → Si Al P ↔ AAEM

*AAEM: Alkali and Alkaline Earth Metal

{ Formation of alkali phosphates, silicates and aluminosilicates [1-3]

Steam gasification biochar
TEM-EDX cartography images



M reactions with ***P, Si, Al***

Inhibits the oxygen transfer mechanism via the metal **M** and its catalytic effect

Water gas reaction inhibition mechanism:

$$C + H_2O \rightarrow CO + H_2$$

Alkali metals (K, Na)

$$M_2CO_3 + 2C \rightarrow 2M + 3CO$$

$$2M + 2H_2O \rightarrow 2MOH + H_2$$

$$\sout{2MOH + CO \rightarrow M_2CO_3 + H_2}$$

$$2MOH + nSiO_2 \rightarrow M_2O \cdot nSiO_2 + H_2O$$

[1] Zhang et al, Fuel, 2008; [2] Y. Niu, et al, Prog. Energy Combust. Sci. 52 (2016) 1–61; [3] D. Nutalapati et al. Fuel Process. Technol. 88 (2007) 1044–1052.

4. Take to home

- The **inorganic content** of biomass has an important impact on the steam gasification reactivity, product yield, and gasification efficiency
- The **beneficial effect** of **AAEM (Alkali and Alkaline Earth Metals)** on the gasification behavior was **confirmed,** as well as the **inhibitory effect** of **Si** and **P**
- The inorganic ratio **K/(Si+P)** is a suitable indicator for gasification reaction of lignocellulosic biomass

Main gasification reactions and mechanisms

Water - gas reaction

$$C + H_2O \leftrightarrow CO + H_2$$

1: $C_f + H_2O \rightarrow C(O) + H_2$

2: $C(O) + H_2 \rightarrow C_f + H_2O$

3: $C(O) \rightarrow CO$

Boudouard reaction

$$C + CO_2 \leftrightarrow 2CO$$

1: $C_f + CO_2 \rightarrow C(O) + CO$

2: $C(O) + CO \rightarrow C_f + CO_2$

3: $C(O) \rightarrow CO$

Intermediate steps [1,2]:

Step 1*:* Dissociation of the reactant at a carbon-free active site (C_f)

Step 2: Formation of a carbon-oxygen surface complex *C(O)*

Step 3*:* Desorption of product species

Other gasification reactions

- *Water - gas shift reaction* $CO + H_2O \rightarrow CO_2 + H_2$
- *Hydrogasification reaction* $C + 2H_2 \rightarrow CH_4$
- *Methanation reactions*
  $2CO + 2H_2 \rightarrow CH_4 + CO_2$
  $CO + 3H_2 \rightarrow CH_4 + H_2O$
  $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

[1] Basu P, Gasification theory, 2013; / [2] Nzihou et al, Energy, 2013; V [3] Di Blasi, Progress in energy and combustion science, 2009