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3rd International Conference on Sustainable Solid Waste Management

ENERGY FROM BIOMASS AND WASTE:

IMPACT OF METAL SPECIES

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OUTLINE

ENERGY FROM BIOMASS AND WASTE: IMPACT OF METAL SPECIES

1. Introduction to pyro-gasification of biomass and waste

2. Structure of pyro-gasification chars containing inorganics

3. Role of Inorganics (Metals)
    - 3.1. Role of Transition Metals
    - 3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

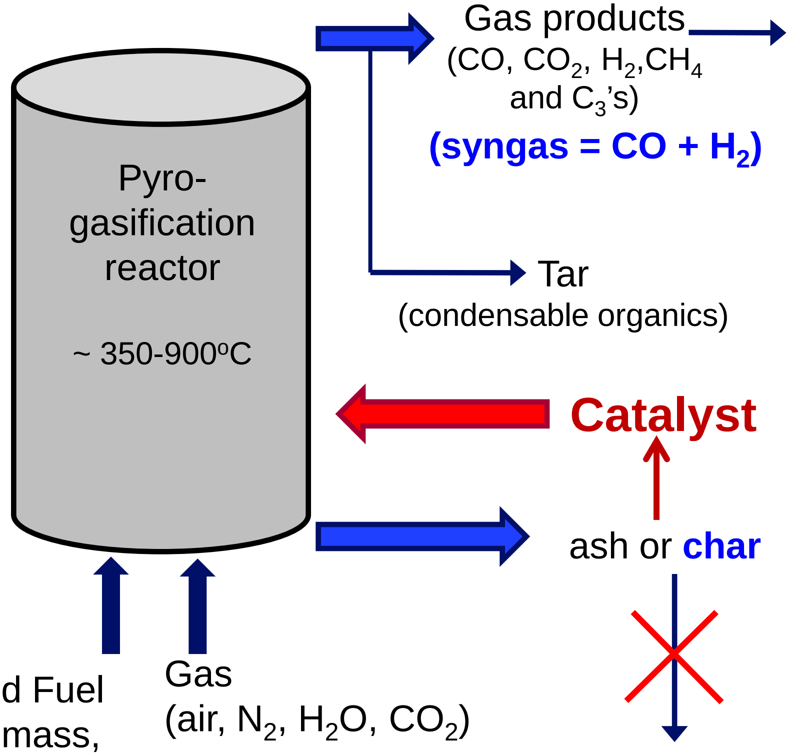
4. Conclusions an Future works

1. Introduction to pyro-gasification of biomass and waste

Pyro-gasification for Energy/Materials Recovery from Waste and Biomass

- Energy recovery from waste/biomass results in reduction of volume of waste, low (or zero) net CO_2 emissions, and presents a distributed energy source

- **Pyro-gasification Process**



Pyro-gasification reactor

~ 350-900ºC

Gas products (CO, CO_2, H_2,CH_4 and C_3's)

(syngas = $CO + H_2$)

Tar (condensable organics)

Catalyst

ash or **char**

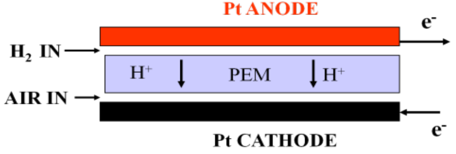
to landfill

Solid Fuel (biomass, waste, RDF)

Gas (air, N_2, H_2O, CO_2)

Energy Recovery

Fuel Cells

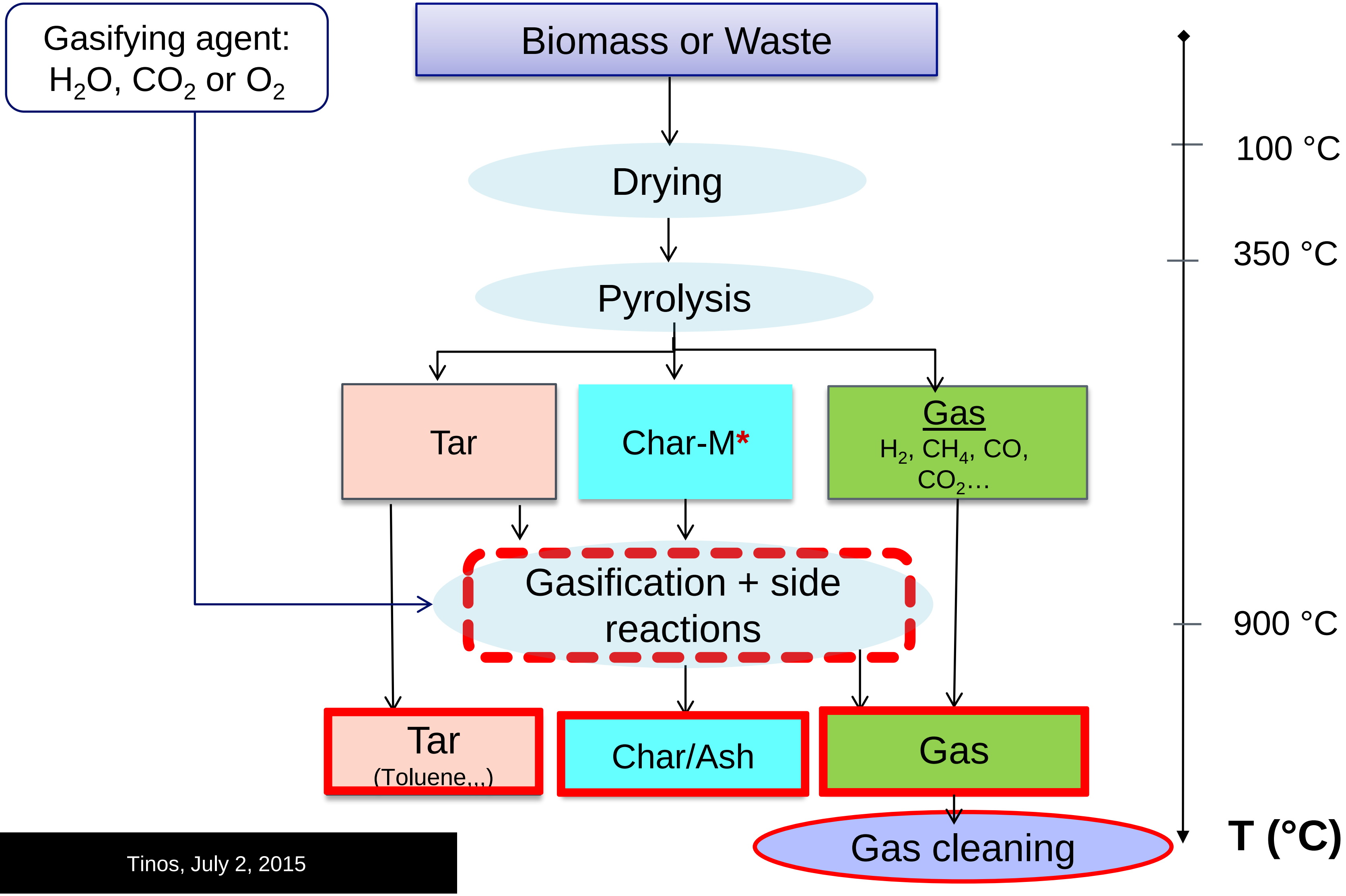


Fuels and chemicals

Gas turbines

1. Introduction to pyro-gasification of biomass and waste

Reaction scheme for biomass and waste pyro-gasification



Char-M*:
char with metal agglomerate at the surface

1. Introduction to pyro-gasification of biomass and waste

Challenges

- ✓ The cost of biomass processing must be decreased by designing new technologies and catalytic systems
- ✓ The decomposition of tar in Syngas
- ✓ Technological Challenges (Corrosion, fouling,…)

1. Introduction to pyro-gasification of biomass and waste

Main and side-reactions

$C + H_2O \rightarrow CO + H_2$ *	***Steam gasification**	**+ 131 MJ/kmol**
$CO + H_2O \leftrightarrow CO_2 + H_2$*	*** Water-gas shift (WGS)**	**- 41 MJ/kmol**
$C + CO_2 \rightarrow 2CO$	**Boudouard**	**+ 172 MJ/kmol**
$C + O_2 \xcancel{\rightarrow} CO_2$	**Combustion**	**- 394 MJ/kmol**

Examples of syngas end-uses and their approximate H_2/CO ratio requirements

Syngas end-use	H_2/CO ratio
Solid oxide fuel cells (SOFC)	4.0 – 6.0
Gas turbine combustion	2.5 – 4.0
Fischer Tropsch (diesel fuels)	1.5 – 3.0
Fischer Tropsch – Fe and Co – based catalyst process	0.5 – 1.5

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2. Structure of pyro-gasification char containing inorganics

Catalysts or inhibitors for pyro-gasification ?
Impact of syngas rate, reaction light off?

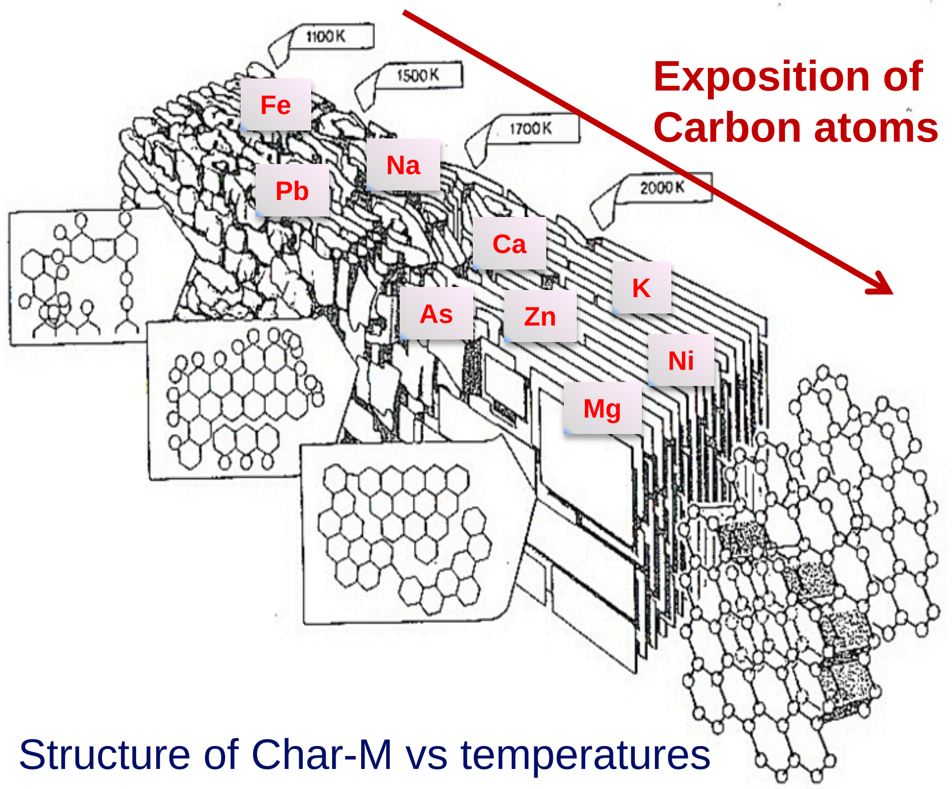
The rate of the gasification process is affected by the process conditions, and is catalysed/inhibited by a number of different species:

Inorganics: Metals :

- Alkali (M^+): Li, Na, K
- Alkaline Earth (Often M^{2+}): Mg, Ca, Be, Ba, Sr
- Transition : Ni, Pb, Zn, …

2. Structure of pyro-gasification char containing inorganics

Catalysts or inhibitors for pyro-gasification ?



Structure of Char-M vs temperatures towards graphitic structures

Small aromatic structural units, with the oxygen present mostly within heterocyclic and phenolic groups. The structural units are cross-linked by ether and olefinic linkages.

Metals :

- ❖ Alkali : Li, Na, K
- ❖ Alkaline Earth : Mg, Ca, Be, Ba, Sr
- ❖ Transition : Ni, Pb, Zn, …

Marsh H., Introduction to Carbon Science. Butterworths, 1989, 52

Nzihou A., Stanmore B., Sharrock P., Energy, 2013, 58, 305-317

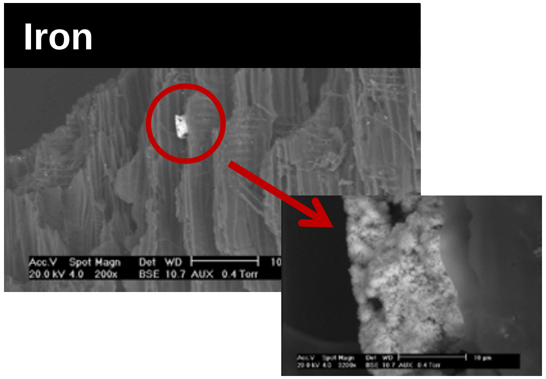
2. Structure of pyro-gasification char containing inorganics

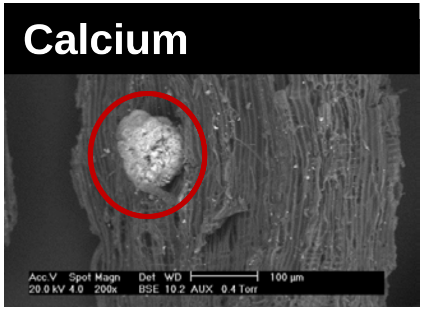
Why is char a good catalyst?

- Char-M often considered a ‘low value’ product
- Opportunity to “valorize” Char-M

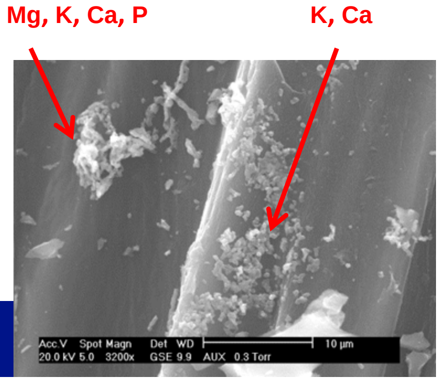
Catalytic metals

Char-M contains metals and minerals used as catalysts in many common processes


Iron


Calcium

ESEM images

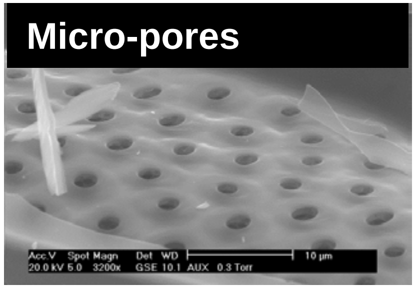


Char-M after heating to 900°C

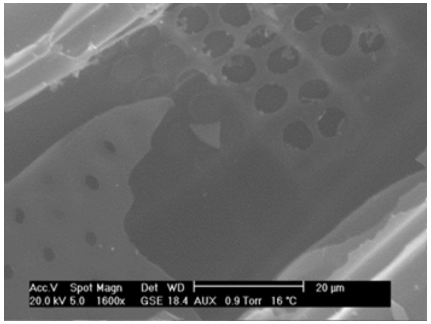
Fe, Ni, Mg, Mn, Ca, Al, Na, K measured in Char-M

Surface area & catalytic sites

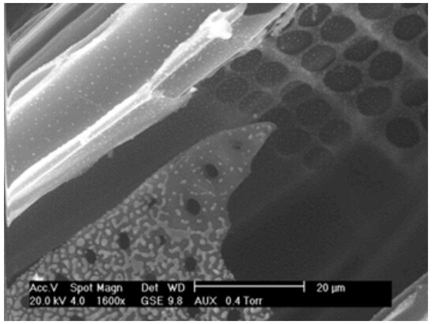
High porosity increases available catalyst sites


Micro-pores

Char-M contains micro- pores (d<2nm)



Char-M from gasification with steam



Char-M after heating to 900°C

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3.1. Role of Transition Metals

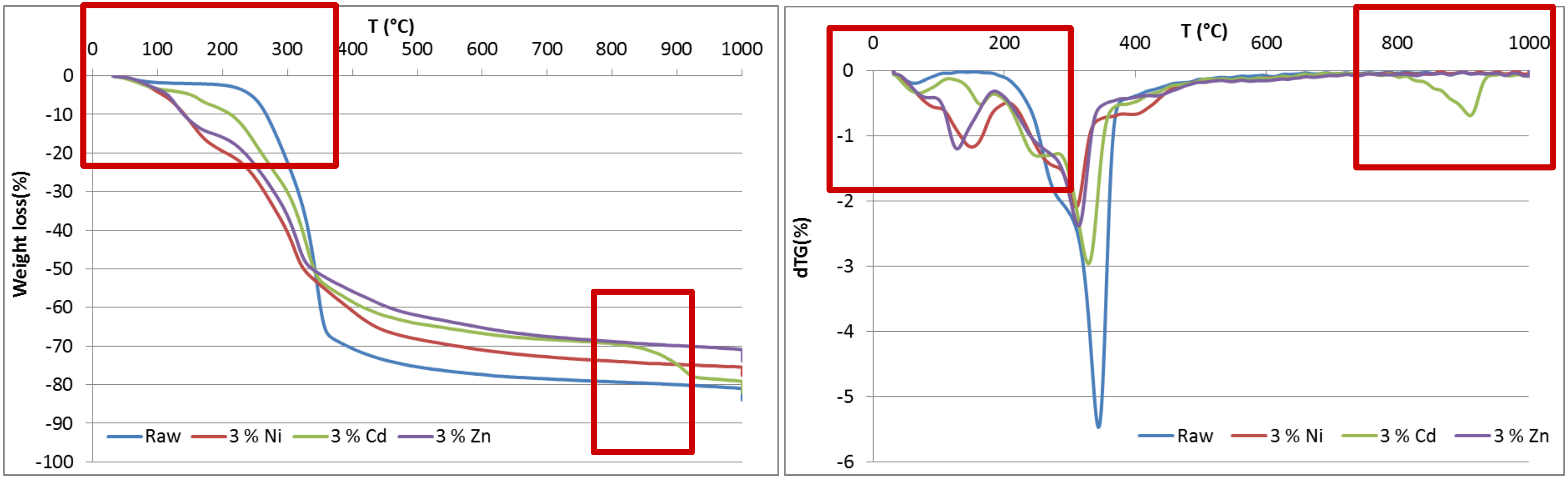
Composition in metals for various biomass and waste

Biomass	Wheat Straw*	Beech Wood*	Demol Timber	Phyto Remed	Sewage Sludge	Chicken Litter	Paper Sludge		Recov Fuel
				Metal content (mg kg^{-1} dry basis)					
As	**0.18**	**3.5**	**550**	**22**	**(10)**	**-**	**8**	**-**	**37**
Cd	0.2	1.0	8	-	38	-	<0.4	350	24
Co	-	-	-	-	-	-	9-12	-	67
Cr	**3.0**	**2.5**	**1060**	**107**	**91**	**112**	**110**	**100**	**1020**
Cu	**25**	**43**	**1080**	**70**	**330**	**71**	**310**	**450**	**2800**
Hg	0.06	0.12	10	8	2.7	-	1000	-	-
Mn	-	(73)	(2500)	-	950	596	55	-	1650
Ni	-	-	-	27	39	<10	-	480	209
Pb	**6**	**33**	**6300**	**55**	**159**	**-**	**160**	**480**	**1100**
Zn	**-**	**(15)**	**-**	**-**	**1318**	**209**	**470**	**170**	**-**

Nzihou A., Stanmore B., Journal of Hazardous Materials, 2013, 256/257, 56-66.

3.1. Role of Transition Metals

Pyrolysis (N_2) of poplar wood contamined with Ni, Cd, Zn

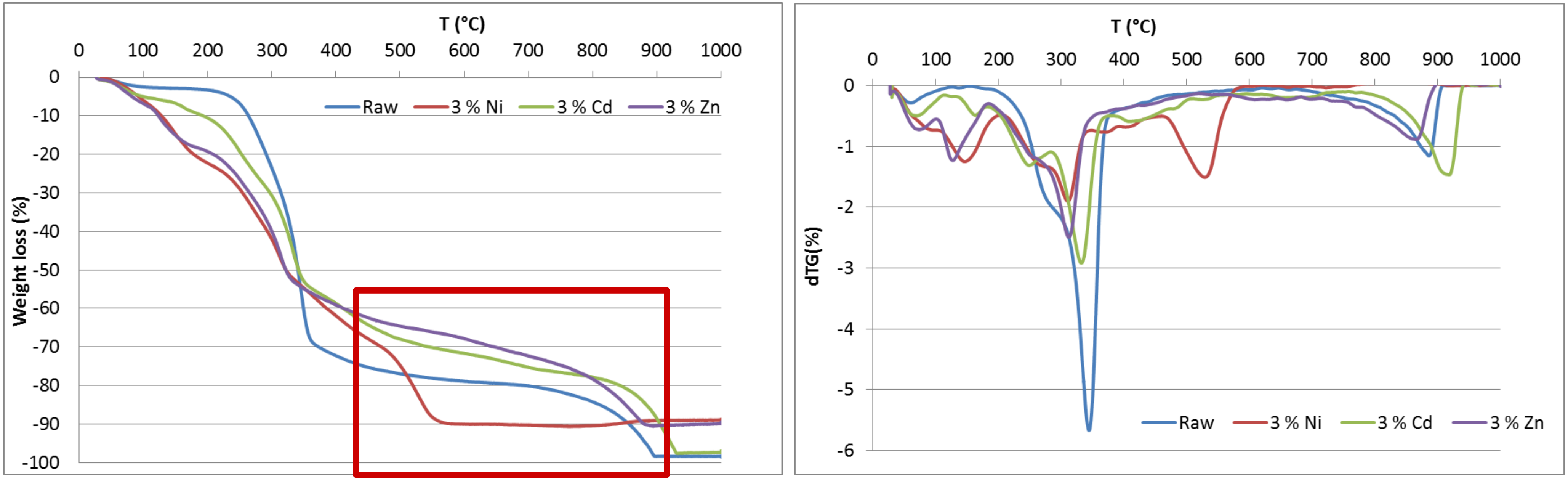


Thermogravimetric analysisc

- ✓ Metals increase and accelerate the wood weight loss from 70 to 370°C and inhibit it from 370 to 900°C in a presence of N_2.
- ✓ 850°C: wood contaminated by Cd has the same weight loss as raw wood
  ⬄ Cd evaporation and not inhibitive effect from this point.
- ✓ No catalytic effect of Ni is observed in a presence of N_2

3.1. Role of Transition Metals

Gasification (CO_2) of poplar wood contamined with Ni, Cd, Zn



Thermogravimetric analysisc

- ✓ Zn inhibits gasification reactions more than Cd
- ✓ Cd and Zn are inhibitors of gasification reactions
- ✓ Ni catalyses gasification reactions

3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

Catalytic effect of alkali carbonates (M: Li, Na, K): Mechanisms

(M^+: Li^+, Na^+, K^+):

- ✓ **CO_2 gasification (Bourdouart)**

$$M_2CO_3 + 2\,C \longrightarrow 2\,M + 3\,CO$$

$$2\,M + CO_2 \longrightarrow M_2O + CO$$

$$\text{or } M_2O + CO_2 \longrightarrow M_2CO_3$$

$$C + CO_2 \longrightarrow 2\,CO$$

- ✓ **Steam gasification**:

$$M_2CO_3 + 2\,C \longrightarrow 2\,M + 3\,CO$$

$$2\,M + 2\,H_2O \longrightarrow 2\,MOH + H_2$$

$$2\,MOH + CO \longrightarrow M_2CO_3 + H_2$$

$$2\,C + 2\,H_2O \longrightarrow \mathbf{2\,CO + 2\,H_2}$$

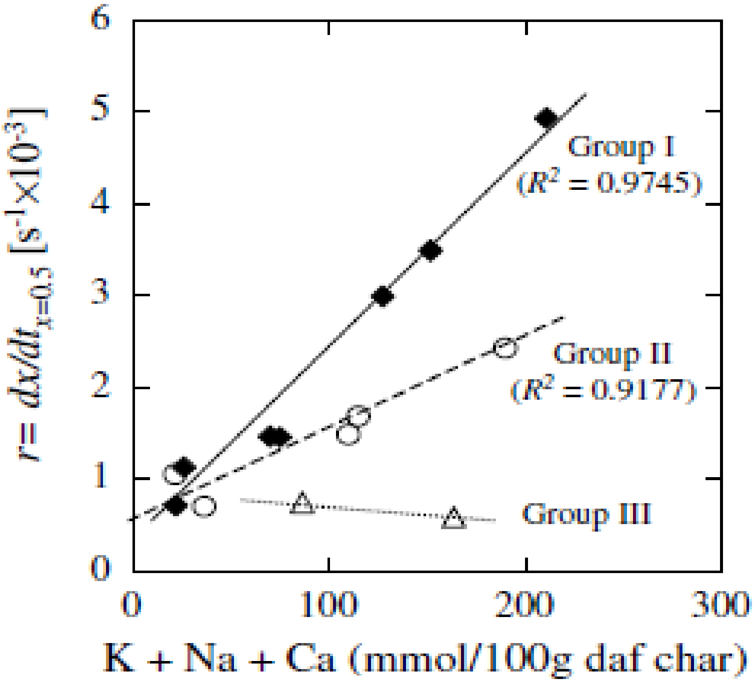
CO loop

Steam-to-carbon ratio: 0.8 to 1.5

- ✓ **Syngas (CO+H2)**
- ✓ **H_2**
- ✓ **CO**

McKee D.W. et al.Carbon 1975; 13: 381-390
McKee DW.. Carbon 1982; 20: 59-66

3.2. Role of Alkali and Alkaline Earth Metals (AAEM)



- Gasification of 14 biomass samples
  (including sawdust, bark, agricultural waste,…)
  Experimental conditions: 50kPa, 850°C

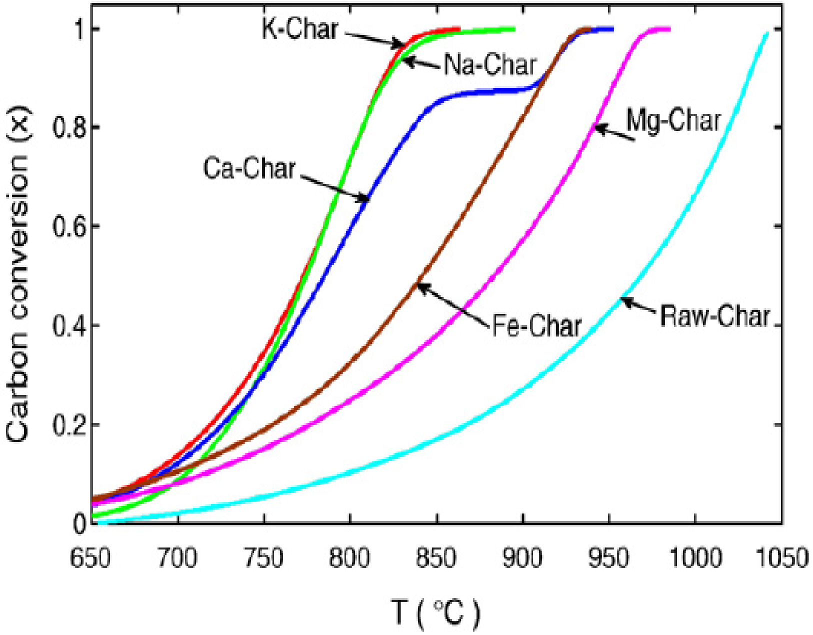
Reactivity towards steam of 14 biomass chars
with respect to the AAEM content

Zhang Y, et al. Fuel 2008; 87: 475–481

Group I: [K]+[Na] > [Ca];
Group II: [Ca] > [K]+[Na];
Group III: high [SiO_2]

- Conversion of fir char with different catalysts under 100% CO_2 at 10^oC/min temperature ramp

Huang Yet al.; Biotechnology Advances 2009; 27: 568–572



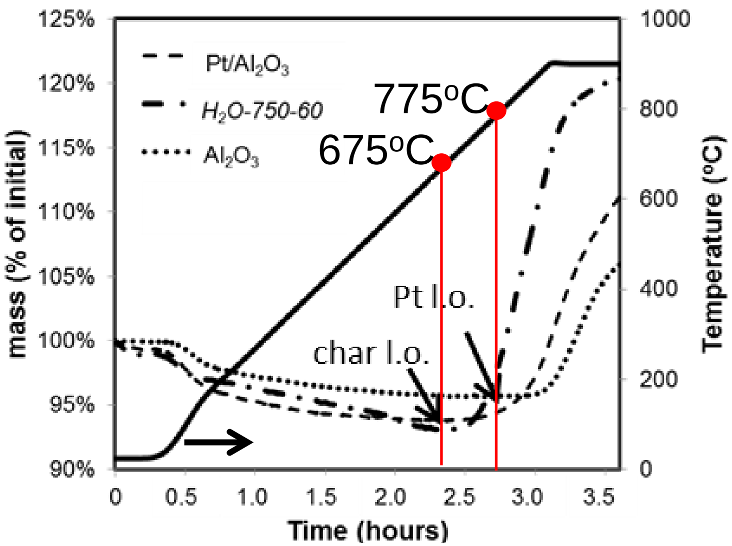
3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

Catalytic performances: Catalyst testing for CH_4 cracking

Reaction: **CH_4 (or Toluene) $\xrightarrow{\text{Char-M}}$ $C + H_2$ (+intermediate hydrocarbons < C6)**

- CH_4 cracking is a reaction with few products
  → easier to compare performance of chars
- Experiments done in a thermo gravimetric analyzer (TGA)
  → enables continuous measurement of reaction via carbon deposition (mass gain)

Comparison to commercial catalysts



	Char-M	Pt/Al_2O_3	Al_2O_3
Light off temperature (°C)	**675**	775	850
Reaction extent (% mass gain)	**20**	11	6

Char catalyst lights off at a lower temperature than commercial metal catalyst

Klinghoffer N., Castaldi M., Nzihou A.; IEC&R, 2012, 51, (40):13113-13122

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CONCLUSIONS and FUTURE WORKS

- ✓ Energy recovery from waste/biomass results in reduction of volume of waste, low (or zero) net CO_2 emissions, and presents a distributed energy source
- ✓ The rate of the gasification process is affected by the process conditions, and is catalysed/inhibited by a number of different species: Inorganics, **Metals :**
  - ❖ Alkali : Li, Na, K
  - ❖ Alkaline Earth : Mg, Ca, Be, Ba, Sr
  - ❖ Transition : Ni, Pb, Zn, …

- ✓ Li, K, Na, Ca, Ni inherent in biomass and waste are the most effective catalysts. **Particular emphasis on Group I (Na, K, Ca)**

Prospects:

- ✓ Initial metal (AAEM) characterization is a key issue
- ✓ Modeling of reaction rate and behavior
- ✓ Make these processes cost-competitive in today's market

RECENT PAPERS FROM OUR GROUP IN THE FIELD

1. **Ducousso M., Weiss-Hortala., Castaldi M., Nzihou M., Reactivity enhancement of gasification biochars for catalytic applications. *Fuel, Accepted June 2015***
2. **Nzihou A., Stanmore B., The Formation of Aerosols During the Co-combustion of Coal and Biomass. *Waste and Biomass Valorization, 2015,* DOI 10.1007/s12649-015-9390-3**
3. **Kinghoffer N., Castaldi M., Nzihou A., Influence of char composition and inorganics on catalytic activity of char from biomass gasification. *Fuel, 2015*,157,37-47**
4. **Nzihou A., Stanmore B., Sharrock P., A review of catalysts for the gasification of biomass char, with some reference to coal. *Energy, 2013*, 58, 305-317**
5. **Nzihou A., Stanmore B., The fate of heavy metals during combustion and gasification of contamined biomass – A brief review. *Journal of Hazardous Materials, 2013*, 256/257, 56-66.**
6. **Kinghoffer N., Castaldi M., Nzihou A., Catalyst properties and catalytic performance of char from biomass gasification. *Industrial & Engineering Chemistry Research, 2012*, 51, 40, 3113-13122**
7. **Nzihou A., Flamant G., Stanmore B., Synthetic fuel from biomass using concentrated solar energy – A review. *Energy, 2012*, 42, 121-131**

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