# Investigation into properties of ash from biomass gasification

Naomi Klinghoffer[1], Marco J. Castaldi[1], Ange Nzihou[2]
[1]Columbia University, Department of Earth and Environmental Engineering, New York, NY
[2]Ecole des Mines d'Albi Carmaux, Centre RAPSODEE, Albi, France

## Motivation

-It is predicted that biomass will make up 15% of energy supply in the future. Gasification is an efficient way to use biomass due to the ability to synthesize a wide variety of fuels from the syn gas.

-Gasification produces 3 main products:
(i) Synthesis gas – gas mixture made of CO + $H_2$ which can be used for fuels synthesis, combustion applications, or fuel cells
(ii) Tar – liquid hydrocarbons such as toluene and naphthalene which must be removed, as they can cause problems with downstream processing
(iii) Ash – solid material that is not converted into the gas phase consisting of metals, minerals, and unburned carbon; considered a low value product often used in construction materials

-Tar is often 'removed' by catalytically reforming it into gases (such as CO/$CO_2$ and $H_2$). Using the ash as a catalyst for tar reforming would provide a low-cost and easily accessible catalyst; if deactivation of the catalyst takes place, it could be disposed of and replaced without great cost or concern

-Ash is a highly porous material with a high concentration of minerals and metals, making it a good candidate for catalytic applications(1). It has been shown that the properties of the ash can be influenced by the gasification conditions (ex. reactive gas, gasification temperature) (2) .

-This research investigates the properties of ash generated under different gasification conditions; specifically, it focuses on properties that would make the ash a good catalyst, such as porosity and surface area

## Experimental

Three experimental apparatuses were used:

*(i) Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC)*
- Experiments were done with a Setaram 111 TGA/DSC.

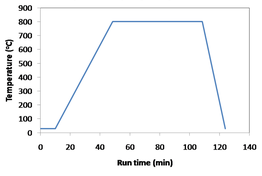
*(ii) Environmental Scanning Electron Microscope (ESEM)*
• Experiments were done using a FEI XL30 ESEM.
• Gasification experiments were done in the microscope by heating the sample to 1000°C at a heating rate of 20°C/minute and images were taken throughout the experiment.

*(iii) Fluidized Bed Reactor*
• An in-house built fluidized bed reactor was used to conduct large-scale gasification experiments.
• Experiments were done at maximum temperatures of 550°C, 750°C, and 920°C; maximum temperature was sustained for 30 minutes or 1 hour.
• $CO_2$, $H_2O$, and $N_2$ were used as reactive gas; flow rate was 400SLPM/kg biomass

## Biomass Decomposition: TGA

Mass loss of biomass during gasification with different gases was measured using a TGA; the temperature program used is shown below

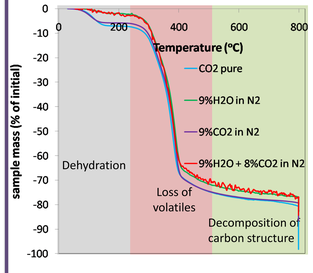
*Temperature program for TGA/DSC*




**Reaction Conditions**

| Reactive Gas | Mass loss (%) |
|---|---|
| 9% $CO_2$ in $N_2$ | 86.66 |
| 9% $H_2O$ in $N_2$ | 81.95 |
| 100% $CO_2$ | 98.25 |
| 9%$H_2O$ & 8%$CO_2$ in $N_2$ | 81.27 |

**Mass Loss**




-$CO_2$ is more reactive than $H_2O$; higher mass loss is achieved with 9%$CO_2$ compared to 9% $H_2O$

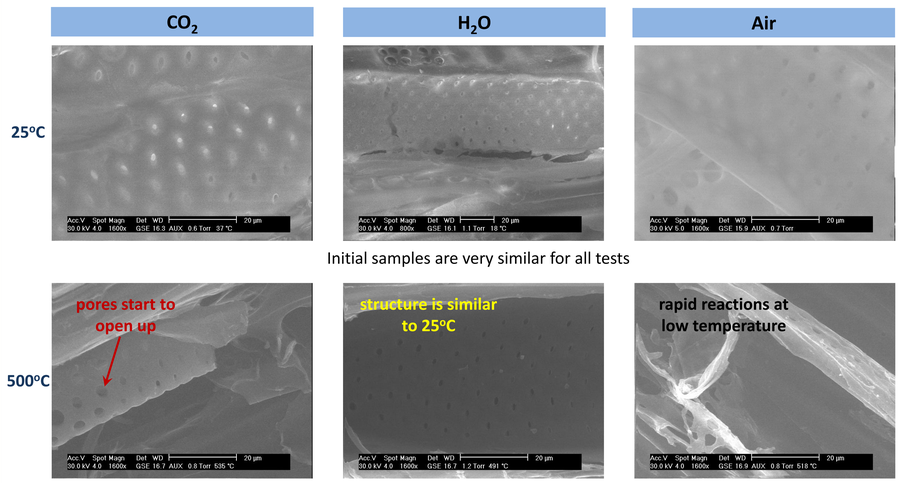
-Mass loss is similar for 9%$CO_2$ and 100%$CO_2$ until 750°C; it is likely that this is when Boudouard* reaction becomes significant

-Mass loss with $CO_2$ + $H_2O$ mix is very close to mass loss with only $H_2O$; this could be indicative of a competitive reaction between $CO_2$ and $H_2O$

*Boudouard reaction: $CO_2$ + C → 2CO

## Gasification Under ESEM

- Biomass samples were heated up to 1000°C under ESEM at 20°C/min; below are images taken during gasification with air, $CO_2$, and $H_2O$; visual analysis of morphological changes can help us understand the reactions taking place




**Observations:** – at lower temperatures, $CO_2$ reaction begins in the small pores of the biomass; this is not observed with $H_2O$
-at higher temperatures, reactions proceed more quickly under $H_2O$ compared to $CO_2$
-reaction under air is very fast, even at low temperatures
- properties of the ash can be modified by changing the process conditions under which biomass is gasified; these properties can affect the catalytic activity of the ash

## Conclusions

- biomass gasification produces a porous ash whose structure is dependent on gasification temperature and gases used
- $CO_2$ produces ash with higher surface area than $H_2O$
- at 800°C, total mass loss is higher with $CO_2$ compared to $H_2O$
- in the presence of both $CO_2$ and $H_2O$ there may be competitive reactions
- at high temperatures, sintering of the ash takes place under $H_2O$ and air but is not observed with $CO_2$

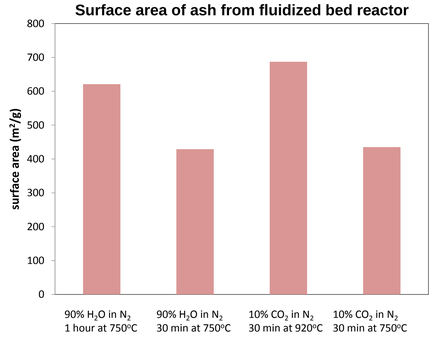
## Future Work

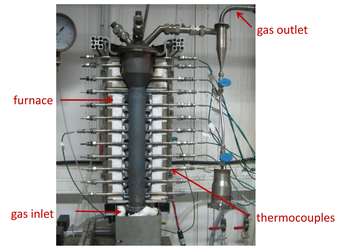
- future work should investigate the catalytic activity of the ash by reforming tars into syn gas or liquids using the ash
- future work should further investigate why the rate of formation of ash is different in different atmospheres and what conditions are ideal in order to avoid sintering

*References*: (1) El-Rub, Z. A.; Bramer, E. A.; Brem, G. *Fuel*. **2008**, 87, 2243-2252
(2) Butterman, H.C.; Castaldi, M. J.; *Environ. Sci. Technol.* **2009**, *43*, 9030-9037

## Ash Characterization

-Biomass was gasified in the fluidized bed reactor, shown on right.
- Reactive gas was varied; test were done with 10% $CO_2$in $N_2$, and 90% $H_2O$ in $N_2$.
- Maximum reactor temperature and time at maximum temperature was varied.
- Surface area of ash was measured using BET method.



**Fluidized bed reactor**

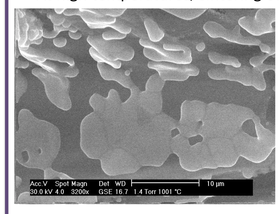
-Higher temperatures or longer reaction times create an ash with higher surface area.

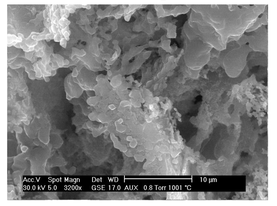
- The porosity of ash generated using only 10% $CO_2$ was the same as that for ash generated using 90% $H_2O$ at the same conditions.

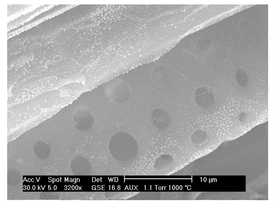
-The ability of $CO_2$ to produce a more porous ash than $H_2O$, could be due to the ability of $CO_2$ to react in the smaller pores of the wood, which is not observed with $H_2O$.

## Ash Sintering

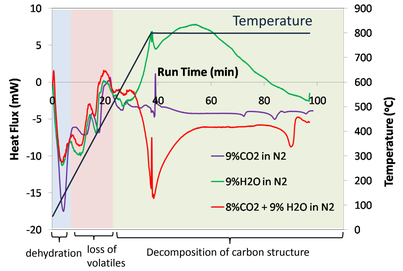
- If ash is to be used as a catalyst, it is desirable to have high surface area, therefore we want to avoid sintering.
- At high temperatures, sintering of the ash was observed with $H_2O$ and with air; no sintering was observed with $CO_2$.


Ash generated under 100% $H_2O$, 1000°C


Ash generated under 100% air, 1000°C


Ash generated under 100% $CO_2$, 1000°C

**DSC heat flux under different reactive gases**




-At 800°C *endothermic* reactions are observed with 9%$CO_2$ and with 8%$CO_2$ + 9%$H_2O$ mix

-At 800°C *exothermic* reactions are observed with 9%$H_2O$

- The mass loss was the same for 9% $H_2O$ and $H_2O$/$CO_2$ mix (see mass loss section) yet DSC shows different reactions; sintering is an example of a reaction that results in no total mass loss; therefore, this could be a sign of sintering taking place with just $H_2O$ while less sintering takes place when $CO_2$ is added

*Possible reasons why sintering is not observed with $CO_2$:*

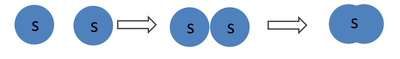
(i) An important decomposition reaction during gasification is:

$$CaCO_{3(s)} \xrightarrow{750^{o}C} CaO_{(s)} + CO_{2(g)}$$

-the rate of this reaction will be slower if the concentration of $CO_2$ in the atmosphere is high
-sintering is more likely if decomposition is fast, therefore increasing $CO_2$ concentration in the atmosphere may decrease the rate of decomposition of carbonate species in the wood

(ii) $CO_2$ has better access to the smaller pores than $H_2O$; therefore it may form a layer of gas in the micro-pores in the wood
- a gas layer may decrease solid-solid contact between particles which may lead to sintering

*In the absence of gas in the micro-pores sintering is more likely to take place:*




*The presence of gas in the micro-pores may decrease sintering:*