# GASIFICATION OF BIOMASS AND $CO_2$ CAPTURE USING CHEMICAL-LOOPING COMBUSTION

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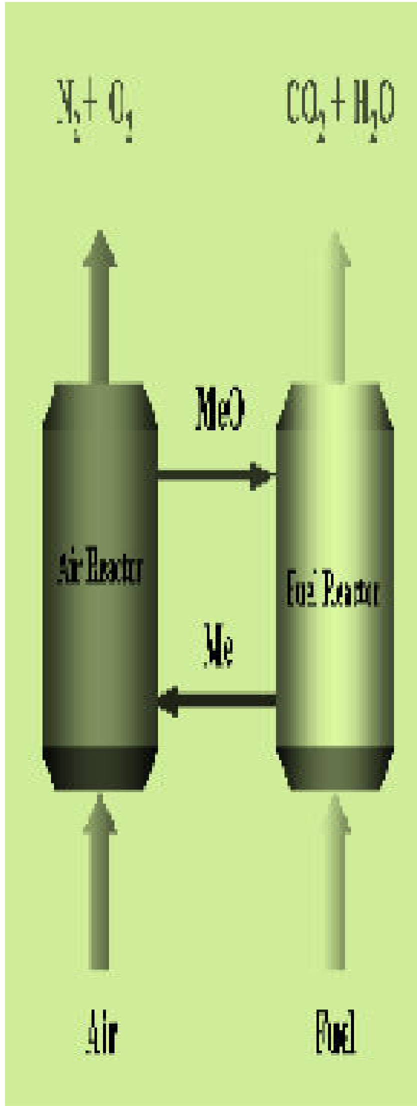
# Chemical-Looping Combustion (CLC)

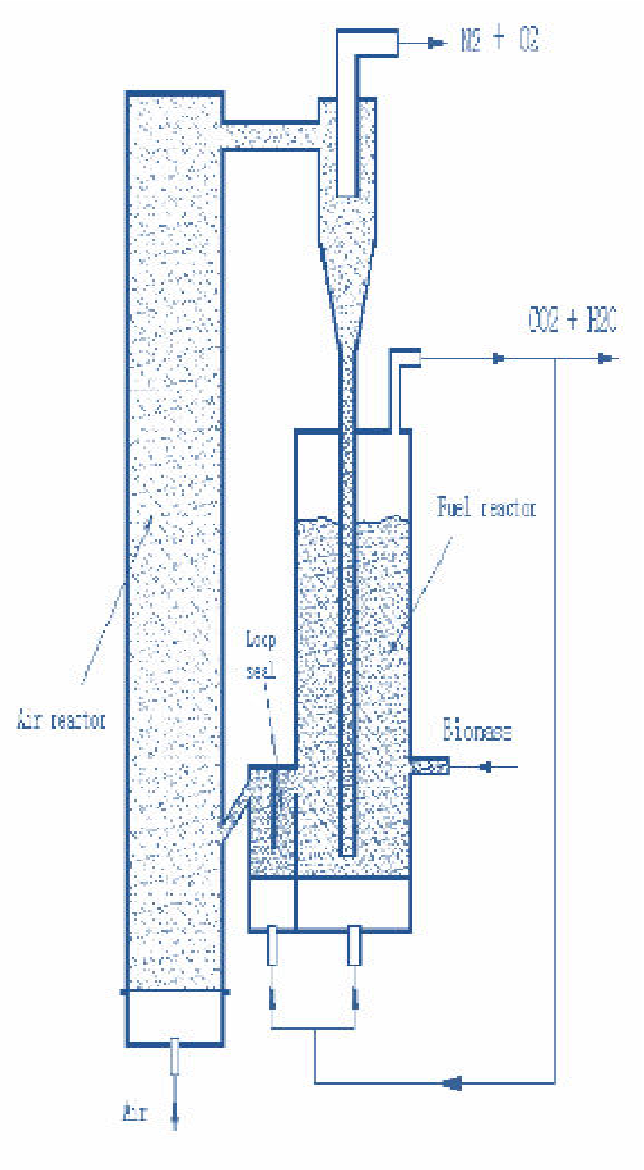
**Fuel reactor: Fuel + 4MeO = $CO_2$ + CO + $2H_2O$ + 4Me**

**Air reactor: 2Me+ + $O_2$ (air) = 2MeO**



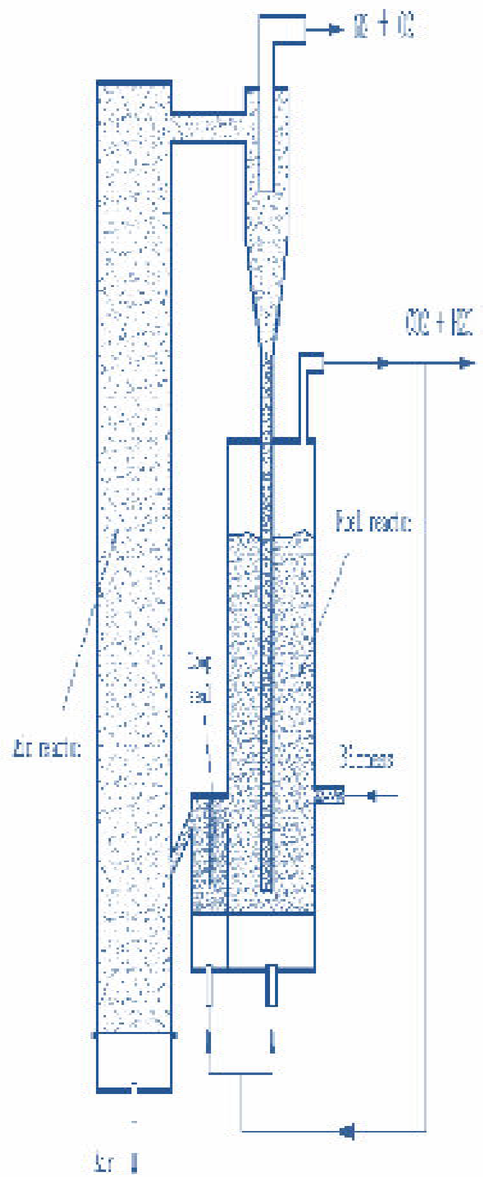

- Direct contact between fuel & air is avoided,
- Pure $CO_2$ can be obtained when $H_2O$ is condensed, eliminated the energy penalty for $CO_2$ separation
- NOx formation is minimal
- The total heat released from the two reactions is equal to that obtained in conventional combustion

# Integrated Biomass Gasification-CLC




- Agricultural & municipal waste are major sources of renewable energy with zero net $CO_2$ emissions,
- Biomass conversion in conjunction with CLC, offers the additional potential of delivering negative $CO_2$ emissions,
- IG-CLC can be accomplished by gasification of the solid fuel producing syngas which can be burned inside the same fuel reactor of the CLC process.

# Integrated Biomass Gasification-CLC



## Fuel Reactor

### Gasification/Pyrolysis Step:

$$C_x\,H_y\,O_z + \omega H_2O \leftrightarrow \alpha H_2 + \beta CO + \gamma CO_2 + \psi H_2O + \zeta CH_4 + \varphi C$$

$$CH_4 + H_2O \leftrightarrow CO + H_2\ (\mathit{SR\ reaction})$$

$$C + H_2O \leftrightarrow CO + H_2\ (\mathit{Heterogeneous\ WGS\ reaction})$$

$$CO + H_2O \leftrightarrow CO_2 + H_2\ (\mathit{WGS\ reaction})$$

$$C + CO_2 \leftrightarrow 2CO\ (\mathit{Boudouard\ reaction})$$

### Combustion Step:

$$4\,M_yO_x + CH_4 \longleftrightarrow M_yO_{x-1} + H_2O + CO_2$$

$$M_yO_x + H_2 \longleftrightarrow M_yO_{x-1} + H_2O$$

$$M_yO_x + CO \longleftrightarrow M_yO_{x-1} + CO_2$$

## Air Reactor

$$M_yO_{x-1} + O_2(N_2) \rightarrow M_yO_x + (N_2)$$

# Experimental Results with OCs

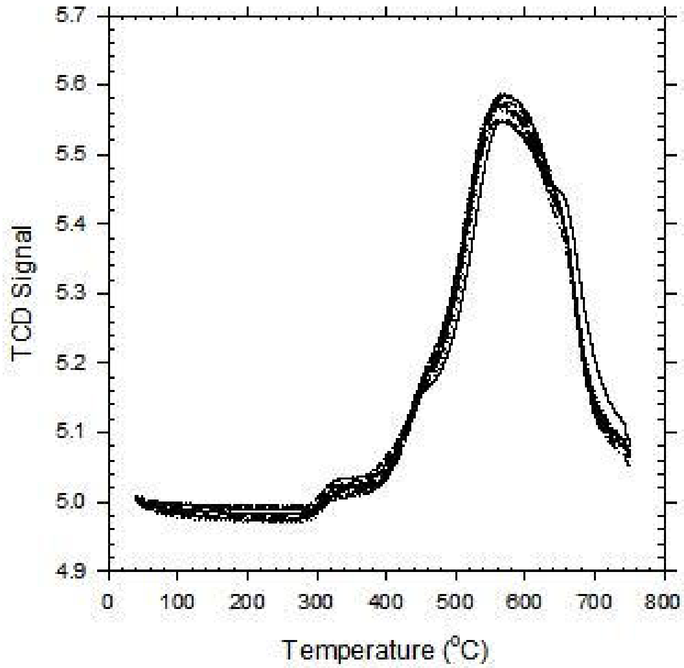
The OCs prepared by the incipient technique, show high reactivity and stability in cyclic TPR/TPO and pulse chemisorption experiments as shown in the figure.

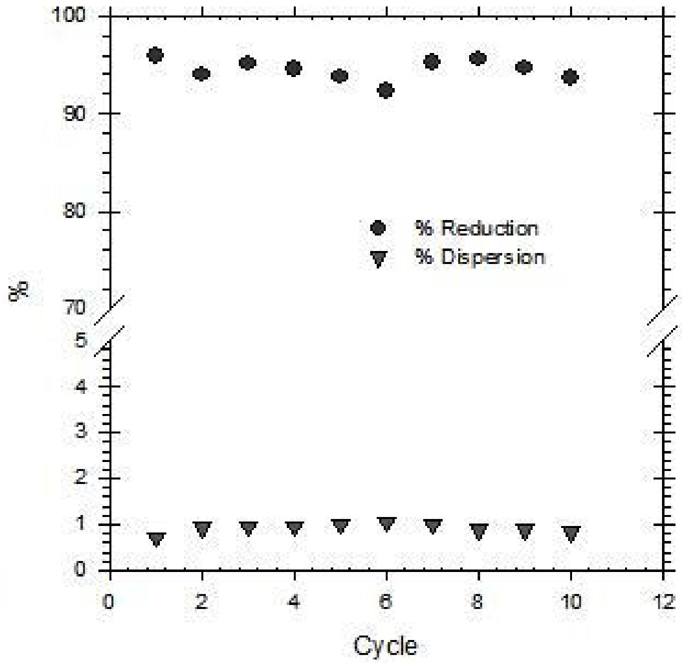
- Approximately **95% conversion** of the loaded Ni is observed. This is consistent over multiple reduction-oxidation cycles.

- Incorporation of Co on γ-$Al_2O_3$ aids the formation of easily reducible NiO species by minimizing **Ni- support interaction** and formation of **non-reactive $NiAl_2O_4$**.

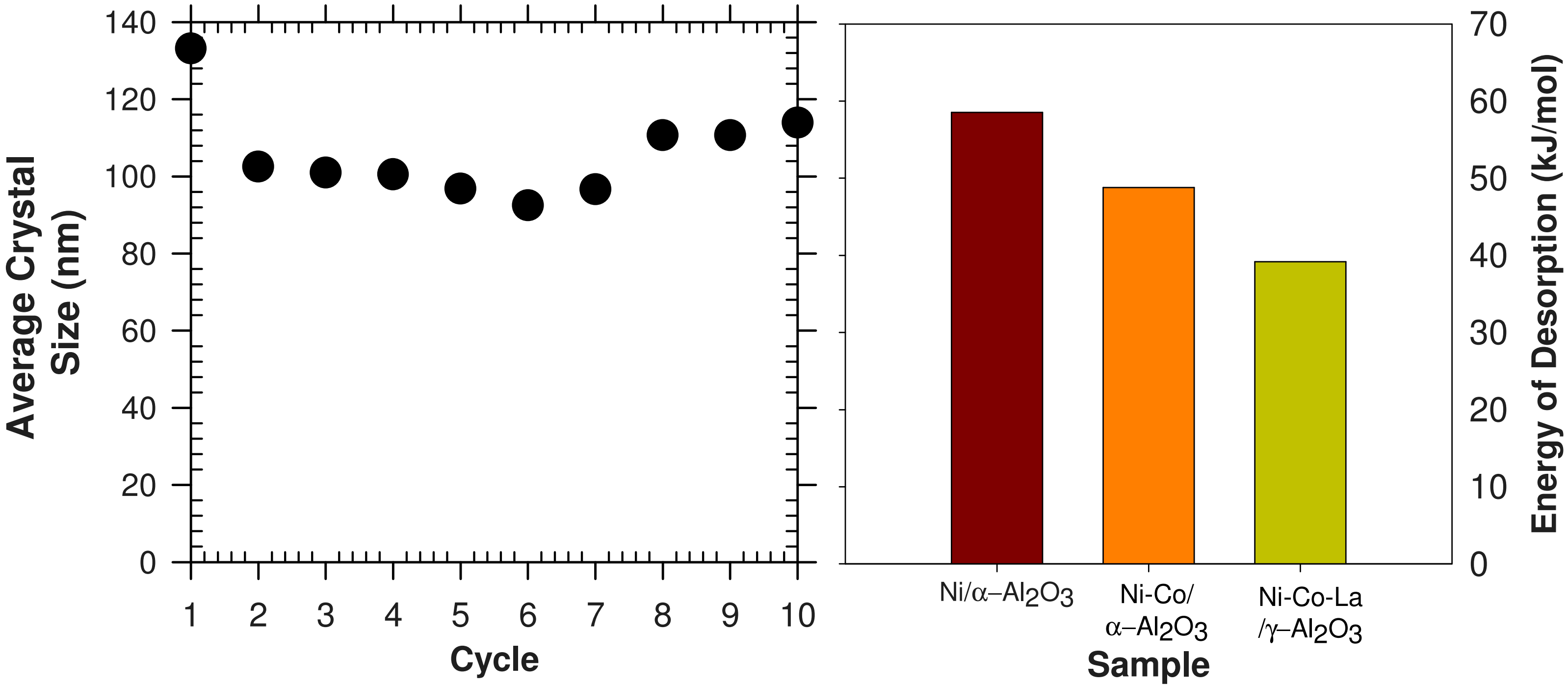
- On the other hand, La on γ-$Al_2O_3$ also minimizes the Ni-support interaction by stabilizing the supports while maintained a **high surface area**.

# Experimental Results with OCs



# Experimental Results with OCs



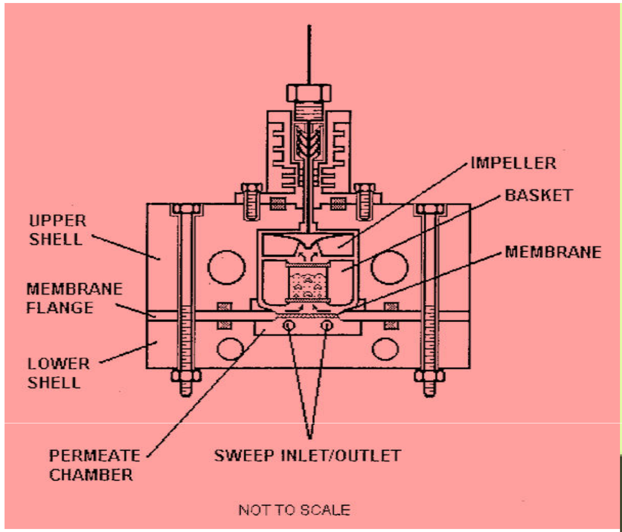
# Experimental Results

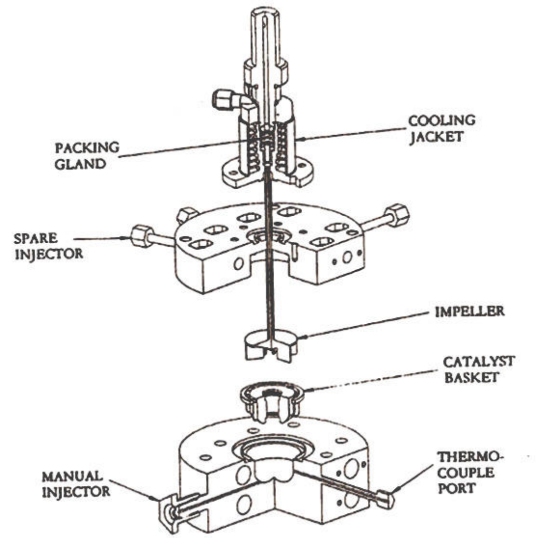
❖Ni particles maintain a relatively low and **stable dispersion** value of 0.94% and average crystal size of around 102 nm. This almost constant metal dispersion and crystal size over repeated reduction–oxidation cycles, is an indicator that the prepared oxygen carrier samples remain unchanged and do not lose active Ni species through solid–solid heterogeneous reactions between the metal species and the support.

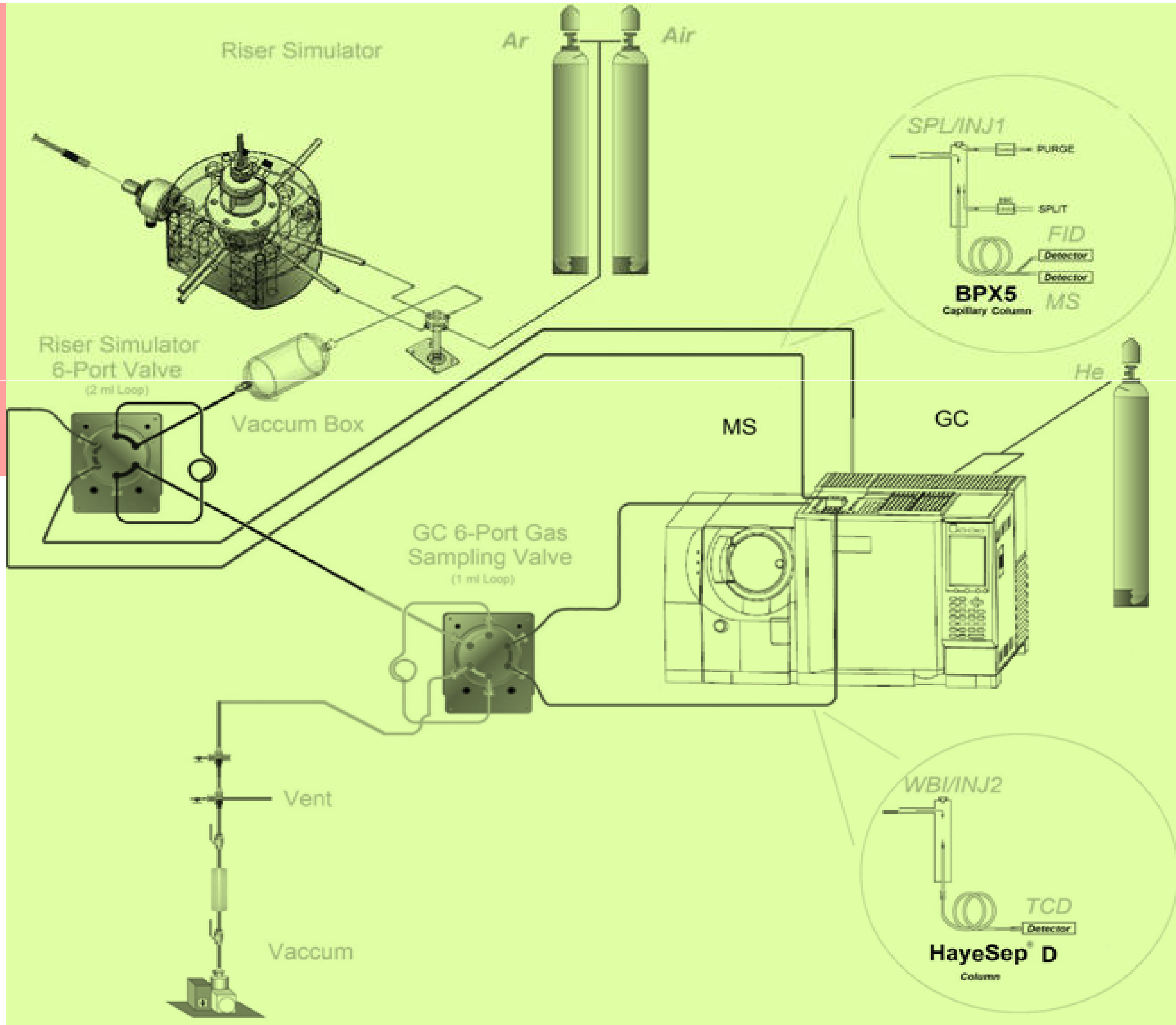
❖ The non-linear regression analysis of $H_2$ TPD results with Amenomiya and Cvetanovic's equation (1990) for the rate of desorption at constant activation energy gives **heat of desorption** 39+/- 20% kJ/mol. This s significantly lower than the 48.8+/-20% kJ/mol value obtained for Ni-Co/α-Al2O36 .with this suggesting a decreased metal oxide support interaction.

**decreased metal oxide support interaction.**

# IG-CLC in a CREC Riser Simulator

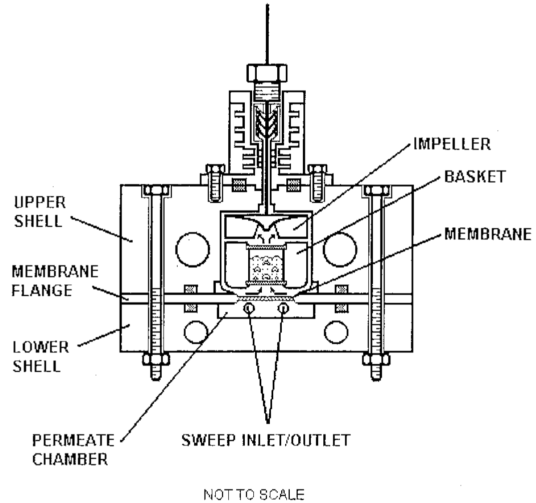


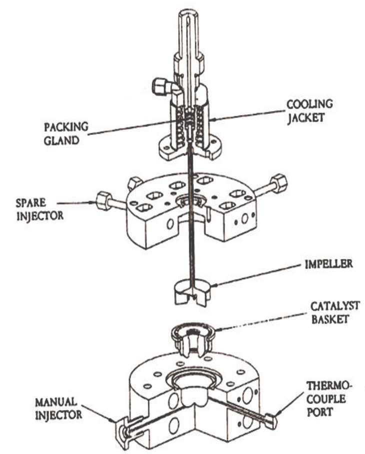



# IG-CLC in a CREC Riser Simulator

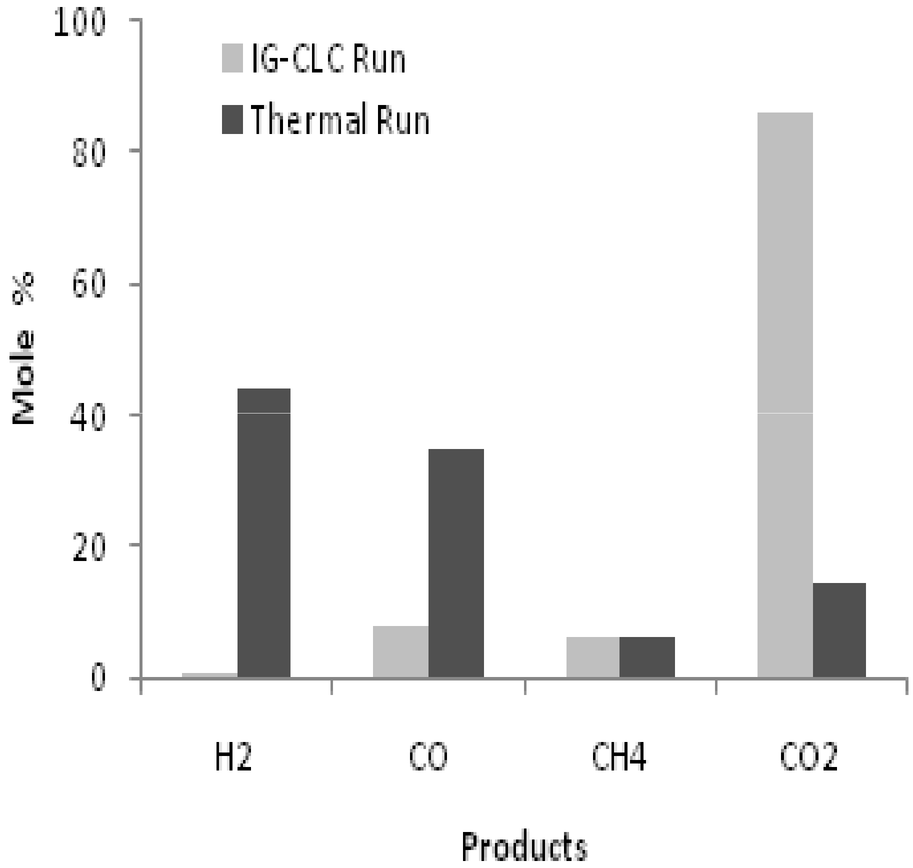
- Fuel: Glucose (C:1, H:2, O:1) as model compound for biomass
- Oxygen Carrier: NiO/La-$\gamma Al_2O_3$(20 % Ni)
- Glucose/Oxygen Carrier: 0.8
- Turbulent fluidization (6000 rpm)
- T: 700 °C, P: 1 atm, t: 30 s
- After each reduction cycle the carrier is re-oxidized in air at 550 °C
- Thermal runs were carried out in order to compare the results




**de Lasa,**
**US Patent 5, 102, 628, 1992**

# IG-CLC in a CREC Riser Simulator: Results

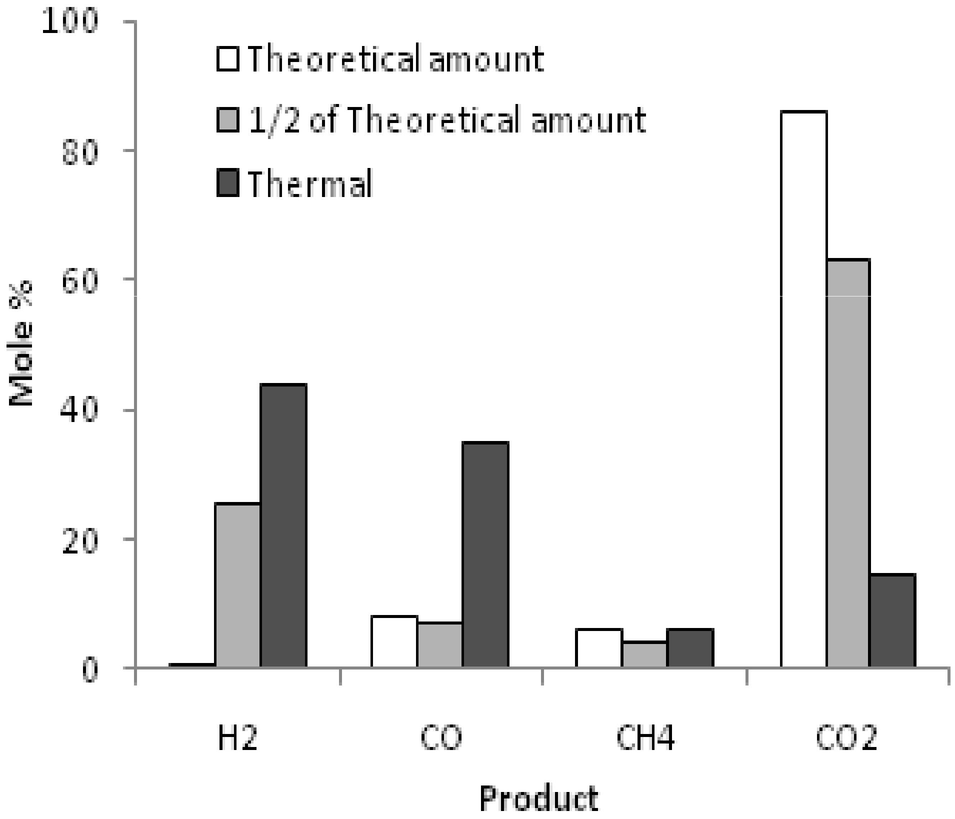



Fuel: Glucose
OC: NiO/La-γ$Al_2O_3$ T: 700 C, P= 1 atm

- Thermal Gasification:7 % $CH_4$, 35 % CO ,44 % $H_2$ and 15 % $CO_2$
- IG-CLC: 7 % $CH_4$, 8 % CO and 0.5 % $H_2$ and 86 % $CO_2$ OC/glucose close to the stoichiometric amounts for complete combustion
- In IG-CLC most of the gas produced during the gasification step is burnt in the subsequent combustion step involving the product gases and the solid oxygen carrier

# IG-CLC in a CREC Riser Simulator: Results

*Product composition for IG-CLC runs using different amount of oxygen carrier using Glucose as feed stock Oxygen in OC/glucose= 1, 0.5 and 0.*

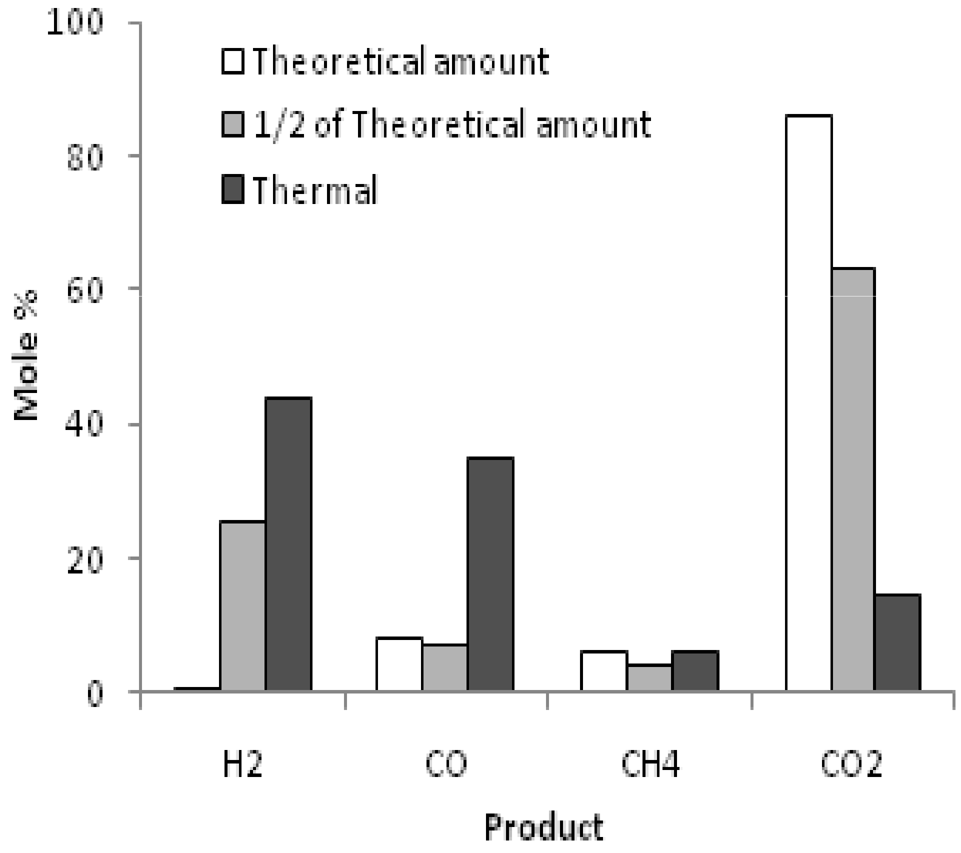



Fuel: Glucose
OC: $NiO/La\text{-}\gamma Al_2O_3$ T: 700 C, P= 1 atm

- Significant variations of $H_2$, CO and $CO_2$ with the amount of oxygen carrier
- Product selectivity of a combustion using a supported metal oxide is closely associated with the degree of the reduction of the oxygen carrier
- At the beginning of the reaction the fully oxidized oxygen carrier favors the total oxidation of the gasification products to form $CO_2$ and $H_2O$system

# IG-CLC in a CREC Riser Simulator: Results

*Product composition for IG-CLC runs using different amount of oxygen carrier using Glucose as feed stock Oxygen in OC/glucose= 1, 0.5 and 0.*




- As the reaction proceeds, the partially reduced oxygen carrier start catalyzing the reactions producing synthesis gas ($CO+H_2$)
- The methane composition in the oxygen deficient runs decreases slightly due to the reforming reaction competition.
- At the same time the CO and $H_2$ remained unreacted due to the oxygen deficiency in the system

Fuel: Glucose
OC: $NiO/La\text{-}\gamma Al_2O_3$ T: 700 C, P= 1 atm

# Thermodynamic Equilibrium Model

## Gasification/Pyrolysis Step complies with stoichiometry:

$$C_x H_y O_z + \omega H_2O \leftrightarrow \alpha H_2 + \beta CO + \gamma CO_2 + \psi H_2O + \zeta CH_4 + \varphi C$$

*The C,H,O balance for the gasification reaction gives:*

$$x = \beta + \gamma + \zeta + \varphi \ (\textit{carbon elemental balance})$$

$$y + 2\omega = \alpha + 4\zeta \ (\textit{hydrogen elemental balance})$$

$$z + \omega = \beta + 2\gamma + 2\psi \ (\textit{oxygen elemental balance})$$

# Thermodynamic Equilibrium Model

## *Gasification Step:*

$$SR: K_{CH_4} = \frac{y_{CO}\, y_{H_2}^3}{y_{CH_4}\, y_{H_2O}} (P)^2 = \frac{\alpha^3 \beta}{\zeta\psi(\alpha+\beta+\gamma+\psi+\zeta+\varphi)^2}(P)^2$$

$$HWGS: K_C = \frac{y_{CO}\, y_{H_2}}{a_C\, y_{H_2O}} = \frac{\alpha\beta}{\varphi\psi}$$

$$WGS: K_{WGS} = \frac{y_{H_2}\, y_{CO_2}}{y_{CO}\, y_{H_2O}} = \frac{\alpha\gamma}{\psi\beta}$$

$$Boudouard: K_{CB} = \frac{y_{CO}^2}{a_C\, y_{CO_2}} = \frac{\beta^2}{\varphi\gamma}$$

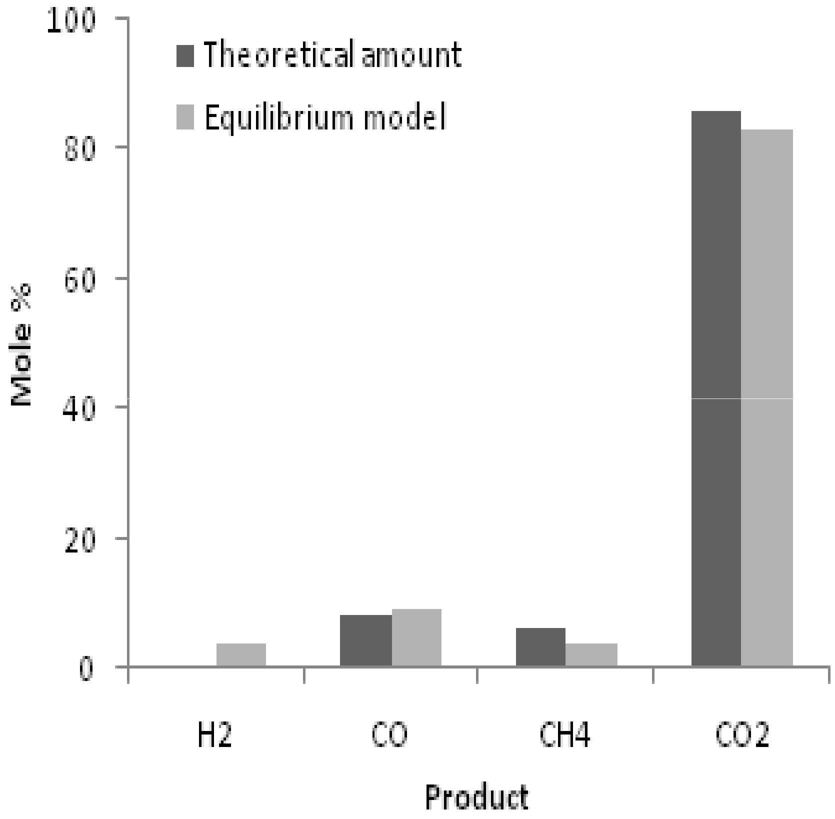
## Combustion Step:

$$CH_4 : K^c_{CH_4} = \frac{a_{M_yO_x} y_{CH_4}}{y_{H_2O} y_{CO_2}} (P)^{-1} = \frac{\zeta}{\psi\gamma^2} (P)^{-1}$$

$$CO : K_{CO} = \frac{a_{M_yO_x} y_{CO}}{y_{CO_2}} = \frac{\beta}{\gamma}$$

$$H_2 : K_{H_2} = \frac{a_{M_yO_x} y_{H_2}}{y_{H_2O}} = \frac{\alpha}{\psi}$$

# IG-CLC Thermodynamic Modeling VS Experimental Results




Fuel: Glucose
OC: NiO/La-γ$Al_2O_3$ T: 700 C, P= 1 atm

- The thermodynamic model simulating the IG-CLC process based on the reaction schemes were studied using the Gibbs free energy minimization to determine the product gas composition
- The product compositions for both the experimental and that of using the equilibrium model are comparable
- This analysis further confirms the potential of an integrated biomass gasification and chemical-looping combustion to provide an innovative technology for $CO_2$ capture

# Conclusions

- Chemical-looping combustion of biomass (model compound glucose) with inherent $CO_2$ separation is investigated using an Experimental and Thermodynamic equilibrium modeling approach.
- The thermodynamic model predicts (close to stochiometric conditions) oxygen carrier $NiO/Al_2O_3$ rapidly reacting with gasified products ($CH_4$, $CO$, $H_2$) forming $CO_2$ and water
- These results are in line with the observed experimental results in the CREC fluidized Riser Simulator.

# Thank You