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Thermodynamic Analysis of Reforming Processes

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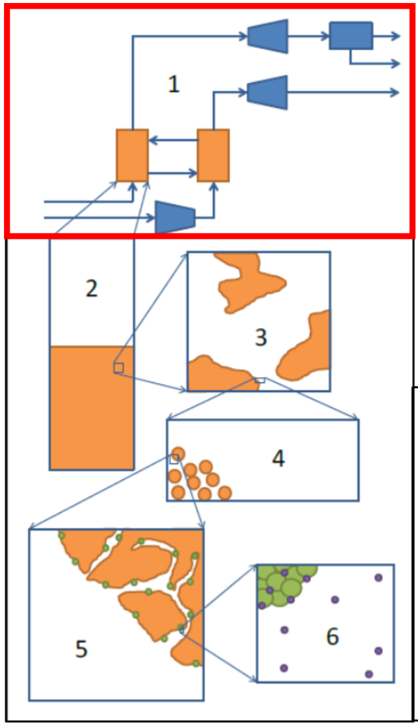
NanoSim – EU FP7 Project

- A Multiscale Simulation-Based Design Platform for Cost-Effective CO_2 Capture Processes using Nano-Structured Materials (NanoSim)



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1. System Scale
2. Equipment Scale
3. Cluster Scale
4. Particle Scale
5. Intra-particle pore scale
6. Atomistic scale

- Connect models at different scales
- Reduce time spent on materials development
- To accelerate rationale development of CO_2 capture processes
- To demonstrate the techno-economic competitiveness of CO_2 capture process based on Chemical Looping Reforming using Nano-Structured materials

Objective of the Current Work

- Identify the thermodynamic potential of a Chemical Looping Reforming (CLR) process

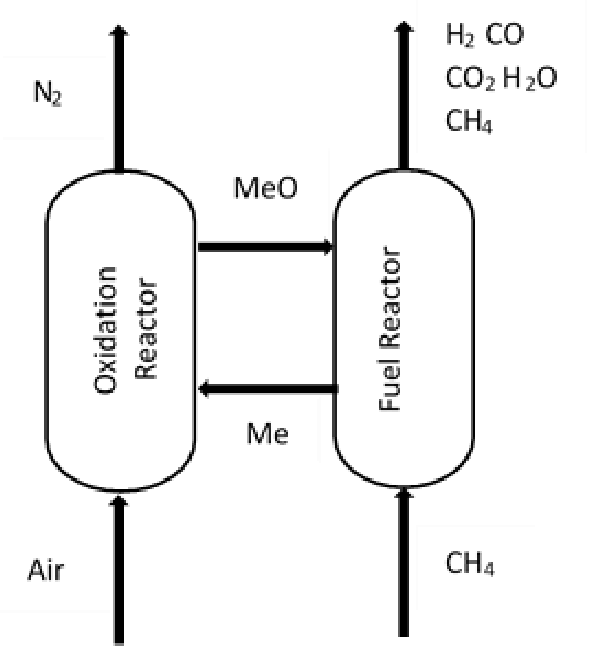
- Exergy analysis of Chemical Looping Reforming (CLR) and conventional Partial Oxidation (POX) process

- Comparison of Exergy Destruction in CLR and POX at different operating conditions

Chemical Looping Reforming (CLR)

$$Me + \frac{1}{2} O_2 \rightarrow MeO$$

$$CH_4 + MeO \rightarrow CO + 2H_2 + Me$$



- Where Me/MeO is the metal oxygen carrier system
- Side reactions occur to yield fractions of CO_2 and H_2O

Chemical Looping Reforming

- Pre-combustion CO_2 Capture
- Inherent Air Separation
- Process Intensification
- Operates at fairly low temperatures
- Gives higher H_2/CO ratio when compared to conventional partial oxidation process

Thermodynamic Analysis - Exergy

Exergy

- Maximum useful work that can be derived from a system
- A method to account for irreversibilites in a system

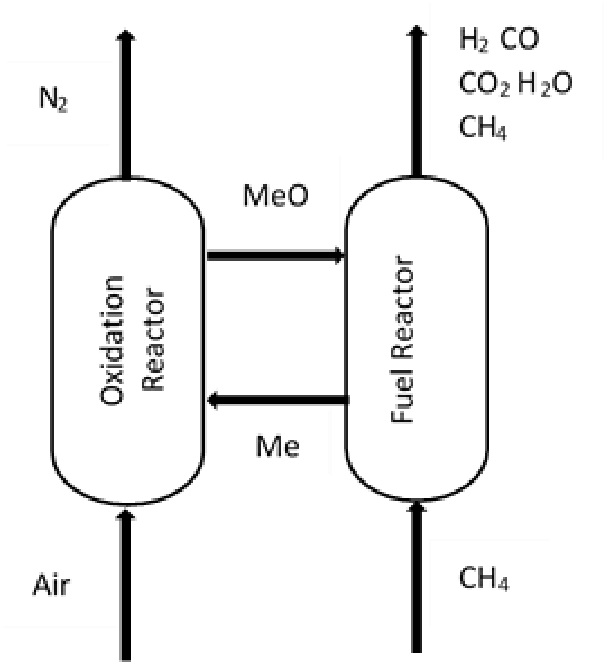
$$E_D = \sum E_Q - W_{CV} + \sum E_i - \sum E_e$$

$$E_Q = Q\,(1- T/T_o)$$

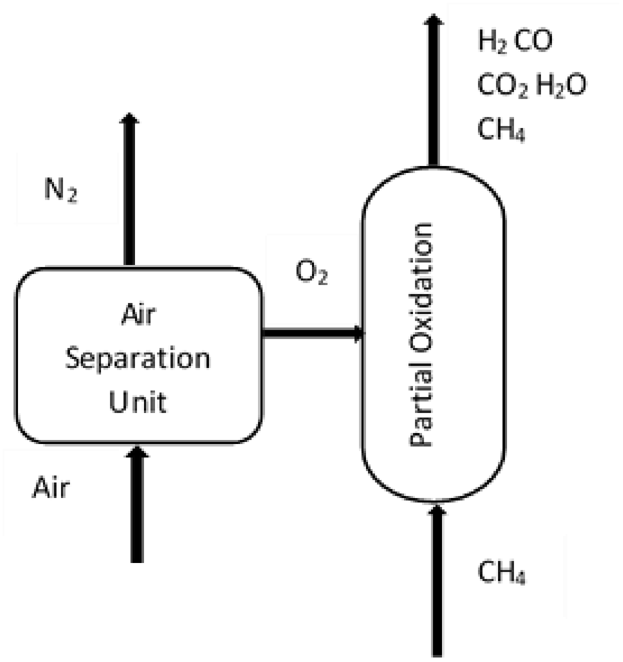
Where

- Q – Heat transfer across the system
- T – Temperature of the system
- T_o – Ambient Temperature
- E_Q – heat transfer exergy
- W_{CV} – Work done by the system
- E_i, E_e – Total exergy of the streams In and Out respectively
- E_D – Exergy destroyed in the system

Methodology



Chemical Looping Reforming



Partial Oxidation

Methodology

$$ExD\% = (E_D/E_{CH4})*100$$

Where

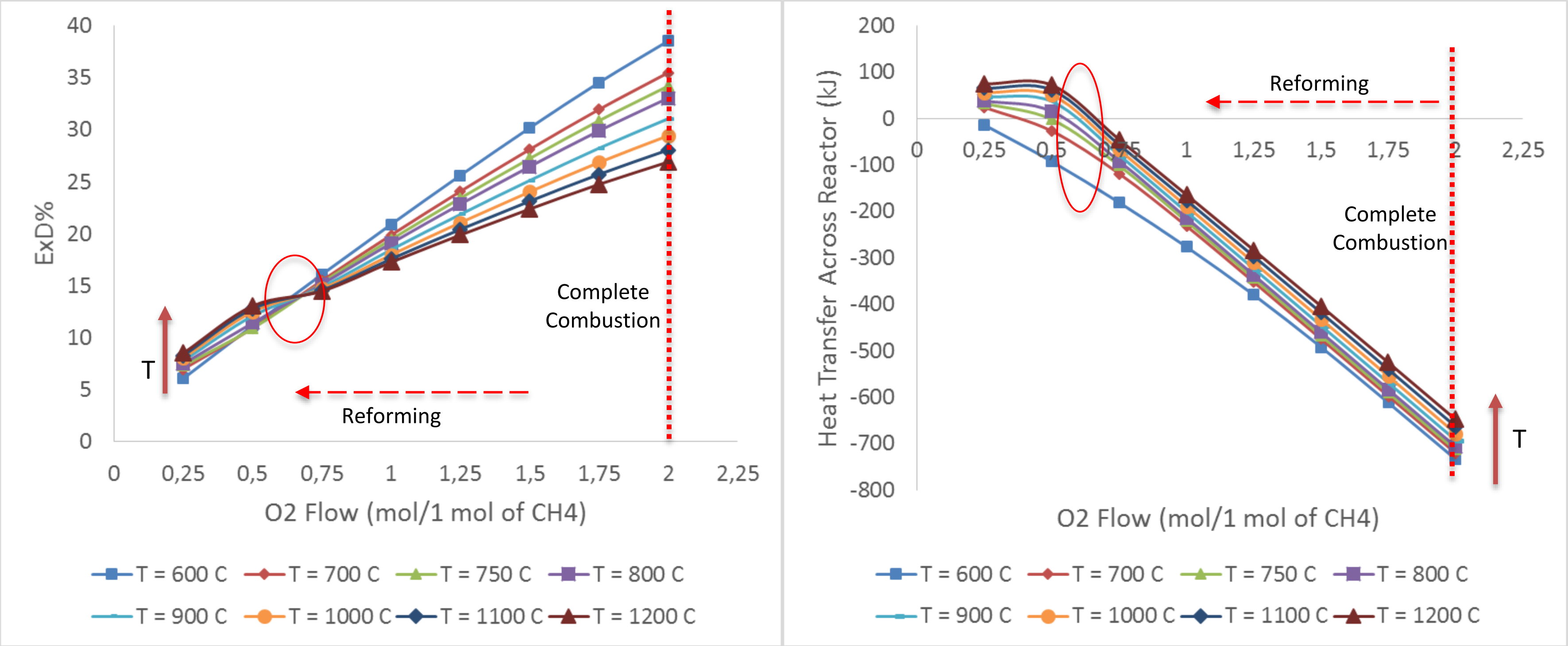
- E_D – Exergy destroyed in the system
- ExD% - Percentage of exergy destroyed
- E_{CH4} – Chemical exergy of fuel (CH_4)

Assumptions and Considerations:

- Air is considered a binary mixture of 21% O_2 and 79 % N_2 (mole fractions)
- Ni/NiO has been considered as the metal-metal oxide system
- Work input to Air Separation Unit (ASU) = 28.51 kJ/mol O2 (0.25 kWh/kg O_2)
- Equilibrium data at different conditions have been taken from ASPEN Plus
- Reactions considered to proceed with minimization of Gibbs Free Energy principle
- Peng Robinson Equation of State has been considered
- Heat transfer across the system boundary occurs at constant temperature

Results and Discussion

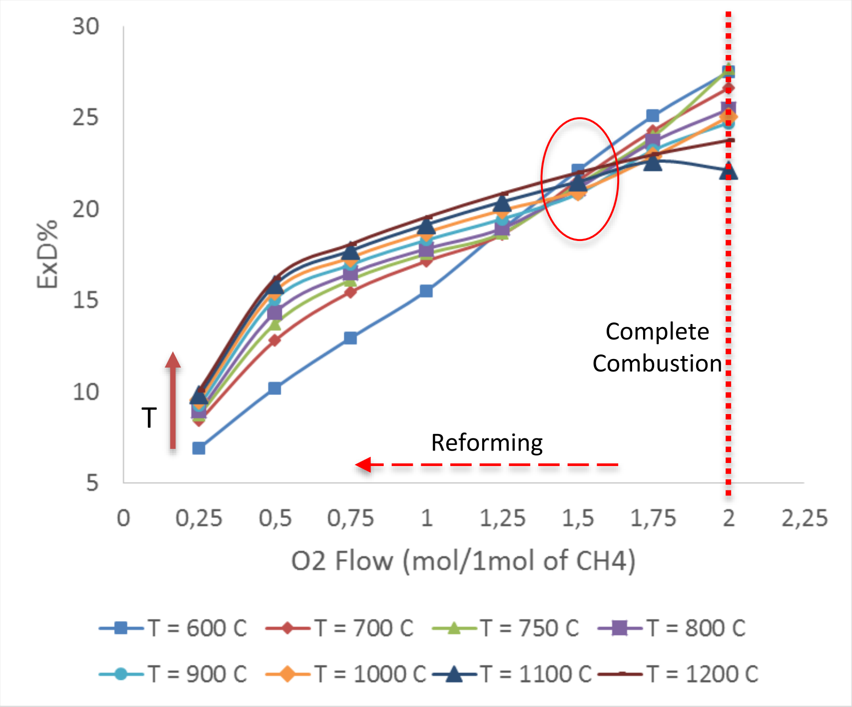
Partial Oxidation

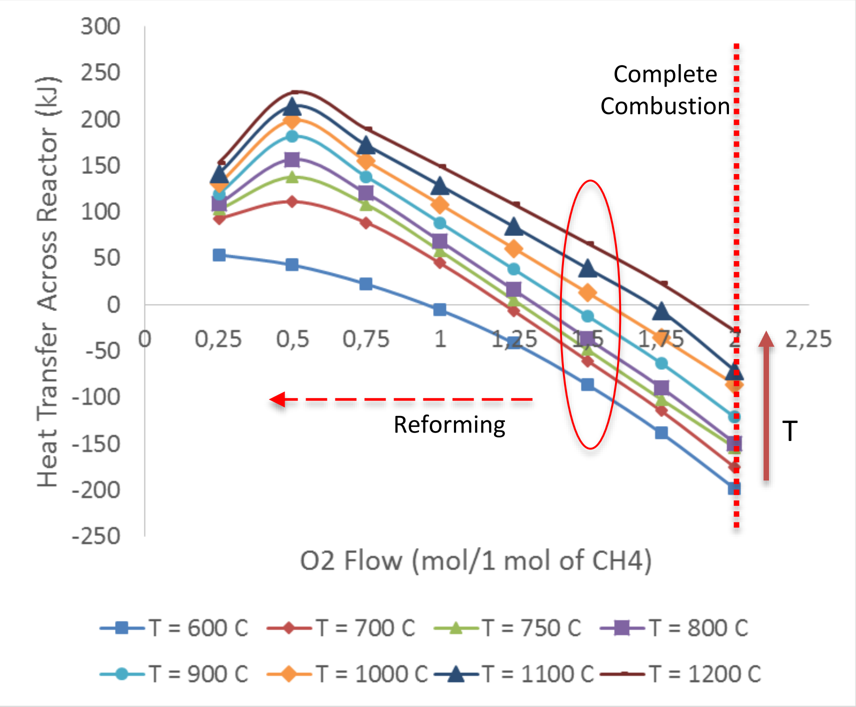


Identifying best way to operate Partial Oxidation

Results and Discussion

Chemical Looping Reforming



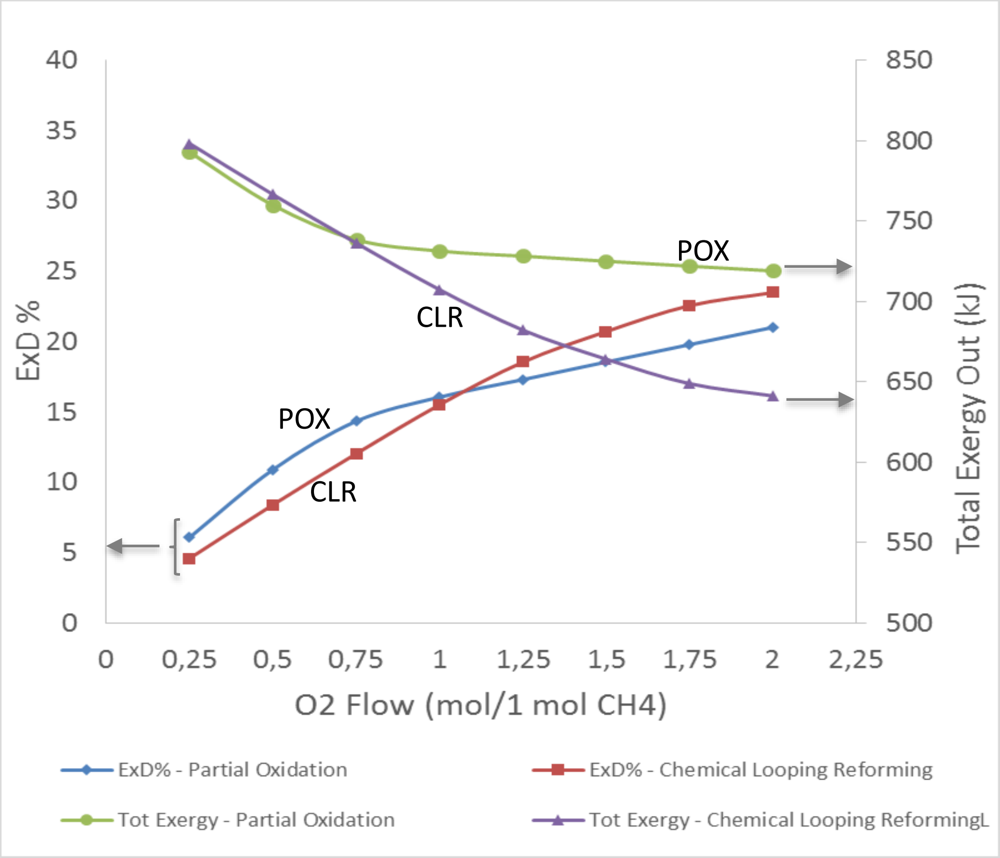


Identifying best way to operate Chemical Looping Reforming

Results and Discussion

Partial Oxidation (POX) vs Chemial Looping Reforming (CLR)

Reactor Conditions Adiabatic

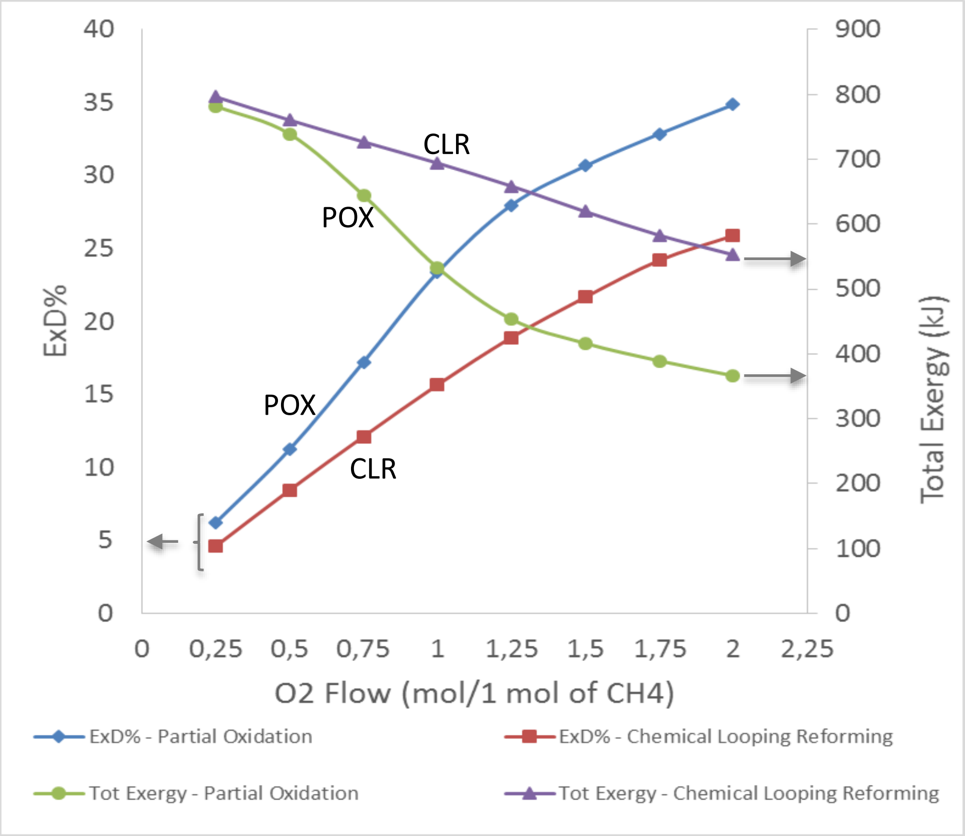


Temperature of reactor exit streams at adiabatic conditions

Results and Discussion

Partial Oxidation (POX) vs Chemial Looping Reforming (CLR)

Reactor
Conditions
Adiabatic
+
Heat
Exchanger
after the
Reactor

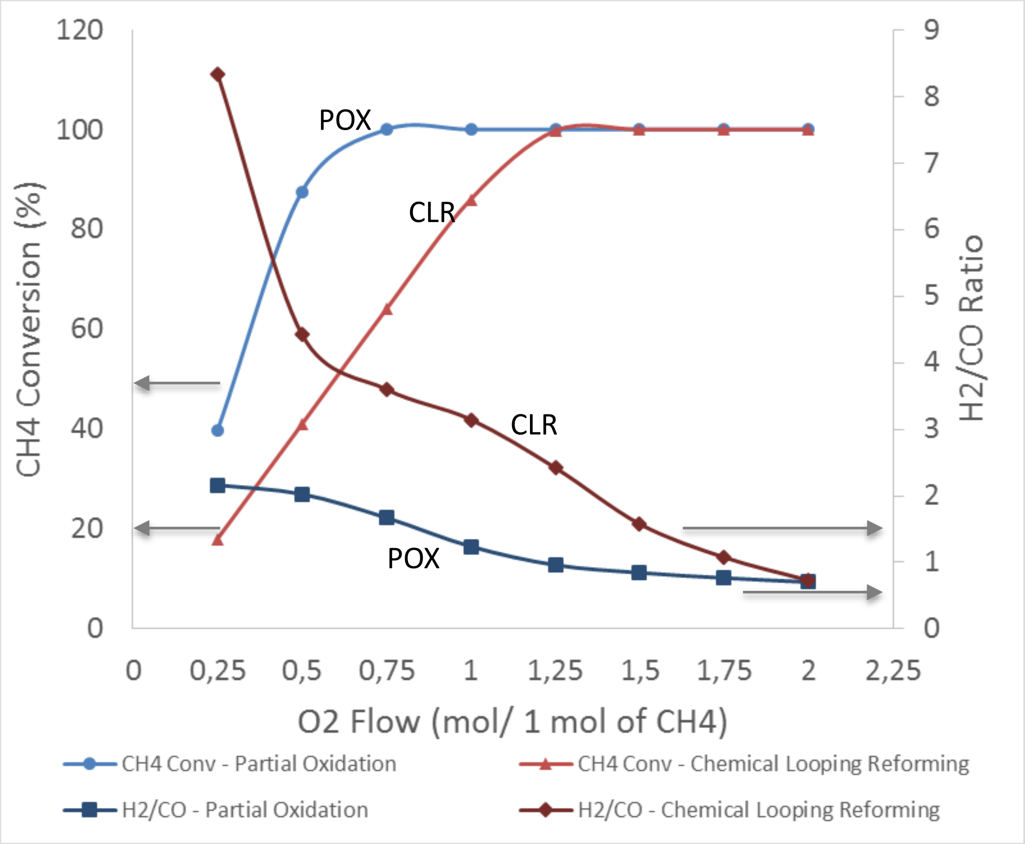


Temperature of exit streams suited to water gas shift reaction

Results and Discussion

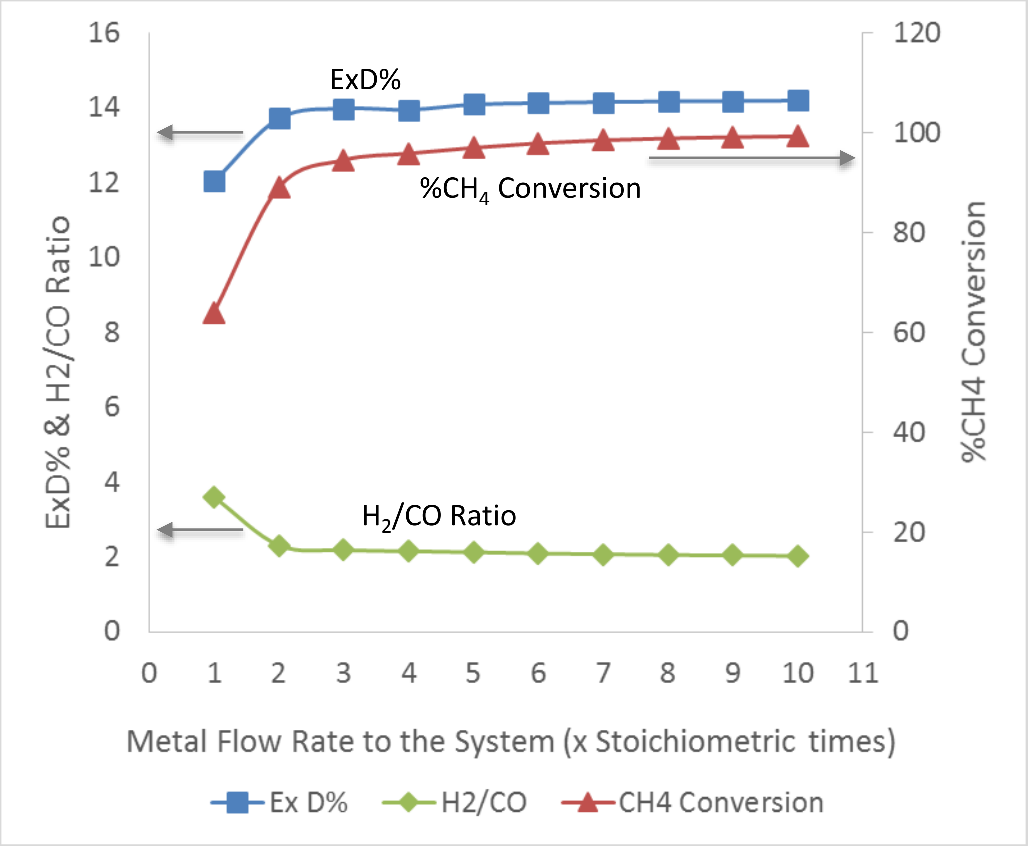
Partial Oxidation (POX) vs Chemial Looping Reforming (CLR)

CH_4 Conversion and H_2/CO ratio



Results and Discussion

High Metal Circulation Rate in Chemical Looping Reforming at constant O_2 input (0.75 mol O_2 / 1 mol CH_4)



Conclusions

- CLR seems to be a promising new method, with small thermodynamic losses and without the need for an air separation unit.

- Chemical Looping Reforming can be adiabatic – no need for external supply of heat

- Exergy destruction in CLR is less than in POX, since the temperature of exit streams from POX is very high, and cooling them down to a suitable water gas shift temperature results in high exergy losses

- CLR reforms CH4 to a product gas with higher H_2/CO ratio when compared to conventional POX

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Thank You