Chemical Looping Gasification for Hydrogen Enhanced Syngas Production with In-Situ CO_2 Capture

2015 DOE Gasification Systems Workshop

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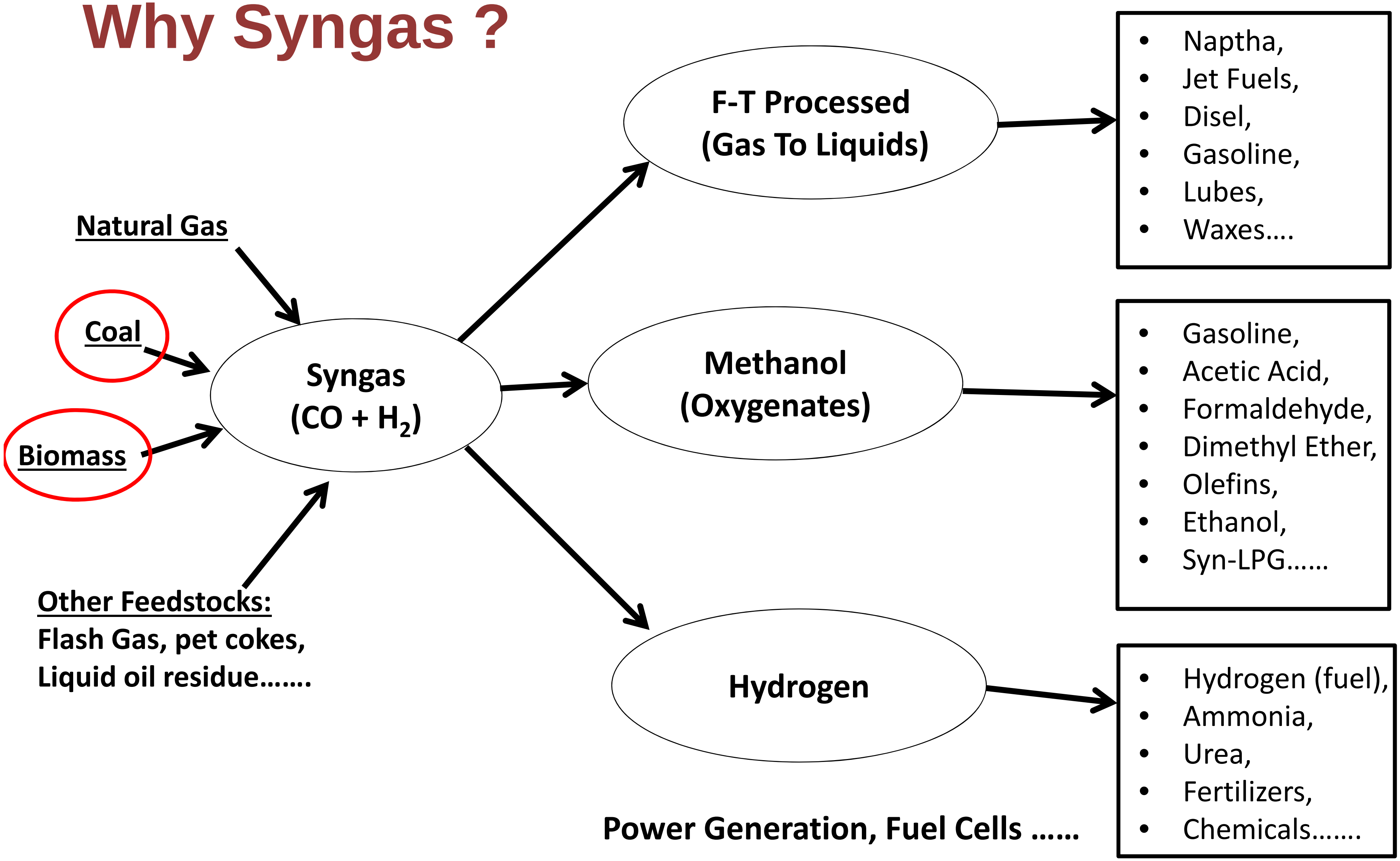
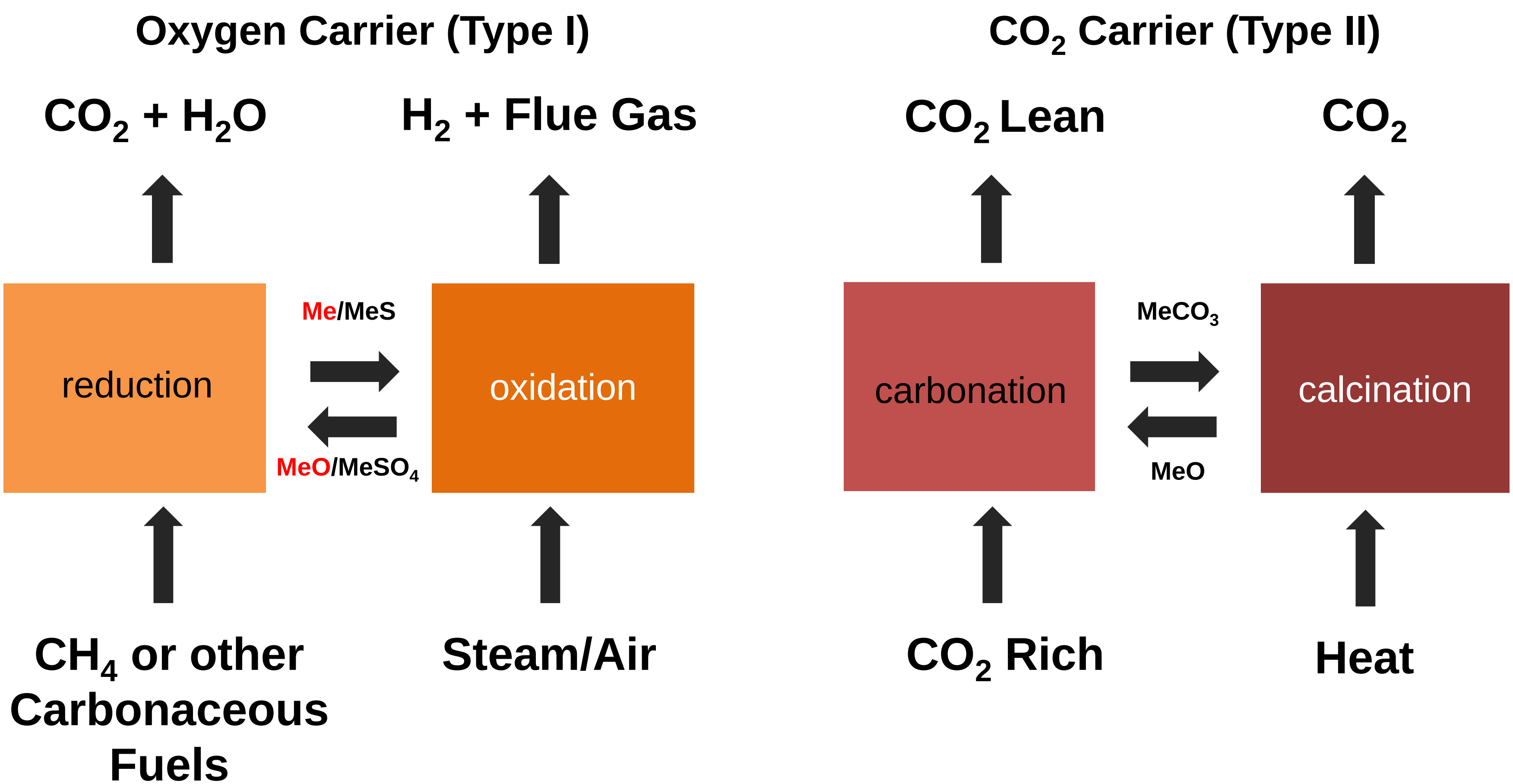
Why Syngas ?


Natural Gas
Coal
Biomass
Other Feedstocks:
Flash Gas, pet cokes,
Liquid oil residue…….
Syngas
(CO + H2)
F-T Processed
(Gas To Liquids)
Methanol
(Oxygenates)
Hydrogen
Naptha,
Jet Fuels,
Disel,
Gasoline,
Lubes,
Waxes….
Gasoline,
Acetic Acid,
Formaldehyde,
Dimethyl Ether,
Olefins,
Ethanol,
Syn-LPG……
Hydrogen (fuel),
Ammonia,
Urea,
Fertilizers,
Chemicals…….
Power Generation, Fuel Cells ……

Chemical Looping Systems with CO_2 Generation or Separation



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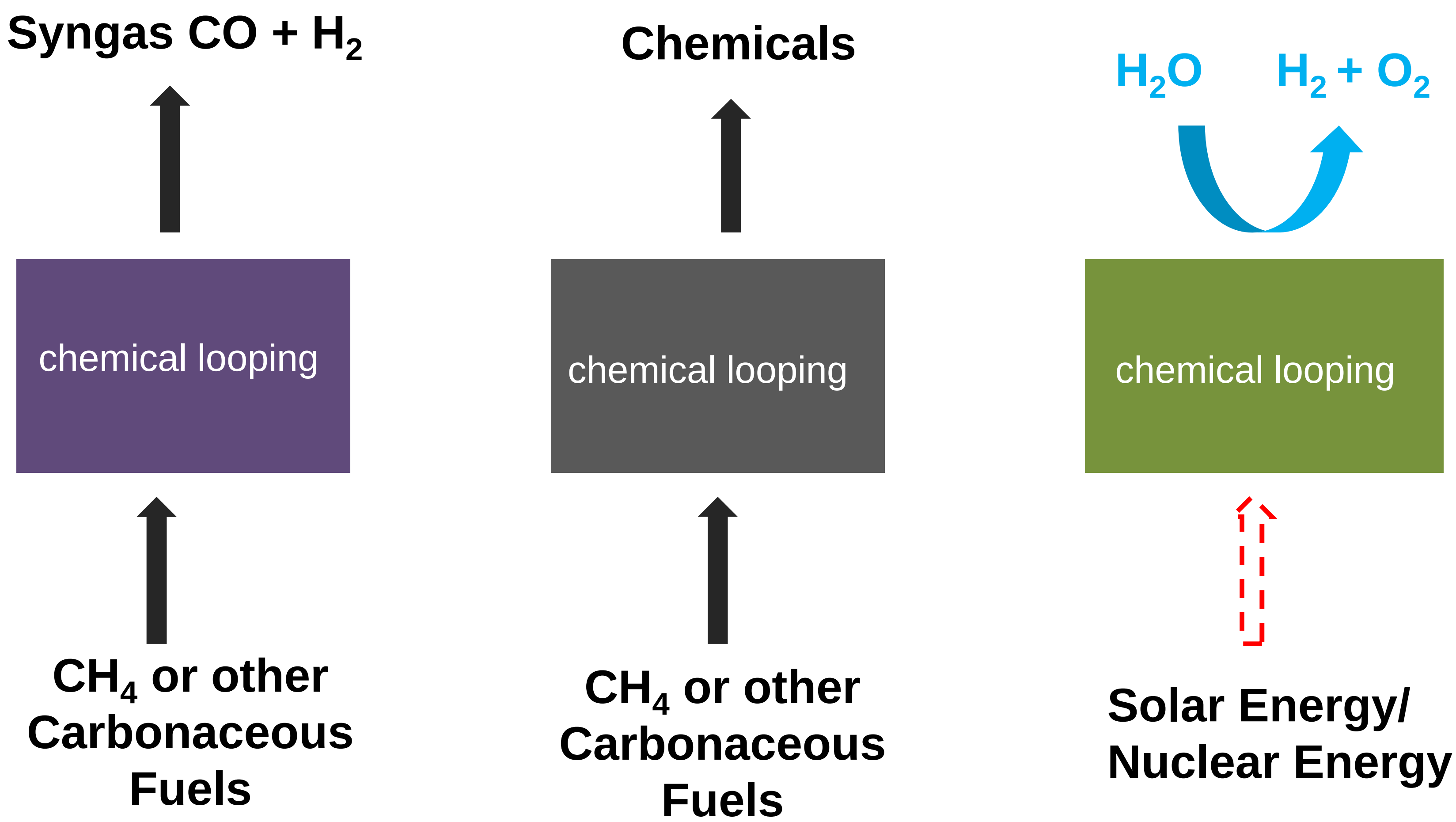
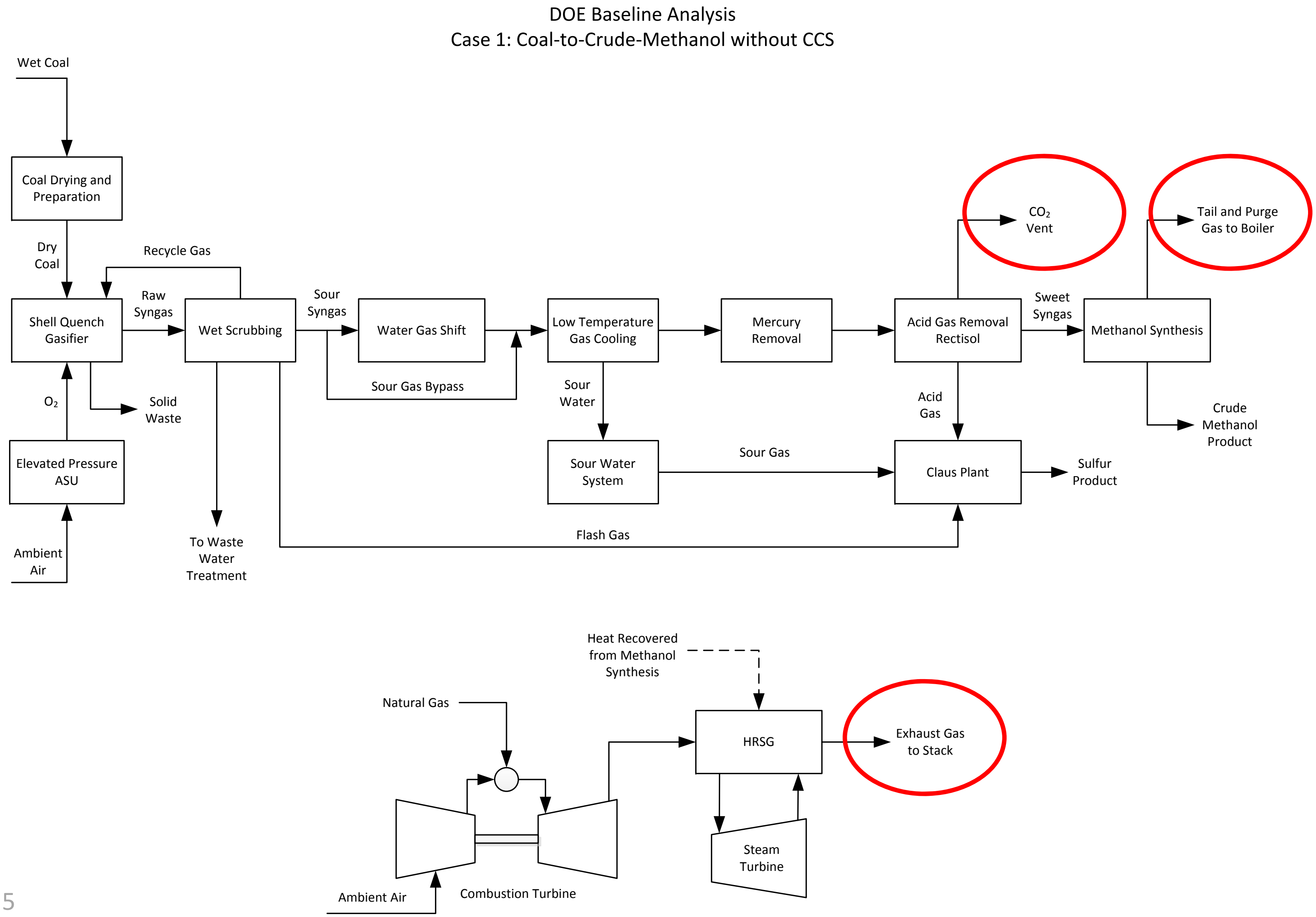
Chemical Looping Systems with Non-CO_2 Generation



Chueh, W. C., Falter, C., Abbott, M., Scipio, D., Furler, P., Haile, S.M., Steinfeld, A. *Science*. 2010. 330(6012), 1797.
Fan, L.-S., Zeng, L., Luo, S. *AIChE Journal*. 2015. 61(1), 2.

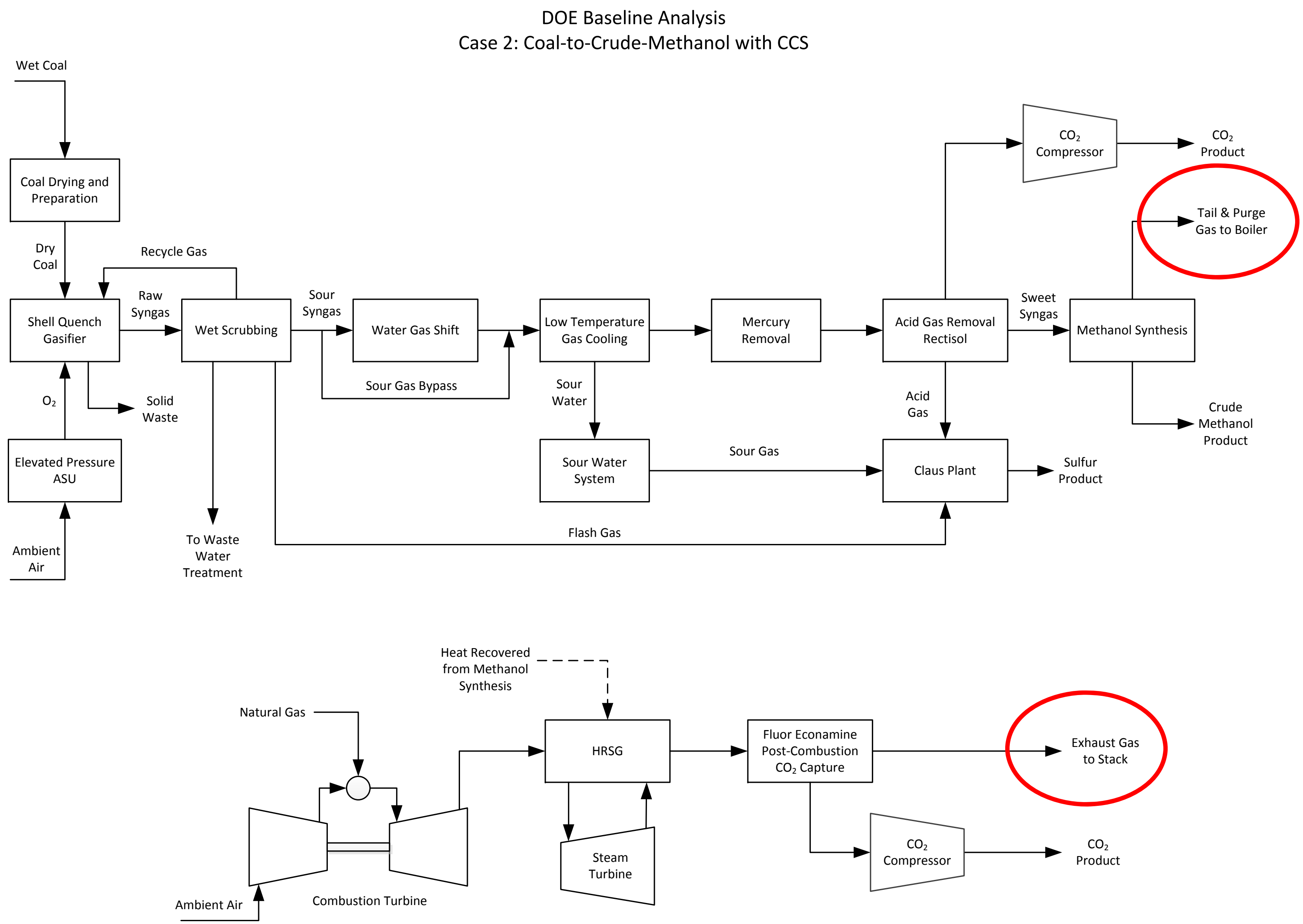
Block Flow Diagrams

DOE/NETL Baseline Configuration Case 1

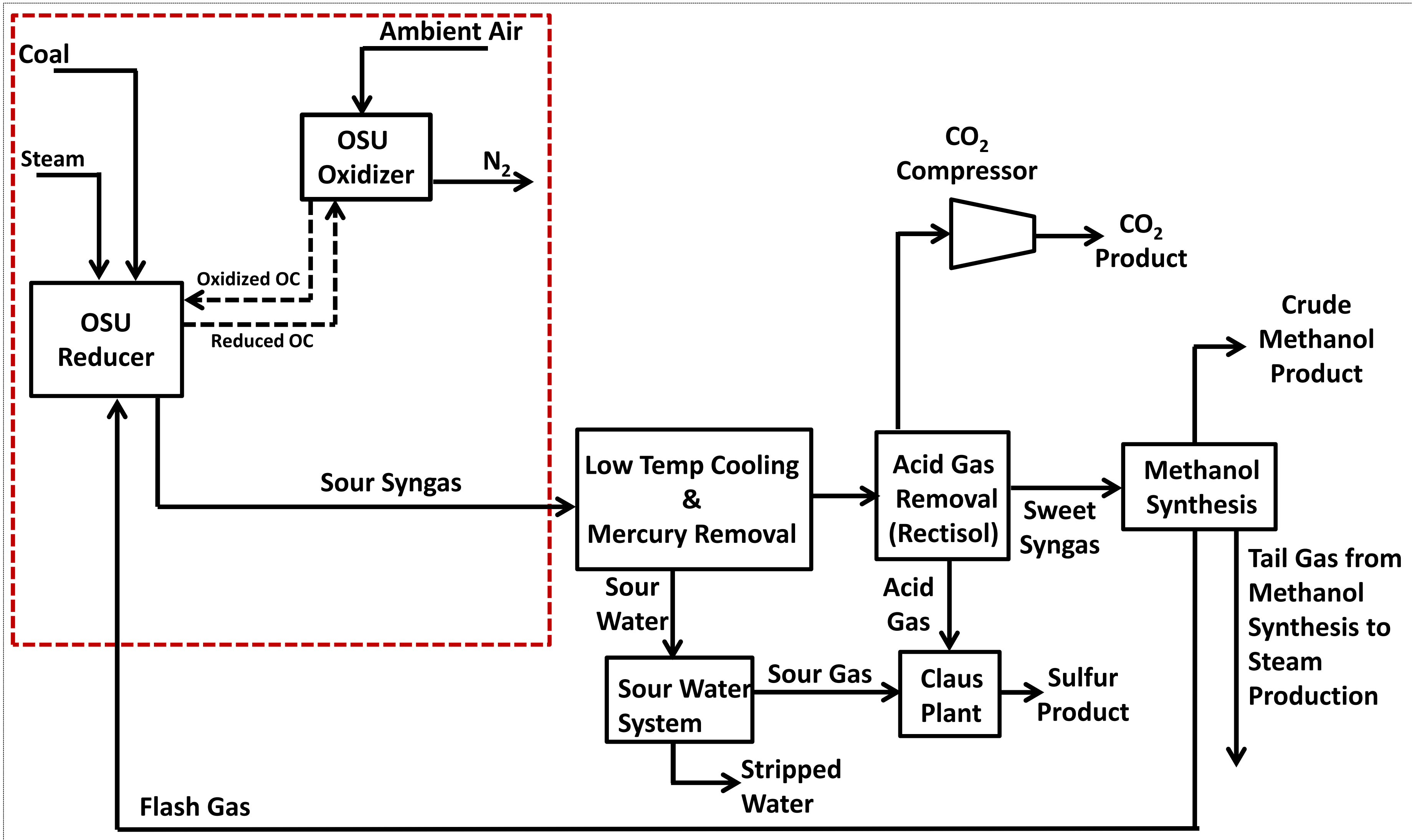


Block Flow Diagrams

DOE/NETL Baseline Configuration Case 2

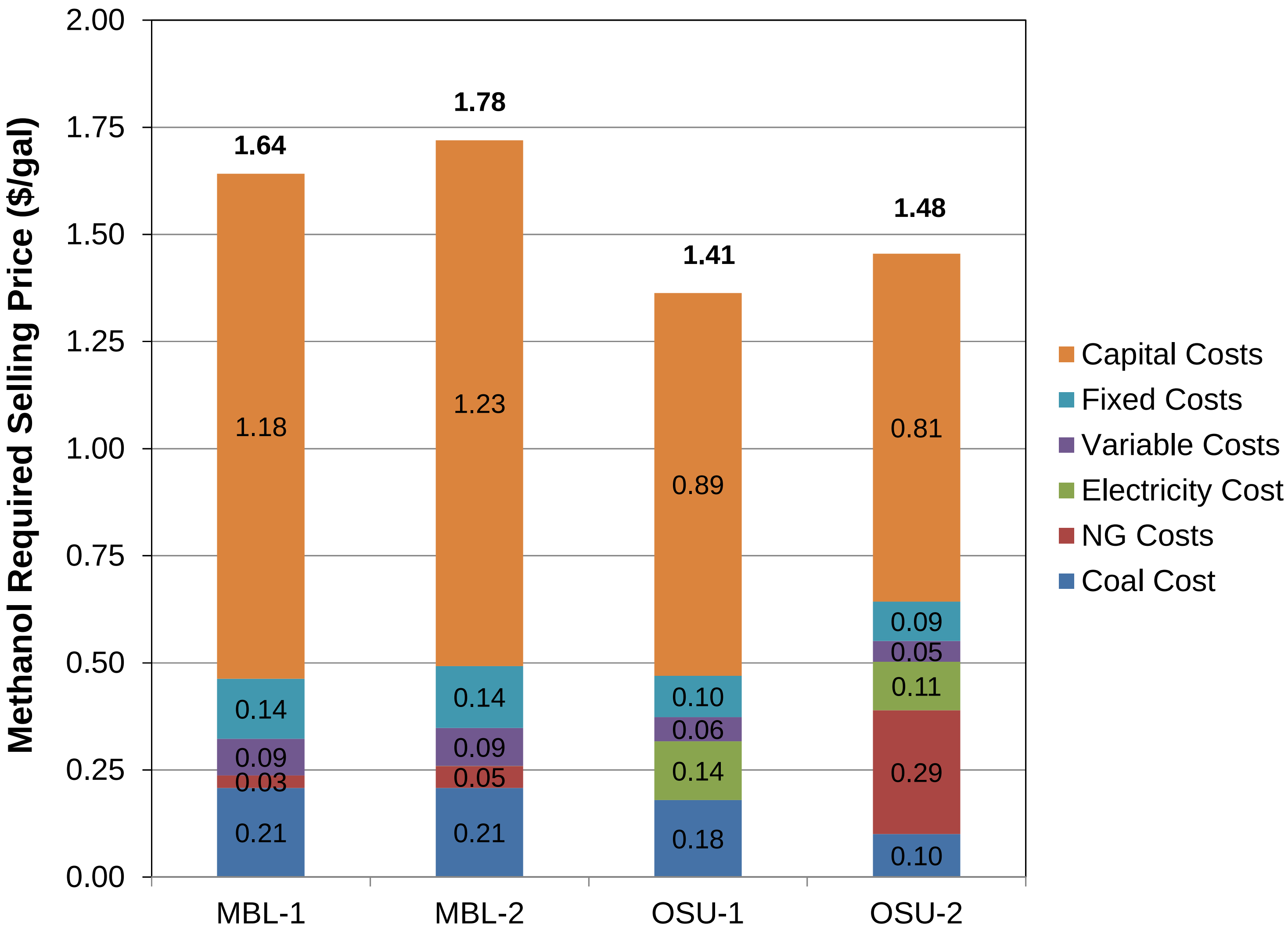


Coal Gasification for Methanol Production: OSU Process

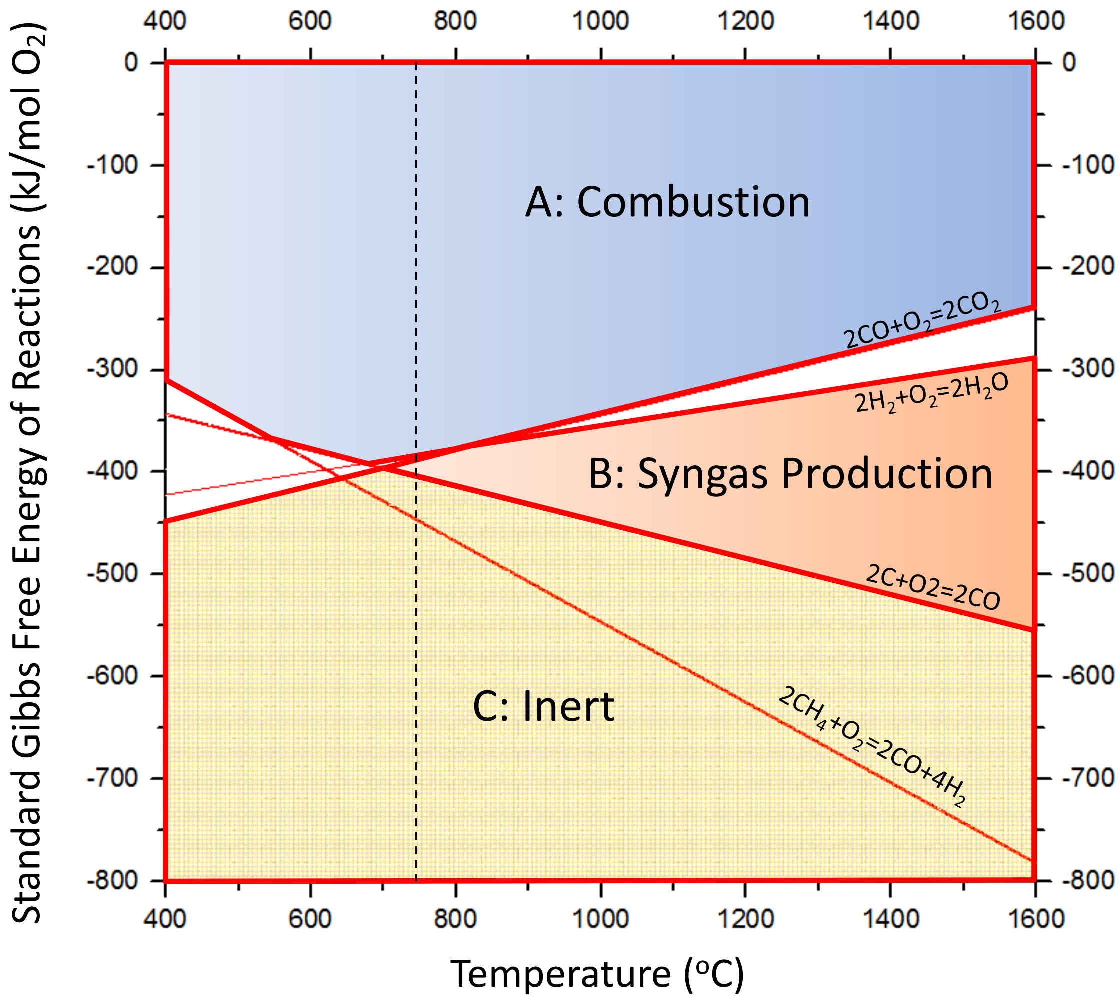


Economic Analyses

Methanol Required Selling Price



Zones of Metal Oxides for Chemical Looping



Recent research focus on **Complex Metal Oxides**

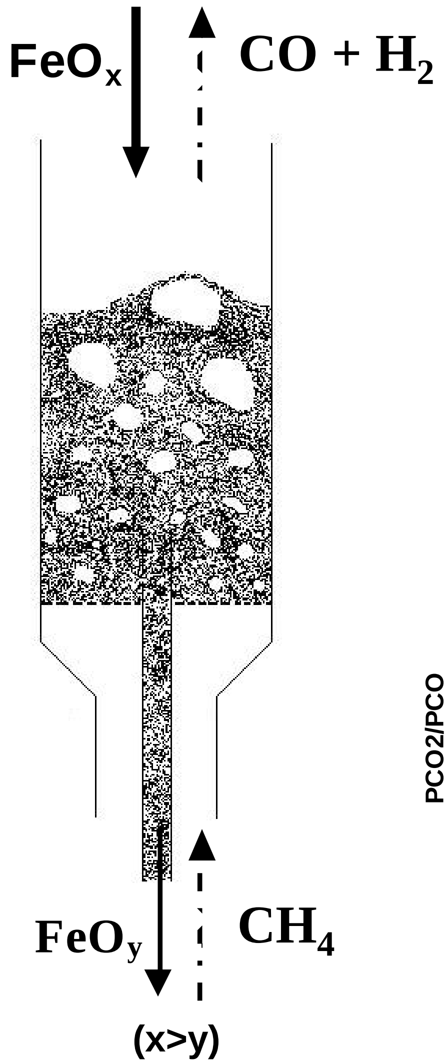
Zone A: They can work as oxygen carriers for both CLFO and CLPO. (NiO, CuO, CoO, Fe_2O_3, and Fe_3O_4, etc.)

Zone B: They are able to work as oxygen carriers for CLPO but not for CLFO (CeO_2, FeO, etc.)

Zone C: They cannot be used as oxygen carriers and are considered as inert materials. (Cr_2O_3 and SiO_2, etc.)

Transition Zone: They are considered as possible CLPO materials with a significant amount of H_2O generated. (SnO_2, etc.)

Reducer Design Concept

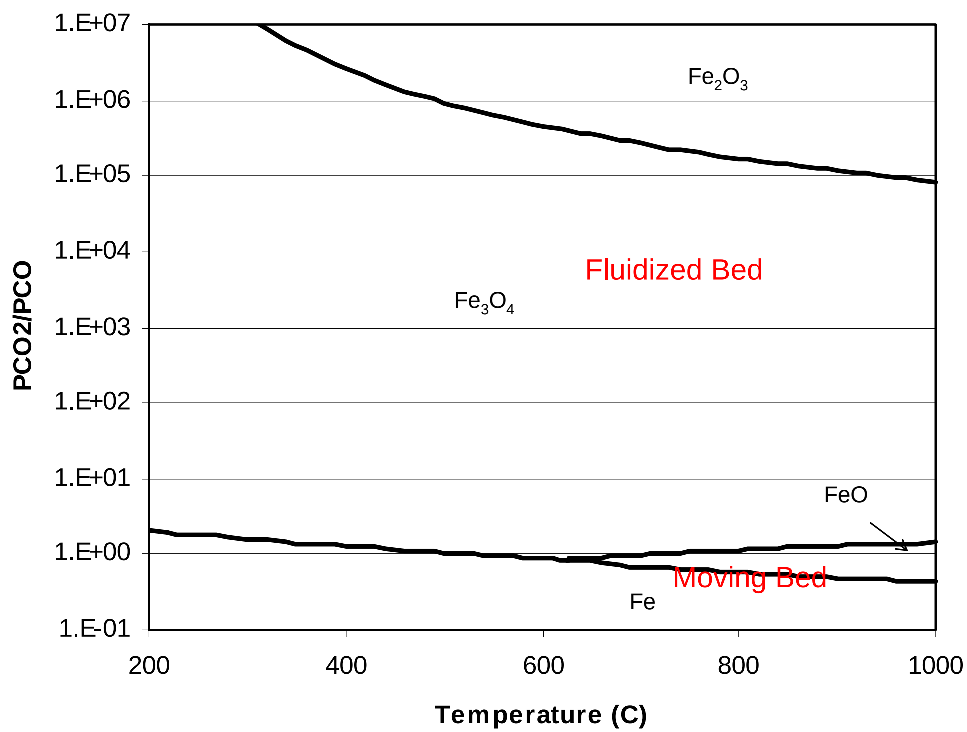


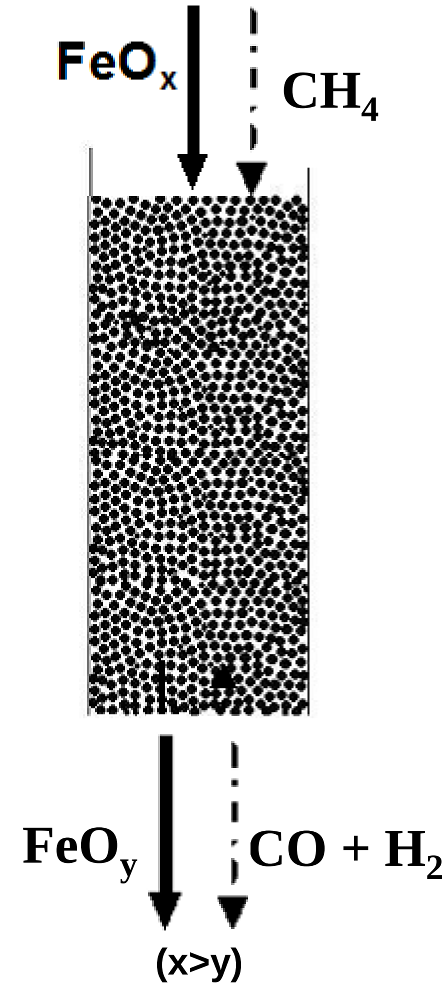
Fluidized Bed

Fluidized Bed V.S. Moving Bed

$> U_{mfv}$ ← Gas Velocity → $< U_{mfv}$

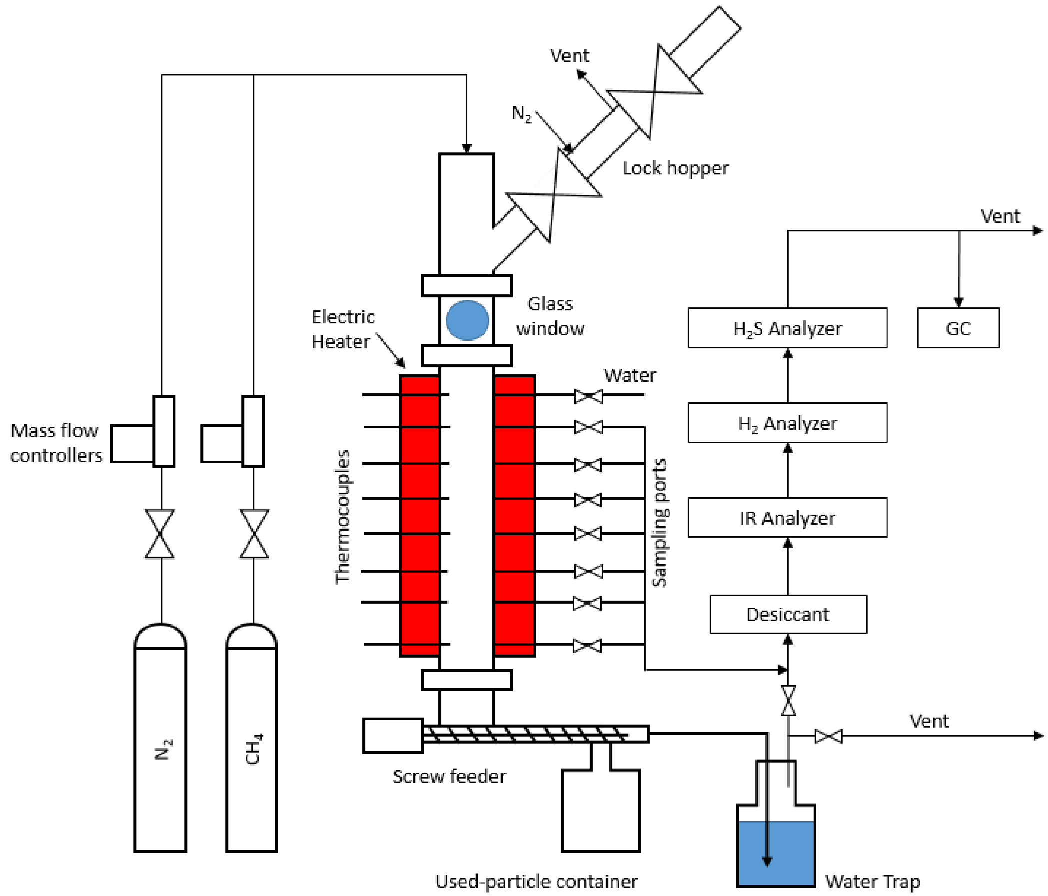
Small ← Particle Size → Large

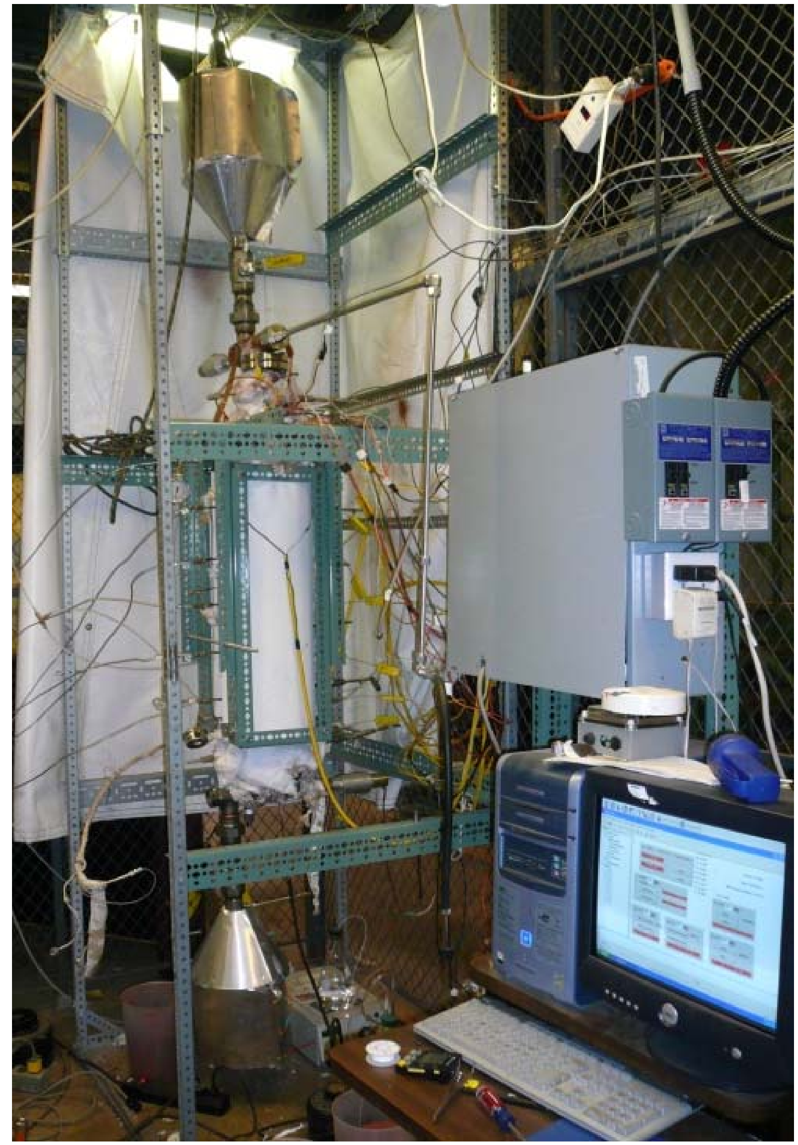




Moving Bed

Bench Moving Bed Reducer

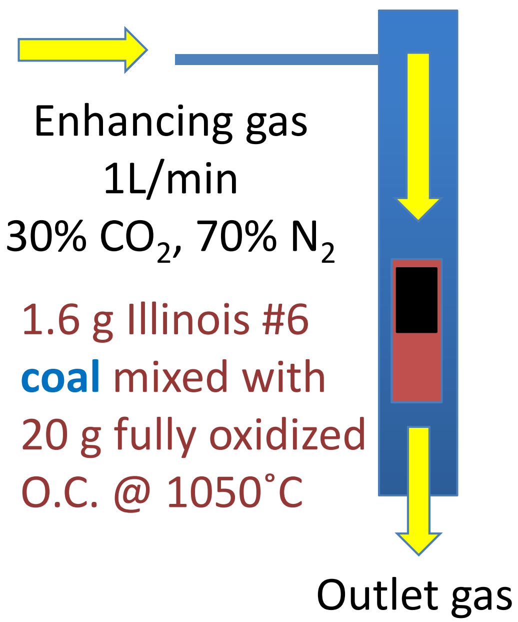




- Coal mixed with Oxygen Carrier particles
- Tests performed:
    - Methane to syngas
    - Sub-bituminous and Bituminous coal
    - Coal to syngas
    - Co-injection of methane
    - Co-injection of methane and steam

Experimental Studies – Fixed Bed Tests

Test Apparatus



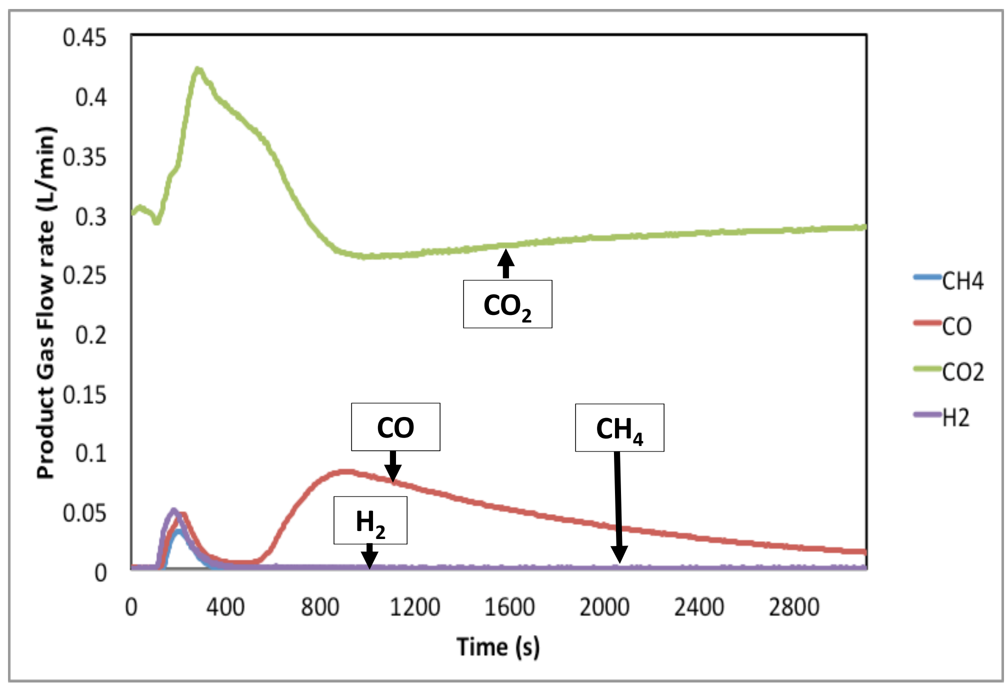
$C + CO_2 \rightarrow 2CO$ (char gasification) (1)

$CH_4 + FeO_x \rightarrow CO + H_2 + FeO_y \ (x>y)$ (volatile conversion) (2)

$CO + FeOx \longleftrightarrow CO_2 + FeO_y \ (x>y)$ (3)

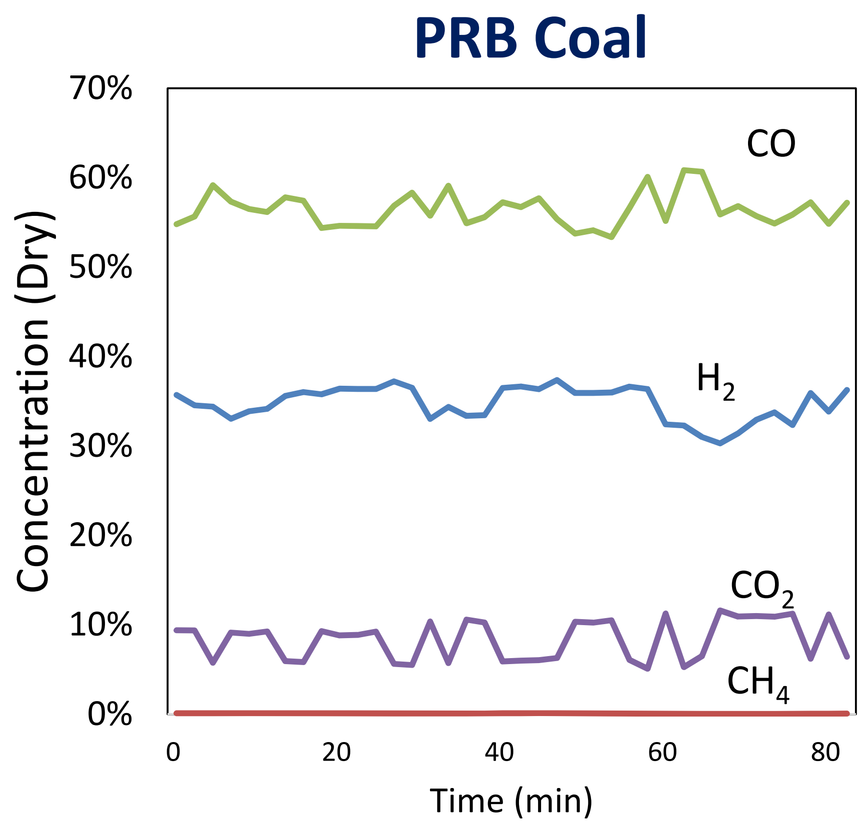
$H_2 + FeOx \longleftrightarrow H_2O + FeO_y \ (x>y)$ (4)

Outlet Gas Results – coal as fuel



- **<u>Coal gasification</u>**
  - Coal gasification with OC confirmed
  - Observed both devolatilization and char gasification
  - Achieved 30 – 34% of OC conversion (FeO)
  - Proved that OC is capable of converting CO_2 to CO
  - Justifies further moving bed studies

Coal to Syngas - Bench Scale Moving Bed Tests



Condition:

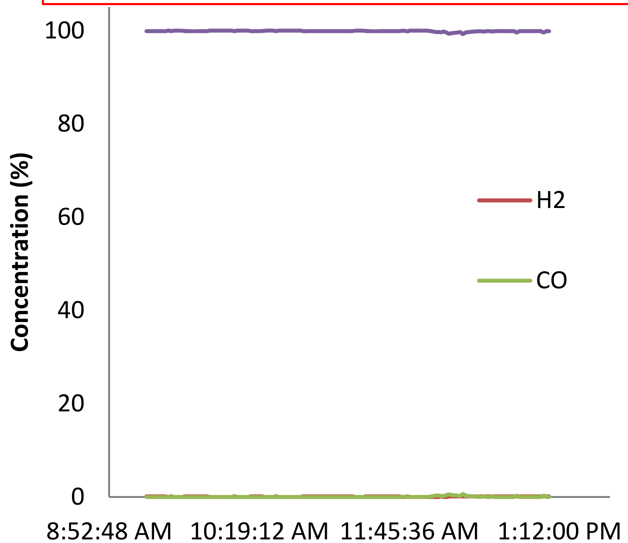
Coal: 4g/min

Oxygen Carrier: 20g/min

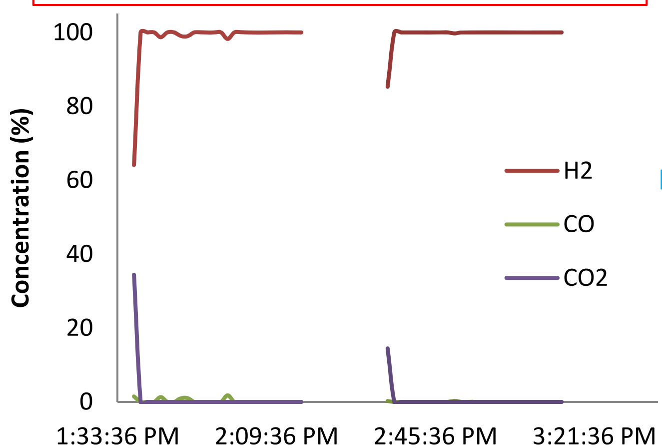
- 100% Conversion
- 85% Syngas Purity

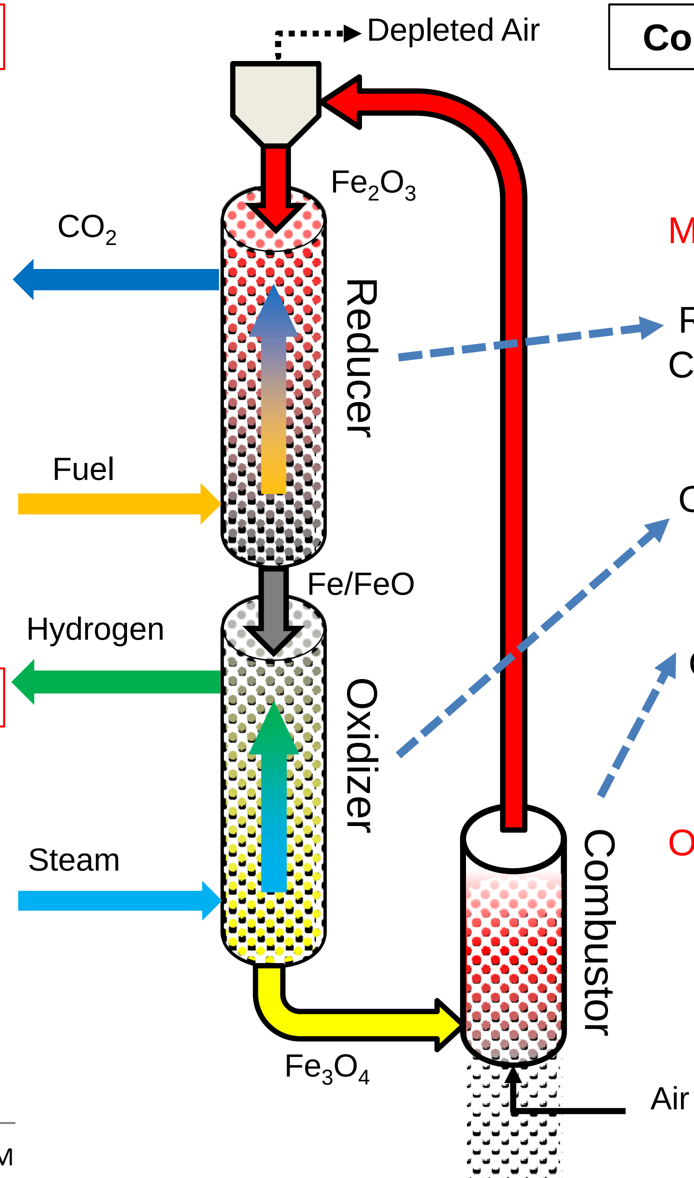
OSU Chemical Looping Hydrogen Production Process

> 99% CO_2 purity generated



>99.99% hydrogen purity at steady state





Counter-current: Full Combustion

Main Reactions

Reducer:
$CO+H_2+Fe_2O_3 \rightarrow CO_2+H_2O+Fe/FeO$

Oxidizer
$Fe/FeO+H_2O \rightarrow Fe_3O_4+H_2$

Combustor
$Fe_3O_4+O_2 \rightarrow Fe_2O_3$

Overall Reaction
$CO+H_2+H_2O+O_2 \rightarrow CO_2+H_2O+H_2$

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Li, F., Zeng, L., Velazquez-Vargas, L.G., Yoscovits, Z., Fan, L.-S. *AIChE Journal*. 2010. 56(8), 2186.
Tong, A., Sridhar, D., Sun, Z., Kim, H.R., Zeng, L., Wang, F., Wang, D., Kathe, M.V., Luo, S., Sun, Y., Fan, L.-S. *Fuel*. 2013. 103. 495.

Concluding Remarks

- From theoretical (thermodynamics and kinetics), experimental (bench and sub-pilot), and economic (third party) evidence, the OSU chemical looping gasification technology using coal, shale gas, and/or biomass as feedstock to produce, in one step without the use of molecular oxygen from air separation, to produce a high purity syngas at H_2:CO at 2:1 for direct application to generate chemicals and liquid fuels downstream can potentially revolutionize the energy and chemical industries in short years.
- The studies from the concluded DOE Phase 1 project activities with independent economic assessment by WorleyParsons have ascertained the technical soundness, process viability and economic attractiveness of these OSU technologies and prepared for further process scale-up efforts.

Concluding Remarks (continued)

- The experience from the on-going high pressure pilot demonstration of H_2 production at NCCC for the OSU Syngas chemical looping technology can accelerate the gasification commercialization process.

Acknowledgements

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Disclaimer