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Carbon Dioxide Conversion Through Tri-Reforming: Reactor/Process Design and Optimization

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Jackson, MS

Carbon Dioxide and the Petroleum Sector

- ✓ **29 Petroleum Refineries**
- ✓ **4.7 MM bbl/day crude**
- ✓ **30% Total U.S. refining**

www.eia.doe.gov

500 scf H_2/bbl crude

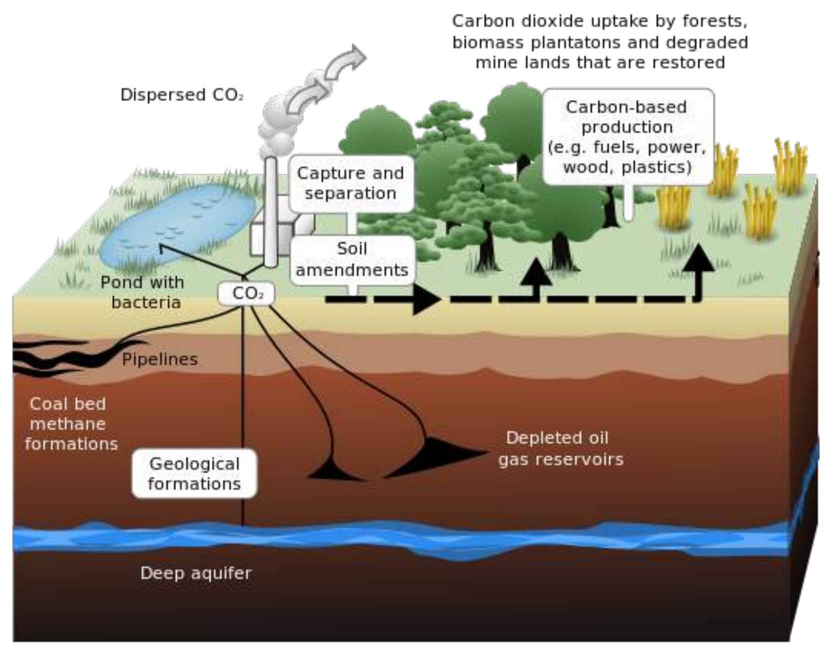
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

Gary, Handwerk, Kaiser (2007)

51,350 tons CO_2/day
(19 MM ton/yr)

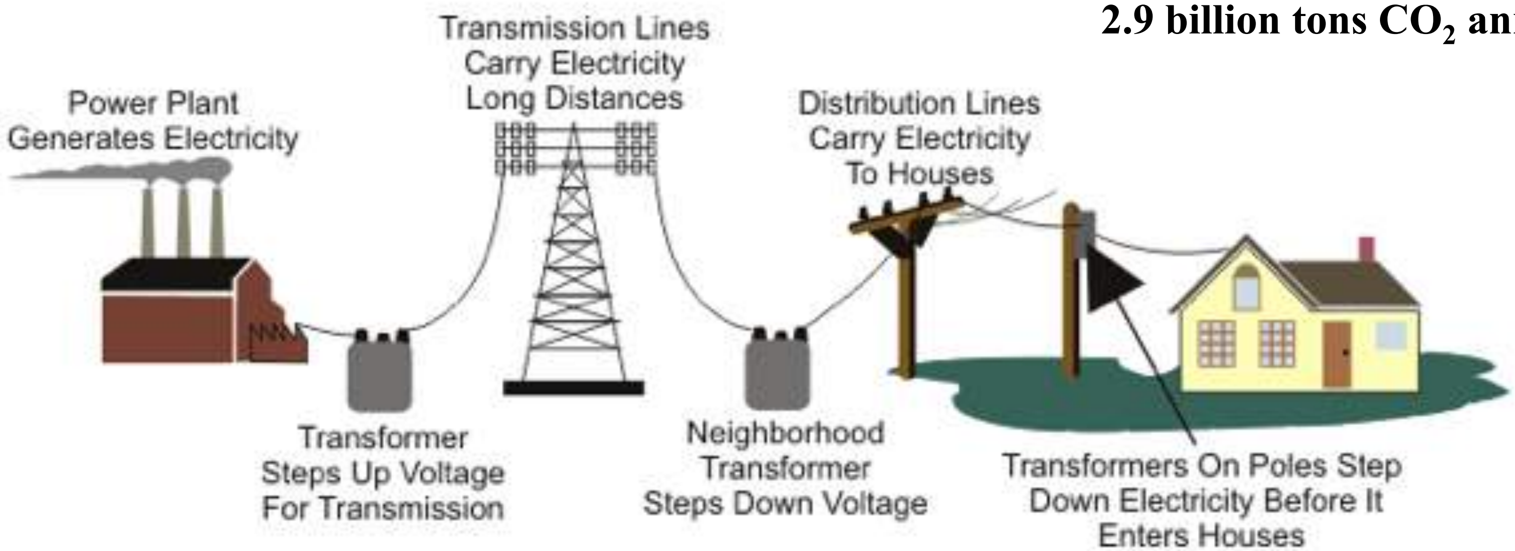
CO_2 Treatment Technologies:

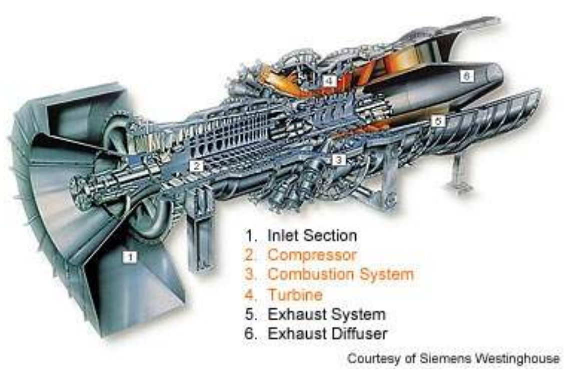
- ✓ Sequestration Technology – CO_2 Capture & storage
- ✓ Conversion – CO_2 to usable compounds

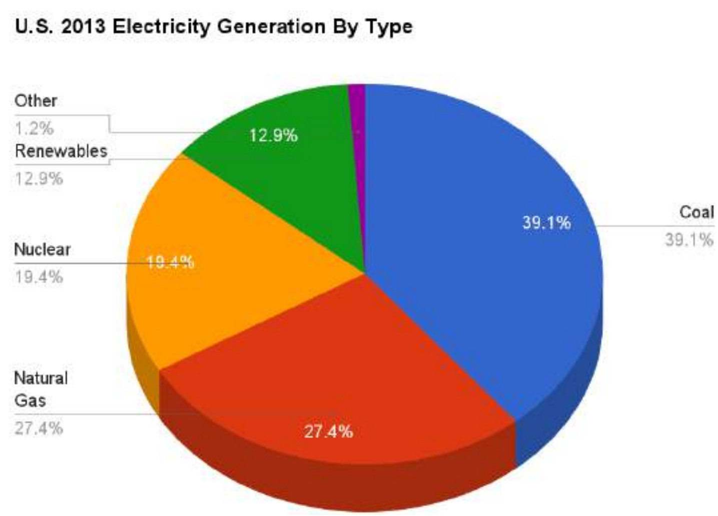


Electricity in the United States

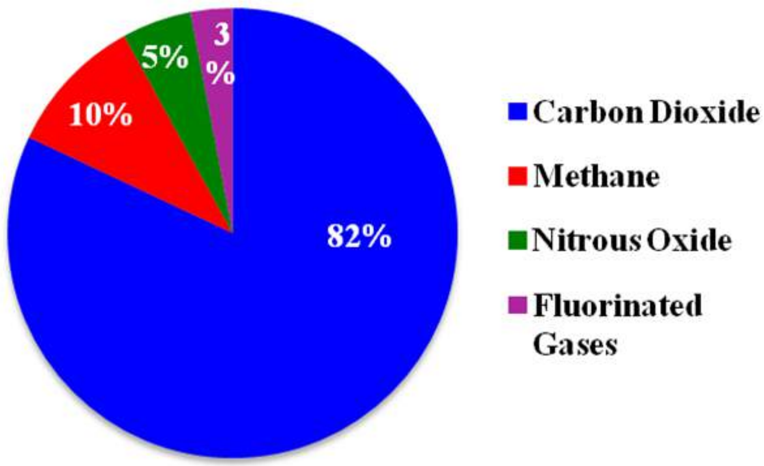
2.9 billion tons CO_2 annually

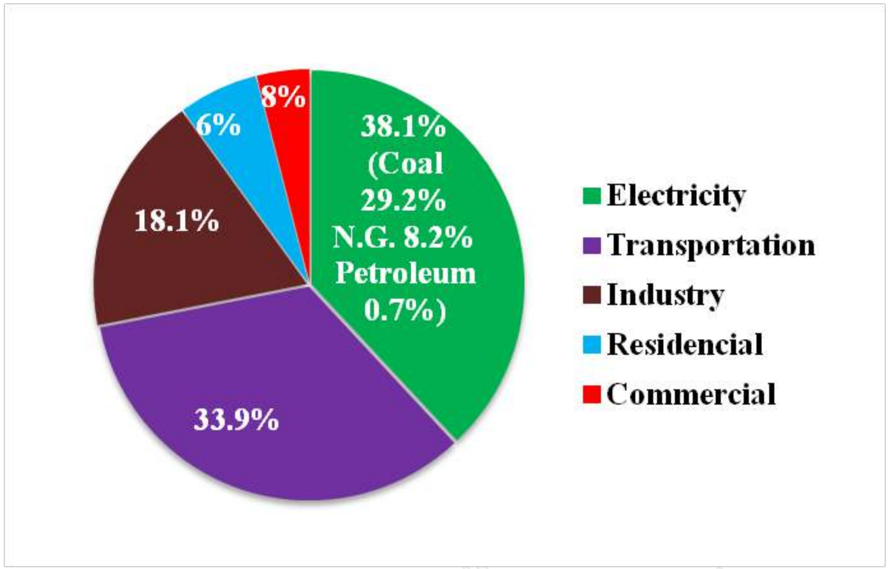






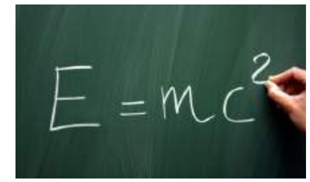
Greenhouse Gases & Their Sources





http://www.epa.gov/climatechange/emissions/co2.html

CO_2 - Birth, Death, and Reuse



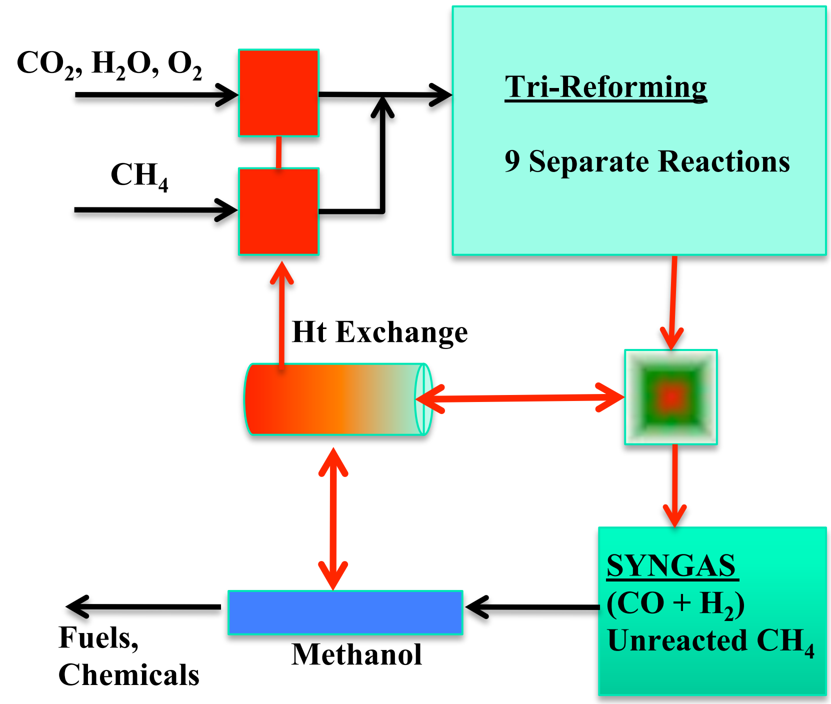
$CO_2 + H_2O$ → (Light, Photocat) → $CO + H_2$ →

Diesel
Methanol
Dimethyl Ether
Long Chain Alcoh

Tri-Reforming: Turning CO_2 into a Fuel

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	ΔH = +247 kJ/mol
$CH_4 + H_2O \rightarrow CO + 3H_2$	ΔH = +206 kJ/mol
$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$	ΔH = - 36 kJ/mol
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	ΔH = - 880 kJ/mol
$CH_4 \rightarrow C + 2H_2$	ΔH = + 75 kJ/mol
$2CO \rightarrow C + CO_2$	ΔH = -172 kJ/mol
$C + CO_2 \rightarrow + 2CO$	ΔH = +172 kJ/mol
$C + H_2O \rightarrow CO + H_2$	ΔH = +131 kJ/mol
$C + O_2 \rightarrow CO_2$	ΔH = -394 kJ/mol

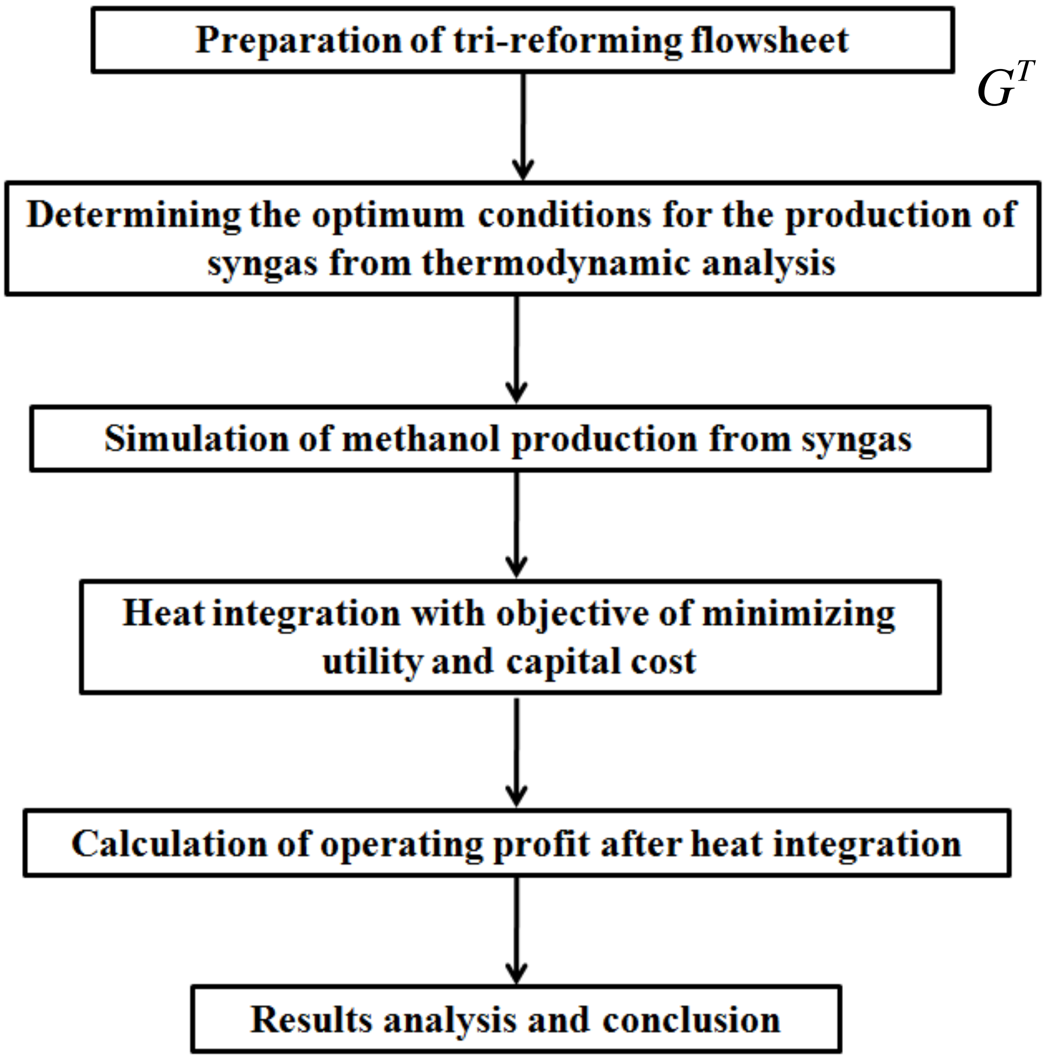
Conversion: >70% CO_2, 98% CH_4
H_2/CO = 1.5 – 2.0



- Conversion and utilization of CO_2 without CO_2 separation from power plant
- Effective production of syngas with desired H_2/CO ratio for methanol synthesis
- Reducing the possibility of carbon formation compared with dry reforming

Song, C. and W. Pan, Catalysis Today, 2004. 98(4): p. 463-484

Framework for Methanol Production via Tri-Reforming



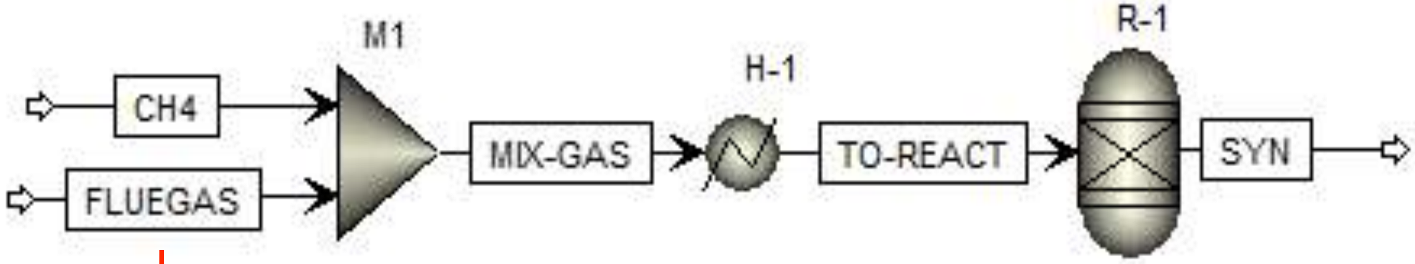
$$G^T = \sum_{i=1}^{n} n_i G_i^0 + R(T + 273.15) \sum_{i=1}^{n} n_i \ln \frac{f_i}{f_i^0}$$

LP Transshipment Model

MINLP Model

Aspen Energy Analyzer

Tri-Reforming Process Flowsheet



$CO_2:H_2O:O_2:N_2 = 0.1:0.2:0.03:0.67$
Basis of 1,000 kmol/hr

Objective

- Converting as much CO_2 as possible
- Obtaining the ideal ratio of $H_2/CO = 2$.

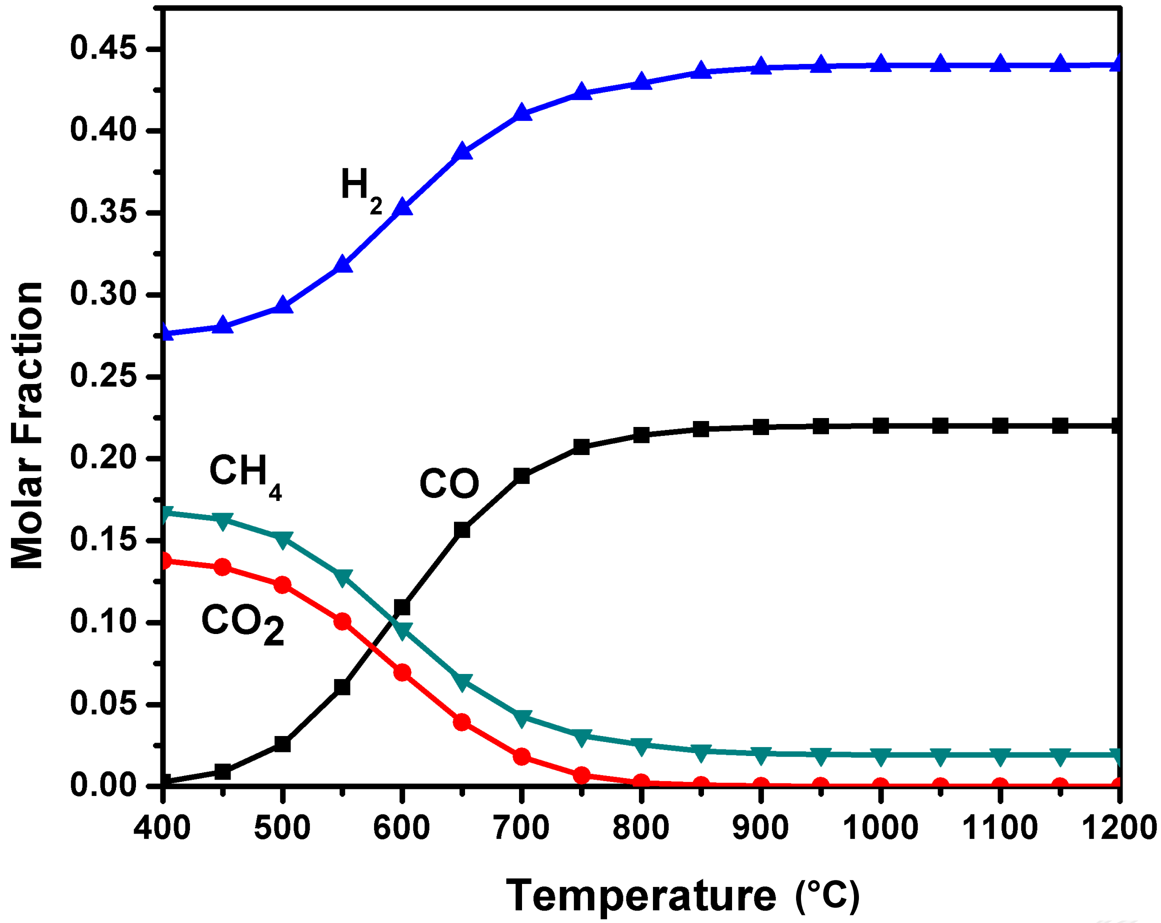
Conditions?

- Reaction Temperature
- Reactor Pressure
- Ratio of CH_4/Flue gas

Tri reforming reactions

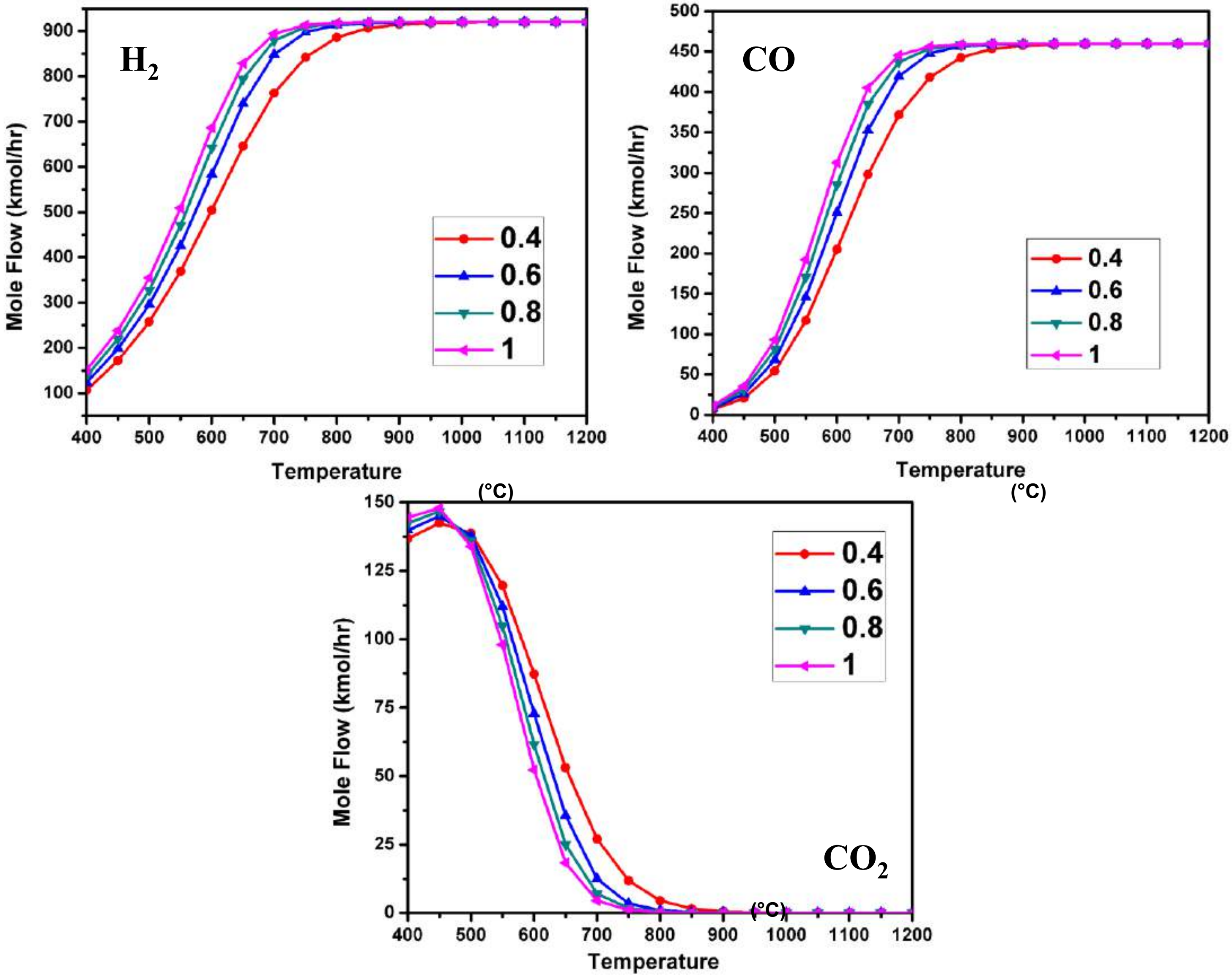
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	$\Delta H = +247$ kJ/mol
$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H = +206$ kJ/mol
$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2$	$\Delta H = -36$ kJ/mol
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$\Delta H = -880$ kJ/mol
$CH_4 \rightarrow C + 2H_2$	$\Delta H = +75$ kJ/mol
$2CO \rightarrow C + CO_2$	$\Delta H = -172$ kJ/mol
$C + CO_2 \rightarrow + 2CO$	$\Delta H = +172$ kJ/mol
$C + H_2O \rightarrow CO + H_2$	$\Delta H = +131$ kJ/mol
$C + O_2 \rightarrow CO_2$	$\Delta H = -394$ kJ/mol

Composition vs Temperature

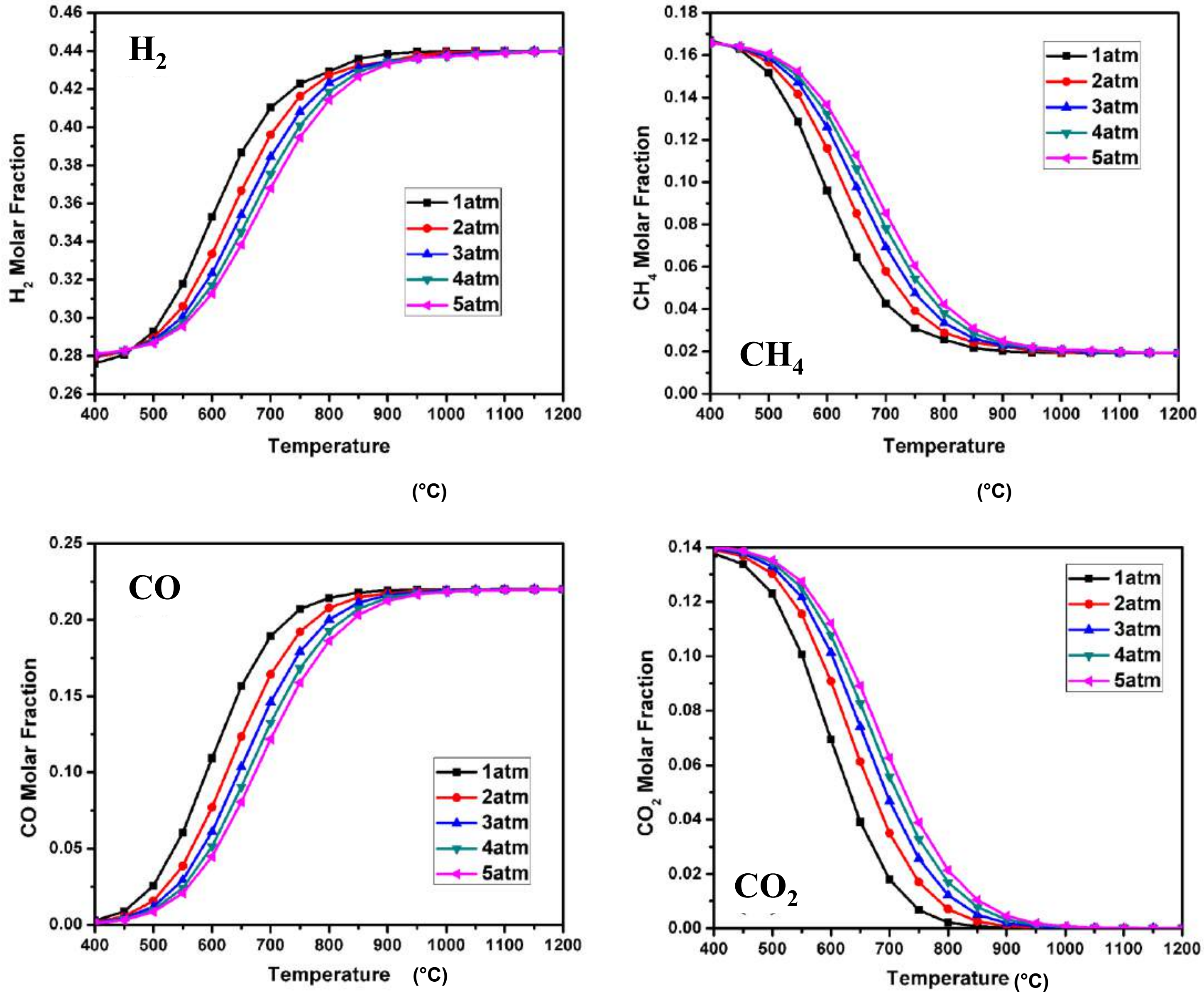


Conditions: CH_4/Flue Gas=0.4 and pressure = 1 atm.

Composition vs CH_4/Flue Gas ratio

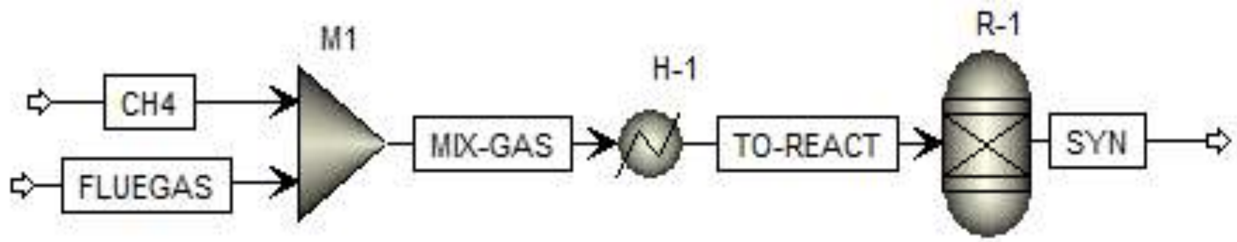


Composition vs Pressure



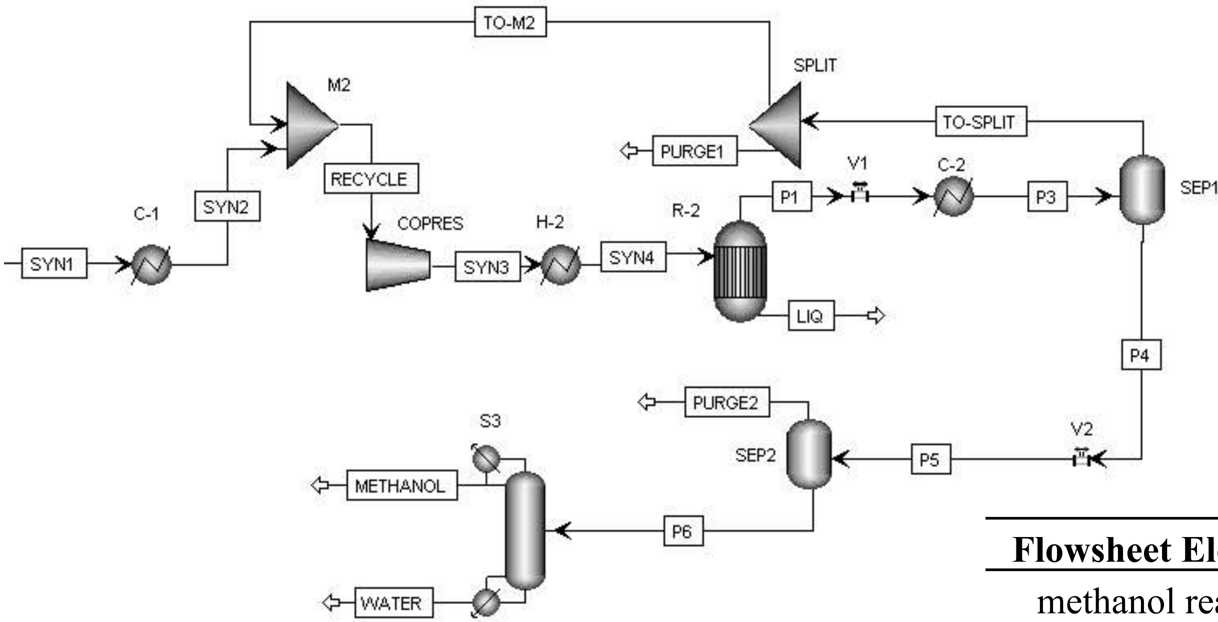
Optimum Conditions

Pressure: 1 atm Temperature: 850 °C CH_4/Flue gas: 0.4



	CH_4	FLUEGAS	MIX-GAS	TO-REACT	SYN
Temperature, °C	25	150	110	850	850
Vapor Frac	1	1	1	1	1
Mole Flow, kmol/hr	400	1000	1400	1400	2080
Mole Frac					
CH_4	1	0	0.29	0.29	0.02
CO_2	0	0.1	0.07	0.07	0
CO	0	0	0	0	0.22
H_2	0	0	0	0	0.44

Combined Methanol Synthesis and Tri-Reforming



R-equil Reactor

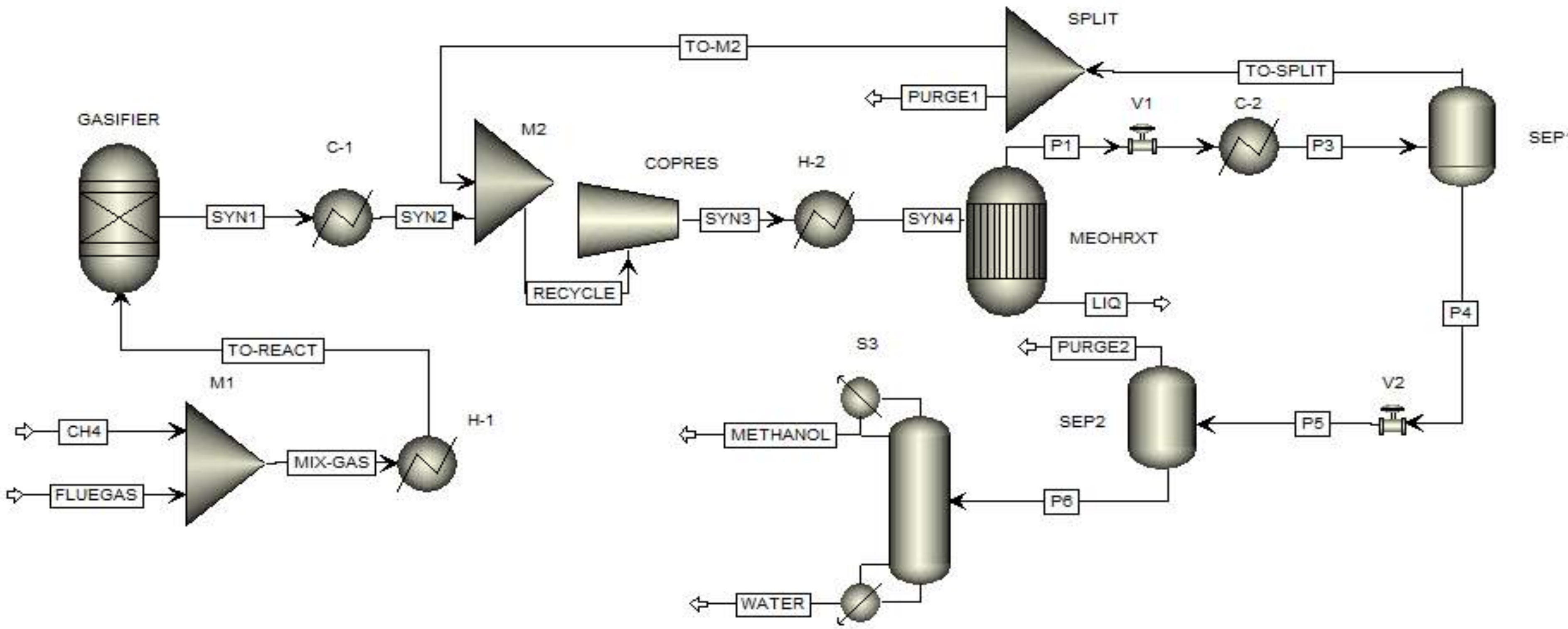
Peng – Robinson EOS

Flowsheet Element	Parameter	Value
methanol reactor	temperature (°C)	220
	pressure (bar)	50
sep1	temperature (°C)	25
	pressure (bar)	24
sep2	temperature (°C)	25
	pressure (bar)	10
S3 (Radfrac)	Number of stages	19
	Feed stage	11
	Reflux ratio	1.5
	Distillate to feed ratio	0.988

$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H = -91$ kJ/mol

$CO_2 + 3H_3 \rightarrow CH_3OH + H_2O$ $\Delta H = -50$ kJ/mol

$CO + 2H_2O \rightarrow CO_2 + H_2$ $\Delta H = -41$ kJ/mol



Variables for heat and cold streams

Blocks	Stream	Tin(°C)	Tout(°C)	Fcp(kW/°C)
H-1	C1	110	850	16
H-2	C2	125	220	154
Reboiler	C3	137	139	4806
C-1	H1	850	60	18
C-2	H2	219	25	170
Conderser	H3	135	96	249

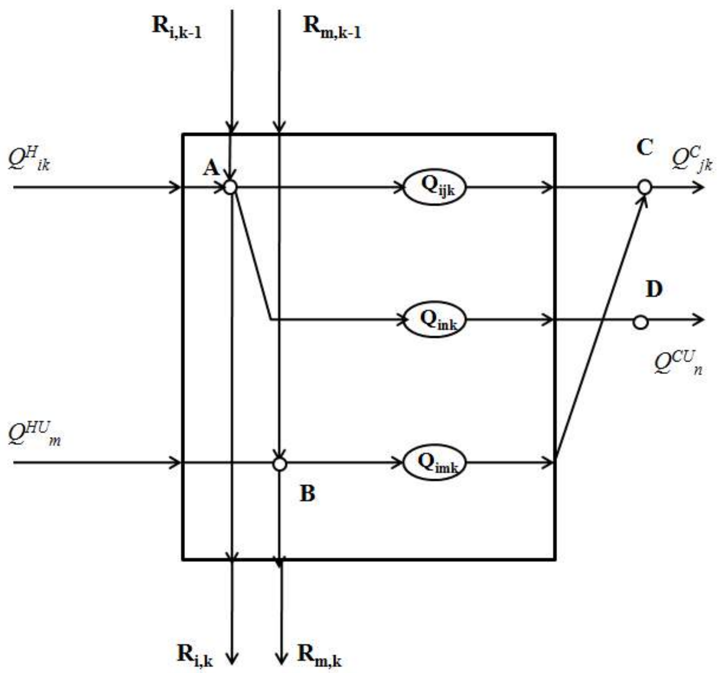
Variables for utilities selected in heat integration

Utility	Temperature(°C)	Cost ($/kW-yr)
Cooling water	20	6.7
Refrigerant 1	-25	86.3
Fired heat	1000	134

Heat Integration strategies

1. Minimizing Utility Cost
2. Minimizing Capital Cost

Transshipment model (Utility Cost)



Heat Flows in interval k

Objective Function:

$$min \sum_{m \in S} c_m Q^S_m + \sum_{n \in W} c_n Q^W_n$$

Equations:

$$R_{ik} - R_{i,k-1} + \sum_{j \in C_k} Q_{ijk} + \sum_{n \in W_k} Q_{ink} = Q^H_{ik}$$

$$R_{mk} - R_{m,k-1} + \sum_{j \in C_k} Q_{mjk} = Q^S_m$$

$$\sum_{j \in H_k} Q_{ijk} + \sum_{m \in S_k} Q_{mjk} = Q^C_{jk}$$

$$\sum_{i \in H_k} Q_{ink} = Q^W_n$$

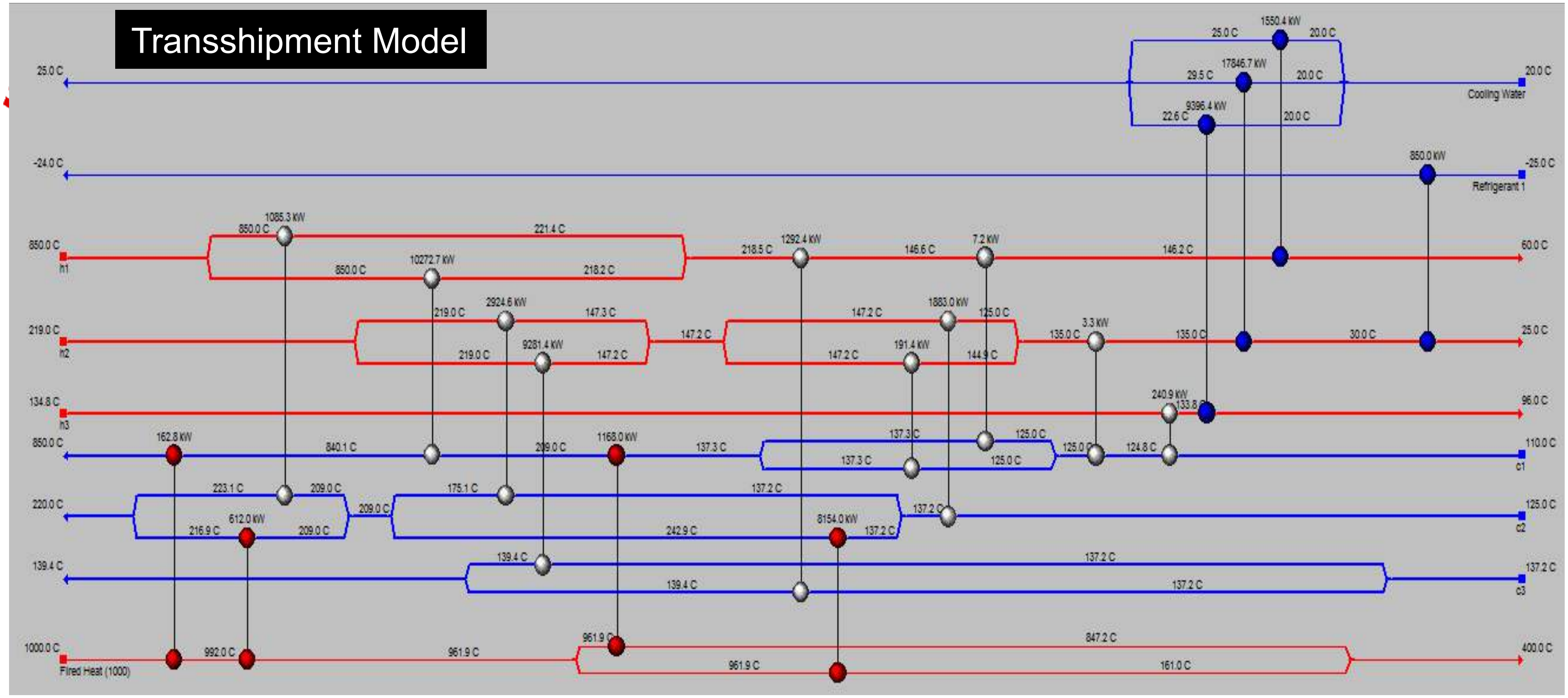
Boundary conditions:

$$R_{i0} = R_{iK} = 0$$

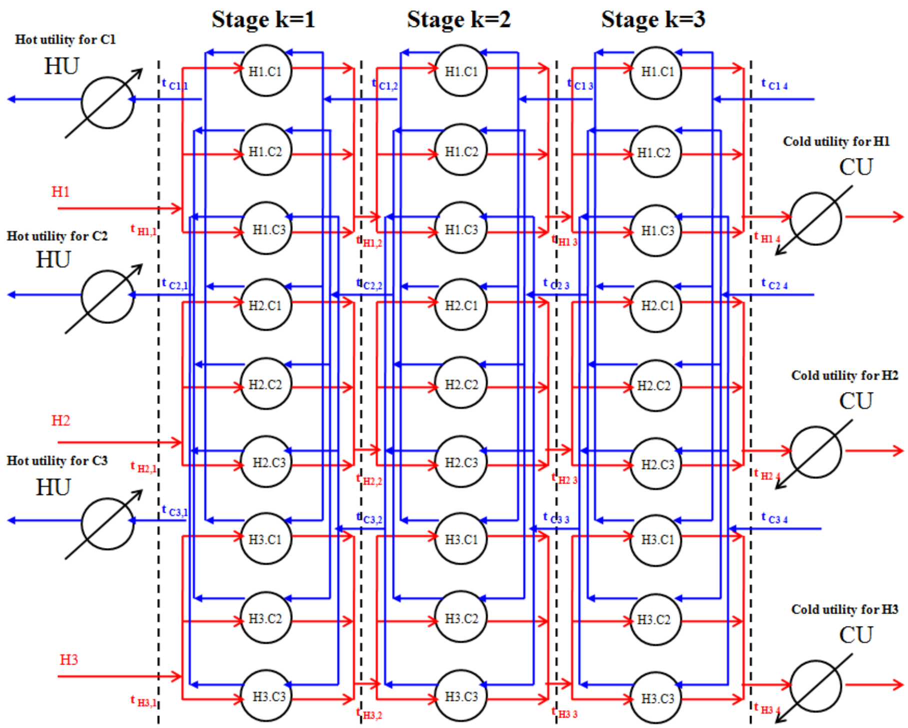
Constraints:

$$R_{ik}, R_{mk}, Q_{ijk}, Q_{mjk}, Q_{ink}, Q^S_m, Q^W_n \geq 0$$

N.V. Sahinidis and I.E. Grossman, Transshipment LP model for minimizing the utility cost in a heat exchanger network 1983



Energy usage before heat integration		Energy usage after heat integration	
streams	Amount (kW)	streams	Amount (kW)
C1	12047	C1	1331
C2	14660	C2	8766
C3	10574	C3	0
H1	14208	H1	1550
H2	32975	H2	18697
H3	9637	H3	9396
% energy savings			**57.8**



Three stage superstructure in MINLP model (Capital Cost)

Minimizing:

Utility cost

$$Min \quad \sum_{m\in HU} c_m Q_m^{HU} + \sum_{n\in CU} c_n Q_n^{CU} +$$

Fixed charges for the exchangers

$$\sum_{i\in HP}\sum_{j\in CP}\sum_{k\in ST} CF_{ij} z_{ijk} + \sum_{i\in HP}\sum_{n\in CU} CF_{i,n} zcu_{i,n} + \sum_{j\in CP}\sum_{m\in HU} CF_{j,m} zhu_{j,m} +$$

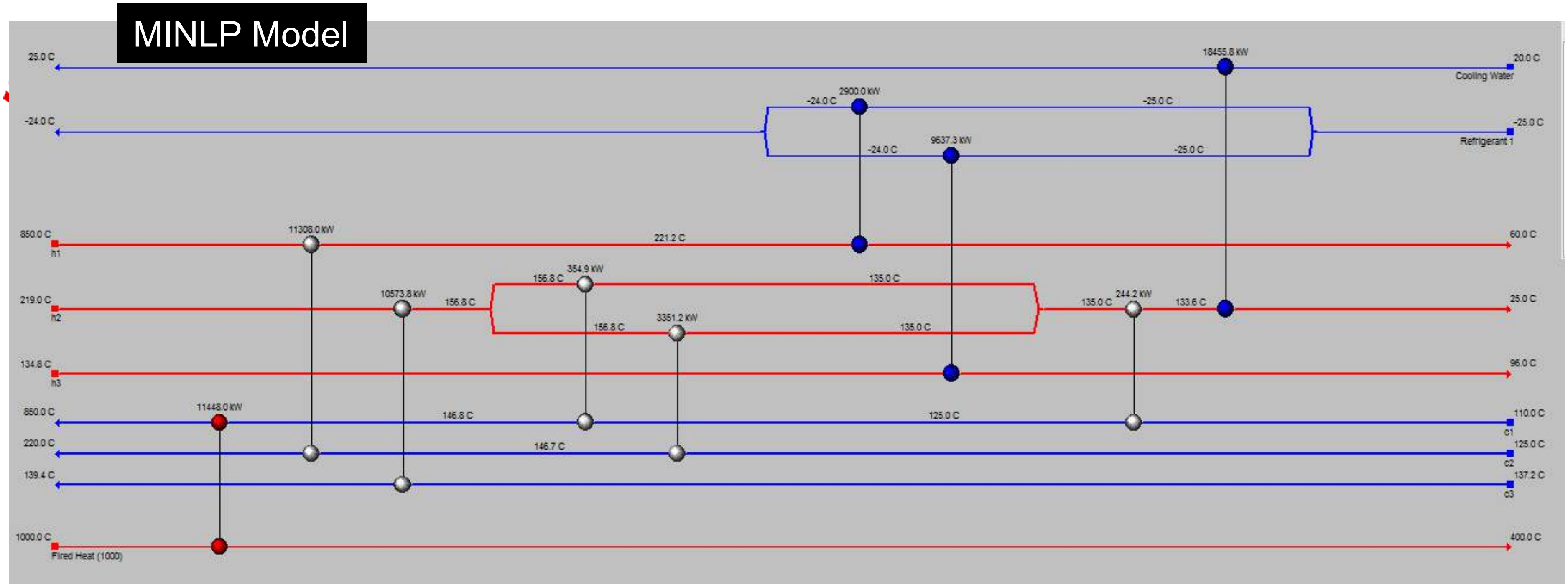
Area cost for each exchanger

$$\sum_{i\in HP}\sum_{j\in CP}\sum_{k\in ST} C_{ij} \left\{ \frac{q_{ijk}}{\left(U_{ij}\left(\frac{(dt_{ijk})(dt_{ijk+1})(dt_{ijk}+dt_{ijk+1})}{2}\right)^{\frac{1}{3}}\right)} \right\}^{B_{ij}} +$$

$$\sum_{i\in HP}\sum_{n\in CU} C_{i,n} \left\{ \frac{qcu_{i,n}}{\left(U_{i,n}\left(\frac{(dtcu_{i,n})(TOUT_i - TIN_n)(dtcu_{i,n} + (TOUT_i - TIN_n))}{2}\right)^{\frac{1}{3}}\right)} \right\}^{B_{i,n}} +$$

$$\sum_{j\in CP}\sum_{m\in HU} C_{j,m} \left\{ \frac{qhu_{j,m}}{\left(U_{j,m}\left(\frac{(dthu_{j,m})(TIN_m - TOUT_j)(dthu_{j,m} + (TIN_m - TOUT_j))}{2}\right)^{\frac{1}{3}}\right)} \right\}^{B_{j,m}}$$

Yee, T.F. and I.E. Grossmann, Comput. Chem. Eng. 1990;14:1165-1184



Energy usage before heat integration		Energy usage after heat integration	
streams	Amount (kW)	streams	Amount (kW)
C1	12047	C1	11448
C2	14660	C2	0
C3	10574	C3	0
H1	14208	H1	2911
H2	32975	H2	18455
H3	9637	H3	9637
% energy savings			**54.9**

Comparison of energy consumption before and after heat integration for the whole process

Energy usage before heat integration			Energy usage after heat integration	
			Minimizing utility cost	Minimizing capital cost
Block	Type	Amount (kWh)	Amount (kWh)	Amount (kWh)
GASIFIER	Reactor	19061	19061	19061
MEOHRXT	Reactor	10762	10762	10762
C-1	Cooler	14209	1550	2912
C-2	Cooler	32975	18697	18456
H-1	Heater	12047	1331	11448
H-2	Heater	14659	8766	0
SEP1	Flash	0	0	0
SEP2	Flash	0	0	0
COMP	Compressor	14255	14255	14255
CONDENSER	RADFRAC	9637	9396	9637
REBOILER	RADFRAC	10574	0	0
Total utility		127605	83818	86531
Energy per kg CO_2		29	19	19.7
% Energy savings			34.3	32.2

Economic Analysis

- Operating hours – 8,000 hr/year
- Flue gas was not considered into the overall costs calculation as it is a waste stream
- Catalyst in the reactions are not considered
- Due to the lack of info for fixed capital cost, depreciation, taxes, operating profit was defined as follows:

PROFIT = INCOME – FCOST – UCOST

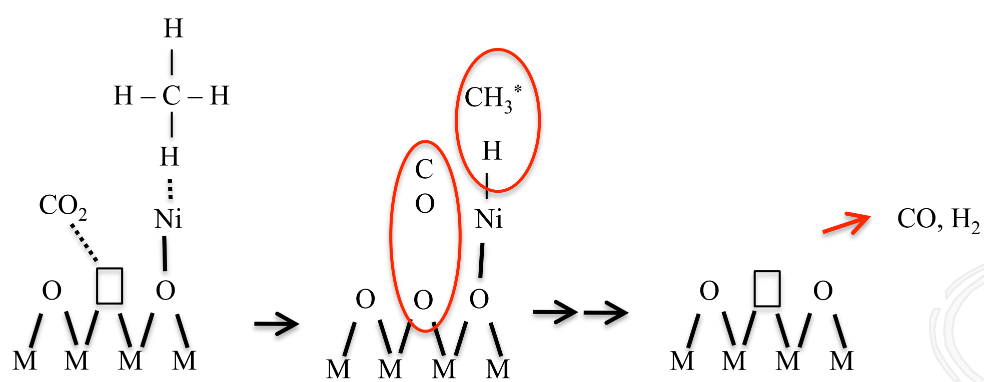
Comparison between steam CO_2 reforming and tri-reforming

CO_2 treatment method	Methanol production (kg/kg CO_2)	Energy consumption (kWh/kg CO_2)
Steam - CO_2 reforming	1.31	11.5
Tri-reforming	2.75	19.0

Aresta, M., Carbon dioxide recovery and utilization. 2003: Springer.

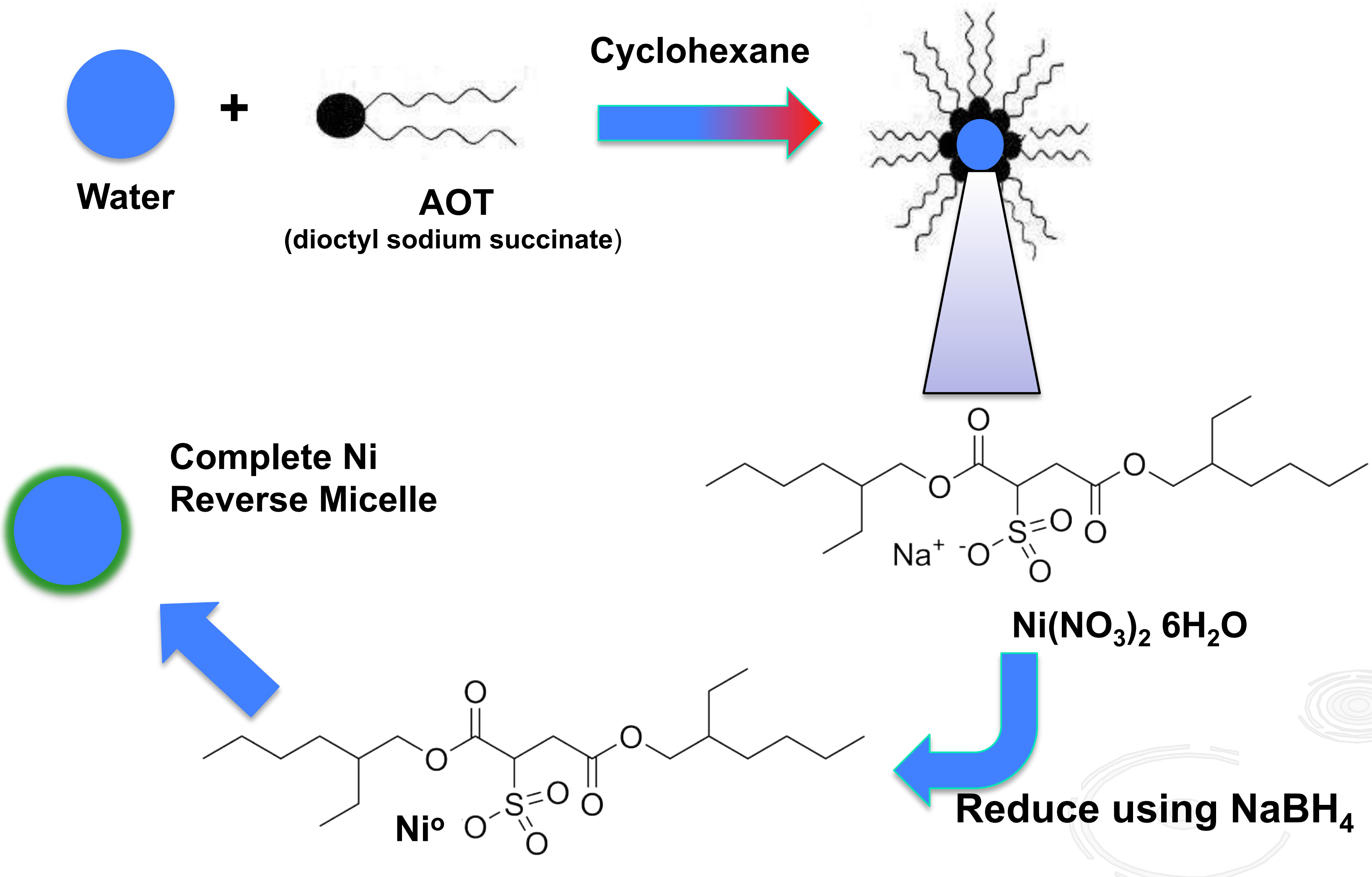
Developing Nanoparticle Catalyst

- ✓ **Synergism between active metal and support**
  - ➢ **Oxygen vacancies within support**
  - ➢ **Adsorption of hydrogen by active metal**
- ✓ **Reverse Micelles for nanoparticle formation**
  - ➢ **Increased active sites per unit mass**
  - ➢ **Intimate contact between reacting species**



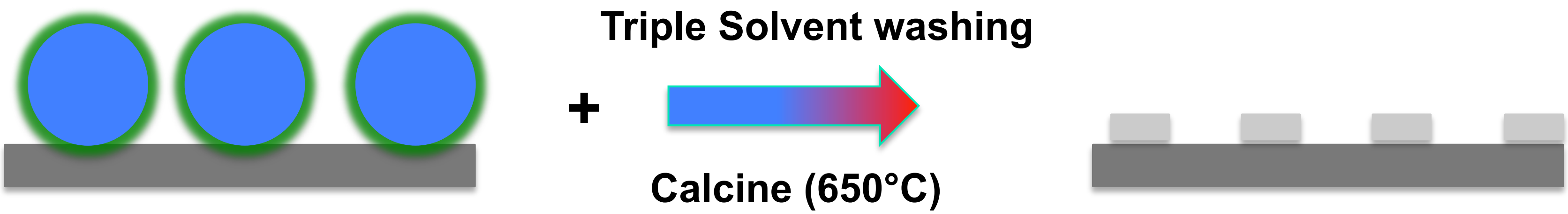
Nanoparticle Catalyst Concept

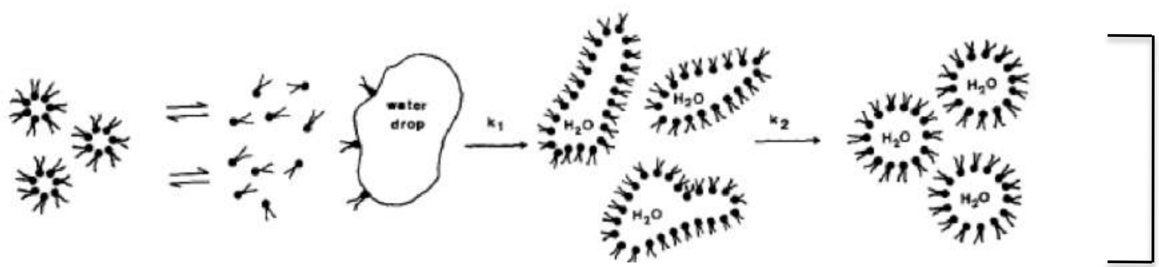
Reverse Micelles
(water in oil micro-emulsions)



Nickel Nanoparticle Catalysts

From Reverse Micelles to Nanoparticle Catalysts



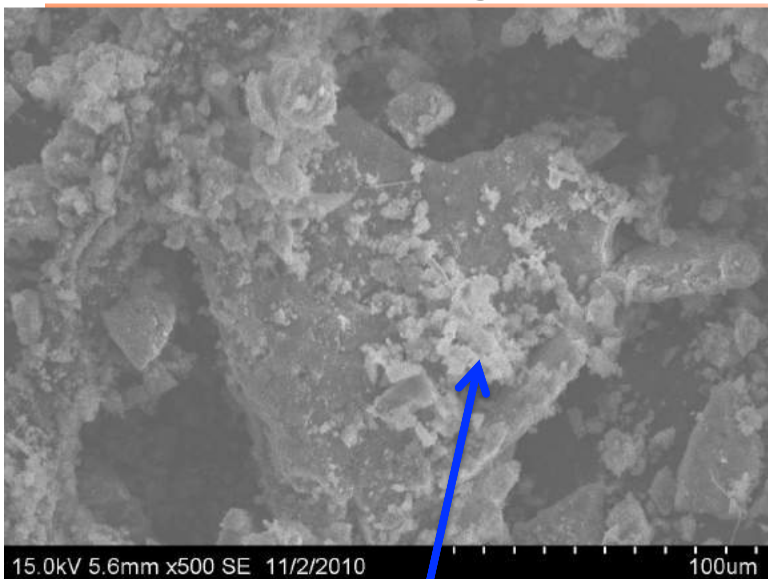


Factors Affecting RM'S

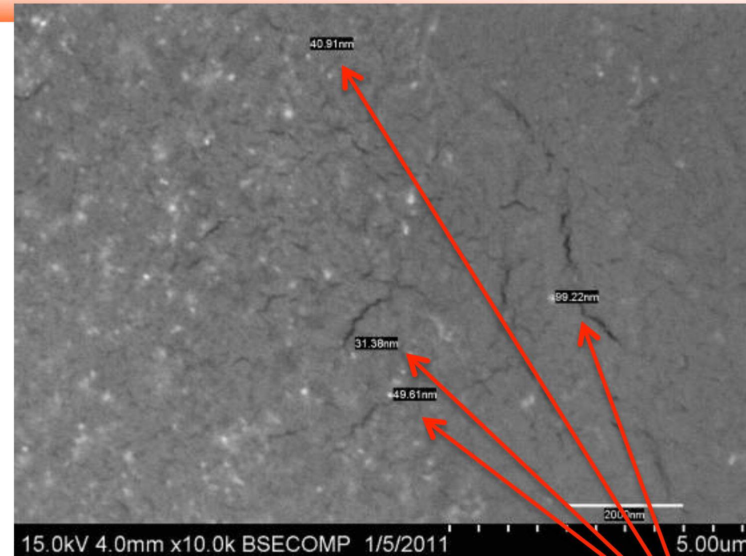
- **Water Pool Size**
- **Surfactant Ligand Size**
- **Sonication**
- **Solvents**

SEM Ni-TiO_2 Support

Wet Impregnation | **Reverse Micelle**



Micron sized Ni particles



30 – 50 nm sized Ni particle

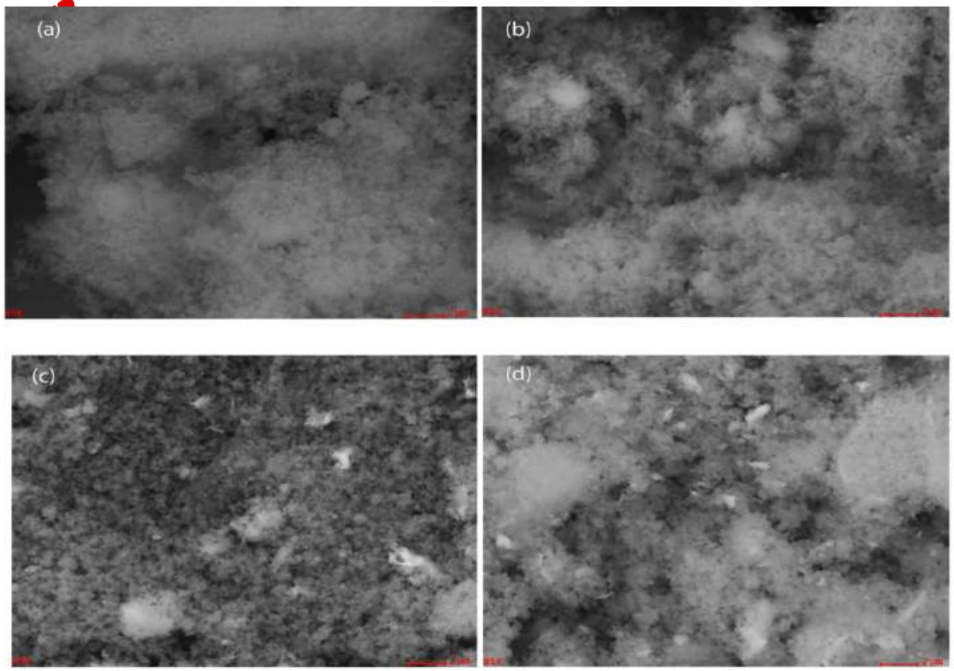
- Nickel nitrate solution, drying, calcination (650°C)
- Narrow particle size range in RM system
- Inconsistent surface converages for Ni (5% ≠ 5%)

$2Cu_2+ + 4BH^- + 12H_2O \rightarrow 2\ Cu + 14H_2O + B(OH)_3$

$2Ni_2+ + 4BH^- + 12H_2O \rightarrow 2\ Ni + 14H_2O + B(OH)_3$

Standard Reduction Potential + -

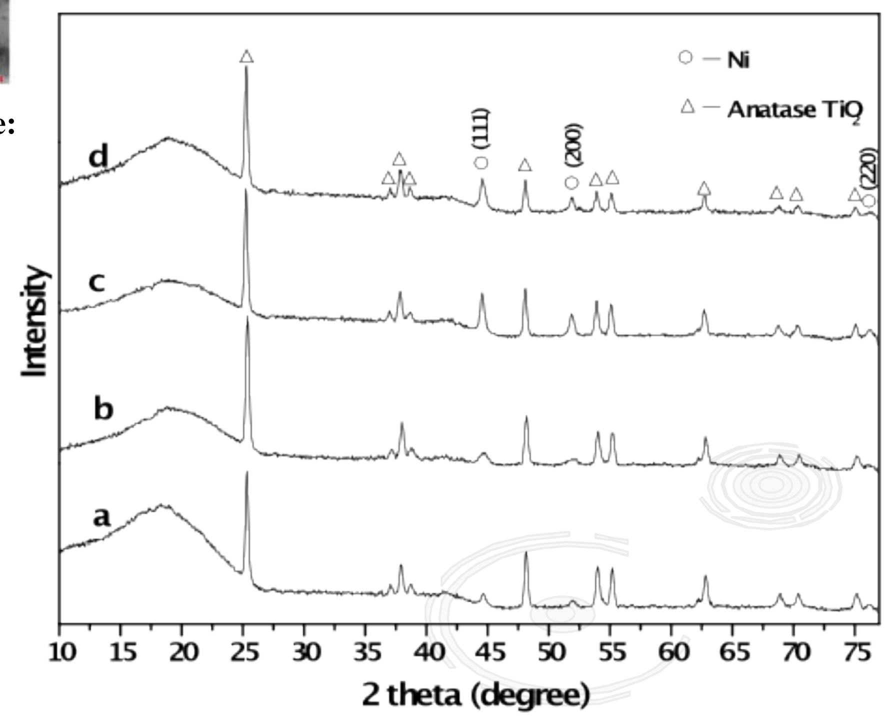
Preliminary Results (Ni/TiO2)



SEM micrograph of (a)5%, (b)10%, (c)15% and (d) 20% Ni/TiO_2 (scale: 2µm)

Ni Content (SEM-EDX)

(a) 5% (7%)
(b) 10% (11%)
(c) 15% (13%)
(d) 20% (21%)

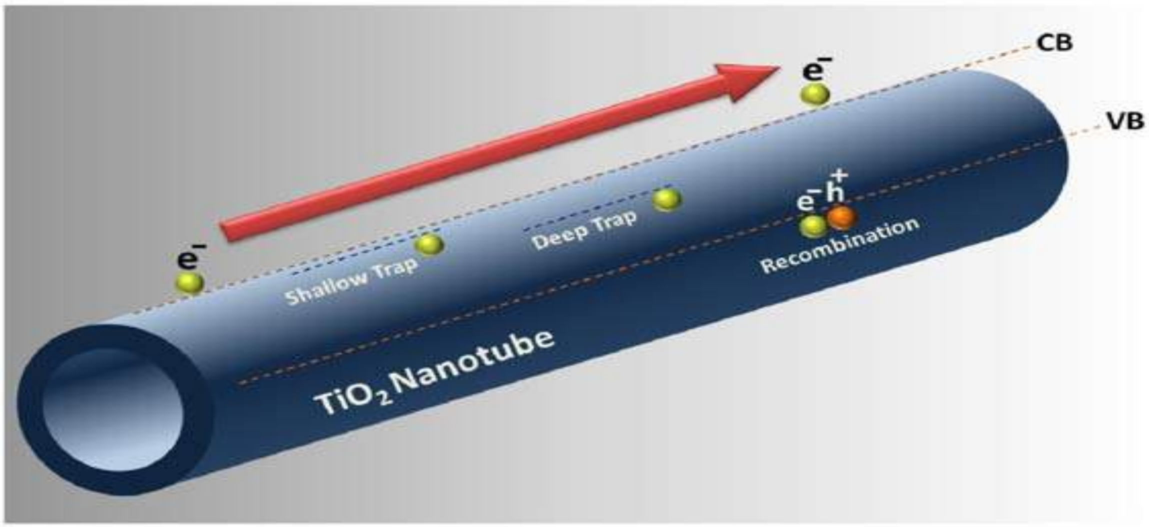


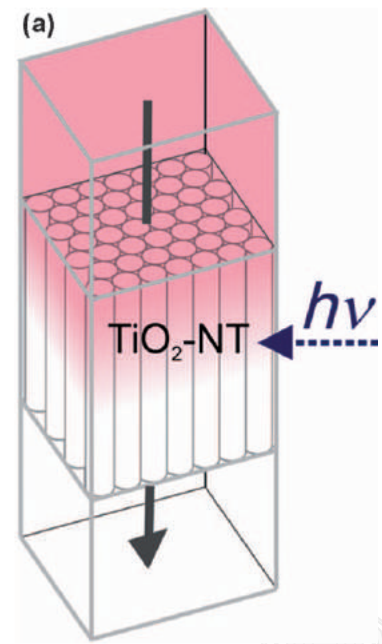
Ni Particle Sizes, nm

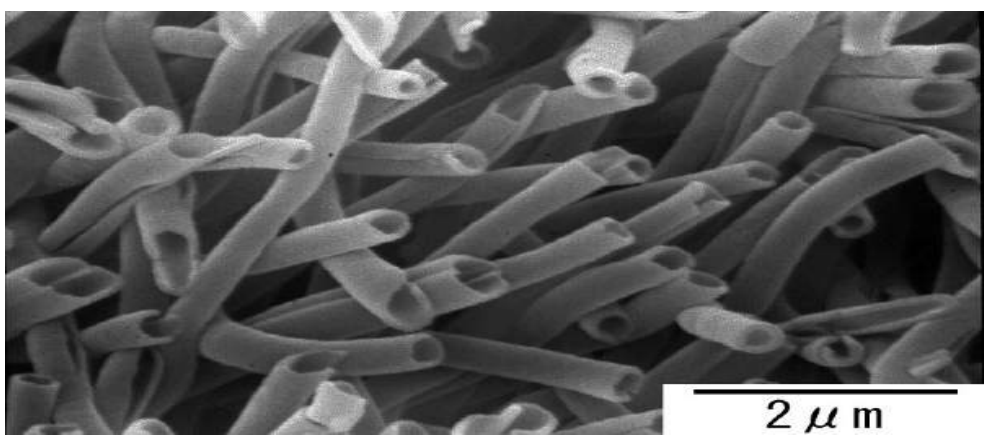
	111	200	220
	16.94	19.17	24.75
	11.25		17.32
	23.16	19.17	19.91
	18.66	21.64	24.75
AVG	**17.50**	**19.99**	**21.68**
St Dev	**4.92**	**1.43**	**3.70**

Photocatalyst Theory

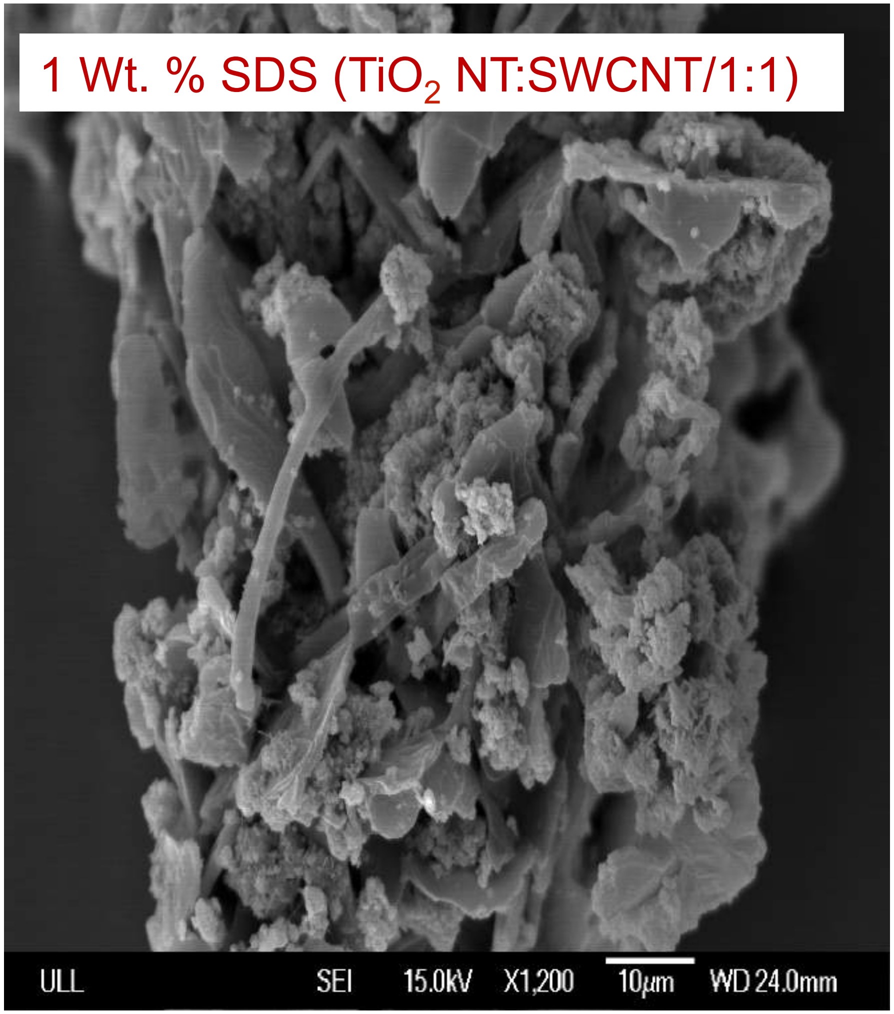
Carbon Nanotubes on Titanium Nanotubes



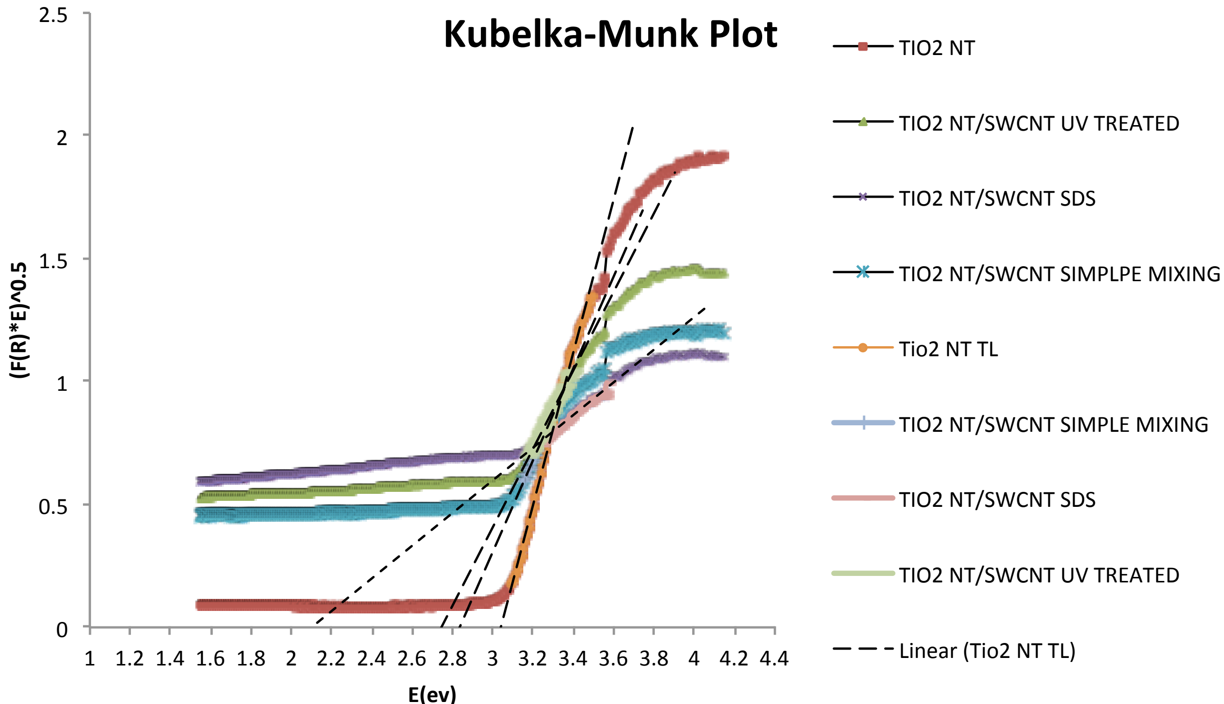




Photocatalyst Development



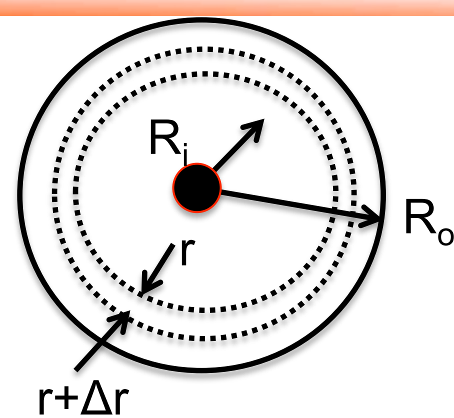
Band Gap Determination

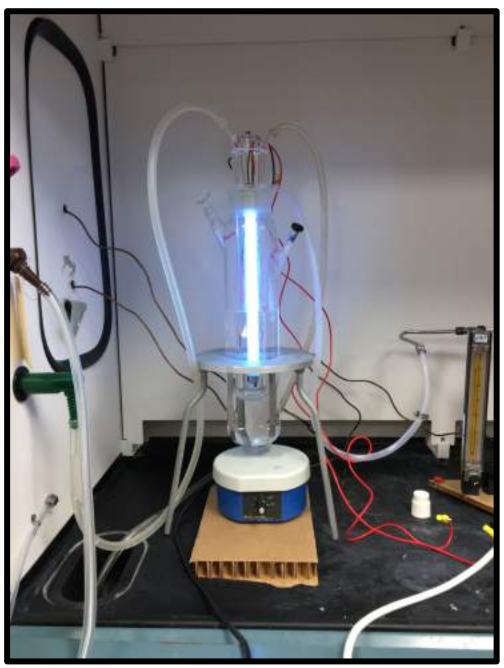


Material	Band Gap Energy, eV
TiO_2-NT	3.1
TiO_2-NT/SWCNT (simple mix)	2.85
TiO_2-NT/SWCNT (uv treated)	2.75
TiO_2-NT/SWCNT (SDS)	2.1

Moving Forward – Photocatalytic Reactions

- **CO_2 Conversion (competing rxn)**
- **Photon Flux**
- **Carbon Balance**
- **Energy Required/mole CO_2**





Photon Balance: In – Out – absorbed = 0

E = Photon Flux
A = Absorbance property of fluid + catalyst

$$2\Pi h[(Er)_r - (Er)_{r+\Delta r}] - 2\Pi hrEA_{\Delta r} = 0$$

Key Closing Thoughts

- Process modeling (equilibrium)
  - Optimum T = 850°C
  - Optimum CH_4/Flue Gas is 0.4
- CO_2 conv 99% and $H_2/CO = 2$
- Catalyst optimization and kinetic evaluation
- Sustainable Carbon Management Strategies

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Erfan Raihan (PhD)
Ashik Mahmud (MS)
Jennifer Watters (UG)

THANK YOU

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