Conversion of CO_2 into Commercial Materials using Carbon Feedstocks

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Developing the Technologies and Building the Infrastructure for CO_2 Storage

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Presentation Outline

- Project benefits and objectives
- Carbon gasification
- Carbon reactivity studies
- Catalyst development
- Techno-economic analysis
- Summary

Benefit to the Program

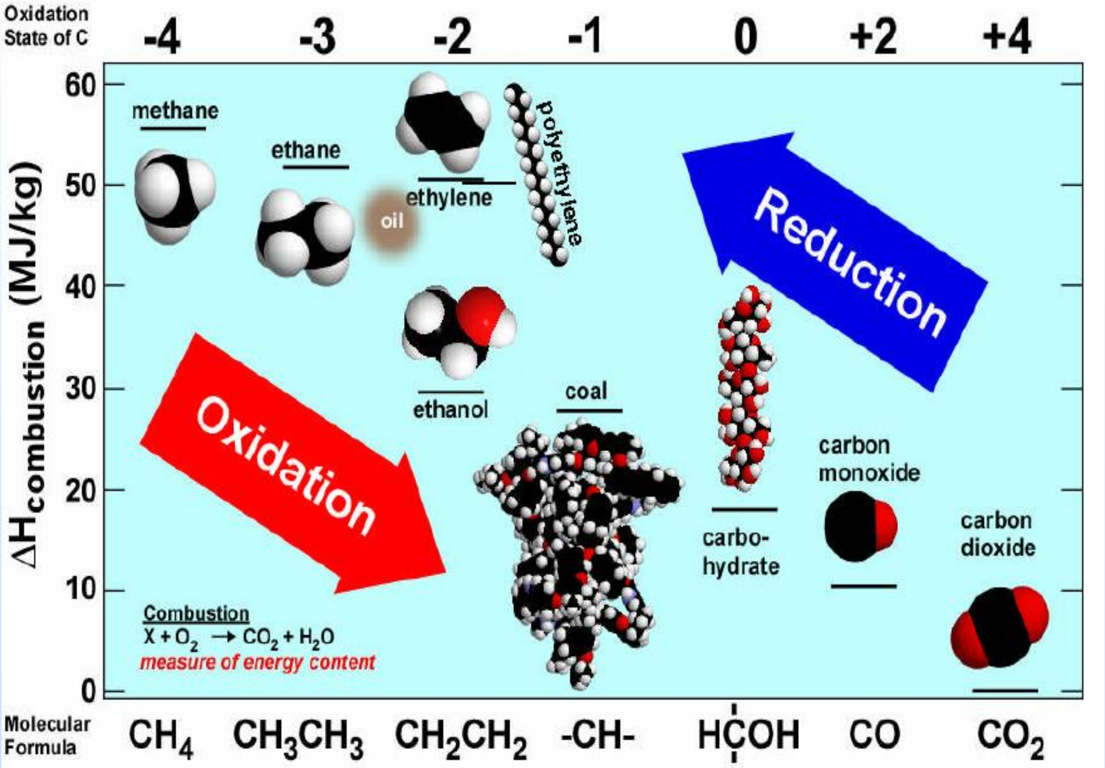
- Program goal: Reduce CO_2 emissions by developing beneficial uses that meet the DOE net cost metric of $10/MT for captured CO_2 that will mitigate CO_2 emissions in areas where geological storage may not be an optimal solution
- Benefits statement: Development of a commercial process for converting CO_2 and a carbon source into a commodity chemical at a cost of < $10 / MT of CO_2.

Project Overview: Goals and Objectives

Overall goal: Develop a process that utilizes carbon as a reductant for CO_2 to produce CO at a net cost of less than $10/MT

- Objectives:
  - Evaluate and identify the most reactive carbon sources for CO_2 gasification
  - Evaluate the potential to increase CO_2 gasification reactivity with catalysts
  - Demonstrate the economic feasibility of CO_2 gasification for the production of CO
  - Evaluate sensitivity of process economics to assist experimental program
  - Evaluate economic feasibility of producing commodity chemicals

Challenges of CO_2 Utilization



CO_2 Properties

- Most fully oxidized form of carbon
- Extremely chemically stable

Challenges

- CO_2 conversion requires abundant low cost reducing agents, energy (heat or electricity), and catalysts

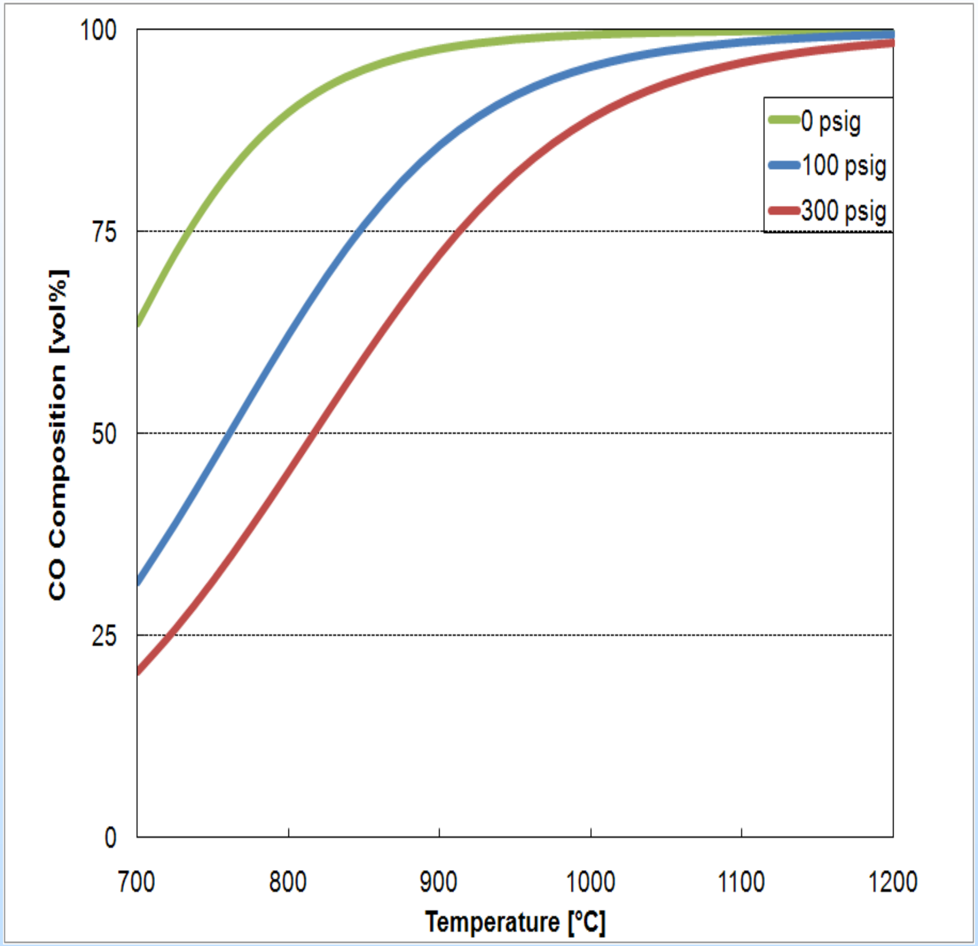
Constraints

- Production of reducing agents, energy, and catalyst requires minimal CO_2 footprint

Banholzer, 2008

CO_2-Carbon Gasification

CO Composition with Temperature and Pressure



CO_2 conversion increases with temperature and decreases with pressure

CO_2 to CO Pathway:

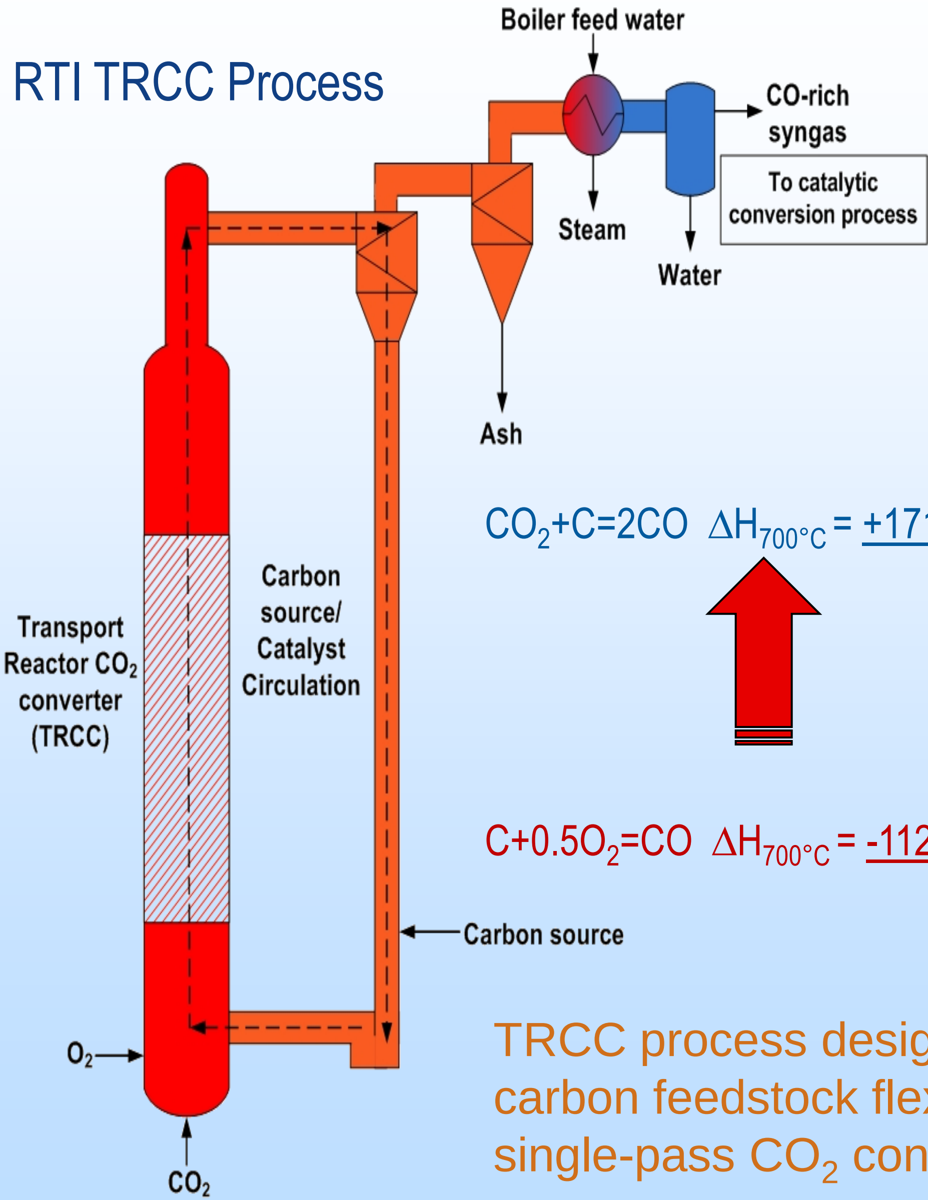
$CO_2 + C = 2CO \quad \Delta H_{25\,°C} = +172.5 kJ/mol$

Challenges:

- Heat transfer
  - Endothermic reaction requires heat addition
- Equilibrium conversion limitations
  - High operating temperature
  - Low operating pressure
- Carbon reactivity
  - Plentiful low-cost carbon sources are not inherently reactive
- Increasing reactivity with catalysts
  - Poor catalyst recovery with impregnation
  - Poor solid catalyst/solid carbon interactions reduce effectiveness of heterogeneous catalysts

TRCC Process Advantages

RTI TRCC Process



$CO_2 + C = 2CO \quad \Delta H_{700°C} = \underline{+171 kJ/mol}$

$C + 0.5O_2 = CO \quad \Delta H_{700°C} = \underline{-112 kJ/mol}$

TRCC process design provides carbon feedstock flexibility and high single-pass CO_2 conversion

Circulating solids

- Partial oxidation of circulating carbon provides energy for endothermic CO_2 char gasification
- Rapid heat transfer throughout the fluidized bed
- Multi-pass carbon conversion compensates for slower reaction kinetics and less reactive carbon sources
- Large mass of circulating carbon results in high single pass conversion of CO_2
- Carbon can be continuously added
- Ash can be continuously removed

Gasification catalyst

- Increases reactivity of low-cost and less reactive feedstock
- Enhances CO_2 conversion at lower temperatures

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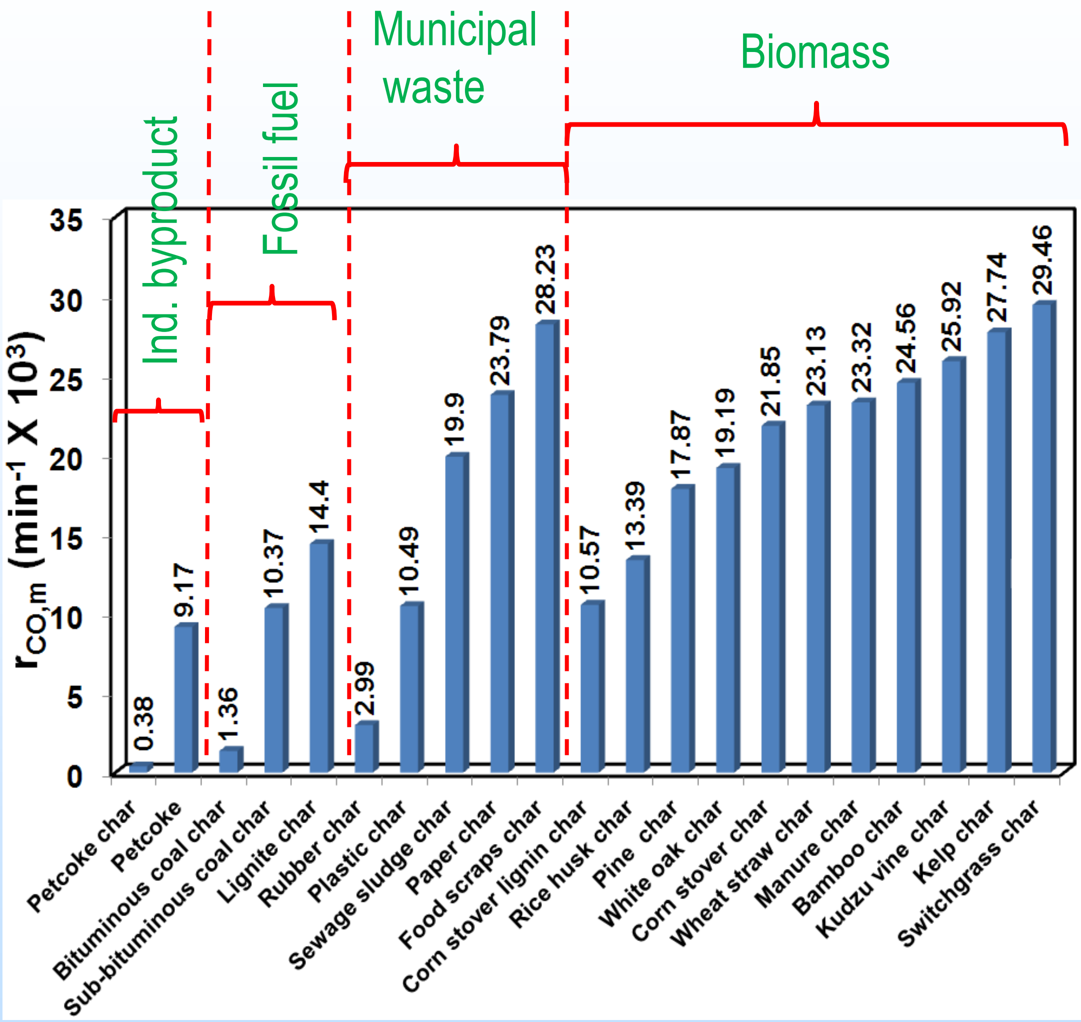
Experimental Evaluation of Reactivity for CO_2 Char Gasification

- **Goals**
  - Rank reactivity with CO_2 of carbon-based reducing agents
  - Establish operational parameters for process development
  - Support catalyst development
- Carbon Reducing Agents
  - Fossil: Bituminous, sub-bituminous coal and lignite
  - Renewable: Biomass Chars (e.g., wood, cornstover, and switchgrass)
  - Industrial byproducts: Petcoke, resid, bitumen
  - Municipal Waste: Plastic, paper, sewage sludge
- Experimental Parameters
  - Temperature: 600-1200 ºC
  - Carbon particle size: 40-120 μm
  - Weight Hourly Space Velocity (WHSV): 0.1- 60 hr^{-1}

Laboratory-Scale Fluidized-Bed Reactor System

Carbon Reactivity Ranking



Reaction conditions:

WHSV=2.36 hr^{-1}; T=800 ^{o}C; P=1 atm

- Reactivity for different carbon sources ranges from about 0.0004 to 0.03 min^{-1} for CO production
- Petcoke char was the least reactivity
- Coal sources have intermediate reactivity
- Biomass and municipal waste has the largest range of carbon reactivity

$$r_{CO,m}\,(min^{-1} \times 10^3) = \frac{28 \times F_{CO,m}}{22.414 \, x \, W_0}$$

$F_{co,m}$ = CO flow rate (SLPM)

W_0 = Initial sample mass (g)

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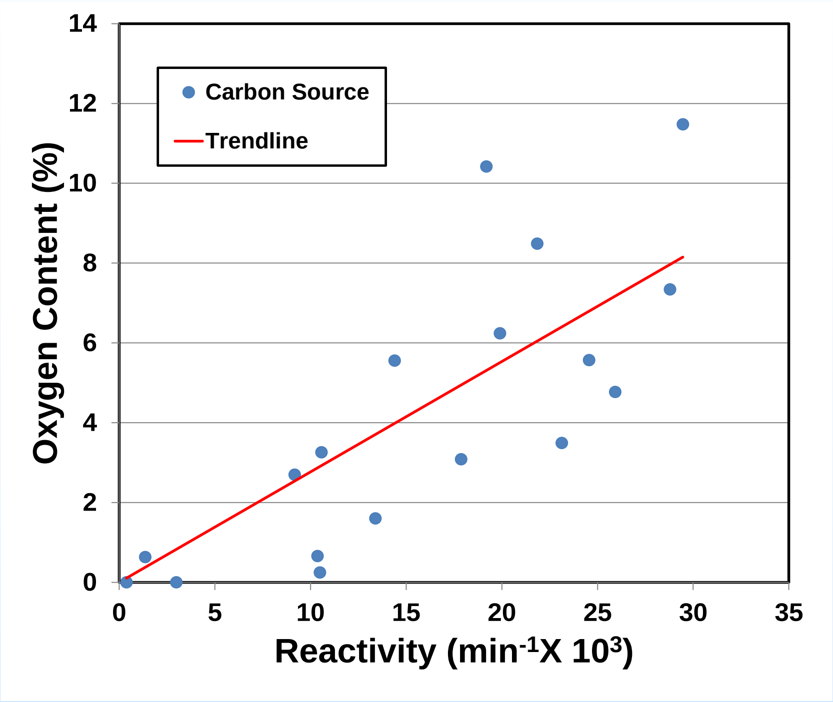
Reactivity and Carbon Properties

Carbon source		Char Preparation		Elemental Analysis (wt%)				Surface Area (m^2/g)
		Temperature (^oC)	Yield (wt%)	C	H	N	O	
Fossil fuel	Petcoke char	800	92.5	94.8	0.5	1.0	0	3.2
	Bituminous coal char	800	52.6	85.9	0.6	1.3	0.6	0.7
	Sub-bituminous coal char	800	43.3	83.4	0.5	0.5	0.7	116.3
	Lignite coal char	800	34.4	75.0	2.1	0.5	5.6	5.6
Biomass	Wheat straw char	500	22.1	97.9	2.2	0.0	3.5	19.0
	Pine char	500	22.5	87.7	2.6	0.0	3.1	278.5
	Corn stover lignin char	500	38.5	87.2	2.3	1.7	3.3	11.7
	White oak char	500	6.1	68.0	3.1	0.0	10.4	2.6
	Switchgrass char	500	18.3	60.4	3.6	0.2	11.5	3.4
	Corn stover char	500	23.4	53.7	2.7	0.0	8.5	2.1
	Rice husk char	500	35.2	45.4	1.6	0.8	1.6	214.2
	Bamboo char	800	13.1	79.4	0.7	1.6	5.6	3.1
	Kudzu vine char	800	21.7	78.6	0.6	1.2	4.8	3.3
Municipal waste	Waste tire char	800	34.3	83.1	0.4	0.3	0	75.9
	Food scraps char	800	14.1	77.5	1.0	2.7	7.3	1.8
	Waste plastic char	800	13.4	90.4	0.7	0	0.2	411.7
	Waste paper char	800	21.3	64.7	0.8	0	0	208.6
	Sewage sludge char	800	30.1	36.3	0.7	2.4	6.2	33.5

- Elemental Composition
  - C,H,O,N (Primary)
- BET surface area

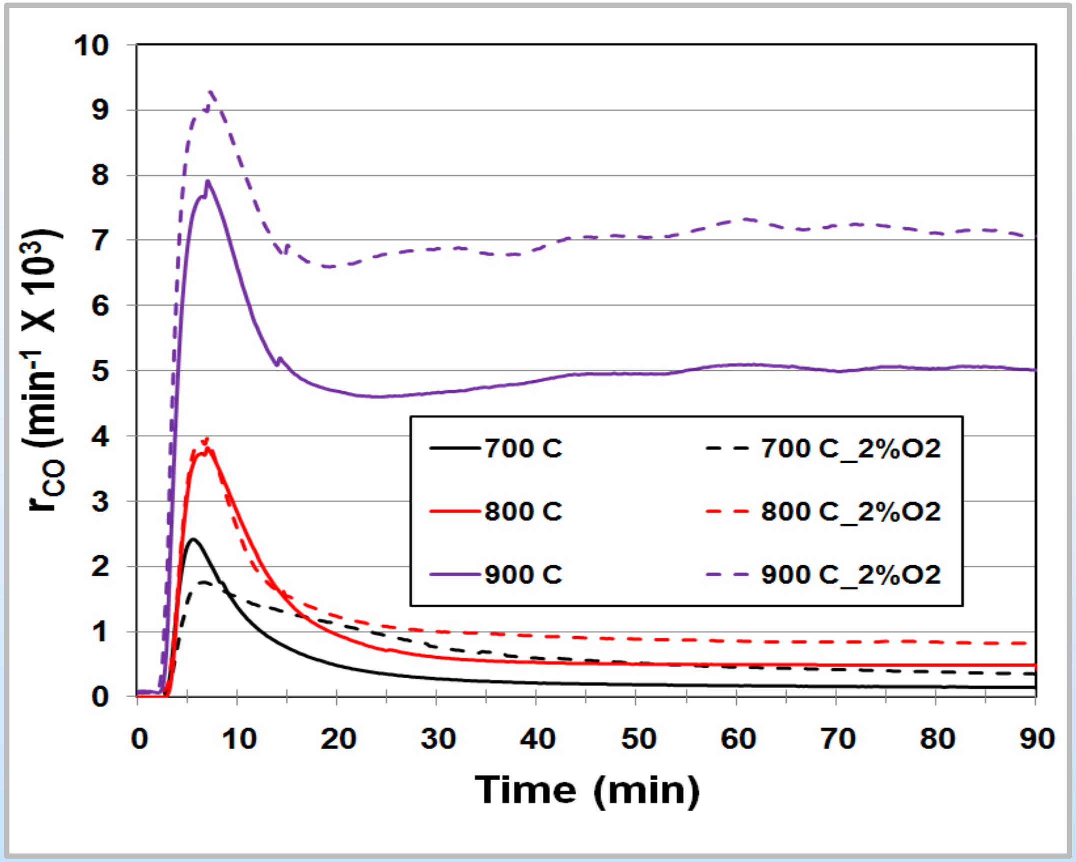
Reactivity and Carbon Properties (cont.)

- Elemental Composition (trace)
  - Mg, Al, Si, P, Si, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Sn, I, Ba, Pb, and Bi (Trace by XRF)
- Crystalline phases identified by XRD



No strong correlation between reactivity and any single factor.

O_2 addition Effect



- O_2 addition results in higher CO production rates at similar CO_2 conversion
  - Direct production of CO from partial oxidation
  - Heat release from partial oxidation provides localized heat for CO_2 char gasification reaction

Reaction conditions:

Carbon source: Petcoke; WHSV=1.18 hr^{-1}; O_2%=2%, P=1 atm

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Catalyst Screening Tests

Catalyst	Reactivity $r_{CO, m}$ (min^{-1} x 10^3)
Cat-1	19.15
$K\text{-}Ca/Al_2O_3$	12.34
Cat-2	11.29
Cat-3	9.43
Cat-4	8.24
Cat-5	7.95
Cat-6	5.13
Cat-7	4.55
Cat-8	2.19
Cat-9	1.86
None	0.38

Reaction conditions:

Carbon source: Petcoke char; WHSV=2.36 hr^{-1}; T=800°C; P- 1atm

- Petcoke char used because of its low reactivity
- $K\text{-}Ca/Al_2O_3$* (best performing catalyst in the literature)
- Demonstrated that catalytic effect improves performance of more reactive carbon sources

*J. Wang, et al., *Fuel*, 89 (2010) 310-317

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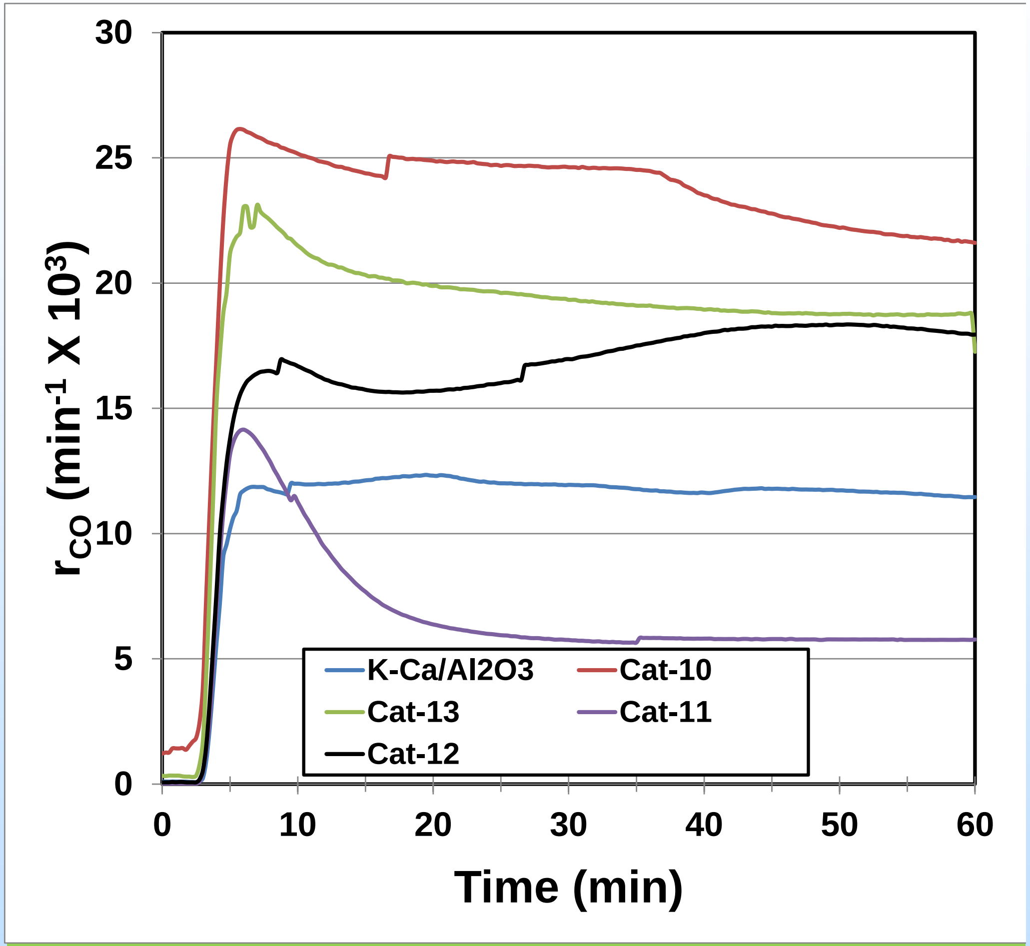
Optimization of Catalyst Formulation



Reaction conditions:

Carbon source: Petcoke char; WHSV=2.36 hr^{-1}; T=800^{o}C; W_{cat}:W_{char}=1:1

- Completed parametric testing of catalyst formulation
  - Active components
  - Promoters
  - Support
- Completed spray dried preparation of most promising catalyst
  - Demonstrated good hydrodynamic properties
  - Demonstrated attrition resistance similar to fluid catalytic cracking catalysts
- Completed extend operation testing with petcoke char

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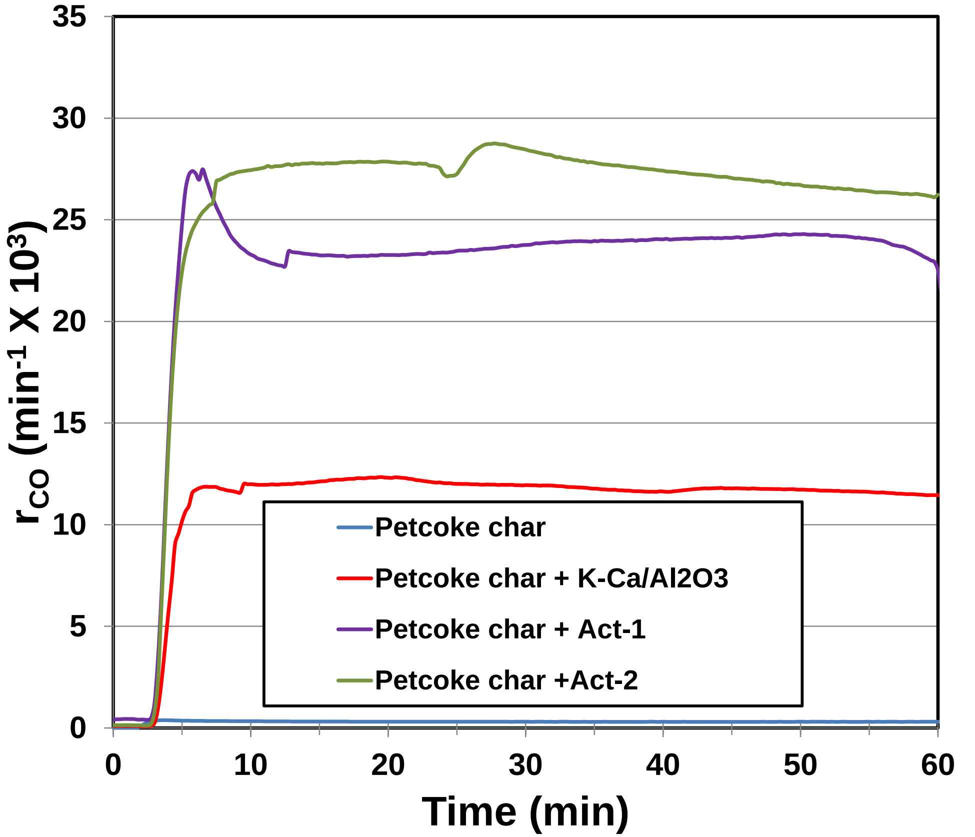
Evaluation of Reaction Mechanism



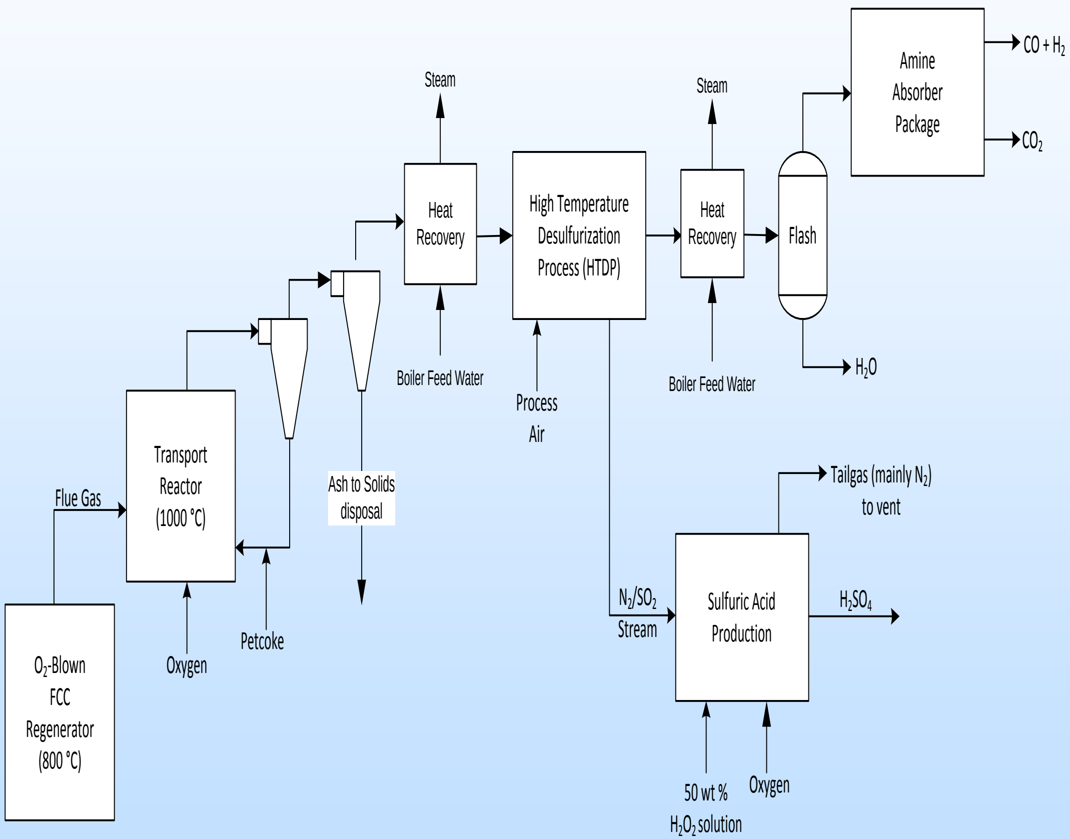
Reaction conditions:

Carbon source: Petcoke char; WHSV=2.36 hr^{-1}; T=800^{o}C; W_{cat}:W_{char}=1:1

- Completed parametric testing to investigate reaction mechanism
  - Catalyst formulations
  - Carbon sources
  - Reaction temperature

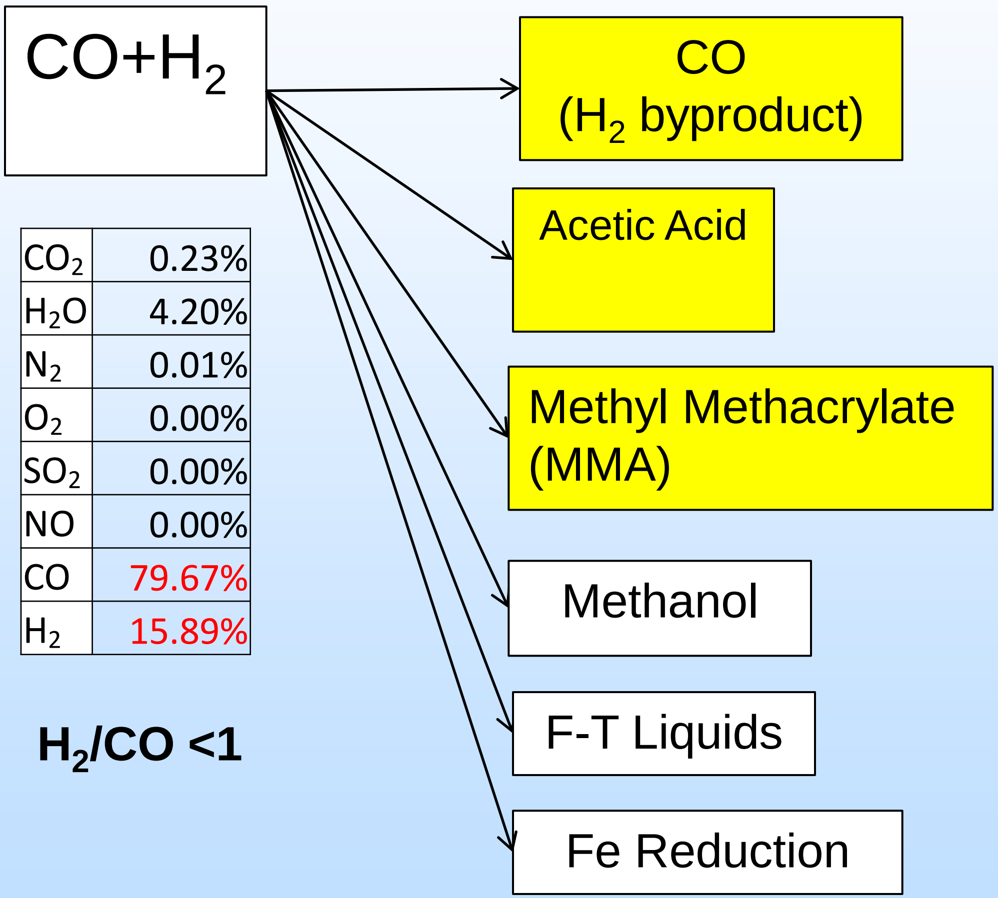
CO_2 Utilization Process Modeling

CO_2 Utilization Process for O_2-enriched fluid catalytic cracking regenerator



- CO_2 source: O_2-based Fluid Catalytic Cracking reactor
- CO_2 feedrate: 3,400 tons/day
- Carbon sources: Petcoke and lignite chars (other carbon sources evaluated)
- Equilibrium-based reactor model
  - Temperature: 800 and 1,000°C
  - 60% CO_2 conversion
- Primary products: CO and H_2
  - Additional syngas cleaning included to remove sulfur, NH_3, and CO_2

Product Selection



CO_2	0.23%
H_2O	4.20%
N_2	0.01%
O_2	0.00%
SO_2	0.00%
NO	0.00%
CO	79.67%
H_2	15.89%

H_2/CO <1

- Favor processes requiring syngas with low H_2/CO ratio
  - Carbonylation chemistry
- Avoid processes requiring high H_2/CO ratios
  - Water gas shift converts the CO back into CO_2
- Market price and production costs available for acetic acid and MMA

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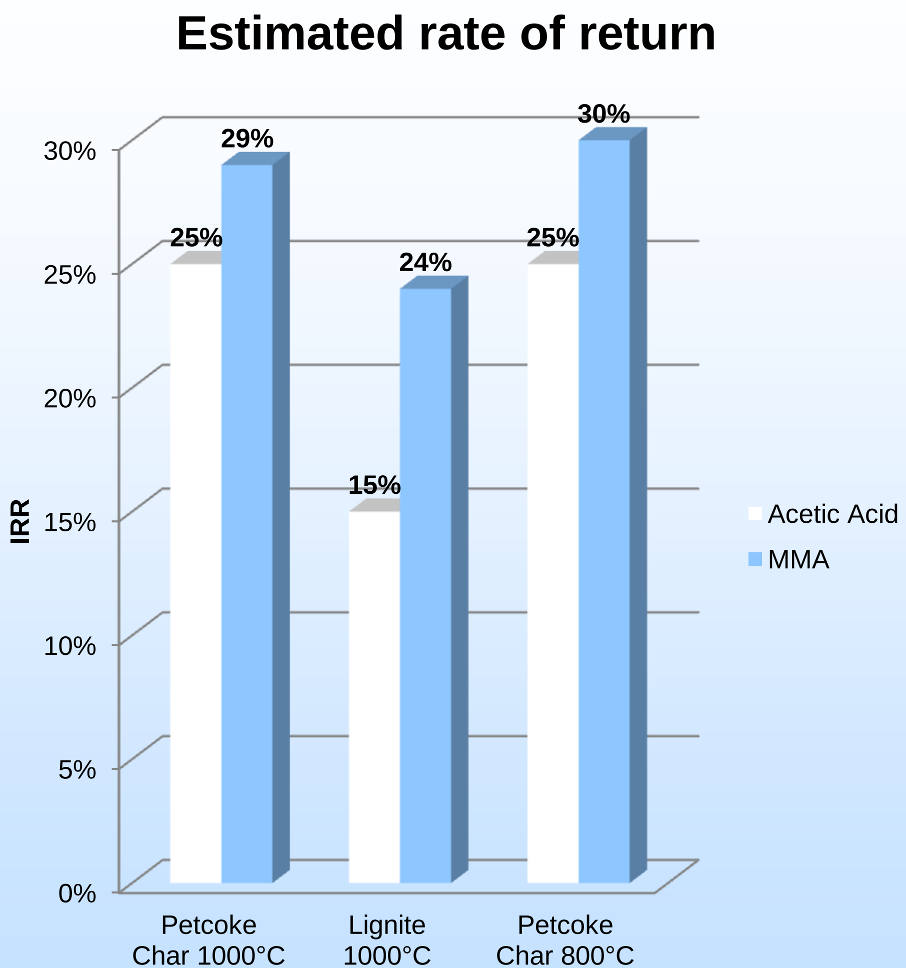
Techno-Economic Results

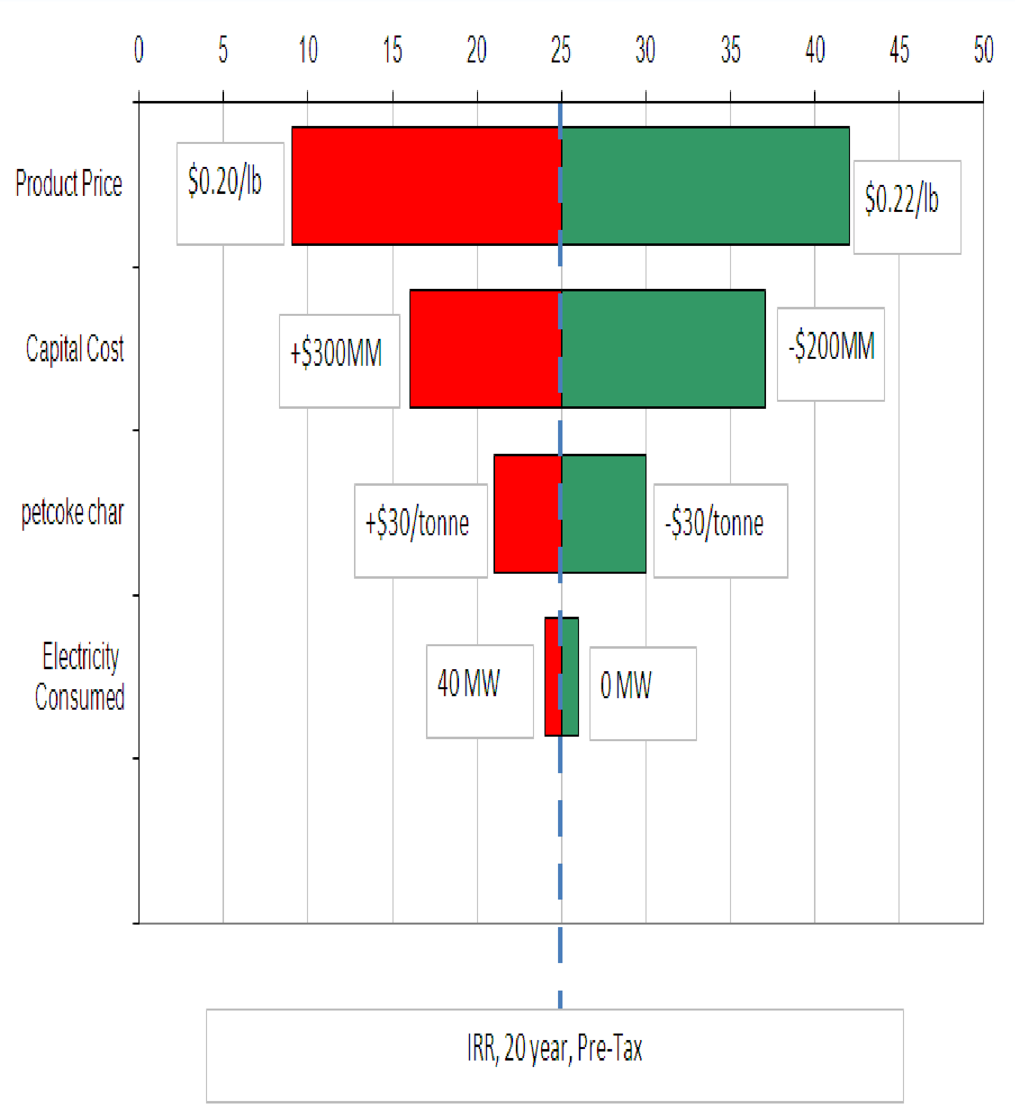


Capital cost (MM \$)	\$597	\$641	\$556

CO_2 conversion ~ 60%

- Production of acetic acid and MMA are economically feasible
- Economics favor carbon sources with higher carbon content (petcoke vs. lignite)
- Lowering operating temperature improves capital cost, but not overall economics

Sensitivity Analysis of Process Economics



- Capital cost: $597 Million
- Feedstock: Petcoke char
- Product: Acetic Acid
- Most sensitive factor: product price

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Accomplishments to Date

- Completed evaluation of reactivity for CO_2 gasification with a variety of carbon sources (Industrial waste, fossil fuels, municipal solids waste, and biomass)
- Investigated correlation between reactivity and physical and chemical properties of carbon sources
- Demonstrated catalyst can significantly improve carbon reactivity
- Implemented catalyst development program
  - Increased reactivity through evaluation of active components and promoters
  - Prepared catalyst samples that are suitable for transport reactor applications
- Investigated catalytic mechanism for carbon reactivity
- Completed techno-economic analysis of process demonstrating economic feasibility of production of acetic acid and MMA

Summary

- Carbon source does affect reactivity
  - Reactivity ranking: Biomass > municipal solid waste > fossil fuels > industrial waste
- No strong link between reactivity and physical or chemical properties of carbon source was identified
- Catalyst increased carbon reactivity by factor of 20 to 30
- Parametric testing enabled identification of optimal combination of active components and promoters
- Fluidizable catalyst prepared for transport reactor applications
- Process is economically feasibly for production of acetic acid and MMA

Future Plans

- Complete the techno-economic analysis for CO and H_2 production
- Initiate catalyst development for direct conversion of CO_2 and carbon into methanol

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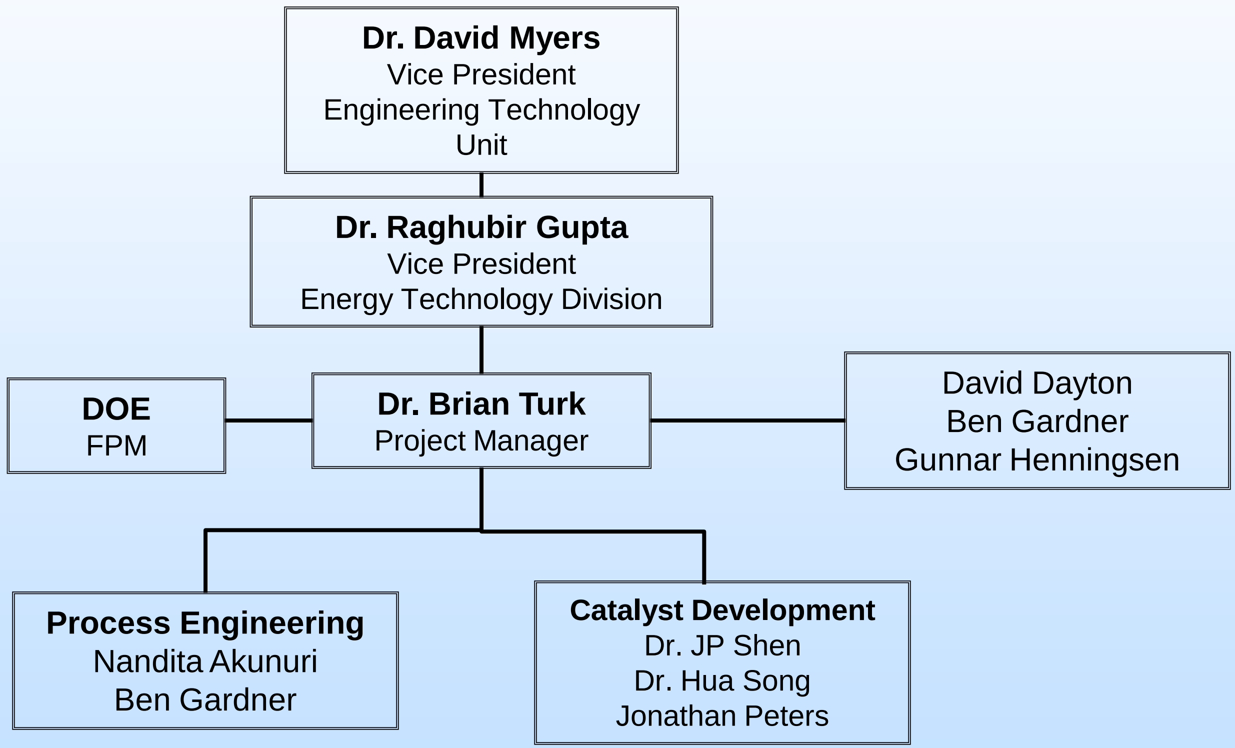
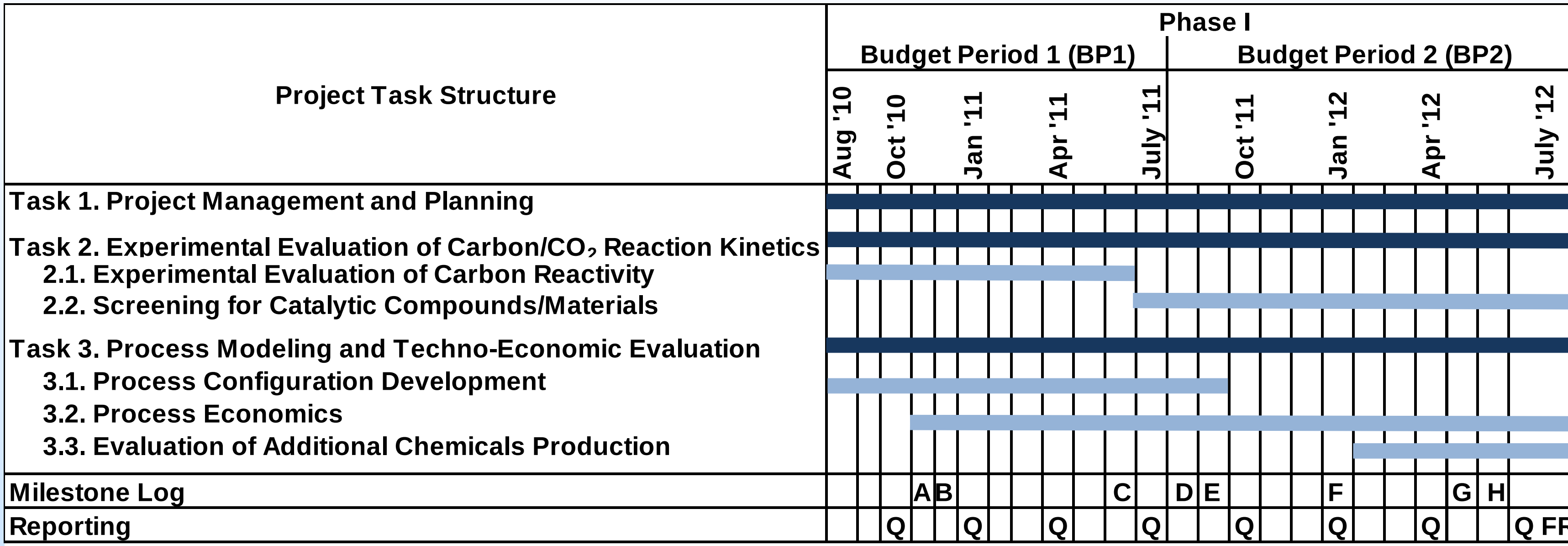
– Nandita Akunuri

Appendix

Organization Chart



Gantt Chart



Q = Quarterly reports due one month after quarter's end; FR = Final report due three months after project's end.

Milestones: A. Updated Project Management Plan, B. Kickoff Meeting, C. Determination of carbon feedstock reactivity with CO2, D. Develop Aspen Plus simulation model for process configuration, E. Begin catalytic compound screening, F. Begin process economic evaluations, G. Determination of catalytic compound impact on carbon feedstock reactivity, H. Complete techno-economic studies

Bibliography

No peer reviewed publications have been generated from project at this time.