



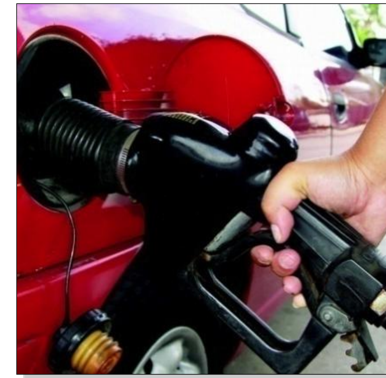

# Biomass to Liquid Fuels and Electrical Power

May 2013

Technology Area Review: Gasification

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# Goals

- Determine economically feasible technologies for production of biomass followed by production of biomass-derived syngas used for:
  - Renewable power generation
  - Liquid fuel production

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# Quad Chart Overview

## Timeline

- Project start date - 2010
- Project end date - 2013
- 80% complete

## Budget

- Funded in FY10
- $1.5 million
- $281k cost share

## Barriers

- Barriers addressed
  - Bt-A Biomass Fractionation
  - Gt-C High Temperature Gas Production from Biomass
  - Gt-G Fuel Synthesis and Upgrading
  - Gt-K Gaseous Intermediates Process Integration

## Partners

- Project conducted at Auburn University
- Collaboration with Rentech

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# Project Overview

- Overall Objectives
  - Determine economic constraints associated with harvesting forest biomass from southern pine and hardwood plantations.
  - Refine techniques for biomass fractionation and conversion into forms suitable for trade in commodity markets.
  - Develop process simulation models for biomass gasification and gas conditioning.
  - Develop models of Fischer-Tropsch synthesis processes.

# Approach

## Continuation of Previous Project

- Models used to evaluate logistics (harvest and transport) systems for young plantations of southern pine and hardwood
- Experimental methods used to identify preprocessing methods to convert biomass into relatively uniform products of cellulose, hemicellulose, and lignin.
- Models developed and validated for biomass gasification, tar formation, and syngas composition using experimental data from a bubbling-bed fluidized-bed reactor.
- Models developed and validated for supercritical phase Fischer-Tropsch conversion of synthesis gases into fuels and chemicals using experimental FT data and gasification modeling results.

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# Auburn Gasification Platforms

Bench-scale
(~1 kg/hr)
Bubbling bed

Pilot-scale
(0.5 ton/day)
Mobile Downdraft CHP

Pilot-scale
(1 ton/day)
Bubbling bed

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# Gasification Research

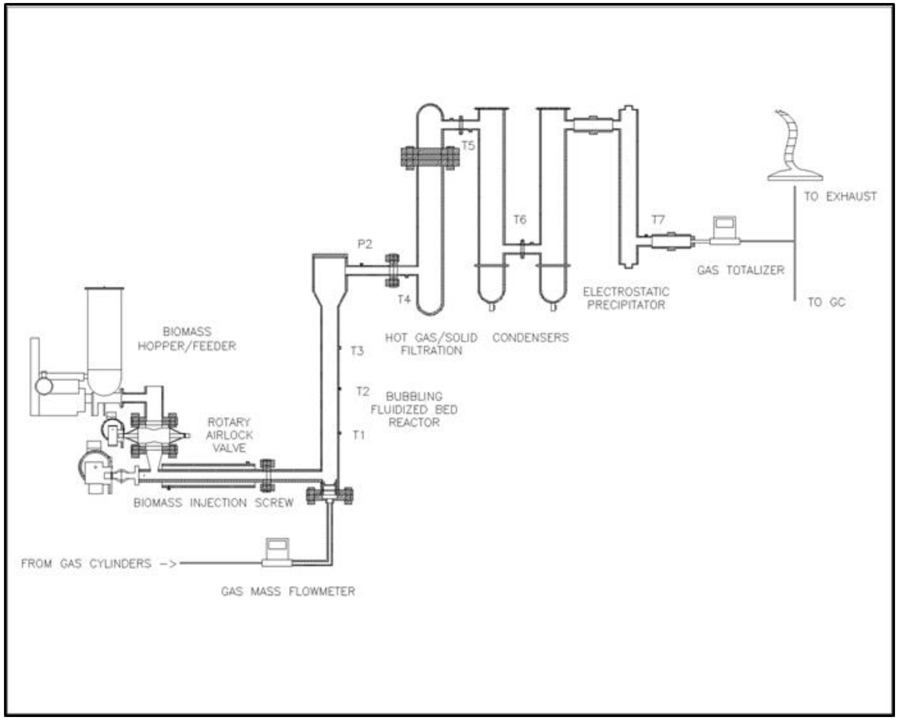
<u>Objectives</u>

- Understand the effect of biomass properties on syngas quality and contaminants (e.g. tar, $H_2S$).
- Understand the fate of contaminants in gasification with different oxidizing media.
- Determine appropriate syngas conditioning and cleanup strategies for subsequent FT synthesis.

<u>Approach:</u>

- Perform gasification studies on different biomass species (e.g. pine, eucalyptus, poplar, and switchgrass) and build process models to predict gasifier performance.

# Gasification Research




**Bench-scale Gasifier Specifications**

- Pressure: atmospheric
- Temperature: 600, 700, 800°C
- Feed rate: ≤ 0.85 kg/h
- Biomass particle size: ~ 850 μm
- Moisture content: ~ 10% (wb)
- Analysis systems:
  - NDIR based gas analyzer (online)
    - $CO$, $CO_2$, $CH_4$, $H_2$, $O_2$
  - HP GC (offline)
    - $H_2S$
  - FTIR based gas analyzer (online)
    - $CO$, $CO_2$, $NH_3$, $HCN$, $HCl$
  - Impinger train for tar analysis (offline)

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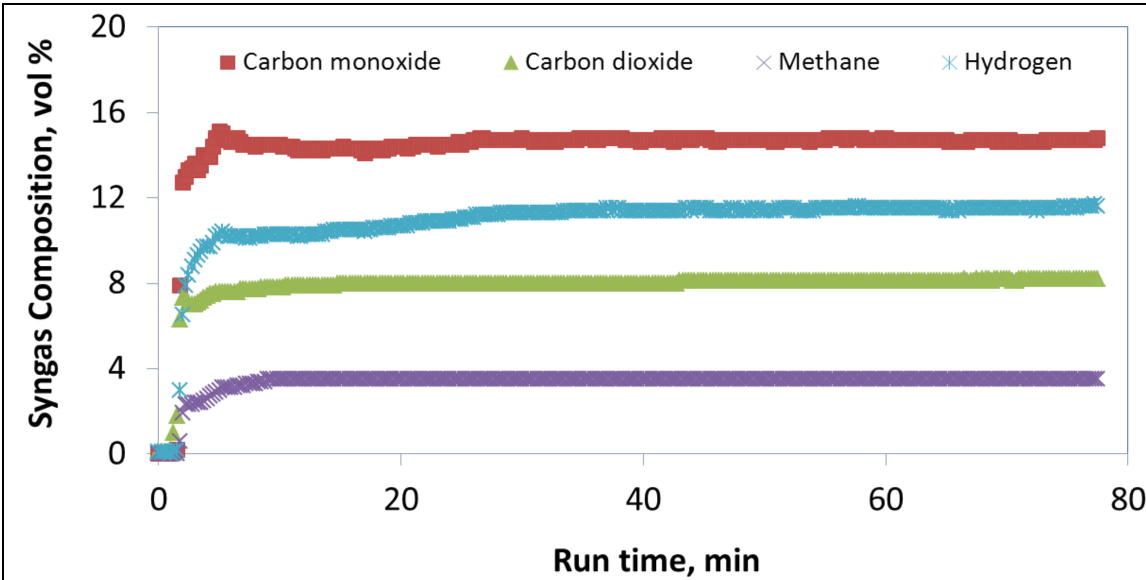
# Syngas Composition
## Example Results




Typical syngas composition profile from southern pine gasification with $O_2$ as oxidant and $N_2$ as fluidization gas

Pine gasification at 700°C from using bench-scale gasifier

| ER | 0.19 | 0.28 |
|---|---|---|
| **Syngas Composition, vol %** | | |
| $O_2$ | 0.7 | 0.0 |
| CO | 15.8 | 12.1 |
| $CO_2$ | 8.0 | 8.1 |
| $CH_4$ | 4.2 | 3.0 |
| $H_2$ | 11.2 | 9.0 |
| $N_2$ | 60.1 | 67. 7 |
| **Contaminants, ppm** | | |
| $NH_3$ | 421.5 | 797.6 |
| HCN | 40.9 | 63.5 |
| HCl | 0.9 | 0.9 |
| $H_2S$ | 31.5 | 25.4 |

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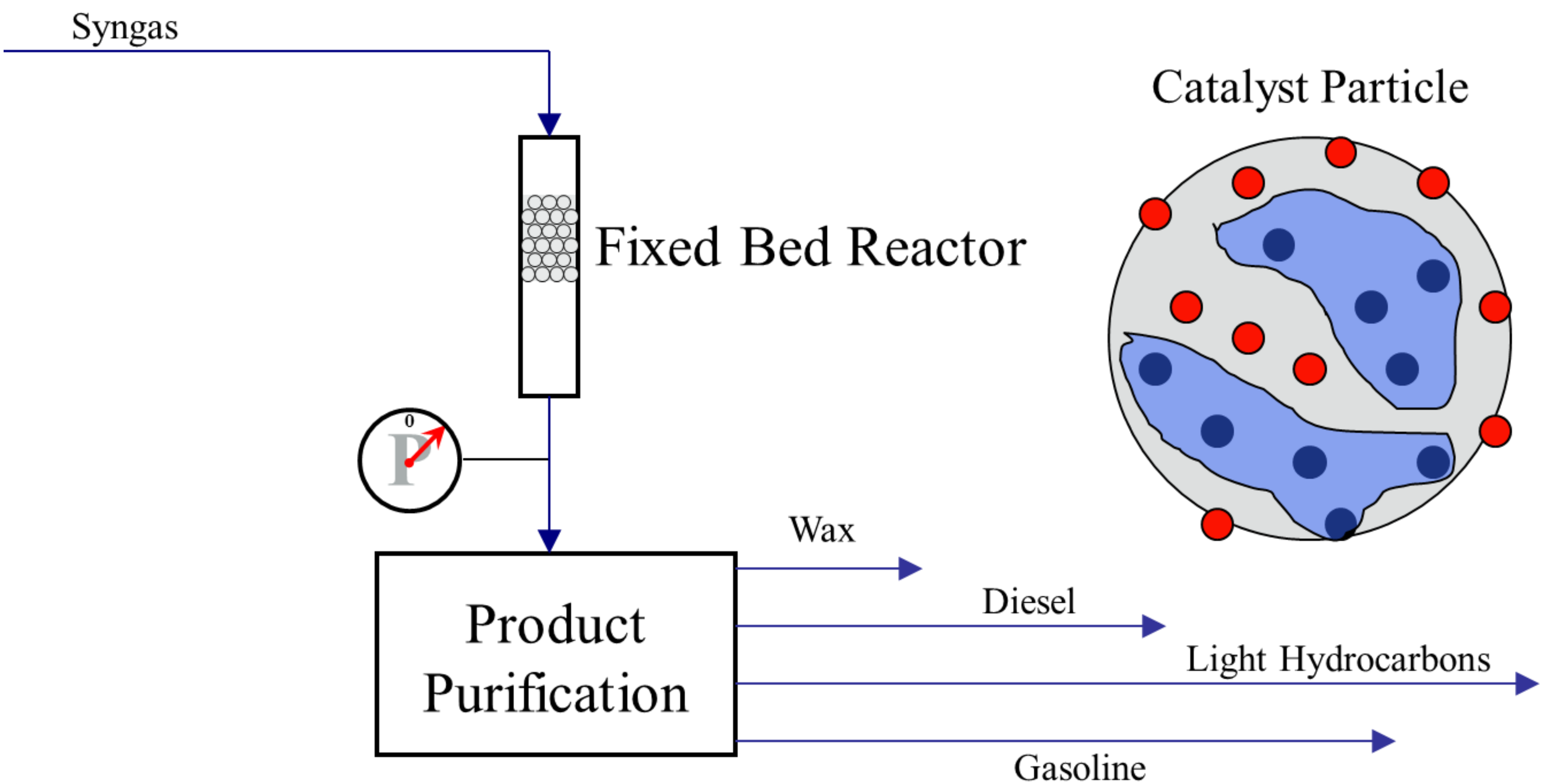
# Fischer-Tropsch Synthesis (Gas Phase)

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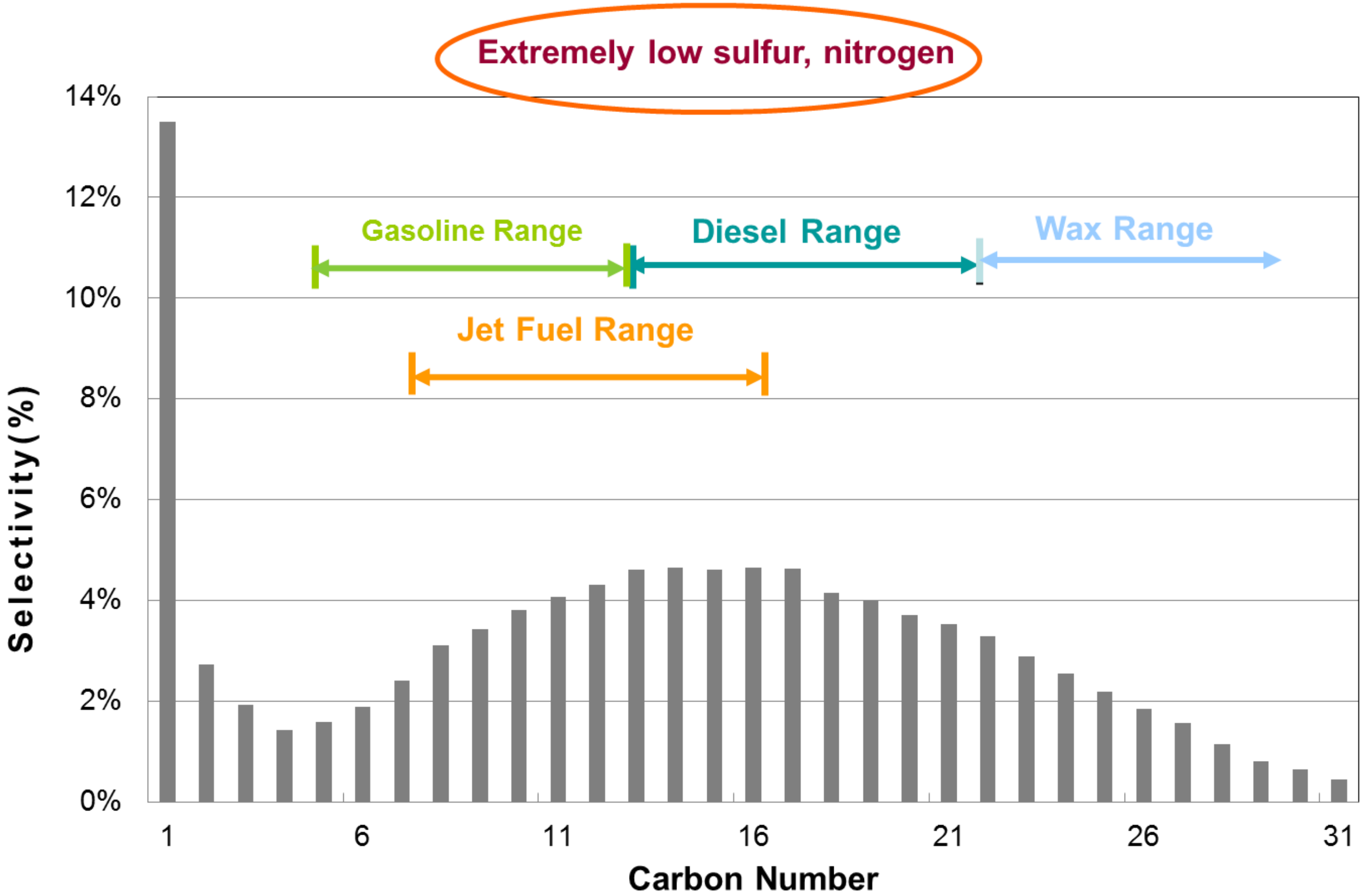
# FTS Product Distribution

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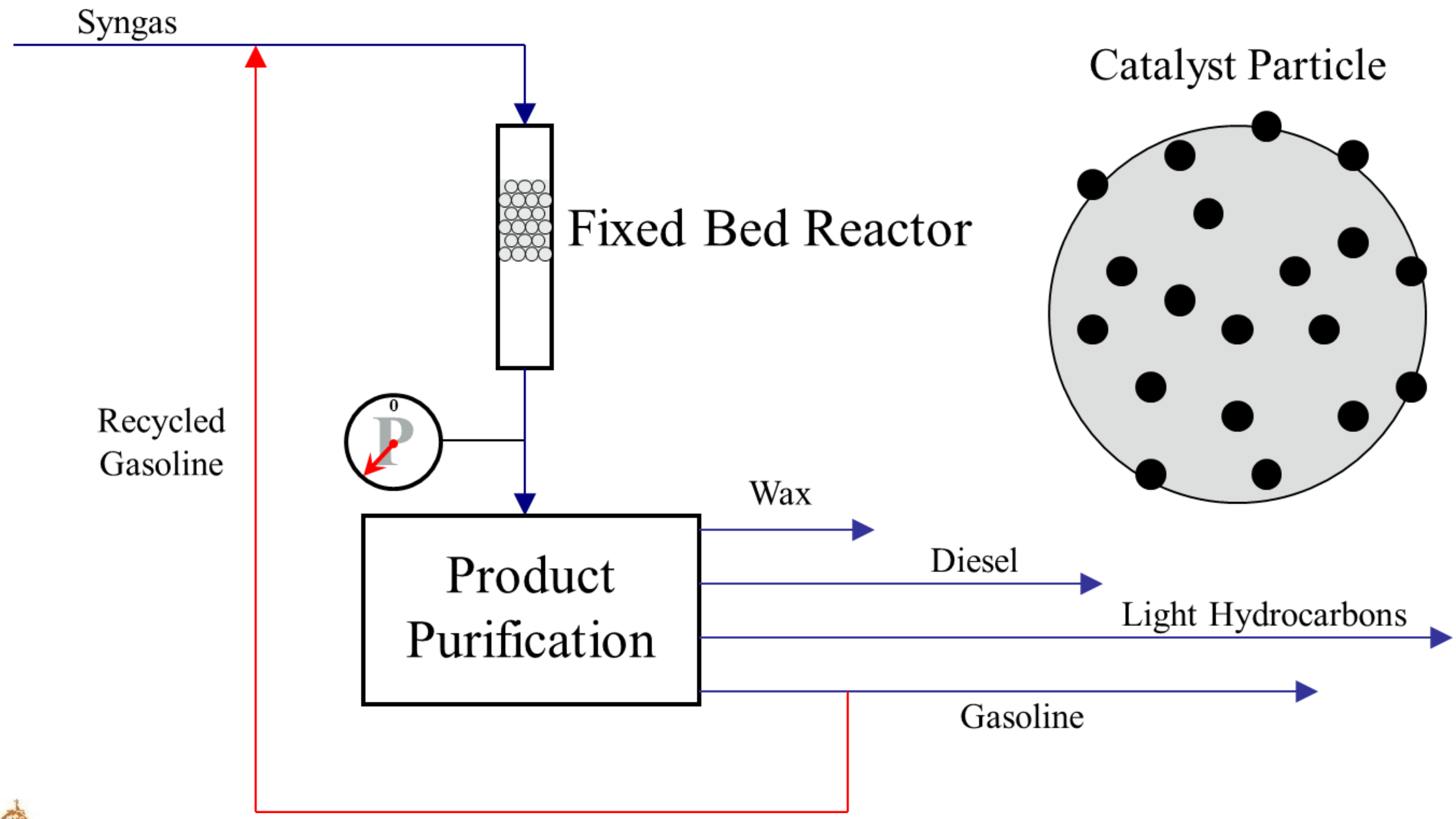
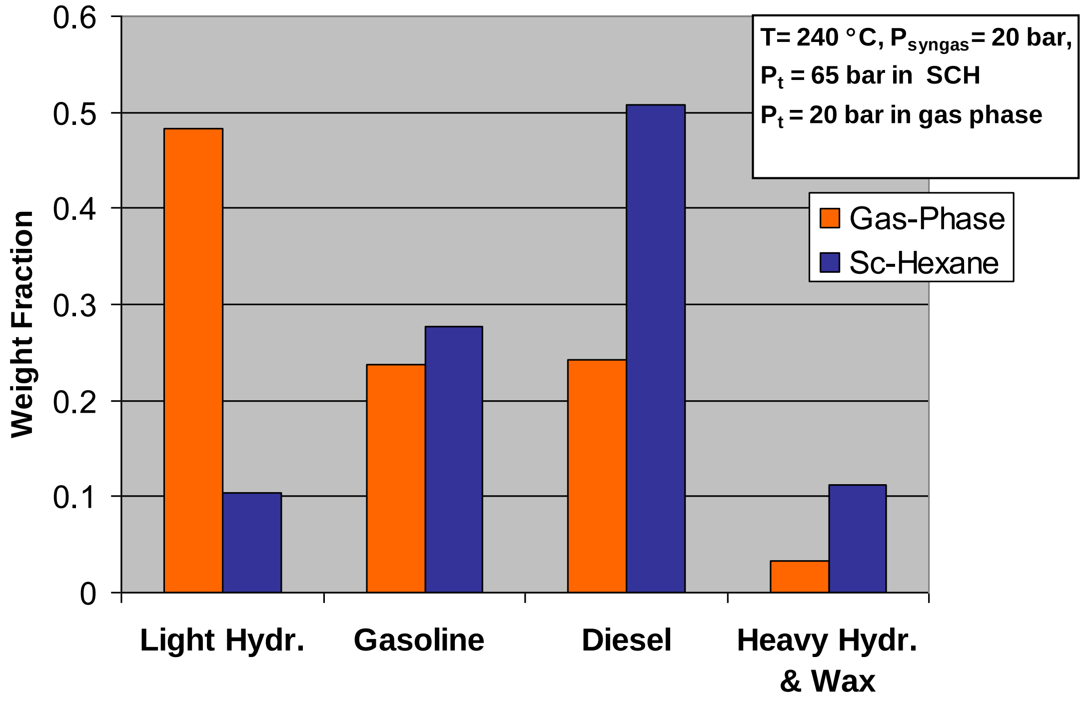
# FTS (Supercritical Phase)



# Benefits of Supercritical FTS

- Suppressed $CH_4$ and $CO_2$ formation
- Increased olefin selectivity at higher carbon numbers
- Improved activity maintenance
- Decreased Adiabatic Temperature Rise
- Higher activity and enhanced diesel and wax selectivity

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# FTS Research

## Objectives

- Synthesize and characterize Fe-based Fischer-Tropsch Synthesis (FTS) catalysts suitable for use with biomass-derived syngas
- Compare gas-phase, slurry-phase, and supercritical phase FTS with syngas obtained from biomass gasification
- Quantify the effect of syngas composition and contaminant levels on FTS performance
  - Characterize this performance relative to syngas conversion, product selectivity, and yield of fuel-range hydrocarbons

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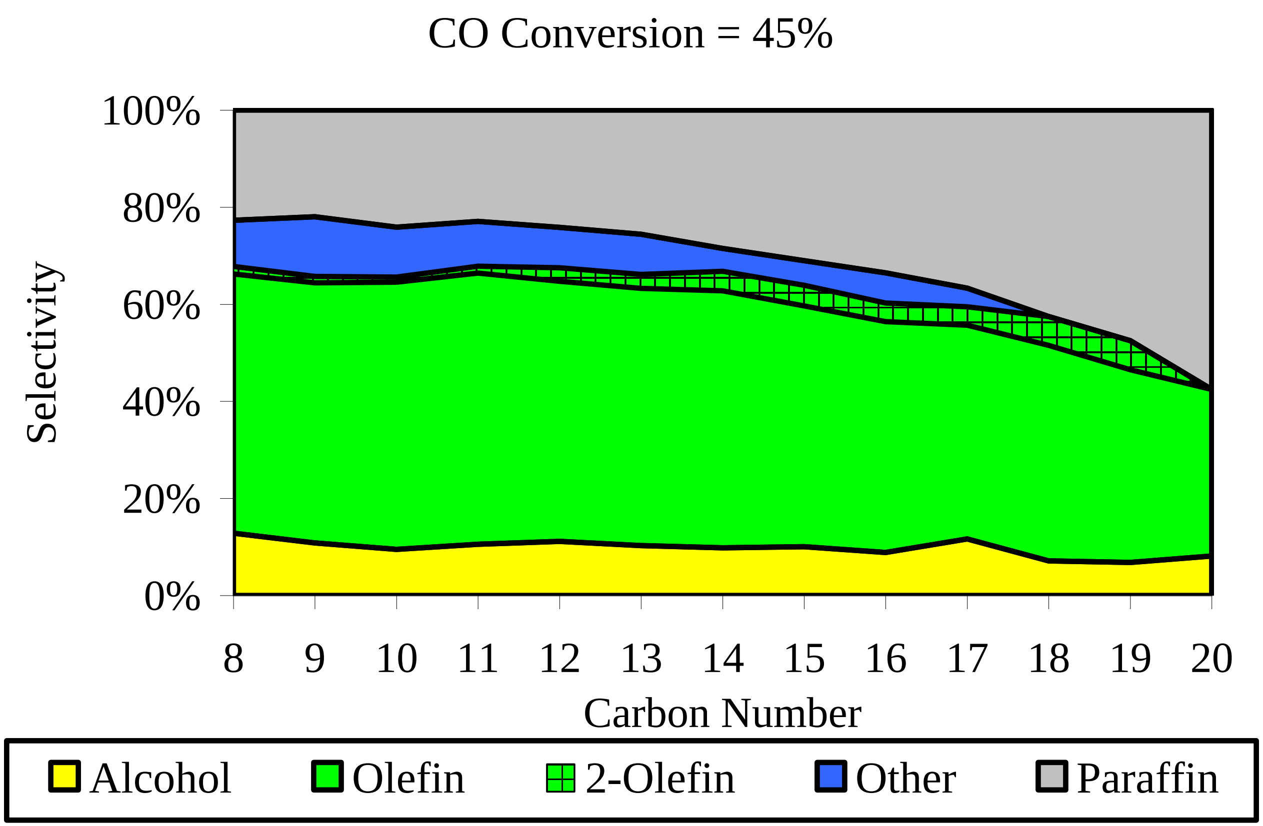
# FTS Liquid Product
## Functionality -v- Carbon Number




- 100 Fe : 10 Zn : 1 Cu : 2 K (by mol) catalyst, T = 240°C, P = 17.5 bar, $H_2$ / CO = 1.65

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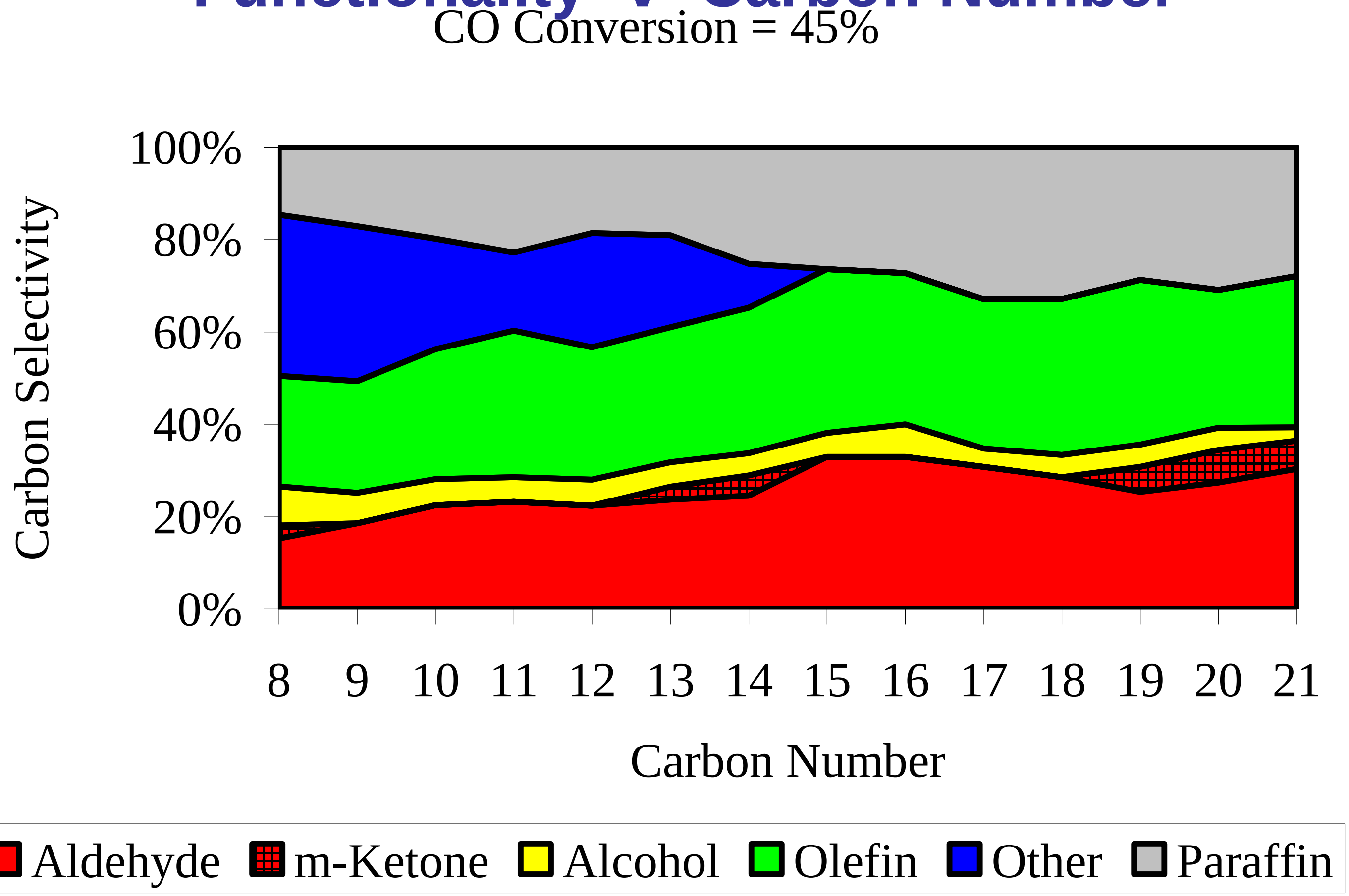
# SCF-FTS Liquid Product

## Functionality -v- Carbon Number




- 100 Fe : 10 Zn : 1 Cu : 2 K (by mol) catalyst
- T = 240°C, P = 79 bar, $H_2$ / CO = 1.65, media = hexanes, media rate = 1 mL/min per 50 SCCM

# Modeling Research

## Objectives

- Optimize gasification-FTS system design using process integration techniques for thermal management and resource conservation.

## Approach

- Models developed using commercial process simulation software.
- Models augmented with customized units for specific equipment, (not be readily available in commercial simulators).
- Models developed in collaboration with other researchers to enable synergistic feedback of design changes identified by simulation to guide targeted validation experiments.

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# Model Formulation

- **Simulation Input**
  - Proximate and ultimate analysis used as simulation input
  - Aspen Plus® process simulation software
  - Gibbs Free Energy minimization approach
- **Initial Analyses**
  - Analyze impacts of increased oxygen (air) content
  - Determining optimal air-to-fuel ratio for each feedstock
  - Examine effects of varying gasifier pressure
  - Steam injection to augment synthesis gas production

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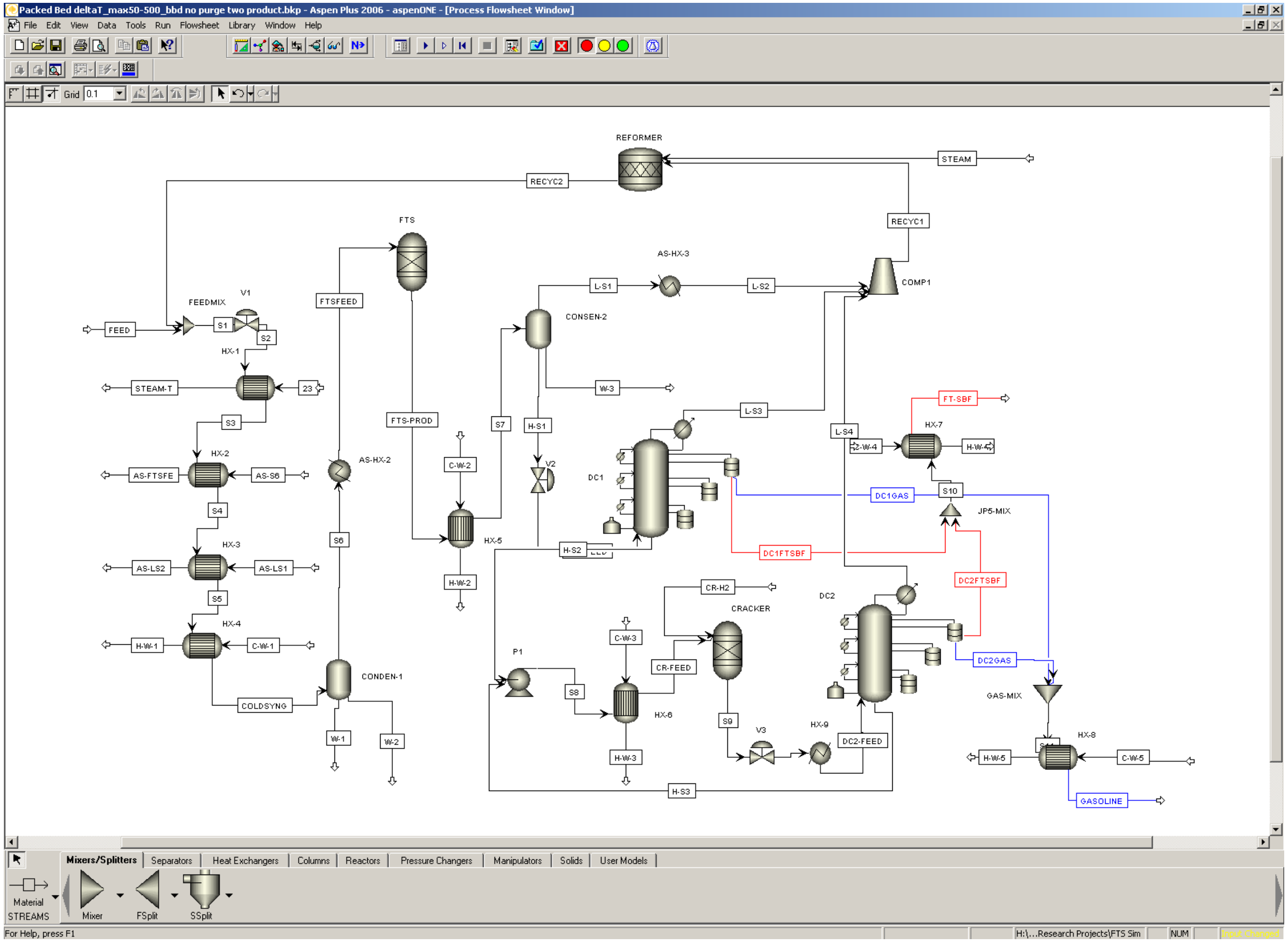
# Gas Phase FTS Model



# Model Specification

- **Fischer-Tropsch Reactor**
  - Based on ARGE reactor (Ruhrchemie and Lurgi)
  - 2050 tubes, 5 cm ID and 12 m length (48.3 $m^3$)
  - Recycle of tail gas (ca. 1/3)
  - Production requires 70.5 gmole CO/sec
  - CO consumption 1.46 gmole CO/$m^3$-sec
  - Heat of Rxn = 170,000 J/gmole CO
  - Volumetric heat generation= 248 kW/$m^3$
  - Packed bed thermal conductivity= 4.49 W/m-K
  - $\Delta T_{max}=S_e R^2/4k$, $\Delta T_{max}$= 8.6K (average)

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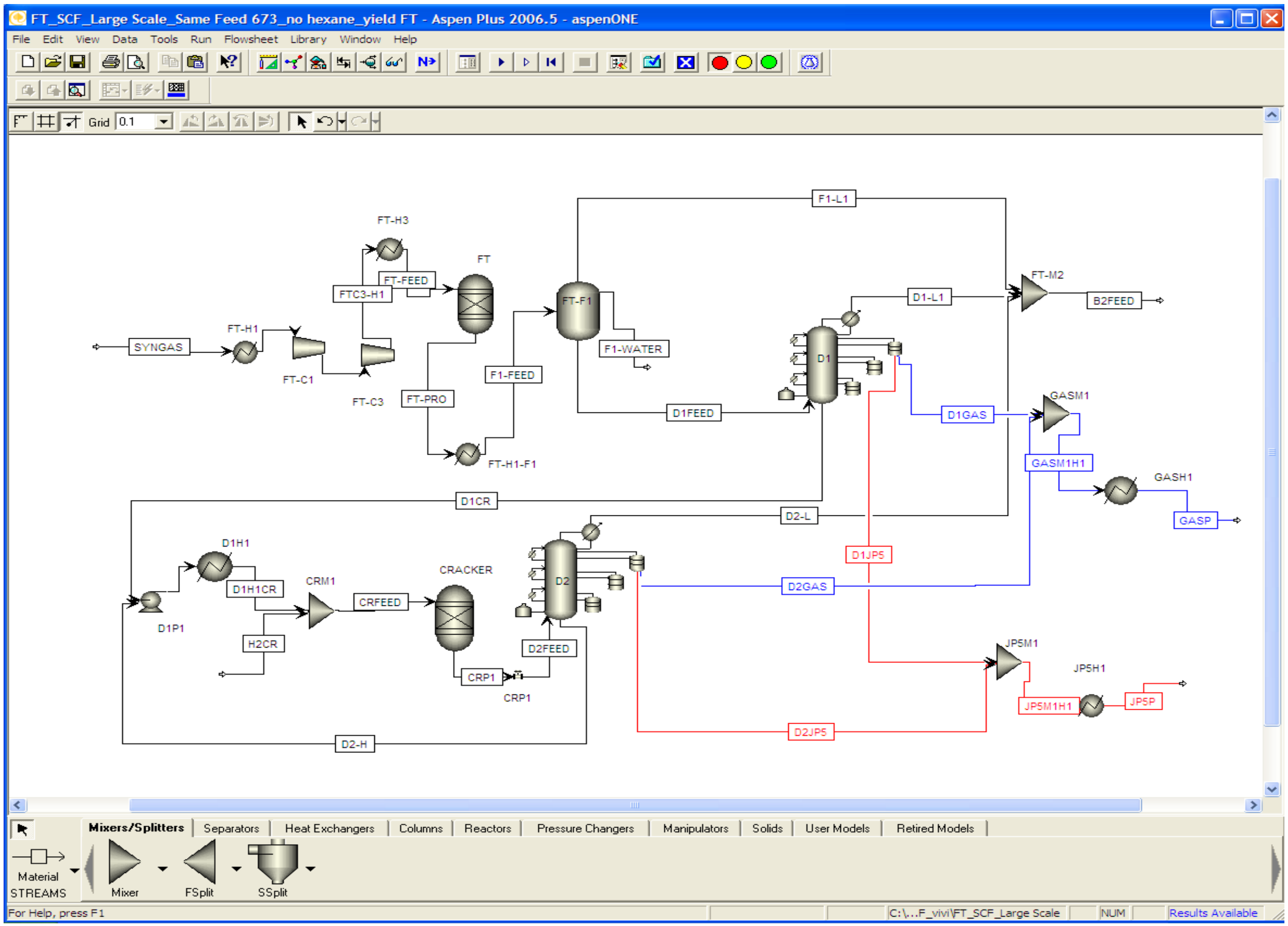
# Supercritical Phase FTS Model

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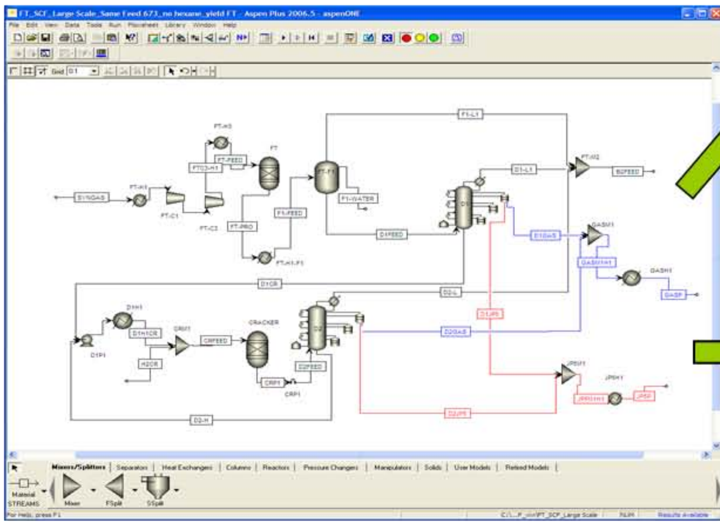
# FTS System Comparison

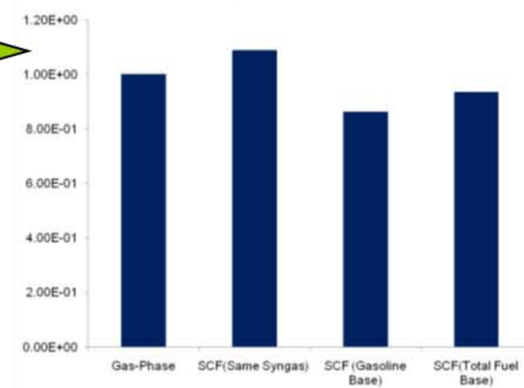
## Supercritical Phase FTS Model



## Fuels Production Analysis

| | | Syngas (kmol/hr) | Gasoline (kg/hr) | | | JP5 (kg/hr) | | | Total Fuel (kg/hr) |
|---|---|---|---|---|---|---|---|---|---|
| | | | D1 | D2 | Total | D1 | D2 | Total | |
| Gas-Phase FTS | | 1524 | 882 | 526 | 1348 | 1271 | 417 | 1688 | 3036 |
| SCF-FTS | Same Syngas Feed | 1524 | 508 | 1318 | 1826 | 1091 | 756 | 1848 | 3674 |
| | Same Fuel Product (based on gasoline) | 1122 | 374 | 974 | 1348 | 806 | 558 | 1364 | 2712 |
| | Same Fuel Product (based on total product) | 1259 | 420 | 1090 | 1510 | 903 | 623 | 1526 | 3036 |

## Energy Analysis




**SCF-FTS is about 20% more expensive than Gas-Phase with the same syngas molar feed rate, but produces about 50% more fuel!**

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# Process Integration

- **Heat Exchanger Network Design**
  - Based on conventional pinch analysis methods
  - Performed using AspenTech HX-Net$^{TM}$
  - Multiple network configurations generated
  - Default setup attempts minimizing total annualized cost based on utility use and equipment size

# FTS System Comparisons

- **Gas Phase FTS[a]**
  - 900˚C adiabatic temperature rise
  - 180 reactor modules
- **Supercritical Phase FTS[a,b]**
  - 30˚C adiabatic temperature rise
  - 6 reactor modules

[a] 50% Conversion with a 5˚C allowable temperature rise

[b] Hexane media with 3.5 mol media per mol syngas

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# FTS System Comparison

| | ARGE | SCAR |
|---|---|---|
| Number of Reactors in Series | 1 | 6 |
| Number of Tubes | 2050 | 1 |
| Tube Diameter (m) | 0.05 | 2.3 |
| Tube Length (m) | 12 | 2 |

| | SCAR |
|---|---|
| Number of Heat Exchangers in Series | 6 |
| Number of Tubes | 128 |
| Tube Diameter (m) | 0.062 |
| Tube Length (m) | 9.74 |

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# FTS System Comparison

| | ARGE | ARGE Modified for SCF-FTS | SCAR (Single Reactor) | SCAR (Multi-Reactor) |
|---|---|---|---|---|
| Number of Reactors | 1 | 1 | 1 | 6 |
| Pressure (bar) | 45 | 200 | 200 | 200 |
| Reactor Volume ($m^3$) | 48 | 48 | 48 | 8 |
| Adiabatic Temperature Rise (K) | N/A | N/A | 5 | 30 |
| Surface Area per Reactor ($m^2$) | 3864 | 3864 | 85.4 | 14.2 |
| Reactor Cost | $2,700,000 | $5,500,000 | $240,000 | $40,000 |
| Number of Heat Exchangers | N/A | N/A | 1 | 6 |
| Surface area per HX ($m^2$) | N/A | N/A | 825 | 241 |
| Cost per HX | N/A | N/A | $1,160,000 | $340,000 |
| Equipment Cost | $2,700,000 | $5,500,000 | $1,400,000 | $2,300,000 |
| Equipment Cost ($/BPD) | $3,000 | $6,000 | $1,600 | $2,500 |

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# Relevance

Technical and economic feasibility of biomass-to-liquid systems will be improved through:

- Enhanced understanding of the relation between biomass physicochemical properties and syngas quality (Tt-C).
- Enhanced understanding of the relation between biomass gasification conditions and feedstock properties on syngas quality (Tt-F).
- Enhanced fuel selectivity and productivity using SCFTS (Tt-G).
- Expanded understanding of the performance of FT catalysts using biomass derived syngas (Tt-H).

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# Critical Success Factors

- Developing information and models that will accurately predict syngas composition from biomass characteristics and gasifier operating parameters.
- Refining models that predict the overall technical and economic feasibility of gasification and SC FTS systems.
- Using models to successfully demonstrate the cost effectiveness of SC FTS and its potential ability to match the scale of biorefineries with biomass logistics systems.

# Future Work

- Continue biomass gasification studies with broader range of feedstocks.
- Test FT catalysts with biomass syngas produced from southern pine.
- Update feedstock definition to match materials used in gasification studies and validate models using experimental gasification data.
- Combine gasification models with FTS models to evaluate optimal integration and recycle scenarios.

# Summary

- Gasification testing using bubbling bed gasification systems was used to expand our understanding of gasification of southern pine.
- Model development is underway to predict gasification performance based on biomass composition and operating parameters.
- Supercritical phase Fischer-Tropsch synthesis has been tested extensively at bench scales.
  1) Suppressed $CH_4$ and $CO_2$ formation
  2) Increased olefin selectivity at higher carbon numbers
  3) Improved activity maintenance
  4) Decreased Adiabatic Temperature Rise
  5) Higher activity and enhanced diesel and wax selectivity
- Process modeling shows that production of liquid fuels and chemicals through supercritical FTS can be more cost effective than traditional gas-phase FTS.

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# Additional Slides

# Publications

- Littlefield*, B.; ***Fasina, O.O.***; Shaw, J.; Adhikari, S.; Via. B. 2011. Physical and flow properties of pecan shells – particle size and moisture effects. Powder Technology 212: 173-180.
- Xie R., Tu M.*, Wu Y., Taylor S. 2012. Reducing sugars facilitated carbonyl condensation in detoxification of carbonyl aldehyde model compounds for bioethanol fermentation. ***RSC Advances***, 2012, 2 (20), 7699 – 7707.
- Durham E., Zhang S., Xu R., Eden M.R., Roberts C.B. 2012. “Novel Adiabatic Reactor Design for Supercritical Fischer-Tropsch Synthesis”, Computer Aided Chemical Engineering, 30B, pp. 1098-1102.
- Durham, E.; Roberts, C.B. 2012. “Supercritical Activity Restoration for Fischer Tropsch Synthesis”, *International Journal for Reactor Engineering*, 10, A19, 2012.
- Durham E., Xu R., Zhang S., Eden M.R., Roberts C.B. 2013. “Supercritical Adiabatic Reactor for Fischer-Tropsch Synthesis”, Industrial & Engineering Chemistry Research (in revision).
- Yang, X., Tu, M.*, Xie, R., Adhikari, S., Tong, Z. (2013) A comparison of three pH control methods for revealing effects of undissociated butyric acid on specific butanol production rate in batch fermentation of Clostridium acetobutylicum. AMB Express, 3(1):3.
- Rui Xu, Ph.D., December 2012, Auburn University Ph.D. Dissertation: Synthesis of Methanol and Higher Alcohols from Syngas over K Prompted Cu Based Catalyst in Supercritical Solvent
- Sihe Zhang, Ph.D., December 2012, Auburn University Dissertation: Production of Transportation Fuel Range Middle Distillates via Fischer-Tropsch Synthesis with Integrated Product Upgrading Under Supercritical Phase Conditions.
- Durham E., Xu R., Zhang S., Eden M.R., Roberts C.B. (2013): “Supercritical Adiabatic Reactor for Fischer-Tropsch Synthesis”, Industrial & Engineering Chemistry Research (published online October 10, 2012, DOI: 10.1021/ie3008677).
- Zhang, S.; Xu, R.; Durham, E.; Roberts, C.B.; “Advancement of Fischer-Tropsch Synthesis with Integrated Product Upgrading via Utilization of Supercritical Fluid Reaction Media,” Proceedings of the 10th International Symposium on Supercritical Fluids, paper 236_004, 2012.
- Xu, R.; Zhang, S.; Roberts, C.B.; “Investigation of Supercritical Fluids as Reaction Media for Higher Alcohol Synthesis over a Cu-Co-Zn Catalyst,” Proceedings of the 10th International Symposium on Supercritical Fluids, paper 297_001, 2012.
- Zhang, S.; Xu, R.; Durham, E.; Roberts, C.B.; “Production of Middle Distillate Range Hydrocarbons via Iron-based Fischer-Tropsch Synthesis with Integrated Product Upgrading under Supercritical Phase Conditions,” submitted to Fuel Processing Technology, 2012.

# Publications

- Xu, R.; Zhang, S.; Roberts, C.B., “Mixed alcohol synthesis over a K promoted Cu/ZnO/Al2O3 catalyst in supercritical hexanes”, revised manuscript submitted to I&EC Research, 2013.
- Zhang, S.; Xu, R.; Durham, E.; Roberts, C.B.; “Production of Middle Distillate Range Hydrocarbons via Iron-based Fischer-Tropsch Synthesis with Integrated Product Upgrading under Supercritical Phase Conditions,” submitted to Fuel Processing Technology.
- Sadhwani N., Liu Z., Eden M.R., Adhikari S. (2013): “Simulation, Analysis and Assessment of CO2 Enhanced Biomass Gasification”, Computer Aided Chemical Engineering (accepted for publication January 2, 2013).
- Bacik, D.; Zhao, M.; Zhao, D.; Roberts, C.B. (2012) “Enhanced Hydrodechlorination of TCE in Aqueous Solution by Polysugar-Stabilized Pd Nanoparticles,” Nanotechnology, 23, 29404.

# Presentations

- Adhikari, S., C. Brodbeck, S. Taylor. 2012. Biomass gasification for heat and power applications. ASABE Technical Paper No. 121338253. ASABE, St. Joseph, MI.
- Durham, E.; Zhang, S.; Xu, R.; Roberts, C.B. 2011. “Aldehydes and Ketones from Fischer-Tropsch Synthesis”, AIChE Annual Meeting, Minneapolis, MN, October 18, 2011
- Durham J.E., Eden M.R., Roberts C.B. 2011. “Supercritical Adiabatic Reactor for Fischer-Tropsch Synthesis”, Paper 265e, AIChE Annual Meeting, Minneapolis, MN.
- Zhang, S.; Xu, R.; Roberts, C.B. 2011. “Production of Middle Distillate Range Transportation Fuels Via Fischer-Tropsch Synthesis With Integrated Upgrading Under Supercritical Phase Conditions”, AIChE Annual Meeting, Minneapolis, MN, October 19, 2011
- Xu, R.; Zhang, S.; Durham, E.; Roberts, C.B. 2011. “Synthesis of Higher Alcohols from Syngas Over a K Promoted Cu-Co-Zn Catalyst in Supercritical Hexanes”, AIChE Annual Meeting, Minneapolis, MN, October 18, 2011
- Durham E., Zhang S., Xu R., Eden M.R., Roberts C.B. 2012. “Novel Adiabatic Reactor Design for Supercritical Fischer-Tropsch Synthesis”, ESCAPE-22, London, United Kingdom.
- Zhang, S.; Xu, R.; Durham, E.; Roberts, C.B. 2012. “Advancement of Fischer-Tropsch Synthesis with Integrated Product Upgrading via Utilization of Supercritical Fluid Reaction Media,” ISSF 2012: 10th International Symposium on Supercritical Fluids, San Francisco, May 13-16, 2012.
- Xu, R.; Zhang, S.; Roberts, C.B. 2012. “Investigation of Supercritical Fluids as Reaction Media for Higher Alcohol Synthesis over a Cu-Co-Zn Catalyst,” ISSF 2012: 10th International Symposium on Supercritical Fluids, San Francisco, May 13-16, 2012.
- Zhang, S.; Xu, R.; Durham, E.; Roberts, C.B. 2012. “Middle Distillates Production Via Fischer Tropsch Synthesis with Product Upgrading Under Supercritical Phase Conditions,” AICHE Spring Meeting, Houston, April 1-5, 2012.
- Xu, R.; Zhang, S.; Roberts, C.B. 2012. “Utilization of Supercritical Fluids As Reaction Media for the Synthesis of Higher Alcohols From Syngas,” AICHE Spring Meeting, Houston, April 1-5, 2012.
- Narendra Sadhwani, Sushil Adhikari and Mario M Eden, 2012. Effect of temperature and oxidizing medium on tar formation in southern pine gasification will be presented at Annual International Meeting of American Institute of Chemical Engineers (AIChE), October 28- November 2, Pittsburgh, PA.
- Shyamsundar Ayalur Chattanathan, and Sushil Adhikari. 2012. Parametric Study of methane and carbon dioxide reforming in synthesis gas presented at 243rd ACS National Meeting, March 25-29, 2012, San Diego, CA.

# Presentations

- M. Tu* (2012) Enzymatic Hydrolysis of Ethanol Organosolv Pretreated Biomass. Frontiers in Biorefining, October 28-November 2, Oral presentation, St Simon, GA
- C. Lai*, M. Tu (2012) Reducing sugars facilitated carbonyl condensation in detoxification of carbonyl aldehyde model compounds for bioethanol fermentation. Bioproducts-2012 meeting, November 19-21, oral presentation, San Antonio, TX.
- M. Tu*, R. Xie (2012) Potential Carbonyl Condensation Reaction in Detoxification of Phenolic Model Compounds for Bioethanol Fermentation. AIChE meeting, October 28-November 2, poster presentation, Pittsburgh, PA.
- R. Xie*, M. Tu (2012) Identification of Nucleophilic Reactions in Detoxification of Phenolic Model Compounds for Bioethanol Fermentation. AIChE Meeting October 28-November 2, poster presentation, Pittsburgh, PA
- Eden M.R. (2012): "Process Systems Engineering Approaches to Sustainable Chemical Product Design", Sustainability Plenary Session, AIChE Annual Meeting, Pittsburgh, PA.
- Roe, D.; Zhang, S.; Xu, R.; Steward, C.; Durham, E.; Roberts, C.B. "Production of Middle Distillate Range Liquid Fuels From Syngas Using Fischer-Tropsch Synthesis and Associated Upgrading Technology Under Supercritical Phase Conditions and Multiple Reactor Configurations," AIChE Annual Meeting, Pittsburgh, PA, October 31, 2012.
- Zhang, S.; Roe, D.; Xu, R.; Roberts, C.B.; "Advancement in Iron-Based Low Temperature Fischer-Tropsch Synthesis with Integrated Product Upgrading Via Utilization of Supercritical Fluid Reaction Media," AIChE Annual Meeting, Pittsburgh, PA, October 29, 2012.
- Eden M.R., Roberts C.B., Taylor S.E. (2013): "Liquid Transportation Fuels and High Value Co-Products from Integrated Biomass Fractionation, Gasification and Advanced Catalytic Conversion", Invited Lecture, Inaugural Southeastern Conference (SEC) Academic Symposium, Atlanta, GA.
- Roe D., Zhang S., Roberts C.B. (2013) "Production of Middle Distillate Range Liquid Fuels From Syngas Using Fischer-Tropsch Synthesis and Associated Upgrading Technology Under Supercritical Phase Conditions and Multiple Reactor Configurations", AICHE Spring Meeting, San Antonio, TX.
- Stewart C., Xu R., Zhang S., Roe D., Roberts C.B. (2013) "Effect of Supercritical Hexanes Reaction Medium and H2/CO Molar Ratio on the Synthesis of Higher Alcohols from Syngas over a K-Promoted Cu-Co-Zn Catalyst.", AIChE Spring Meeting, San Antonio, TX.