National Renewable Energy Laboratory

A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

# Pilot-Scale Thermochemical Technologies for Integrated Biorefinery Development – The Thermochemical Conversion Platform


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**National Bioenergy Center**

**Golden, CO USA**


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Golden, CO USA

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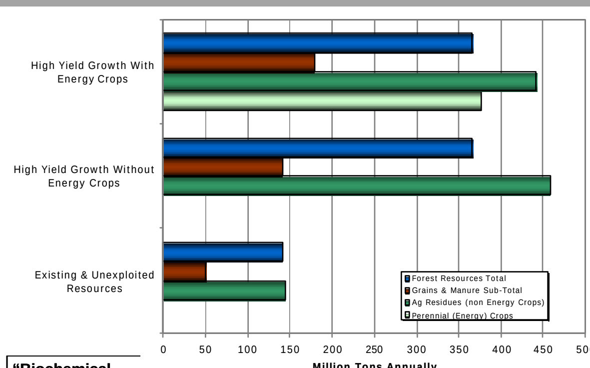
# The President's Biofuels Initiative – The 30x30 Vision



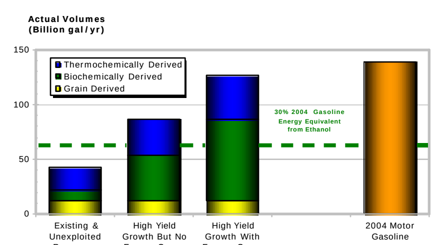

**Transformation through Intermediates (sugars)**

**"Biochemical conversion"**

*main difference is in the primary catalysis system*

**Reduction to building blocks ($CO$, $H_2$)**

**"Thermochemical conversion"**



# Opportunities for Thermochemical Biofuels

## Near-term - gasification/mixed alcohol synthesis for $1.07 by 2012

- Cost-competitive with High Potential Biofuel Yields

## Mid-term (30x30)

- Biorefinery residues in integrated BC/TC plants
- Pyrolysis

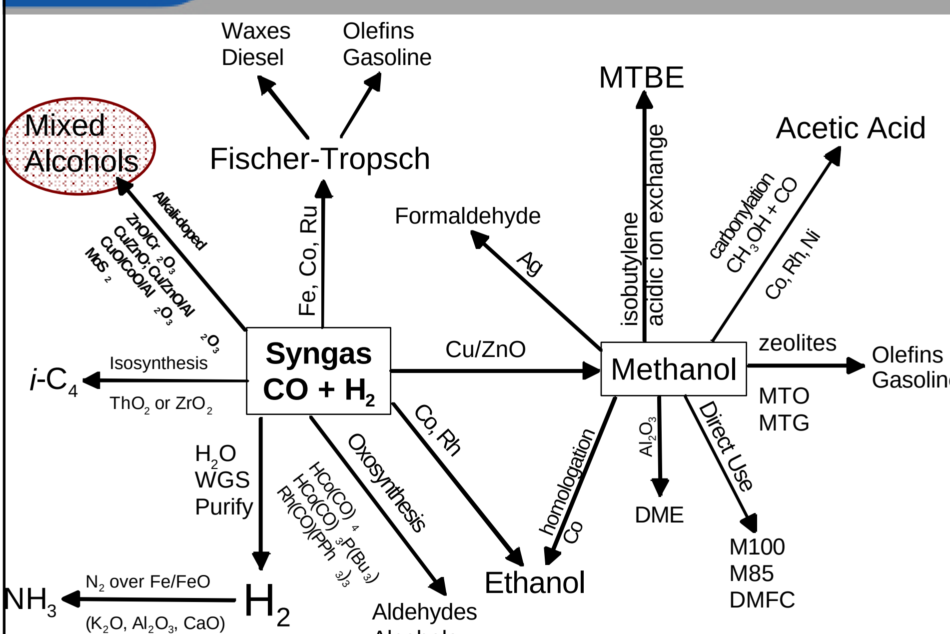
## Long-term (30x30)

- Selective Thermal Transformation (improve yields and selectivity)

Challenge: *Develop thermochemical technologies that are technically and economically feasible at the appropriate scale for reasonably available biomass resources*



# Products from Syngas



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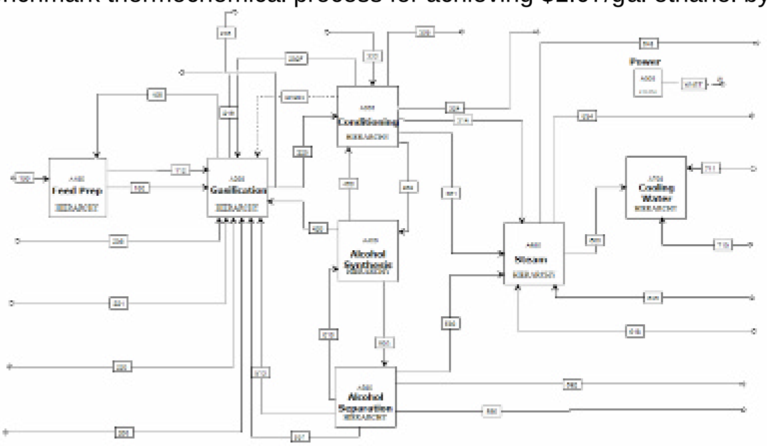
## Mixed Alcohol Design Report

**Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass**

http://www.nrel.gov/docs/fy07osti/41168.pdf (PDF 3.3 MB) NREL-TP-510-41168

Targeted to appropriate feedstock, level of technologies, and market conditions to provide a benchmark thermochemical process for achieving $1.07/gal ethanol by 2012

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### Feedstocks

Forest resources as primary feedstock

- Base design using wood composition
- Scenarios for alternate feedstocks

Costs consistent with forest resources per Billion Ton Study

- $35 per bone dry ton at plant gate
- Scenarios for other feedstock costs, moisture content, ash content, …

### Integration & Economic Issues Economic

Mixed C3OH+ by-product

- Final separation of C3OH+ mixture done "over the fence line"
- Scenarios for alternate C3OH+ values
  - Fraction of chemical feedstock value (target case)
  - Equivalent to ethanol
  - Kerosene value (fraction of gasoline value)

Scenarios – 2005 Dollars

- Total Project Investment
- Average Installation Factors
- Contingency
- Return on Investment
- Loan vs. Equity Financing

Additional Fossil Fuel

- fossil fuel for energy deficiency

### Conversion Technologies

Indirect gasification

- BCL correlations with decreased methane production
- Scenarios
  - Costs of catalyst impregnated olivine
  - Gasifier temperature
  - Yields: hydrocarbon, CO2, char, …

Cleanup & Conditioning

- Tar reforming consistent with "goal case"
  - Includes on-line catalyst regeneration
- Scenarios
  - Reforming conversions
  - Catalyst lifetime
  - Reformer costs (non catalysts)
  - Acid removal costs

Catalytic fuel synthesis

- Specified conversions
  - Kinetic calculations done "off line"
  - High single pass conversions
- Scenarios
  - Single pass yields
  - Selectivity to ethanol
  - Alcohol distribution
  - Catalyst lifetime
  - Catalyst specs (sulfur & $CO_2$ allowability)

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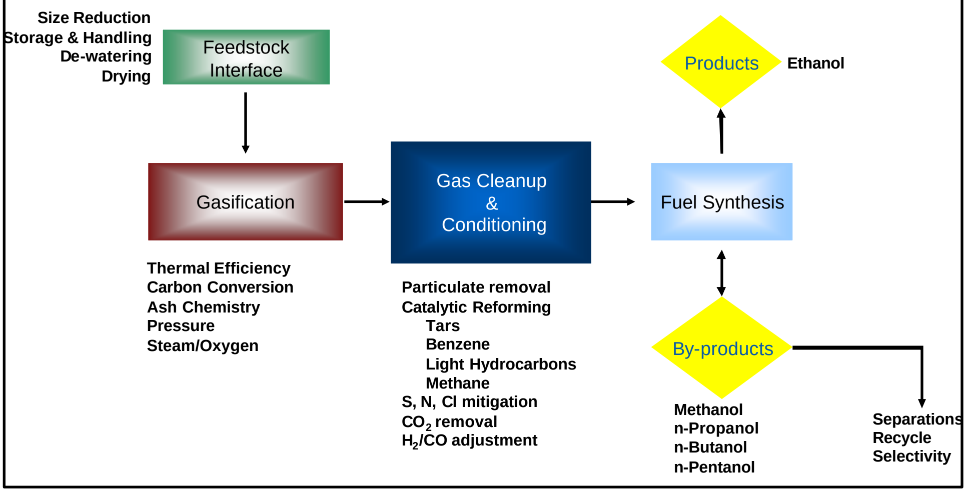
## Technical Barrier Areas

### Gas Cleanup & Conditioning has the largest economic impact

January 9-10, 2007 in Washington, DC,  70 Attendees from Industry, Academia, Government, http://www.thermochem.biomass.govtools.us/

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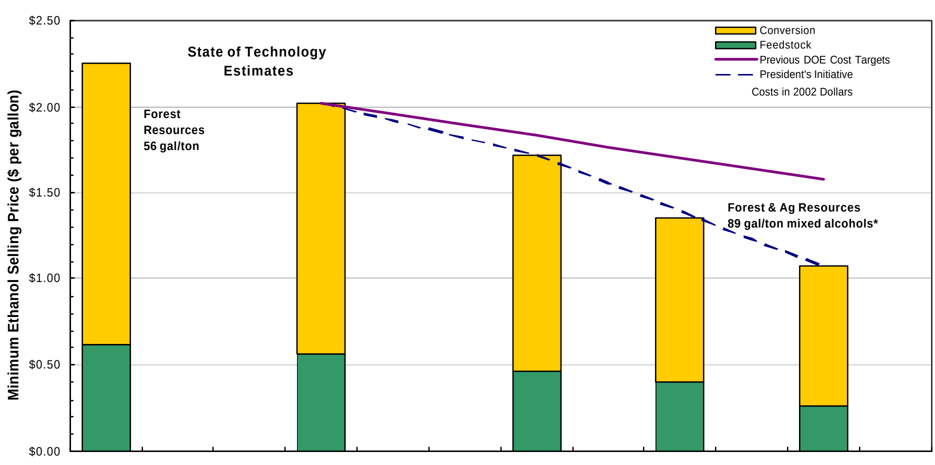
## Targets – Minimum Ethanol Selling Price



## Gasification R&D for "$1.07" Thermochemical Ethanol Targets

### Gas Cleanup and Conditioning – Tar Reforming Catalyst Development

- Consolidated tar and light hydrocarbon reforming to reduce capital and operating costs

Tar Reformer Performance - % Conversion

| Compound | Current | Goal |
|---|---|---|
| Methane ($CH_4$) | 20% | 80% |
| Ethane ($C_2H_6$) | 90% | 99% |
| Ethene ($C_2H_4$) | 50% | 99% |
| Tars (C10+) | 95% | 99.9% |
| Benzene ($C_6H_6$) | 70% | 99% |
| Ammonia ($NH_3$) | 70% | 90% |

### Advanced Catalysts and Process Improvements for Mixed Alcohol Synthesis

- Increase single pass conversion efficiency (38.5% to 50%)
- Improve selectivity (80% to 90%)
- Improve yields at lower synthesis pressure

### Fundamental Gasification Studies

- Technical validation of comparable syngas quality from biorefinery residues and wood residues



## Core Expertise to Address Barriers

### Thermochemical Analysis

- Conceptual integrated thermochem/biochem process
- Detailed stand-alone thermochemical process

### Thermochemical Conversion

- Feedstock dependent performance and syngas quality

### Gas Clean-Up & Conditioning

- Fluidizable tar reforming catalyst evaluation for IBR applications
- Catalyst regeneration for maximizing catalyst performance and lifetime

### Integration of Operations

- Reforming catalyst performance integrated with gasifier operations to consolidate unit operations for capital cost reductions

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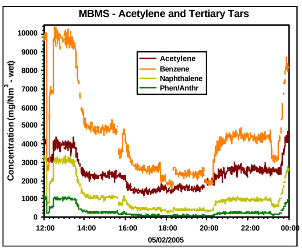
## Thermochemical PDU

- Gasification – feed dependent syngas quality, reforming catalyst performance
- Pyrolysis – medium quantity oil production, gas and liquid solids filtration, real time product optimization
- Gas Clean-Up and Conditioning
- Integrated tar reforming - catalyst lifetime & deactivation kinetics
- On-line tar and product analysis

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## MBMS Tar Sampling

**Advantages**

- Universal detection (low and high molecular weight species)
- Real-time monitoring
- Preserves reactive and condensable species
- Rapid screening/fingerprinting
- Large dynamic range ($10^6$ to $10^{-1}$ ppmv)
- High-pressure, high-temperature system monitoring

Typical Hydrocarbons/Tars Observed

| Molecular Weight | Formula | Chemical Name(s) |
|---|---|---|
| 15,16 | $CH_4$ | methane |
| 26 | $C_2H_2$ | acetylene |
| 78 | $C_6H_6$ | benzene |
| 91,92 | $C_7H_8$ | toluene |
| 94 | $C_6H_6O$ | phenol |
| 104 | $C_8H_8$ | styrene |
| 106 | $C_8H_{10}$ | (m-, o-, p-) xylene |
| 108 | $C_7H_8O$ | (m-, o-, p-) cresol |
| 116 | $C_9H_8$ | indene |
| 118 | $C_9H_{10}$ | indan |
| 128 | $C_{10}H_8$ | naphthalene |
| 142 | $C_{11}H_{10}$ | (1-, 2-) methylnaphthalene |
| 152 | $C_{12}H_8$ | acenapthylene |
| 154 | $C_{12}H_{10}$ | acenaphthene |
| 166 | $C_{13}H_{10}$ | fluorene |
| 178 | $C_{14}H_{10}$ | anthracene, phenanthrene |
| 192 | $C_{15}H_{12}$ | (methyl-) anthracenes/phenanthrenes |
| 202 | $C_{16}H_{10}$ | pyrene/fluoranthene |
| 216 | $C_{17}H_{12}$ | methylpyrenes/benzofluorenes |
| 228 | $C_{18}H_{12}$ | chrysene, benz[a]anthracene, … |
| 242 | $C_{19}H_{14}$ | methylchrysenes, methylbenz[a]anthracenes |
| 252 | $C_{20}H_{12}$ | perylene, benzo[a]pyrene, ... |
| 266 | $C_{21}H_{14}$ | dibenz[a,kl]anthracene, … |
| 278 | $C_{22}H_{14}$ | dibenz[a,h]anthracene, … |

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## On-line Analytical Capabilities

- Non-dispersive infrared (NDIR) Analyzer for $CH_4$ (range: 0-50 vol%)
- NDIR Analyzers for $CO_2$ and CO (0-50 vol% range)
- Paramagnetic Oxygen Analyzer (range of 0-25 vol%)
- $H_2$ thermal conductivity analyzer (range of 0-50 vol% and analog inputs for %CO, %$CH_4$ and %$CO_2$ to correct the $H_2$ value)
- Quad Micro Gas Chromatograph
  - 4 channel, on-line GC with 2-3 min cycle time
  - $H_2$, $O_2$, $N_2$, $CH_4$, CO, $CO_2$, $C_2H_6$, $C_2H_4$, $C_2H_2$, $C_3H_8$, and $C_4$ paraffin's and olefins
- Transportable molecular beam mass spectrometer (TMBMS)
  - Continuous, real-time monitoring of all gas phase products with particular emphasis on condensible tars and heteroatoms

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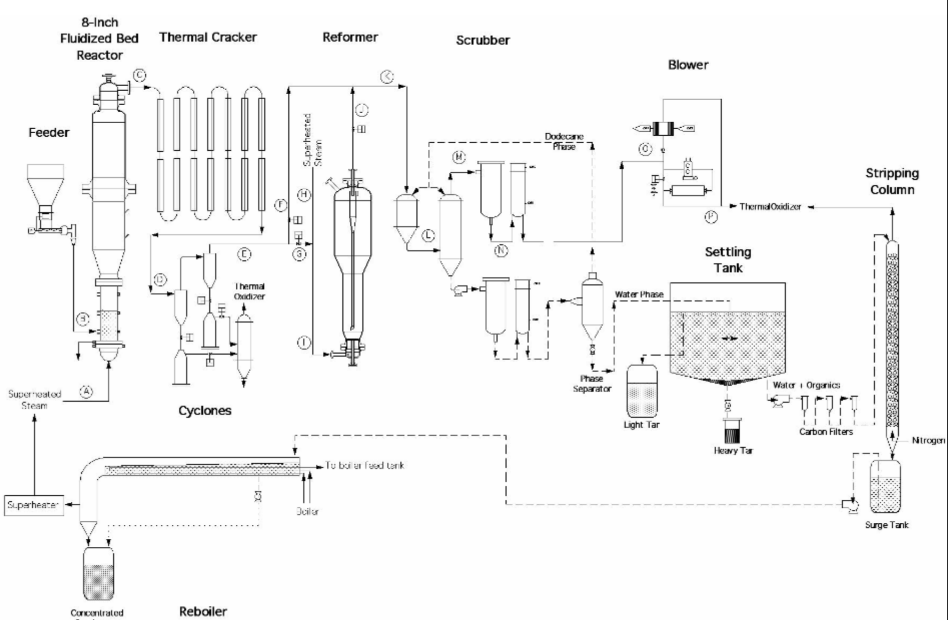
## NREL 150 kWt Thermochemical Process Development Unit



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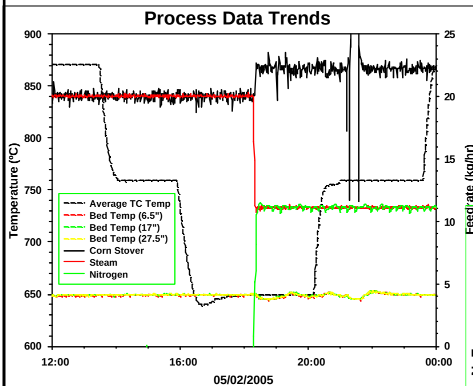
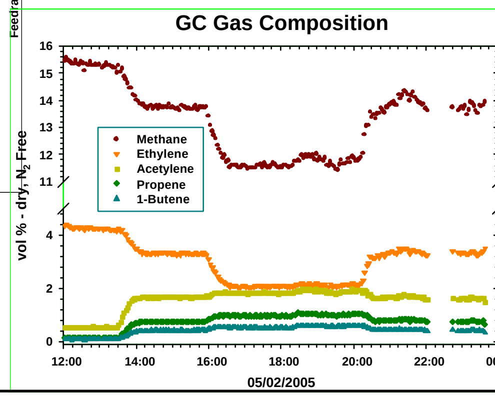
## Real-time data from corn stover gasification

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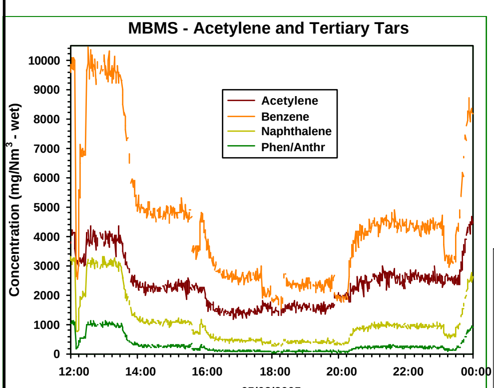
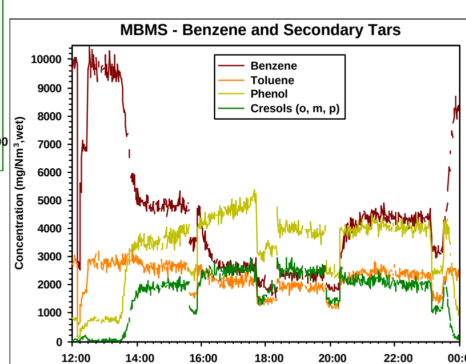
## On-line Tar Measurements



## Feedstock Fuel Variability

| Feedstock Composition | | | |
|---|---|---|---|
| | Wood | Corn Stover | BioChem Residue |
| **Proximate Analysis (wt %)** | | | |
| Moisture | 3.74 | 5.78 | 0 (63.76) |
| Ash | 0.63 | 10.69 | 14.02 |
| Volatiles | 82.68 | 67.35 | 60.25 |
| Fixed C | 12.95 | 16.18 | 25.73 |
| **Ultimate Analysis (wt%)** | | | |
| C | 51.36 | 44.0 | 55.95 |
| H | 6.25 | 4.68 | 5.20 |
| N | 0.11 | 0.68 | 2.27 |
| O | 37.89 | 34.09 | 22.37 |
| S | 0.02 | 0.08 | 0.19 |

| NREL TCPDU Syngas Composition (S/B = 1) | | | |
|---|---|---|---|
| Vol% | Wood | Corn Stover | BioChem Residue |
| $H_2$ | 28.1 | 25.4 | ? |
| CO | 25.5 | 23.4 | ? |
| $CO_2$ | 25.2 | 22.5 | ? |
| $CH_4$ | 15.3 | 14.5 | ? |
| $C_2H_4$ | 3.7 | 4.4 | ? |
| Benzene (mg/Nm$^3$) | 6,500 | 10,000 | ? |



## NREL Catalyst Development

**Objective:** Long duration catalyst activity to maintain syngas quality (tar destruction >99%) to meet accepted gas quality standards

### Performance requirements

- Tar reforming: $CxHyOz + H_2O(g)?\ H_2 + xCO$
- Water gas shift: $H_2O + CO?\ CO_2 + H_2$
- Coke gasification: $C + H_2O(g)\ ?\ COx + H_2$
- Steam methane reforming: $CH_4 + H_2O?\ CO + 3H_2$

### Improve reforming catalyst performance

- Develop attrition resistant reforming catalysts
  - Support type/treatment/particle size/surface area
  - Optimize catalyst regeneration
- Characterize and understand catalyst behavior
  - Catalyst components and promoters
  - Understand/minimize catalyst deactivation
  - Predict pilot scale behavior from MATS behavior
- Preparation
  - Incipient wetness
  - Calcination
  - Reduction

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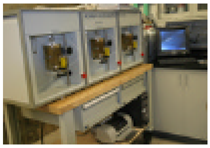
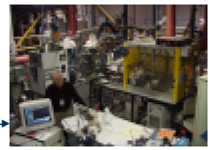
## Tar Reforming: Micro – Pilot Scale Evaluation



MATS 1*
- Fixed bed 1 g catalyst
- TPR* characterization

Rapid catalyst preparation

**MATS 2**
- Fixed bed 1 g catalyst
- Tar destruction
- Steam reforming
- TCPDU slipstream



**2" FBR***
- Fluid bed 250 g catalyst
- Kinetic data
- Lifetime data
- TCPDU slipstream
- Online analysis

**TCPDU-FSR***
- Fluid bed 50 kg catalyst
- Process data
- Kinetic data
- Lifetime data
- Online analysis

MATS: Microactivity test system
FBR: Fluidized bed reactor
FSR: Full stream reformer
TCPDU: Thermochemical process development unit
TPR: Temperature programmed reaction

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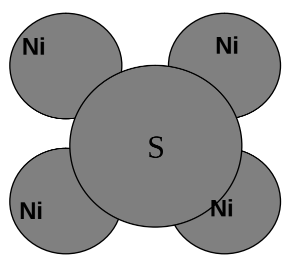
## S Deactivation of $Ni/Al_2O_3$ Catalysts

- S blocks Ni active sites and eliminates sites for $H_2$ adsorption and HC cracking
- Little S adsorption on  a-alumina
- Surface-mediated mechanism




- HT oxidation causes S to penetrate catalyst surface
- S removal depends on temperature and steam content
- Current research to achieve regeneration at process conditions

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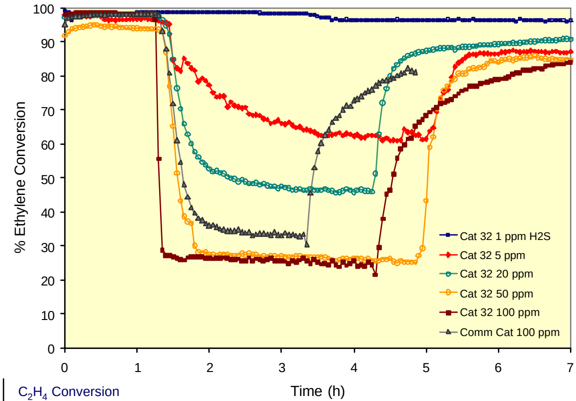
## Catalyst Deactivation by $H_2S$

| | |
|---|---|
| $C_2H_4$ Flow | 150 sccm |
| $[H_2S]$ | 1-100 ppmv |
| Temp ºC | 820-850 |
| S/C | 4.0 |
| GHSV | 90,000 $h^{-1}$ |
| $t_{res}$ | 0.3 s |
| Bed Height | 18 mm |
| Catalyst | 32 |




| $[H_2S]$ ppmv | $C_2H_4$ Conversion % Pre Deact. | $C_2H_4$ Conversion % Post Deact. | $C_2H_4$ Conversion % Post Regen. |
|---|---|---|---|
| 100 | 100 | 35 | 80 |
| 50 | 100 | 35 | 85 |
| 20 | 100 | 45 | >90 |
| 5 | 100 | 60 | >90 |
| 1 | 100 | 93 | >95 |

$$\frac{\text{Time on stream (TOS)}}{\text{Regeneration time}} > 1.0$$

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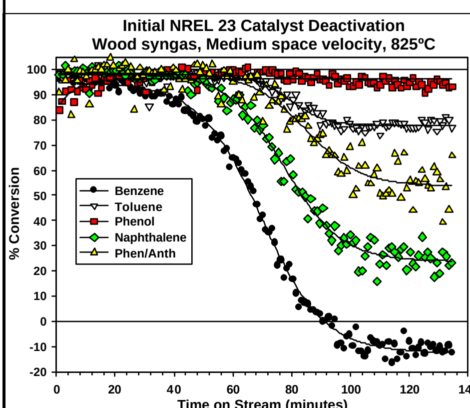
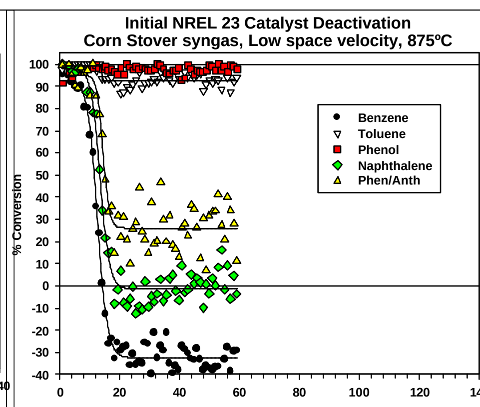
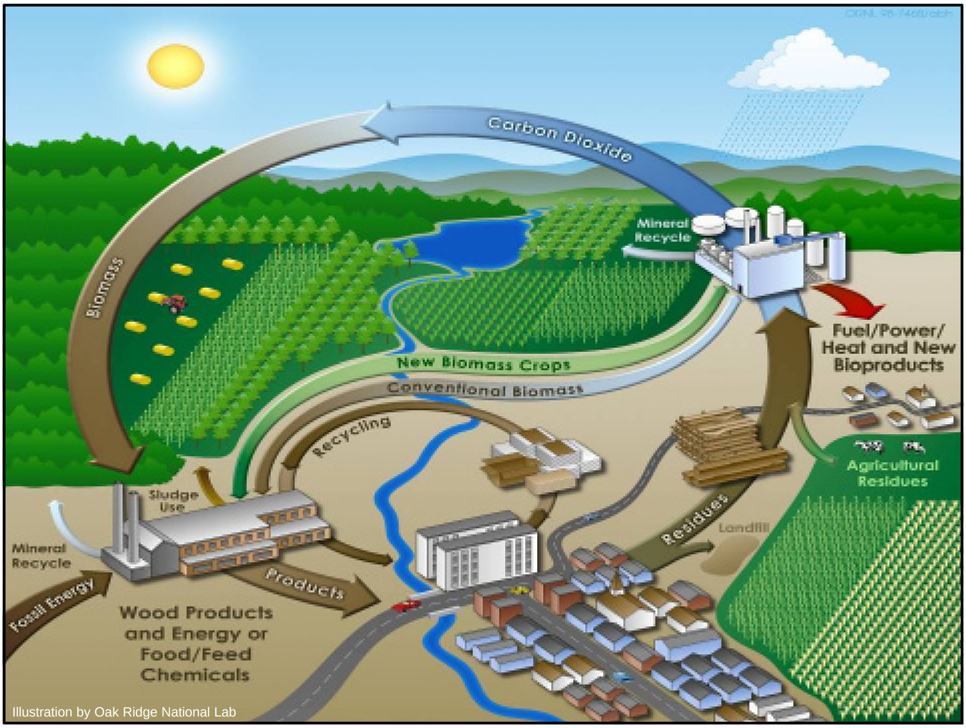
## Tar Cracking Catalyst Evaluation

**Technical Goals**

- Deactivation kinetics; Steady-state conversion efficiency
- Bench and pilot-scale efforts aligned to determine optimized reforming catalyst performance
- Provide technical data for design of regenerating tar reforming reactor and refined technoeconomic analyses





Carbon Dioxide
Biomass
Mineral Recycle
Fuel/Power/
Heat and New
Bioproducts
New Biomass Crops
Conventional Biomass
Recycling
Agricultural
Residues
Sludge
Use
Mineral
Recycle
Residues
Landfill
Fossil Energy
Products
Wood Products
and Energy or
Food/Feed
Chemicals
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