the Energy to Lead

# IH$^2$ for the Direct Production of Gasoline and Diesel from Biomass


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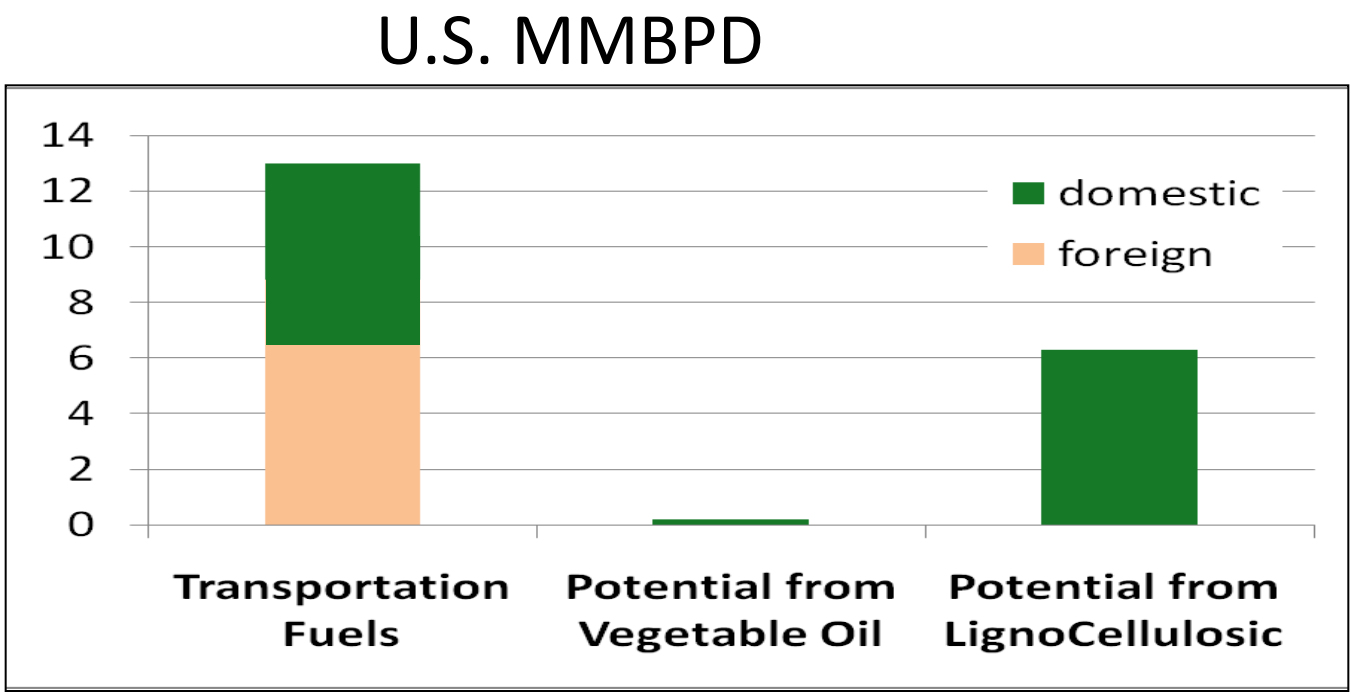
# Potential for Liquid Fuels from Lignocellulosic Feedstocks




Based on 28 wt. % conversion to liquid; US based on 1 Billion ton/yr of biomass

Lignocellulosic conversion could replace much of the imported oil and is renewable each year – it won't run out !

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# Challenges for Pyrolysis or Pyrolysis Plus Upgrading

## >Undesirable Pyrolysis Oil Properties

- > Limited demand
- > Expensive to transport
- > Incompatible with oil refinery metallurgy

## >Expensive and Difficult Upgrading to Make Fungible Fuels

- > High $H_2$ requirements
- > Severe conditions (low LHSV, high pressures)
- > Catalyst Fouling - Plugged reactors

Overcoming Pyrolysis Problems has proved to be difficult



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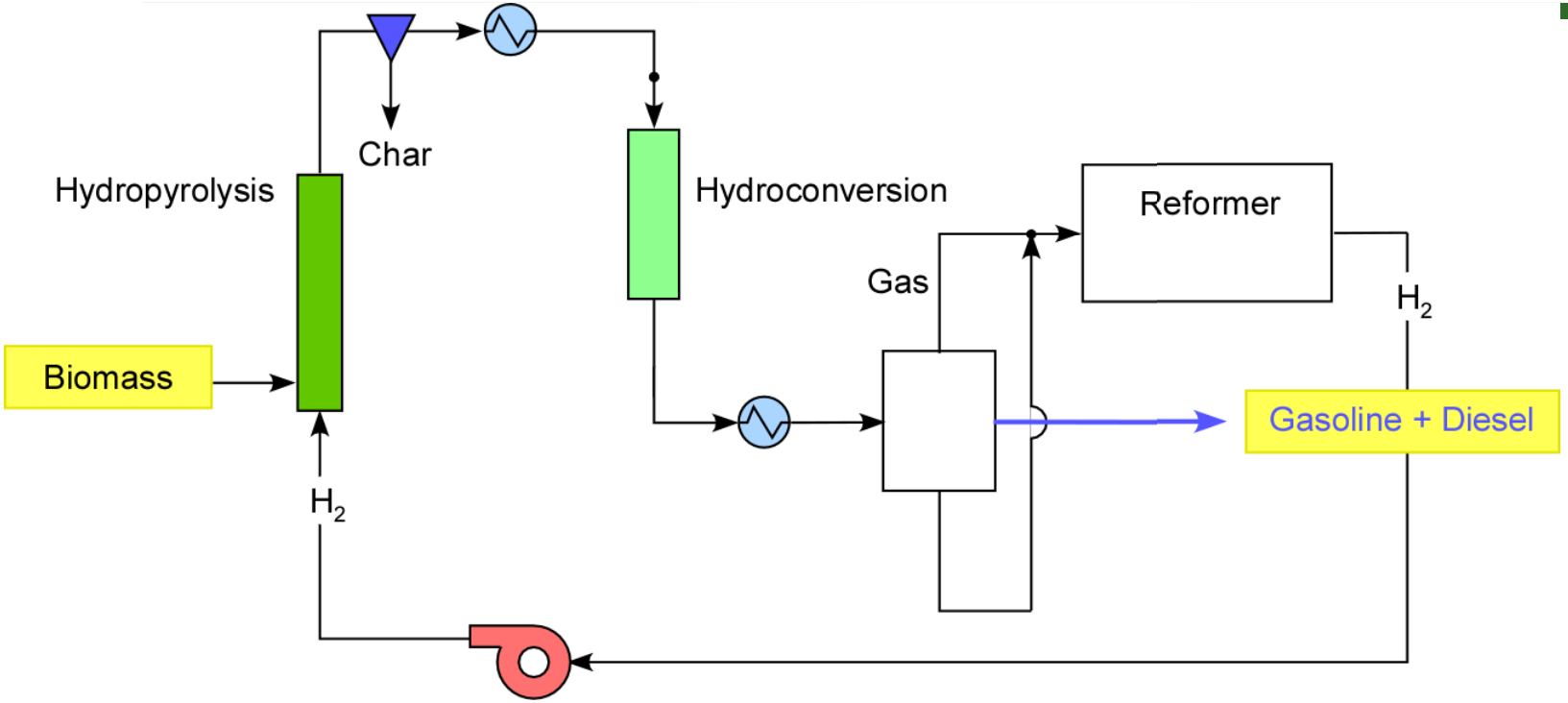
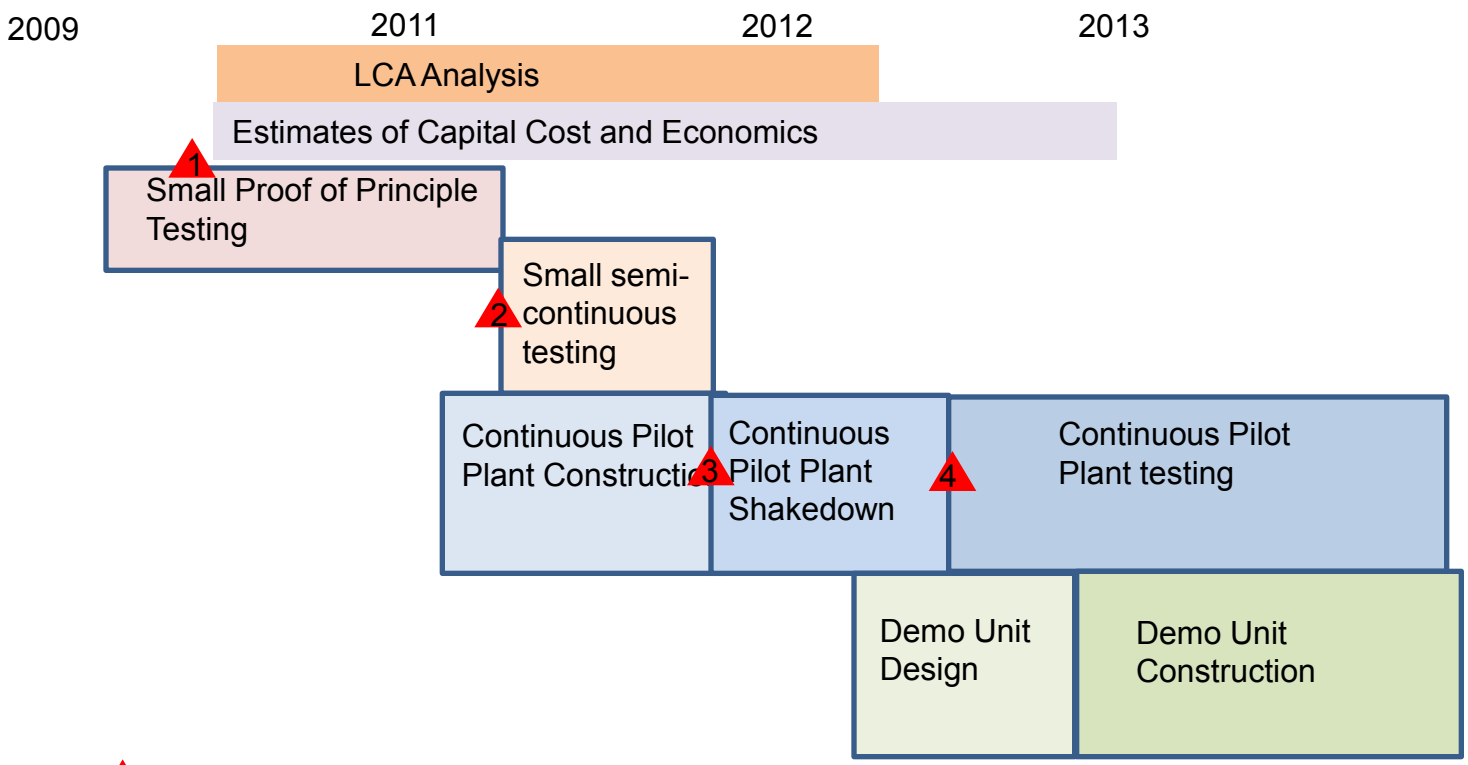
# Integrated Hydropyrolysis and Hydroconversion ($IH^2$)



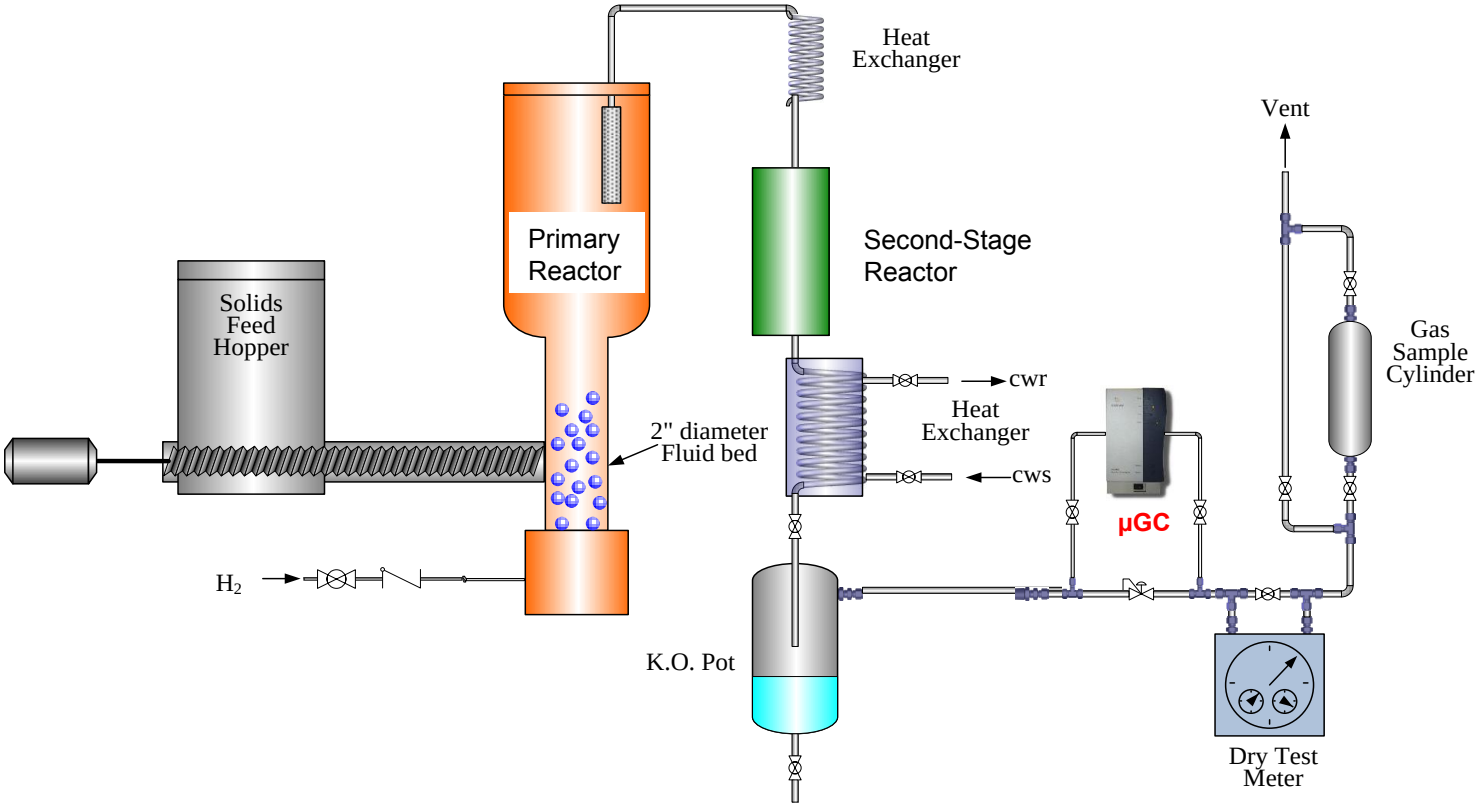

- Directly make desired products
- Run all steps at moderate hydrogen pressure (100-500 psi)
- Utilize $C_1$-$C_3$ gas to make all hydrogen required
- Avoid making "bad stuff" made in pyrolysis – PNA, free radicals

# IH$^2$ Development Timeline




1. Demonstrated good yields and stable operation in proof of principle tests
2. Demonstrated continuous char and catalyst separation
3. Continuous pilot plant constructed and delivered
4. Matched product quality and yields in pilot plant with laboratory unit

# IH$^2$ Proof of Principle Unit

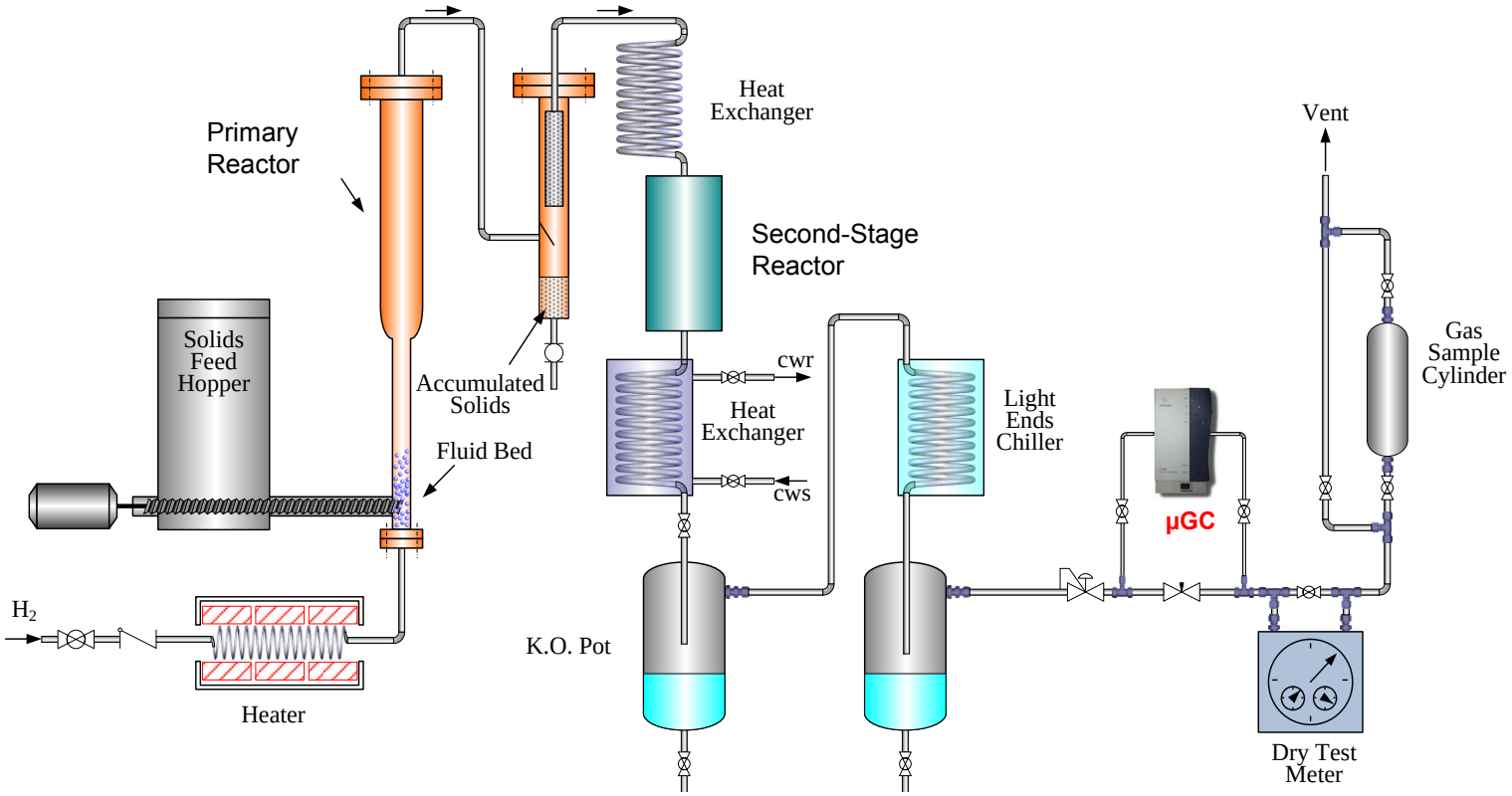



- 360 g/hr of biomass feed
- batch reactor
- typically 4 hours of operation

**Multi-purpose lab reactor – gasification, pyrolysis, IH$^2$ configurations.**

# IH² Semi-Continuous Lab Unit

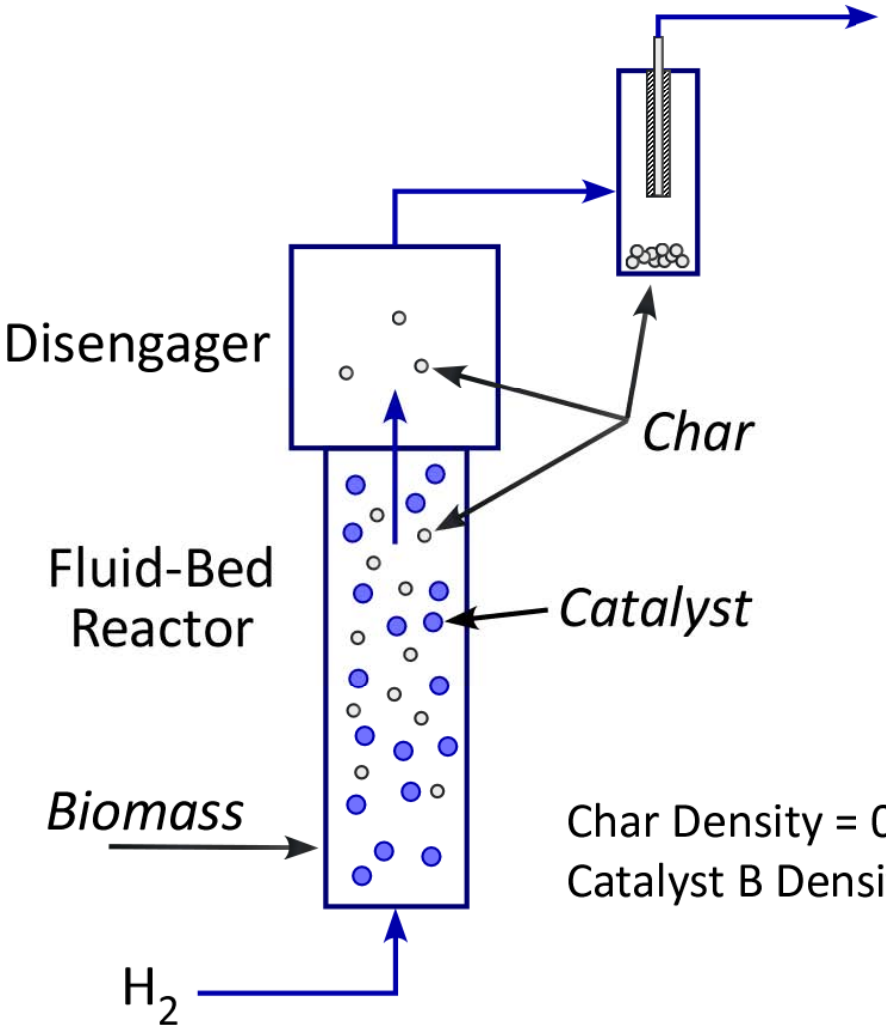
Improved IH2 MBU Pilot Plant




- 360 g/hr of biomass feed
- Continuous char-catalyst separation
- Discontinuous operation: ~6-hour test – idle increments for reloading feed

**Dedicated laboratory unit for IH² process testing.**

# Mechanics of Char - Catalyst Separation In IH$^2$ Pilot Plant




Char Density = 0.3 g/cm$^3$
Catalyst B Density = 1.0 g/cm$^3$

# Lab Scale Test Results: IH$^2$ Liquid Yields and Feedstock Flexibility

| | Wood | Lemna | Aquaflow Micro Algae | Bagasse | Blue Marble Macro Algae | Corn Stover |
|---|---|---|---|---|---|---|
| Feed % C | 49.7 | 46.3 | 43.1 | 43.1 | 34.0 | 40.2 |
| Feed %H | 5.8 | 5.8 | 6.1 | 5.0 | 4.43 | 5.0 |
| Feed %O | 43.9 | 35.7 | 20.4 | 35.3 | 23.6 | 35.7 |
| Feed %N | 0.11 | 3.7 | 6.5 | .34 | 4.6 | 1.0 |
| Feed %S | 0.03 | 0.3 | 0.7 | .10 | 1.9 | 0.05 |
| Feed % Ash | 0.5 | 8.2 | 23.1 | 16.2 | 29.4 | 18.1 |
| Feed H/C | 1.40 | 1.50 | 1.70 | 1.39 | 1.56 | 1.49 |
| **Typical % $C_4$ + Liquid Yield (MAF)** | **25-28** | **30** | **46** | **30** | **35** | **21** |
| **$C_4$+ Gallon/Ton MAF** | **82** | **100** | **157** | **100** | **119** | **67** |
| **% Oxygen** | **(BDL)** | **(BDL)** | **(BDL)** | **(BDL)** | **(BDL)** | **(BDL)** |
| **TAN #** | **<1** | **<1** | **<1** | **<1** | **<1** | **<1** |

BDL = Below detectable limit of 0.5%



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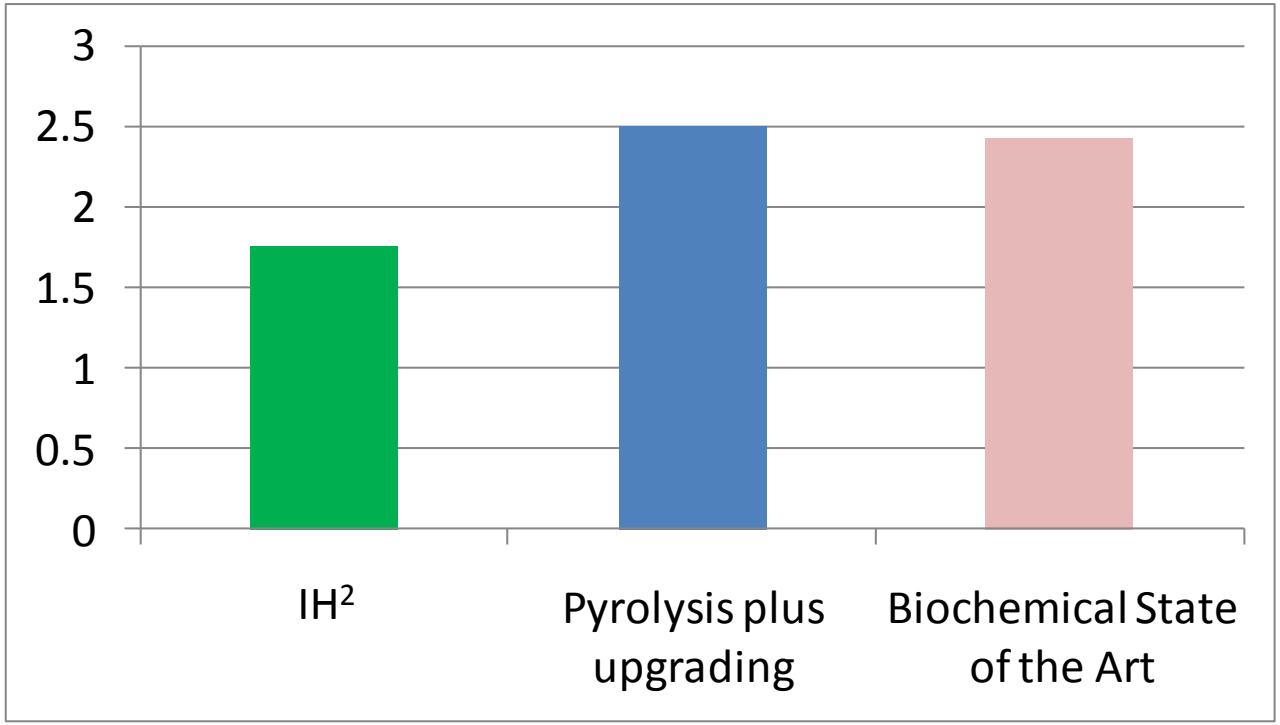
# $IH^2$ Typical Detailed Yields

| Feedstock | Wood | Algae |
|---|---|---|
| $C_4$ + Liquid yields (MAF) wt% | 26 | 46 |
| % Oxygen in liquid | <1 | <1 |
| Gasoline liquid product, wt% | 16 | 24 |
| Diesel liquid product, wt% | 10 | 22 |
| Char (MAF) wt% | 13 | 5 |
| $CO_X$ (MAF) wt% | 17 | 7 |
| $C_1$-$C_3$ (MAF) wt% | 13 | 13 |
| Water (MAF) wt% | 36 | 31 |
| $H_2$ uptake (MAF) wt% | 4.6 | 4.4 |
| External $H_2$ required for integrated system | None | None |
| Ammonia wt% | 0.18 | 2.4 |

- Enough $C_1$-$C_3$ is made so that all the process $H_2$ requirements

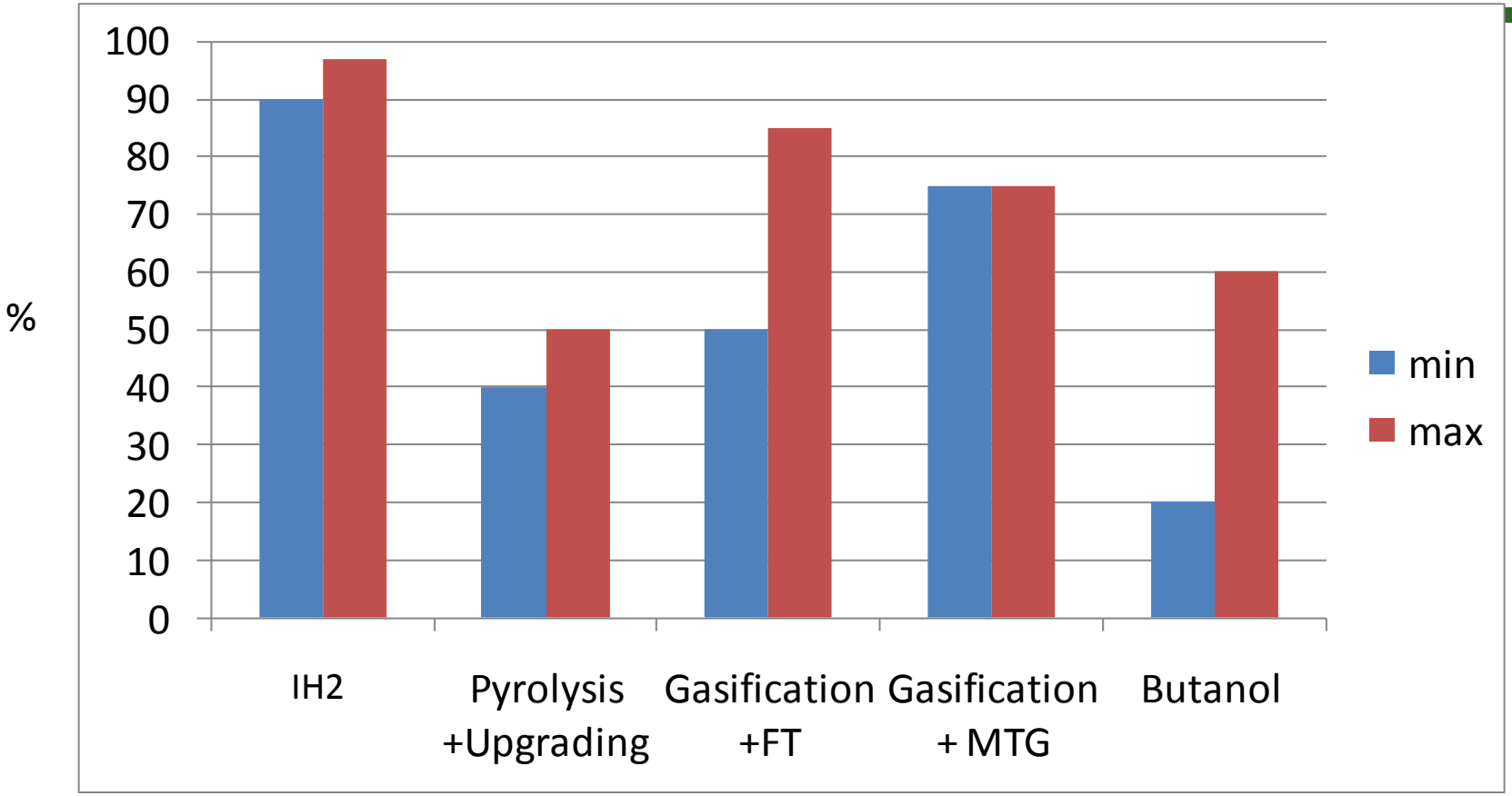
# Economic Comparison

FCOP +ROI - $/gal




Based on 2000 t/d of biomass feed

# Comparison of Greenhouse Gas Reduction- by Technology

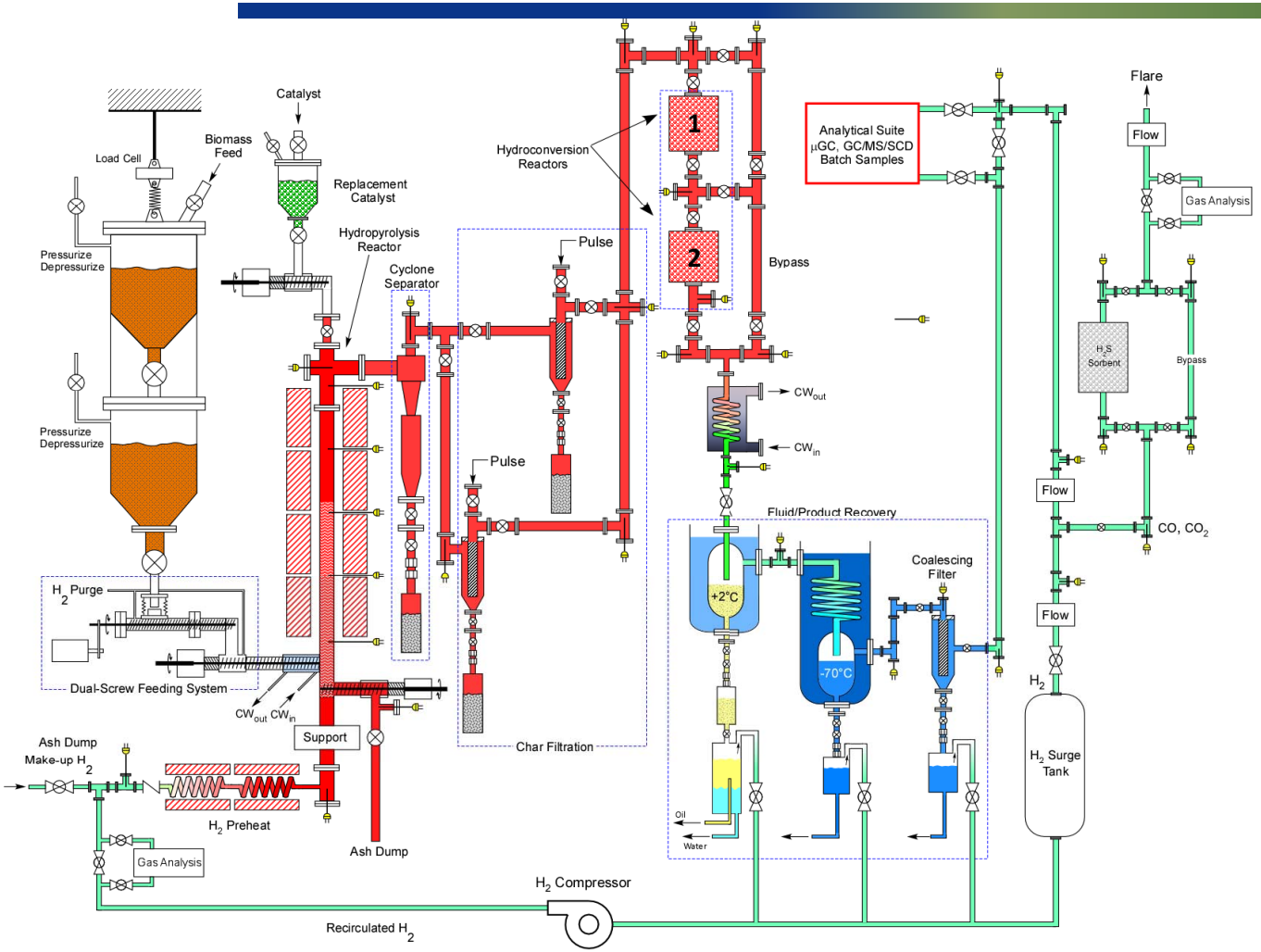



•Other technologies LCA from David Hsu "Biofuels Beyond Ethanol" Sept 9, 2008

# $IH^2$ Pilot Plant Goal

- Transform semi-continuous $IH^2$ process to continuous $IH^2$ process
- Quantify catalyst life and stability with multiple feedstocks
- Incorporate continuous biomass feeder and on-stream catalyst make-up systems

# Schematic Diagram of Continuous IH$^2$ Process Unit




- 2 kg/hr of biomass feed
- Continuous char-catalyst separation
- Continuous operation

# NEW CONTINUOUS 50kg/d IH$^2$ PILOT PLANT
# Delivered to GTI Sept 20, 2011

# IH$^2$ 50 kg/d Continuous Pilot Plant

# New 50kg/d IH$^2$ Pilot Plant Control Room

# Differences between Lab & Pilot Units

| | Pilot Plant | Laboratory Unit |
|---|---|---|
| Mode of operation | Continuous | Semi-continuous |
| Amount of biomass feed | 2000g/h | 360g/h |
| Automation/control system | yes | little |
| Lock hopper – continuous feed | yes | No (batch) |
| Continuous char removal | yes | No (batch) |
| Compressor/recycle gas | yes | No ( once through) |
| Automated valves/interlocks | yes | No |
| Primary reactor diameter | 2.5x | 1x |
| Cyclone | yes | No |
| Gas velocity in Primary Rx | 2x | 1x |

# Shakedown Issues

| Problem | Solution |
|---|---|
| Mechanical transport of biomass and mechanical removal of char | Agitation added, vessels redesigned |
| Leaking valves | Metal seated lapped valves, Nitrogen Padding |
| Incomplete biomass conversion | Matching biomass/char residence time in fluidized bed reactor |

**Mechanical Issues related to moving solids were primary issues.**

# Liquid Product Quality Excellent from Lab and Pilot Units

| | Lab | Pilot |
|---|---|---|
| | | |
| %C | 88.40 | 88.20 |
| %H | 11.00 | 11.60 |
| %S | 0.02 | 0.02 |
| %N | <0.1 | <0.1 |
| %O | BDL | BDL |
| TAN | <1 | <1 |

**100% gasoline + diesel**

BDL = Below detectable limit of 0.5%

# Liquid Products Collected from Recent Continuous IH$^2$-50 Testing with Wood

Gasoline-Range Hydrocarbons

Diesel/Jet-Range Hydrocarbons

Aqueous Product



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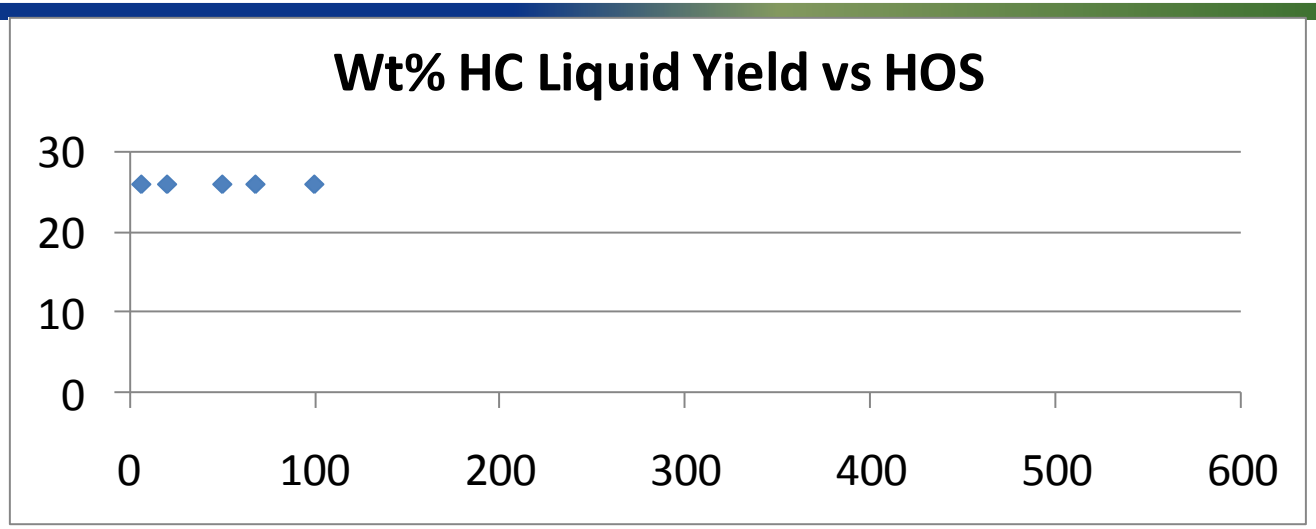
# Comparison of Lab & Pilot Yields

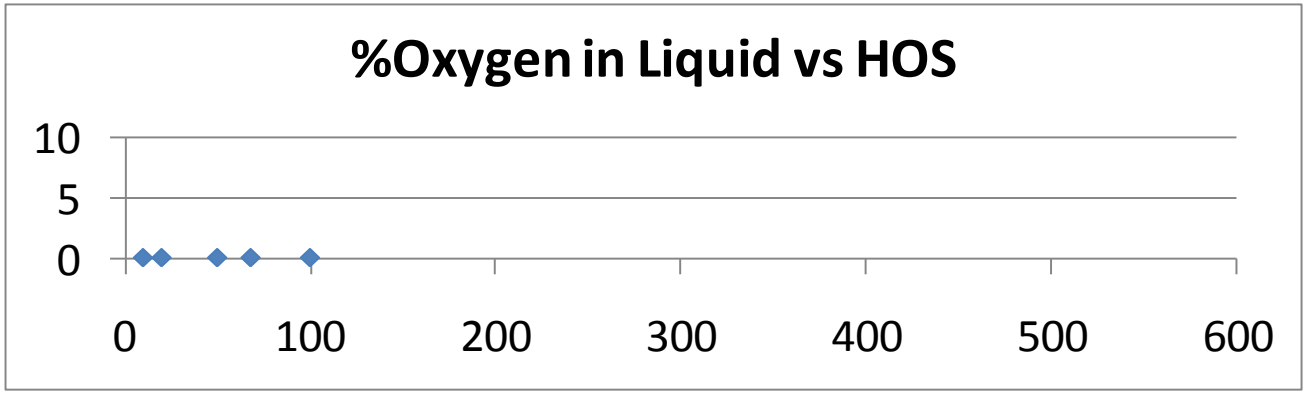
Yields in wt% of biomass feed (wood) on a moisture and ash free basis

| | Lab | Pilot |
|---|---|---|
| **Gasoline + Diesel** | **26** | **26** |
| char +ash | 13 | 14 |
| water | 36 | 39 |
| $CO+CO_2$ | 17 | 9 |
| C1-C3 | 13 | 15 |
| TOTAL* | 105 | 105 |

* Total greater than 100% due to hydrogen uptake

# Continuous Pilot Plant Yields and Quality



# Conclusions and Future Work

- $IH^2$ is a Differentiated Thermochemical Process
  - Produce valuable fuel products *directly* from multiple and mixed biomass feedstocks
  - Self-sufficiency produces fuels with excellent life cycle carbon benefits (>90% lower than fossil fuels)
  - Excellent economics of production (estimated <$2/gallon minimum selling cost)
- Remaining work to be done
  - Long-term testing just begun to confirm OPEX
  - Scale up - larger demonstrations

# Acknowledgments

> DOE Funding was essential to develop this process

U.S. DOE Award DE-EE-0002873
U.S. DOE Award DE-EE-0004390

> CRI Catalyst is essential for the process to work

- > 1st stage catalyst
- > 2nd stage catalyst

> CRI Catalyst is our development partner and are licensing this process commercially

# Background

# Fundamental Limitation of Pyrolysis of Biomass

> Biomass has a low Effective H/C ratio so it needs more hydrogen in its structure which Pyrolysis (or catalytic pyrolysis ) can't provide

>When water is formed during pyrolysis it removes hydrogen forming reactive olefins and depleting the biomass of hydrogen

> Pyrolysis of biomass rapidly makes acids

> High Acid Content Rapidly catalyzes undesirable pyrolysis reactions such as

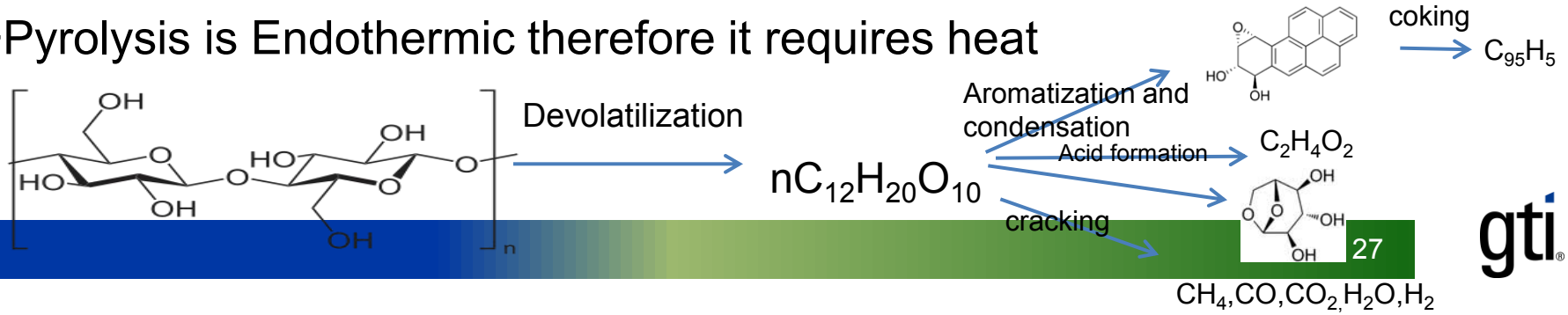
> Polymerization

> Aromatization ( and PNA formation)

> Coking

> Once PNA's are formed it is very expensive and difficult to upgrade them – Hydroconversion cost is directly proportional to feed molecular weight and PNA content

>Pyrolysis is Endothermic therefore it requires heat



# IH$^2$ Catalytic Hydropyrolysis Fundamentals

> IH$^2$ first stage hydropyrolysis rapidly **adds hydrogen to biomass fragments, removes oxygen** and caps free radicals, as soon as the biomass devolatilizes

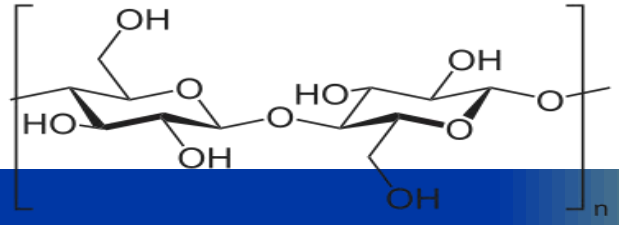
> Removing oxygen from biomass is quite rapid with the right catalyst and conditions

> Hydropyrolysis produces hydrocarbons and few oxygenates

>Hydropyrolysis reactions are exothermic reactions which produce substantial heat

>Minimize coking

>Reactions controlled by catalyst and hydrogen




Devolatilization →

$nC_{12}H_{20}O_{10}$

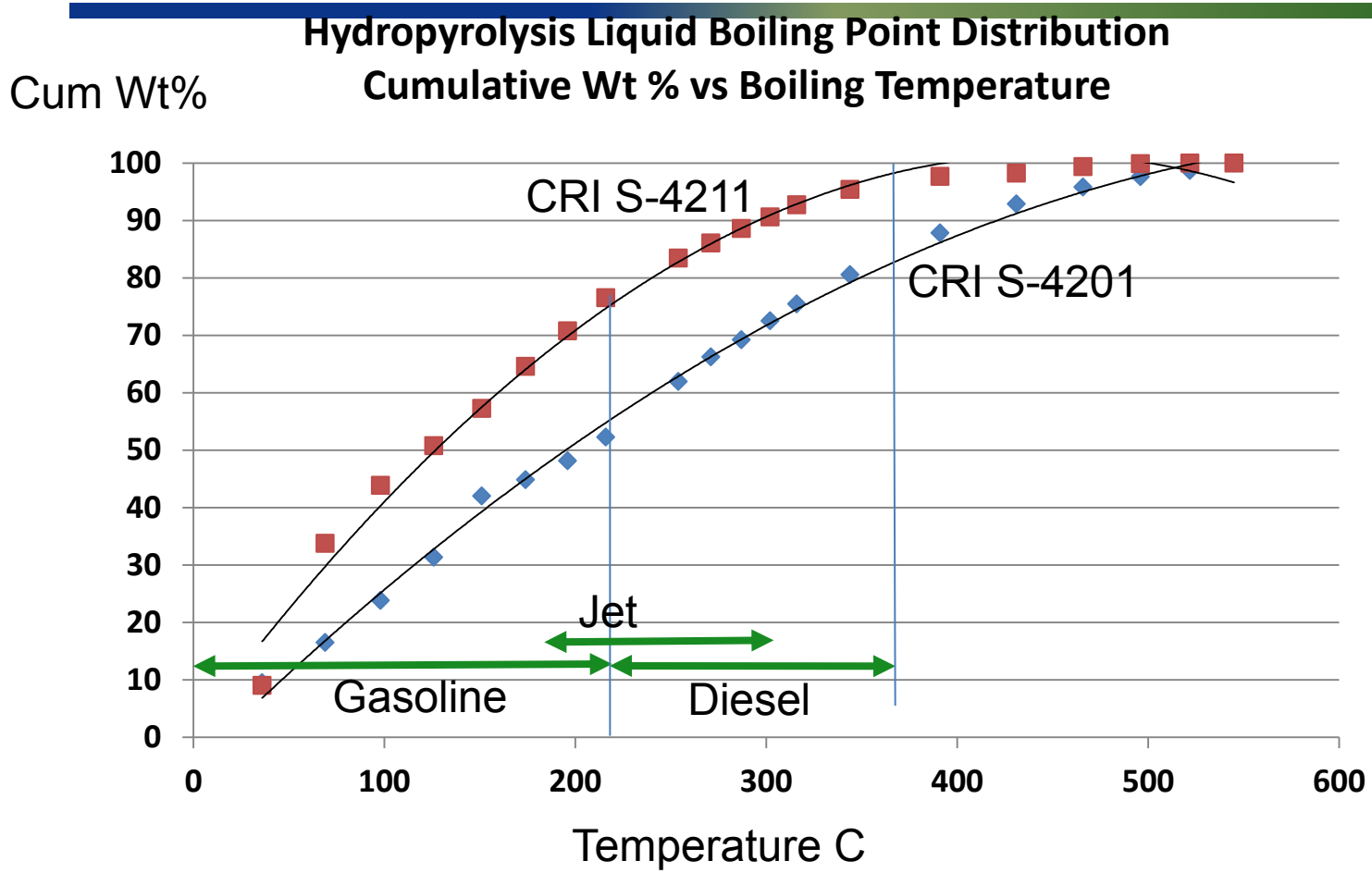
Hydrodeoxygenation
Decarbonylation

$H_2$

**Catalyst**

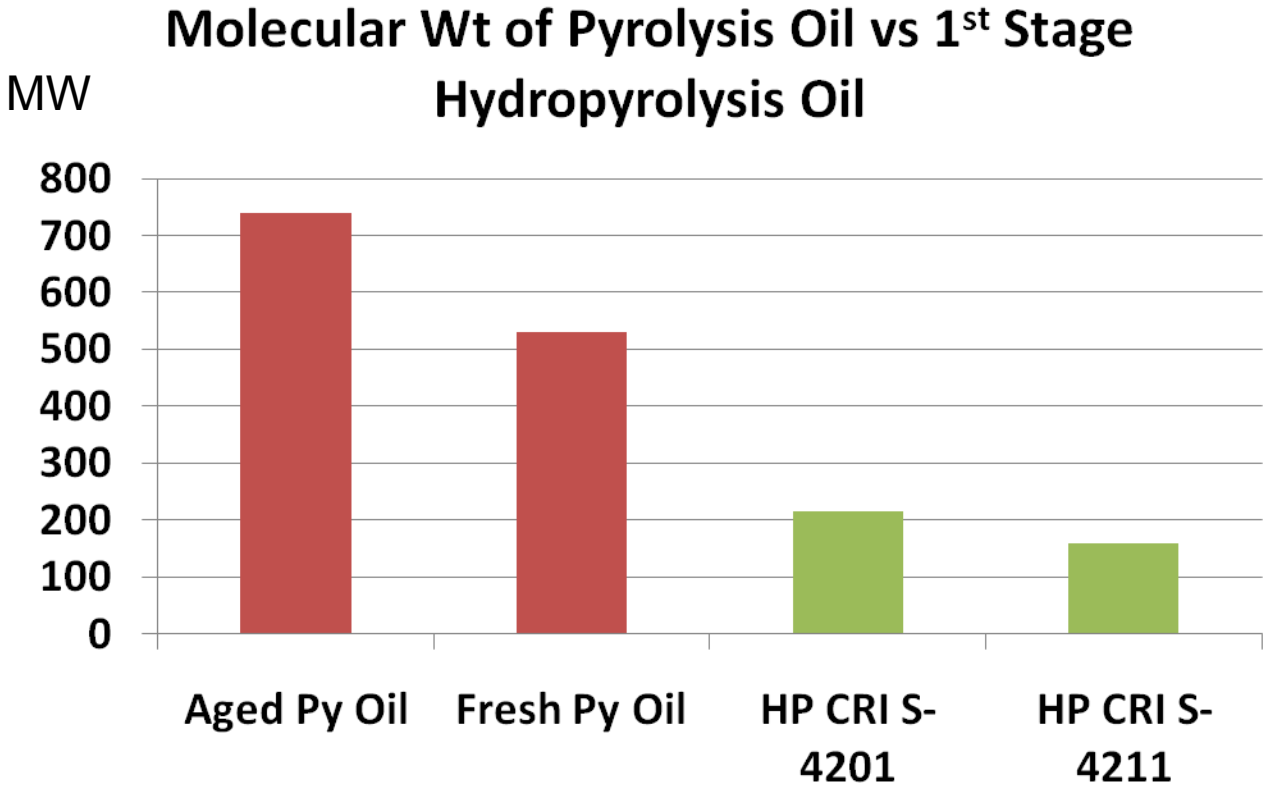
→ $C_{10}H_{22}$+ 8 $H_2O$+2CO,
$C_7H_8$+ $C_7H_8$+5CO
$C_{14}H_{30}$+$H_2O$+CO
HEAT

# 1st Stage Hydropyrolysis Liquid Boiling Point Distribution

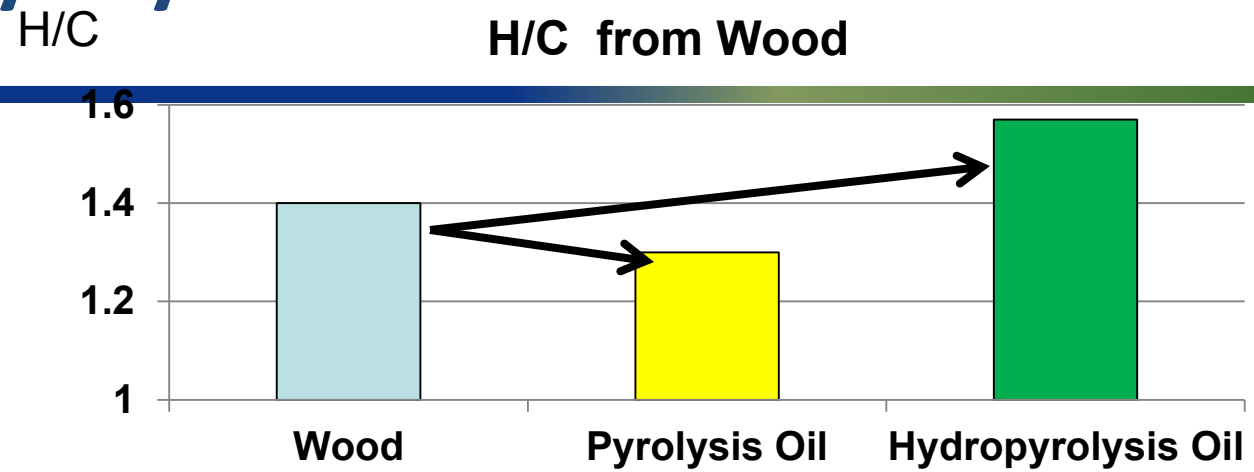



1st stage Hydropyrolysis Liquids have smooth boiling point distribution and are primarily gasoline, jet and diesel

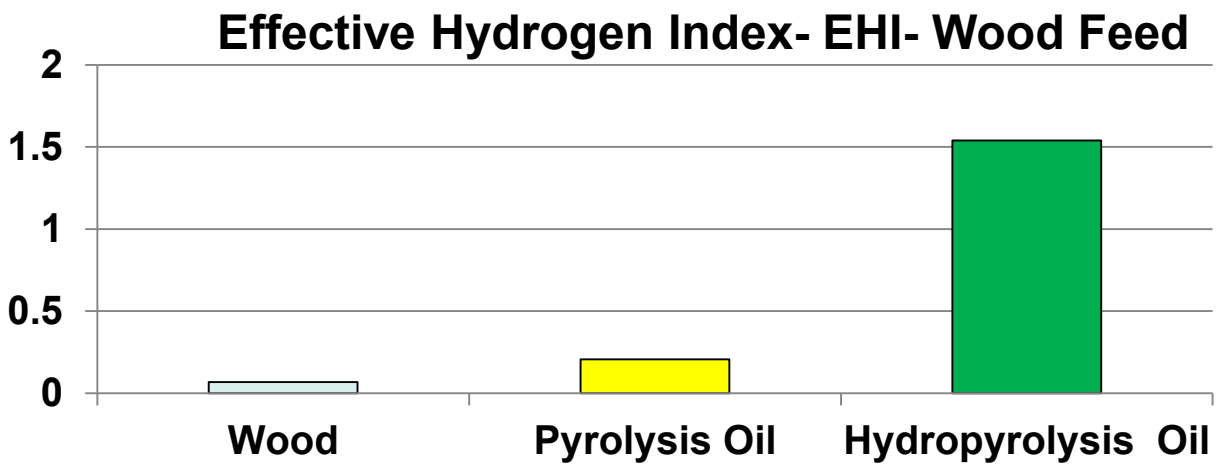
# Lower Molecular Weight of 1st Stage Hydropyrolysis Oil compared to Pyrolysis Oil



# Advantages of Hydropyrolysis vs Pyrolysis




H/C ratio goes up with hydropyrolysis, down with pyrolysis




EHI=(H-2O-3N-2S)/C is a measure of coking, higher EHI=less coking

# Hydropyrolysis vs Pyrolysis
# 1st Stage Product Comparison from wood

| | Hydropyrolysis Step of IH² | Hydropyrolysis Step of IH² | Pyrolysis |
|---|---|---|---|
| Catalyst | CRI S-4201 | CRI S-4211 | None |
| H2 Partial pressure,psi | 325 | 325 | No |
| % Oxygen in C4+ Product | 2.6 | 0.5 | 50 (40 water free basis) |
| % TAN in C4+ product | 0.35 | 0.5 | 100 |
| % water in C4+ product | <0.2 | 0.3 | 20 |
| density, g/ml | 0.85 | 0.82 | 1.2 |

- There is a big difference between Hydropyrolysis products and pyrolysis products
- Much easier to upgrade hydropyrolysis product than pyrolysis product

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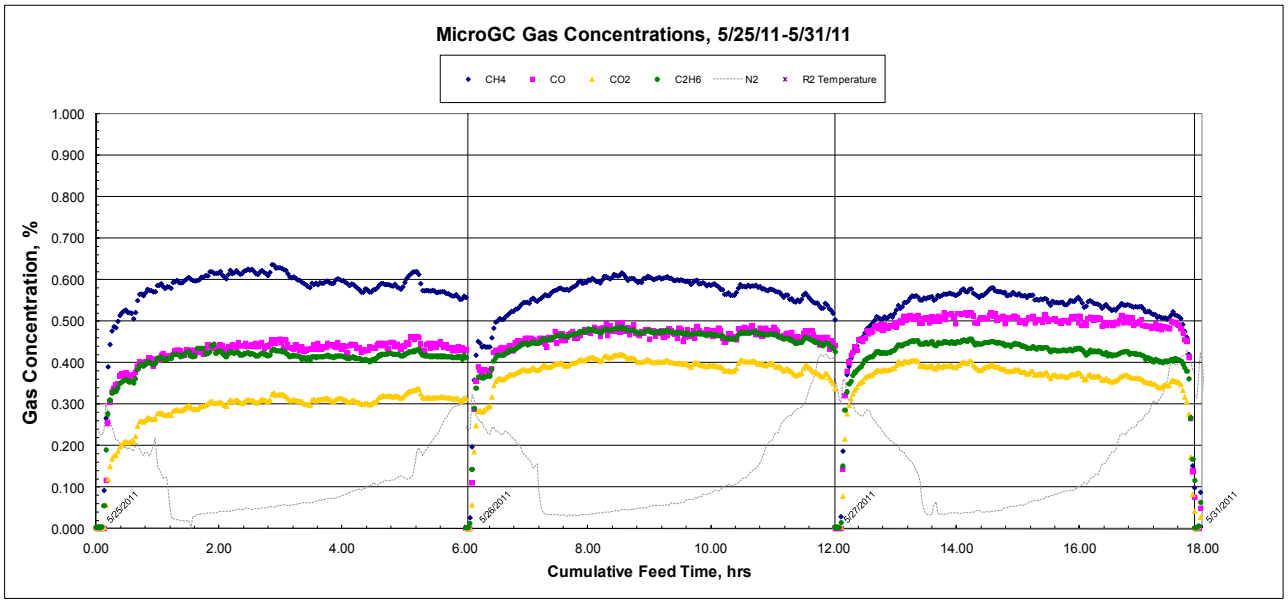
# Semi-Continuous Tests – Shows good stability over 3 day period (wood feed)

**C1-C2 data for Semi-continuous IH$^2$ testing**




| | | | |
|---|---|---|---|
| Wt % O in Liquid | <1% | <1% | <1% |

**Overall Liquid Yield 26-28 wt %**
**Good Catalyst-char separation**
**Startup-shutdown with same catalyst in bed**
**234g cat bed in, 229g cat bed out**