DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Refinery Upgrading of Hydropyrolysis Oil from Biomass

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Technology Area Review

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Goals

- Develop a cost-effective route for converting biomass to transportation fuels by first converting biomass to hydropyrolysis oil and then upgrading the hydropyrolysis oil in existing refinery equipment
  - Study properties and corrosion characteristics of first-stage hydropyrolysis liquids
  - Upgrade hydropyrolysis oils at standard diesel hydrotreating conditions to demonstrate how this would be done at a refinery
- Compare the advantages/risk of refinery upgrading of hydropyrolysis oil (from refiners viewpoint) to locating an IH$^{2®}$ process next to a refinery
- Obtain specific data on costs of bring wood to a Valero refinery or cornstover to a Valero corn-ethanol plant
- Develop a preliminary engineering design for a hydropyrolysis plant and commercial-scale facility to be located next to a Valero refinery
- Develop the best possible real project for a Valero location

Quad Chart Overview

Timeline

Project start: 1/1/2013
Project end: 12/31/2015 or sooner
Percent complete: 75% billed, 90% actual

Budget

	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	1.2M	.84M	1.2M
Project Cost Share total	.26M	.35M	.26M
GTI cost share	.24M	.12M	.02M
CRI cost share	.02M	.17M	.22M
Johnson Timber cs		.03M	
MTU cost share		.04M	.02M

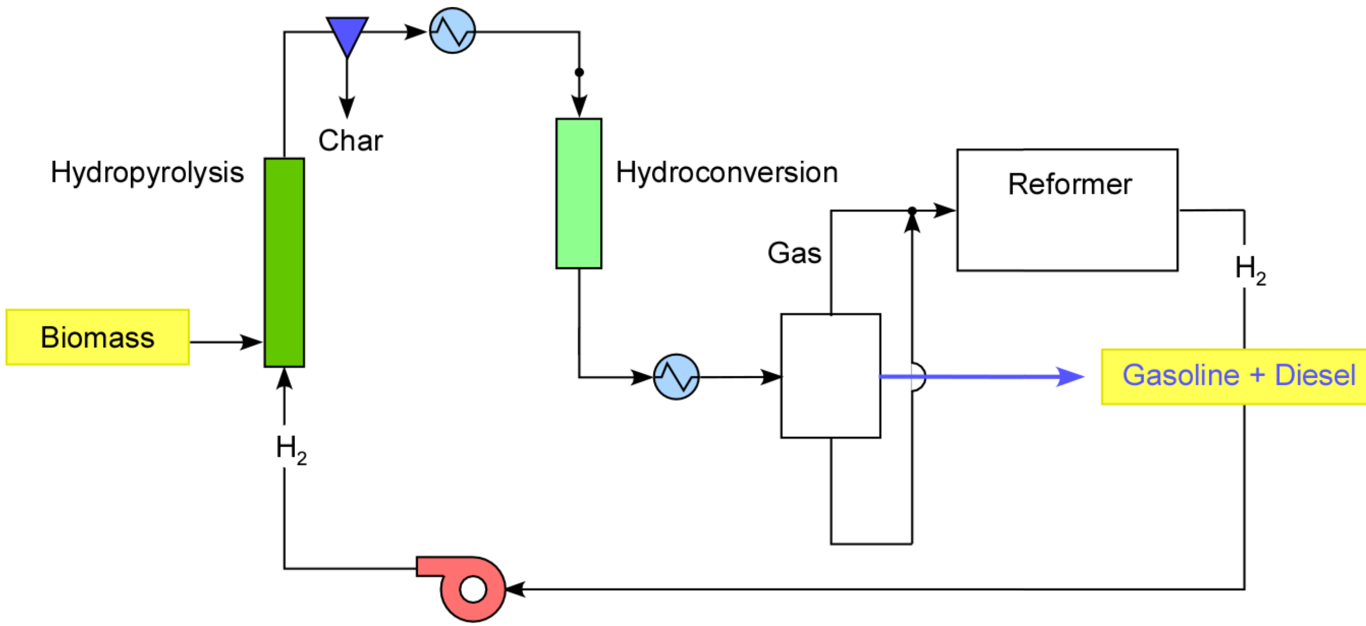
Barriers Addressed

- Pyrolysis of biomass
- Fuels Catalyst Development
- Thermochemical Process Integration
- Feeding or Drying Wet Biorefinery Streams
- Lack of Understanding of Environmental/ Energy Tradeoffs

Partners

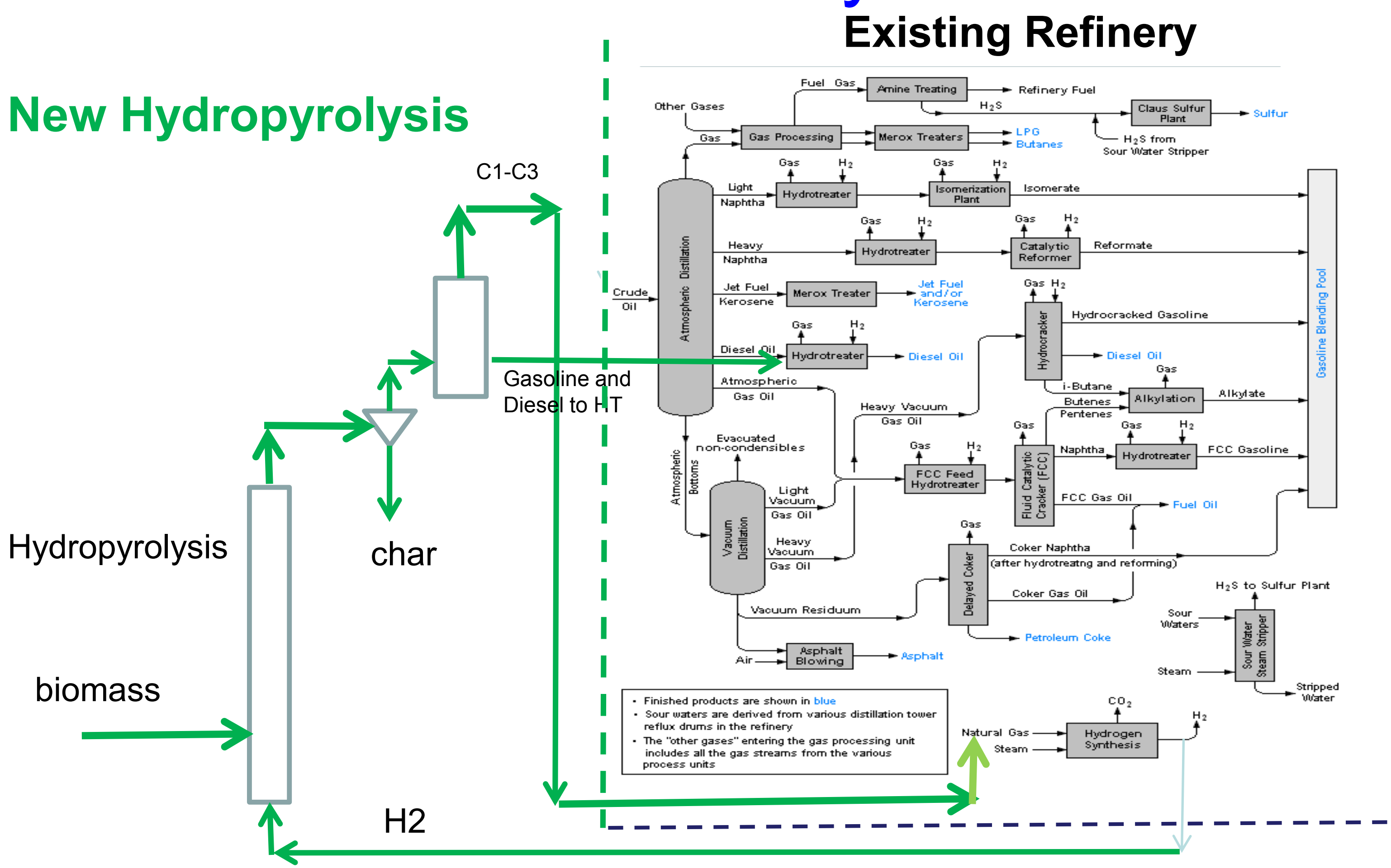
GTI: 55%
CRI Catalyst: 27%
Valero: 2%
Cargill: 4%
Johnson Timber: 6%
MTU: 6%

Integrated Hydropyrolysis and Hydroconversion (IH²®)



- 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–such as PNA, free radicals

Adjacent Hydropyrolysis Integration with a Refinery



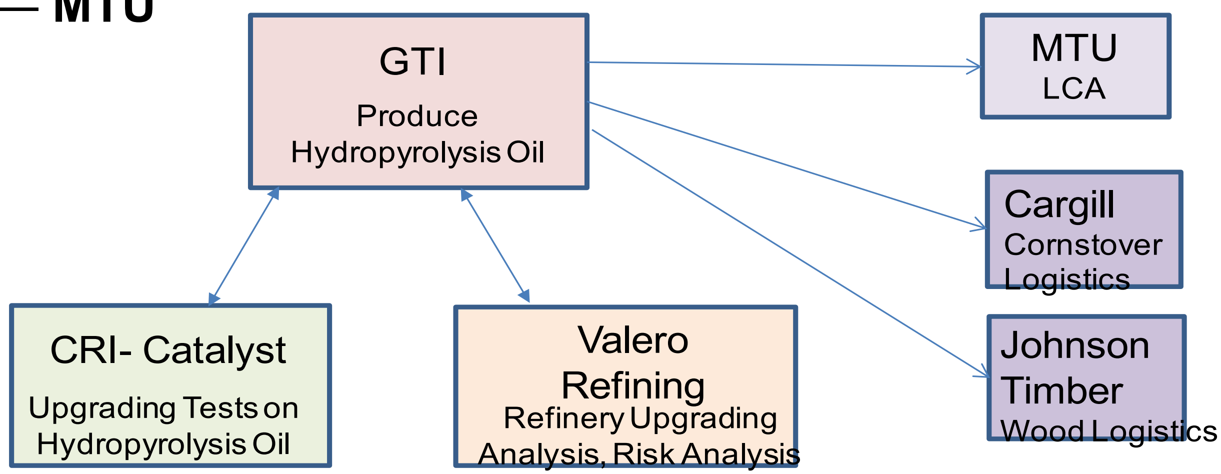
Best integration system depends on oil refinery specifics – hydropyrolysis products have low TAN's and can be blended into refinery streams

Project Team/Project Steps

Project Steps

1. Make Hydropyrolysis Oil + Analyze Properties—— **GTI**
2. Upgrade Hydropyrolysis Oil and IH$^{2®}$ Oil —— **CRI**
3. Evaluate Risks of Refinery Upgrading —— **Valero**
4. Evaluate Feed Costs and Logistics —— **Johnson Timber + Cargil**
5. Engineering Design —— **KBR**
6. LCA Analysis —— **MTU**

PROJECT TEAM



Project Status

- ☑ **GTI Work Completed**—All feedstocks prepared
  - ☑ 25 liters of IH²® liquid from wood
  - ☑ 25 liters of IH²® Liquid from cornstover
  - ☑ 25 liters of hydropyrolysis liquid from wood
  - ☑ 25 liters of hydropyrolysis liquid from cornstover
- ☑ **CRI Catalyst Upgrading** — Completed *(except for final report)*
  - ☑ Demonstrated hydropyrolysis liquid upgrading at Diesel hydrotreating conditions
  - ☑ Demonstrated 3rd stage diesel dearomatization to make 43 cetane diesel from IH²® liquid
- ☑ **Valero**
  - ☑ Risk analysis complete — Negative on refinery upgrading but open to drop-in fuel blending
- ☑ **Johnson Timber** — Report complete
- ☑ **Cargill on Cornstover** — Report completed
- ☑ **KBR** — Engineering finished
- ☑ **MTU** — LCA analysis in progress
  - ❑ Wood LCA completed

3 – Technical Accomplishments/ Progress/Results

- Production of hydropyrolysis liquids
- Characterization of hydropyrolysis liquids
- Upgrading of hydropyrolysis liquids
- Valero risk analysis for refinery upgrading
- Costs and logistics to deliver wood to a Valero refinery
- Costs and logistics to deliver cornstover to a Valero corn ethanol plant
- Engineering analysis – cost of hydropyrolysis or IH$^{2®}$ near a refinery
- LCA

Hydropyrolysis and IH$^{2®}$ Liquid Properties

	Hydropyrolysis Product from Wood	IH$^{2®}$ of Wood	Hydropyrolysis of Cornstover	IH$^{2®}$ of Cornstover
Wt % C	84.71	88.62	80.39	86.10
Wt % H	10.25	11.69	10.00	12.48
Wt % N	<0.1	<0.1	1.19	0.24
Wt % S	<0.1	<0.1	0.14	<0.1
Wt % O	4.96	<0.4	8.29	1.18
Density g/ml	0.850	0.789	0.874	0.792
TAN	4.4	<0.05	9.95	0.05
% Gasoline	59	76	59	70
% Diesel	41	24	41	30
Liters Prepared	25+	25+	25+	25+

Oak Ridge National Laboratories – Comparison of Hydropyrolysis Liquids vs. Pyrolysis Liquids

	Pyrolysis Liquids, Wood, Avg	Hydropyrolysis Wood	Pyrolysis Liquids, Cornstover, Avg	Hydropyrolysis Cornstover
ppm Formic Acid	**4855**	**297**	**2317**	**0**
ppm Acetic Acid	**30819**	**309**	**13871**	**0**
Oakridge Modified TAN	**119**	**14**	**93**	**16**
GTI/CRI TAN		**4.4**		**15**

Component Types in Hydropyrolysis Oil from Wood

Compound Group	Wt %
C5-C11 Monocyclics (saturates and olefins)	9
Linear Paraffins	5
C17-C18 Olefin Isomers	1
Groups of Saturated Fused Ring Systems	11
Monaoaromatics	19
Indanes/Indenes	8
Phenols	9
2 Ring Aromatics (Naphthalenes)	9
Napthalenes with Additional Saturated Ring	6
3 Ring Aromatics	6
3 Ring Aromatics with Additional Saturated Ring	2
Unknowns	15

Oak Ridge National Laboratory Corrosion Tests with Hydropyrolysis Liquids vs. Pyrolysis Liquids

Hydropyrolysis Liquids from Wood

(in mm/yr)

Exposure Time (hr)	Carbon Steel		2¼Cr-1Mo Steel		409 Stainless Steel		304L Stainless Steel		316L Stainless Steel	
	Coupons	U-bends	Coupon	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C GTI sample C (wood)										
250 hr	0.02	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50°C GTI sample C (wood)										
250 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
1000 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Pyrolysis Liquids from Wood

Exposure Time (hr)	Carbon Steel		2¼Cr-1Mo Steel		409 Stainless Steel		304L Stainless Steel		316L Stainless Steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C Pyrolysis (wood)										
250 hr	1.35	1.41	2.07	1.95	.12	.12	<0.01	<0.01	<0.01	<0.01
500 hr	.90	1.04	1.61	1.46	.06	.08	<0.01	<0.01	<0.01	<0.01
1000 hr	.69	.99	1.46	1.41	.03	.04	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50C Pyrolysis Liquid (wood)										
250 hr	5.07	5.21	4.08	4.25	.89	1.79	<0.01	<0.01	<0.01	<0.01
500 hr	2.96	2.90	2.45	2.61	.44	.90	<0.01	<0.01	<0.01	<0.01
1000 hr	1.66	1.62	1.59	1.77	.23	.45	<0.01	<0.01	<0.01	<0.01

Hydropyrolysis oils much less corrosive than pyrolysis oils

CRI Upgrading of Hydropyrolysis Oils

- Hydropyrolysis oils can be upgraded to diesel and gasoline **at standard diesel hydrotreating conditions with standard diesel hydrotreating catalyst**
- CO_2, CO and water will be produced in the hydrotreating step which may require some refinery hydrotreater unit modifications depending on the amount of hydropyrolysis oil treated in the refinery unit
- Diesel produced from hydrotreating hydropyrolysis oil at typical conditions will have low cetane of 27 – does not meet fuel specification
- An aromatic saturation process using optimized catalyst integrated with an external IH$^{2®}$ process can produce diesel product of 43 meeting all specifications – aromatic saturation is not typically present in refineries

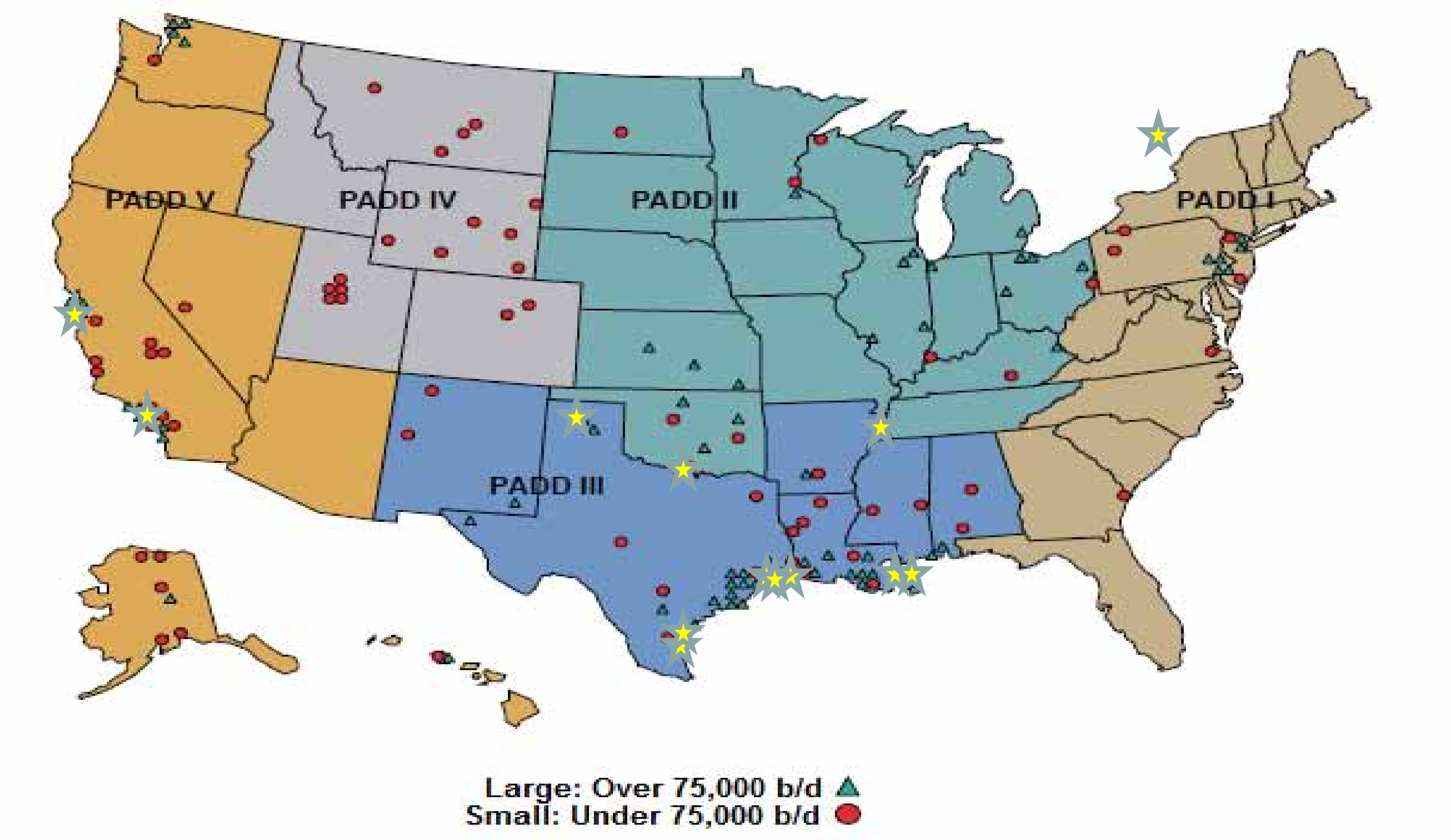
	U.S. Diesel Specification	**Hydrotreated Hydropyrolysis Oil**	**IH$^{2®}$ Diesel**	**IH$^{2®}$ Plus Integrated Aromatic Saturation**
Diesel Cetane	GT 40	27	27	43

Valero Risk Analysis of Hydropyrolysis + Refinery Upgrading

- Valero believed risk of hydrotreating hydropyrolysis oil in their refineries was **unacceptable** because of metallurgy and catalyst deactivation concerns
- Cost of integrated hydrotreating step in IH2® is very small only 3% of IH2® cost
- Valero prefers a 43 cetane product – which cannot typically be produced in refinery hydrotreating equipment
- **Best option to mitigate risk in Valero analysis was IH2® plus integrated diesel upgrading and blending IH2® gasoline and diesel into the pool with no refinery upgrading**

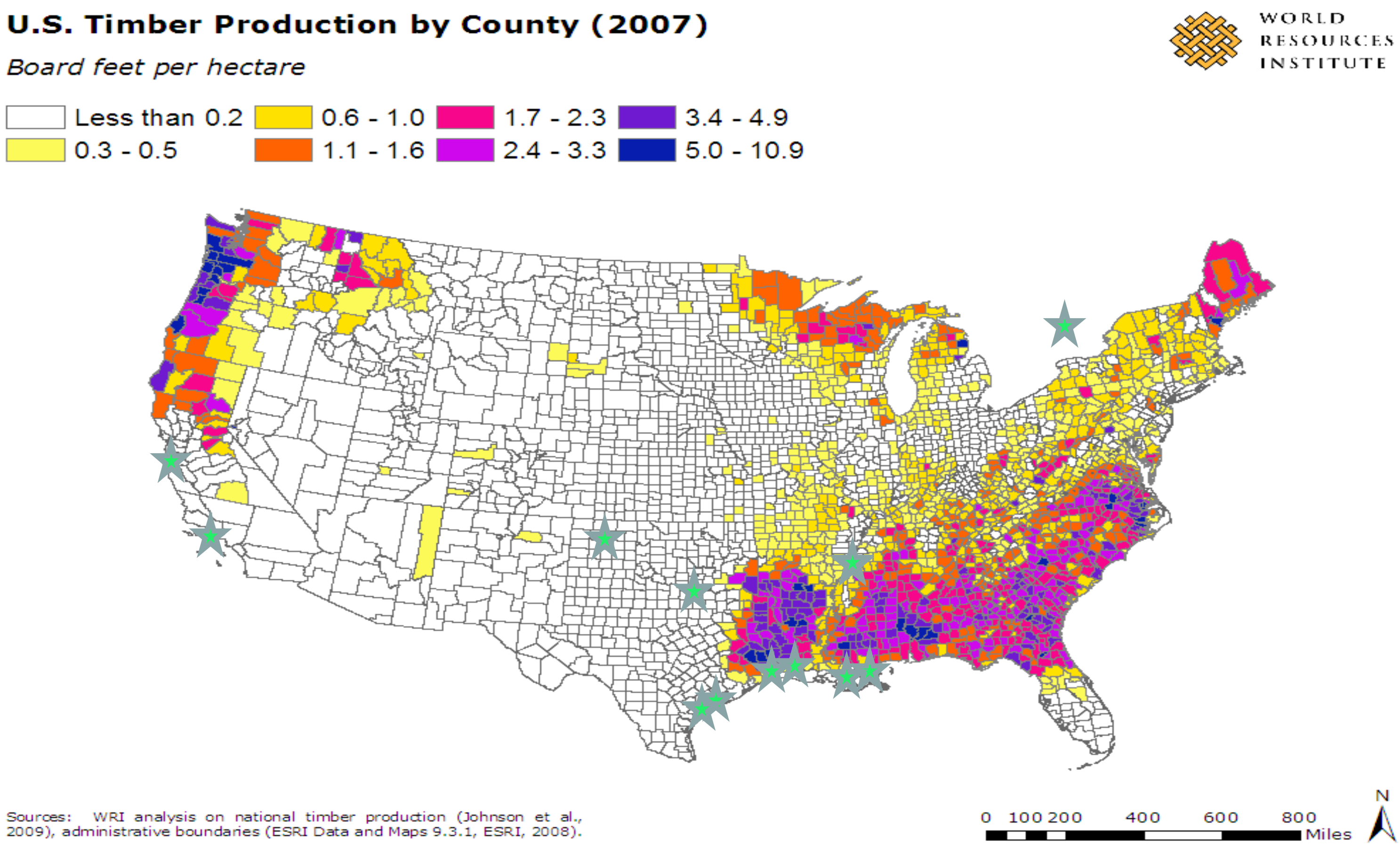
U.S. Oil Refinery Locations

Valero Locations ★



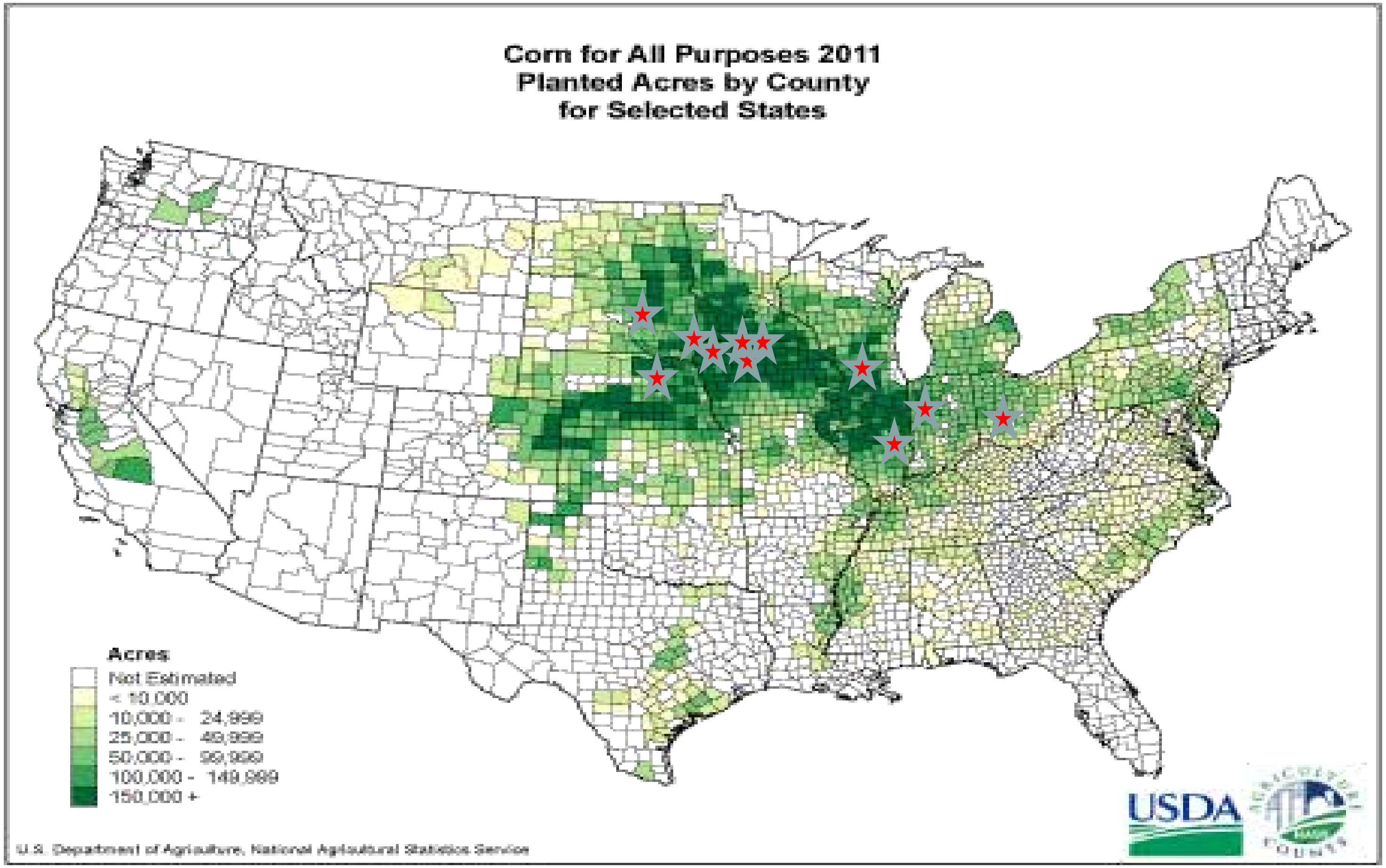
U.S. Timber Production by County

Valero Refinery ★



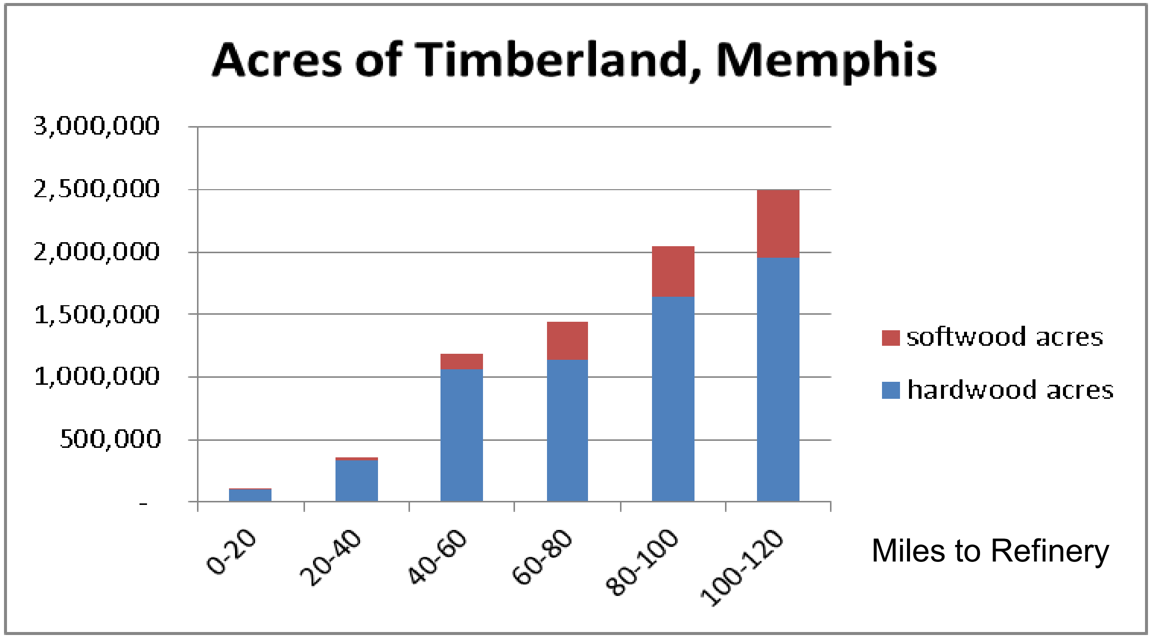
U.S. Corn Production

Valero Ethanol ★



Wood Delivered Costs–
500 t/d to Memphis Refinery

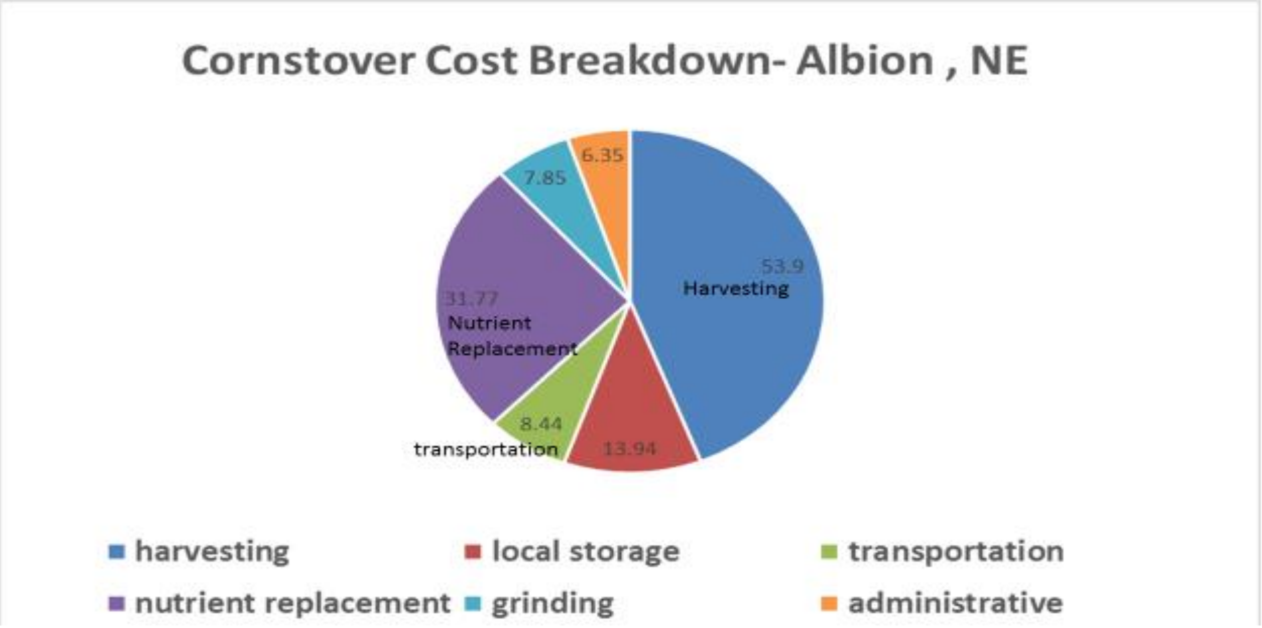
	Johnson Timber est
Delivered Feed Price $/ton	72



JT Evaluation of possible Valero refinery locations found Memphis best

Cornstover Delivered Costs 500 t/d

	$/ton (MF)
Welcome Mn Ethanol Plant	119.5
Albion NE, Ethanol Plant	120.6
Memphis TN Refinery	134.0



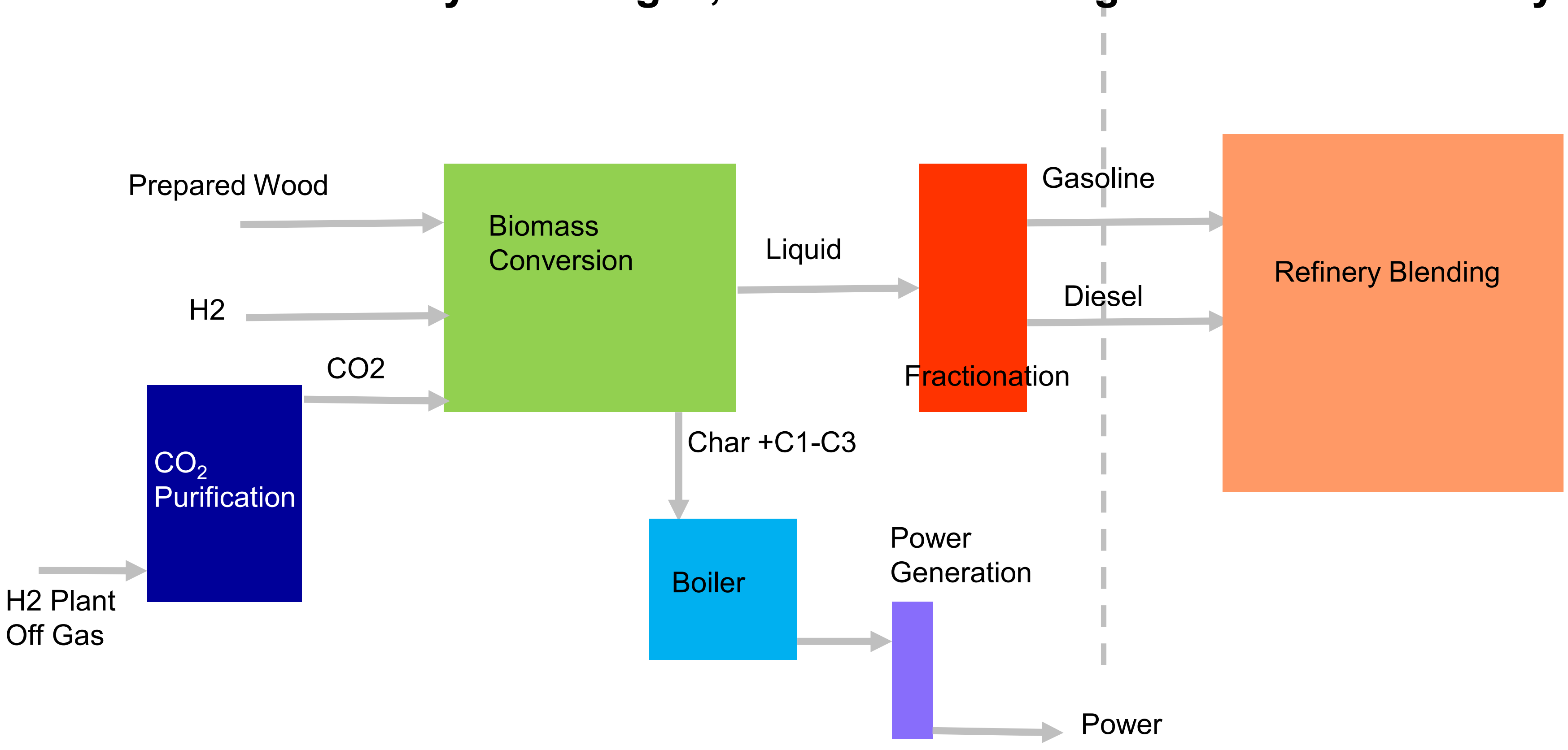
Hydropyrolysis or IH$^{2®}$ Finished Fuel Yield for Wood vs. Cornstover

	Wt% C4+Liquid Yield	Gallon per ton
Wood	26-30	86-92
Cornstover	21	67

Wood is best feed for initial IH$^{2®}$ units since it has higher liquid yields and lower feedstock costs

Engineering Case 1 – Hydropyrolysis or IH²® Next to a Refinery – Case 1

All H2 from refinery natural gas, burn char+C1-C3 gas to make electricity



Simplest Possible Configuration – Utilizes Refinery H2 Plant

KBR Capital Cost(in $Million) – Hydropyrolysis or IH$^{2®}$ next to Refinery – Case 1

500t/d wood feed = 14MM gal/yr gasoline + diesel

	500 t/d
Biomass conversion	18.7
Hydrotreating Section	2.5
Hydrocarbon Separation	10.8
Hydrogen Axuillaries	3.0
Amine Regenerator	6.0
Char Boiler	18.5
Power Generation	11.1
Cooling Tower System	3.6
Total Capital	74.1
Catalyst	2.0
Infrastructure	11.2
Field Cost Total Direct	87.3
Total Indirects	43.7
Total Project	131.0

Only 2% increase in cost from integrated hydrotreating stage

Utilities Case 1 – Hydropyrolysis or $IH^{2®}$ Power Production

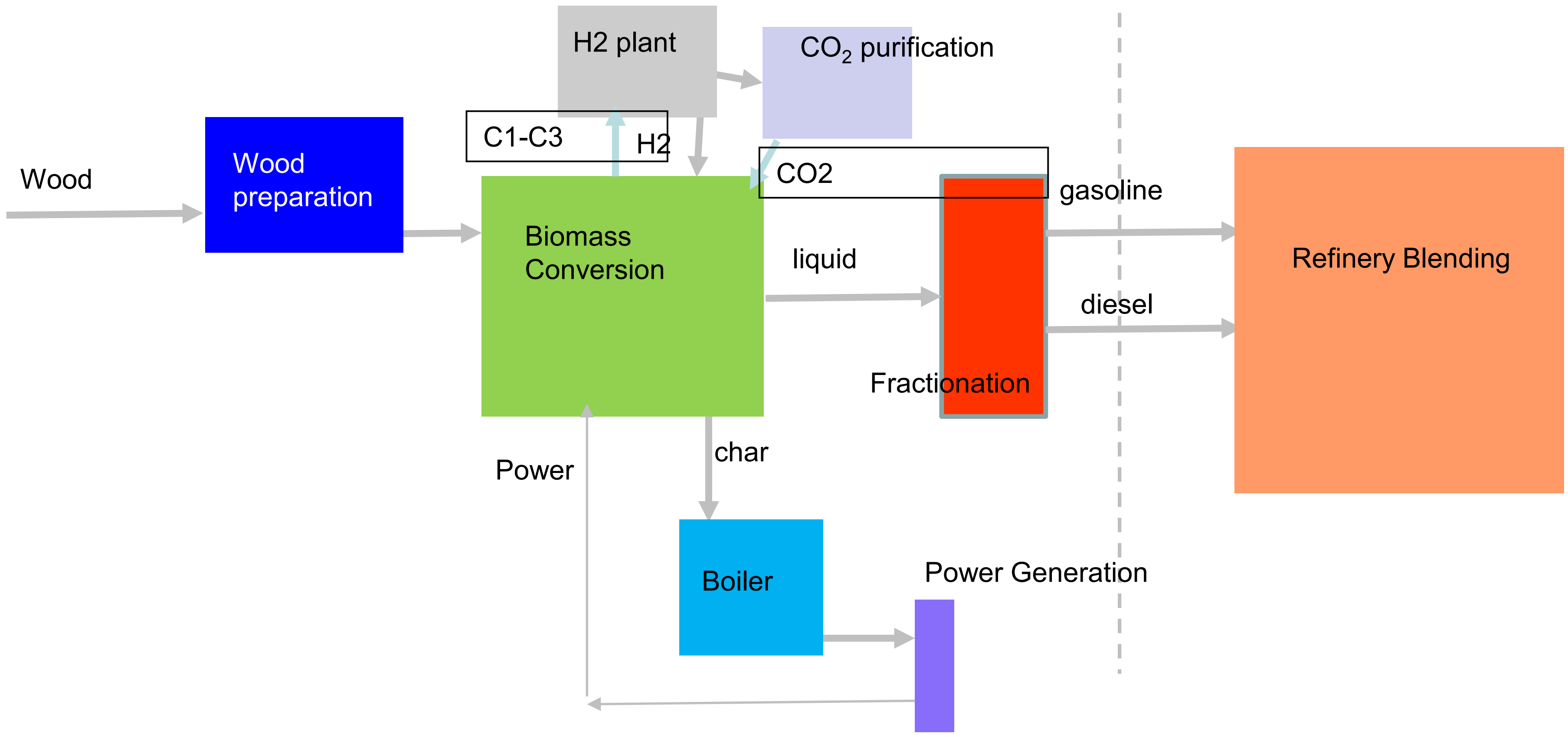
When H2 is produced from refinery natural gas and Char +C1-C3 burned

	500t/d
MW	12

In this case hydropyrolysis or $IH^{2®}$ actually produces power

IH2® Next to a Refinery – Case 2

Stand alone IH2® next to a refinery includes 3rd stage + Integrated Hydrogen plant



More Complex – standalone system next to refinery

Case 2 – IH$^{2®}$ Capital Cost – KBR(in $Million)

including H2 plant and 3rd stage

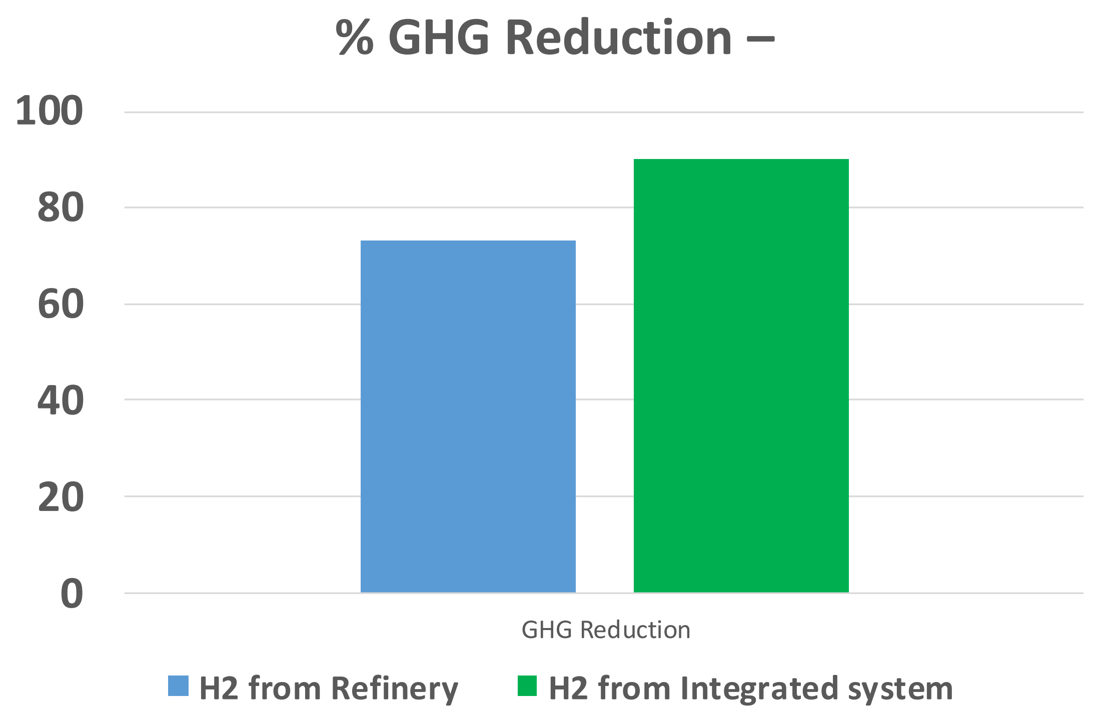
	500t/d
Base total project cost	131
+ 3rd stage	10
Total	141
+ H2 Plant	38
Total	179

Case 2 – Utility Requirements – KBR

For IH2® next to refinery including 3rd stage + H2 plant and H2 made from IH2® C1-C3+ no natural gas use

	500t/d
Electric ,MW	2.0
Natural Gas, MW	-
Raw Water makeup L/sec	17.9
Waste water out L/sec	7.1
Nitrogen kg/h	<2.5

GHG Reduction Comparison for H2 from Refinery vs. Integrated IH^{2}®



Using integrated hydrogen production significantly decreases GHG emission compared to using refinery generated hydrogen

Summary

- There are many locations in the U.S. where refineries are located near enough to biomass to be viable locations for biomass conversion processes
- **Valero believes there is too much risk to upgrade liquids containing any oxygen in their refinery units**
- Valero prefers a standalone unit next door providing drop in fuels for blending
- Engineering study shows there is only a small capital cost savings for refinery upgrading versus upgrading in the integrated hydrotreater for hydropyrolysis case
- **An integrated 3rd stage allows production of drop in diesel (43 cetane) as well as drop in gasoline from woods all products are 100% drop in gasoline and diesel**

4. Relevance

- This Project is relevant to BETO goals by
  - Providing a clear path to make drop-in gasoline and diesel fuels from biomass for less than $2/gal with low GHG emission
  - Providing information on integration of intermediate products with petroleum refineries

Summary

- Cornstover is more expensive, has lower yields and is less economically viable than wood feed
- **LCA and GHG reduction is better when hydrogen is produced from biomass derived gas rather than fossil fuel derived gas**
- Memphis is the best location in the Valero system (in U.S.) for an integrated wood to gasoline + diesel process
- Integrated systems which go all the way to drop in fuels rather than producing intermediates save money, reduce greenhouse gas emissions, and reduce risk when entire fuel generation process and LCA are included

5 – Future Work for this project

- Finish LCA for Cornstover
- Receive CRI upgrading report
- Finish final report

Additional Slides

Oakridge National Laboratory Corrosion Tests with Hydropyrolysis Liquids vs. Pyrolysis Liquids

Hydropyrolysis Liquids from Cornstover

(in mm/yr)

Exposure Time (hr)	Carbon Steel		2¼Cr-1Mo Steel		409 Stainless Steel		304L Stainless Steel		316L Stainless Steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C hydropyrolysis (cornstover)										
250 hr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
1000 hr	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Samples immersed in 50°C hydropyrolysis (cornstover)										
250 hr	0.09	0.08	0.07	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
500 hr	.06	.06	.04	.04	<.01	<.01	<.01	<.01	<.01	<.01
1000 hr	.04	.07	.02	.02	<.01	<.01	<.01	<.01	<.01	<.01

Pyrolysis Liquids from Cornstover

Exposure Time (hr)	Carbon Steel		2¼Cr-1Mo Steel		409 Stainless Steel		304L Stainless Steel		316L Stainless Steel	
	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends	Coupons	U-bends
				Corrosion Rates in mm/yr						
Samples suspended above 50°C Pyrolysis (cornstover)										
250 hr	.75	1.52	1.27	1.86	.29	.26	<0.01	<0.01	<0.01	<0.01
500 hr	1.25	1.25	1.48	1.71	.20	.20	<0.01	<0.01	<0.01	<0.01
1000 hr	1.01	1.31	1.48	1.67	.16	.15	<0.01	<0.01	<0.01	<0.01
Samples immersed in 50C Pyrolysis Liquid (cornstover)										
250 hr	4.86	4.88	5.84	5.91	3.85	3.52	<0.01	<0.01	<0.01	<0.01
500 hr	3.41	3.31	4.97	5.20	3.0	1.76	<0.01	<0.01	<0.01	<0.01
1000 hr	2.14	2.07	3.69	3.83	1.52	.88	<0.01	<0.01	<0.01	<0.01

Hydropyrolysis oils much less corrosive than pyrolysis oils

Publications, Patents, Presentations, Awards, and Commercialization

- 5 U.S. Patents have been issued related to hydropyrolysis and IH$^{2®}$ Technology
- Early work on this project was presented at 2014 EU biomass conference, GTI and CRI have presented many talks on IH$^{2®}$ technology in general
- CRI, our Commercialization partner, is in talks with several customers to build commercial units or build 5t/d demonstration units
- CRI has sold 3 licenses for Engineering studies of the IH$^{2®}$ technology

Future Requirements for IH^2® Commercialization

- Demonstration unit probably required to provide customer confidence, de-risk technology
- Current pilot plant could be expanded economically to 1t/d