2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Refinery Upgrading of Hydropyrolysis Oil from Biomass

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Bio-Oil Technology Area Review

Terry Marker
GTI

Project Goals and Objectives

- *Develop a cost effective route for converting biomass to transportation fuels by*
  - Converting biomass to hydropyrolysis oil
  - Upgrading the hydropyrolysis oil in a petroleum refinery using existing refinery equipment
  - Working closely with a major petroleum refining company to develop the best integration
  - Developing a preliminary engineering design for a hydropyrolysis pilot and commercial scale facility to be located next to a Valero refinery
  - Developing an engineering design package for locating a hydropyrolysis unit converting cornstover at one of Valero's 10 midwest corn ethanol plants
  - Comparing risk versus benefits from a refiners point of view for Integrated hydropyrolysis and hydroconversion (IH^2) vs hydropyrolysis plus refinery upgrading

Selected from FOA DE-FOA-0000686 Bio-Oil Stabilization and Commoditization

Project Quad Chart Overview

Timeline

- Jan 2013
- April 2016
- 8.7% spent – project just started

Barriers

- Barriers addressed
  - Pyrolysis of Biomass and Bio-Oil Stabilization

Budget

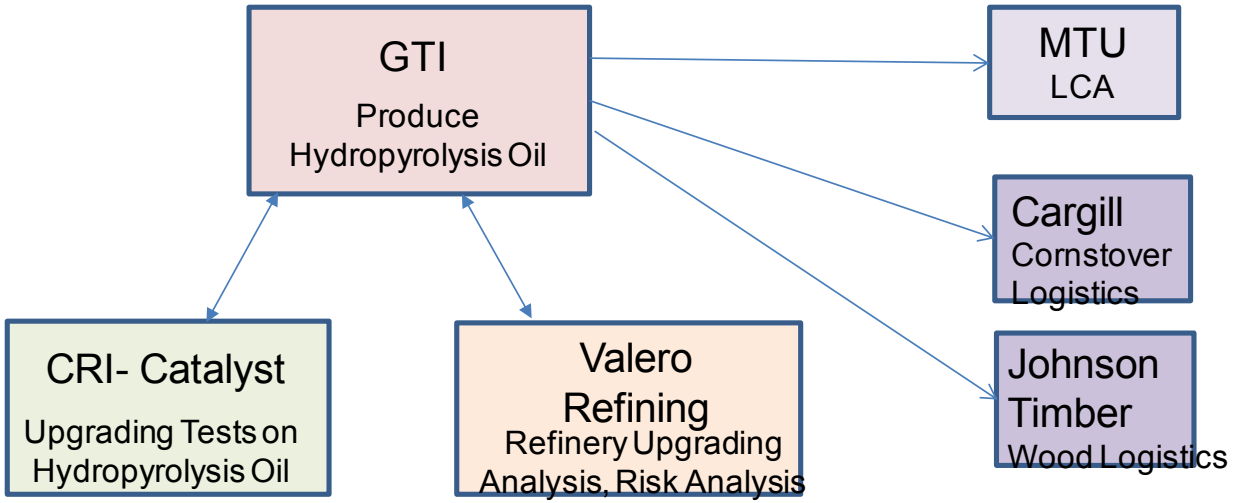
- Total $4.1MM, $3.2MM DOE,$.88MM CS
- 2013 to date $356K, $280K DOE, $74K CS
- 3 years funding,$1.4MM/year

Partners & Roles

- GTI,CRI Catalyst, Valero, Johnson Timber, Cargill, MTU

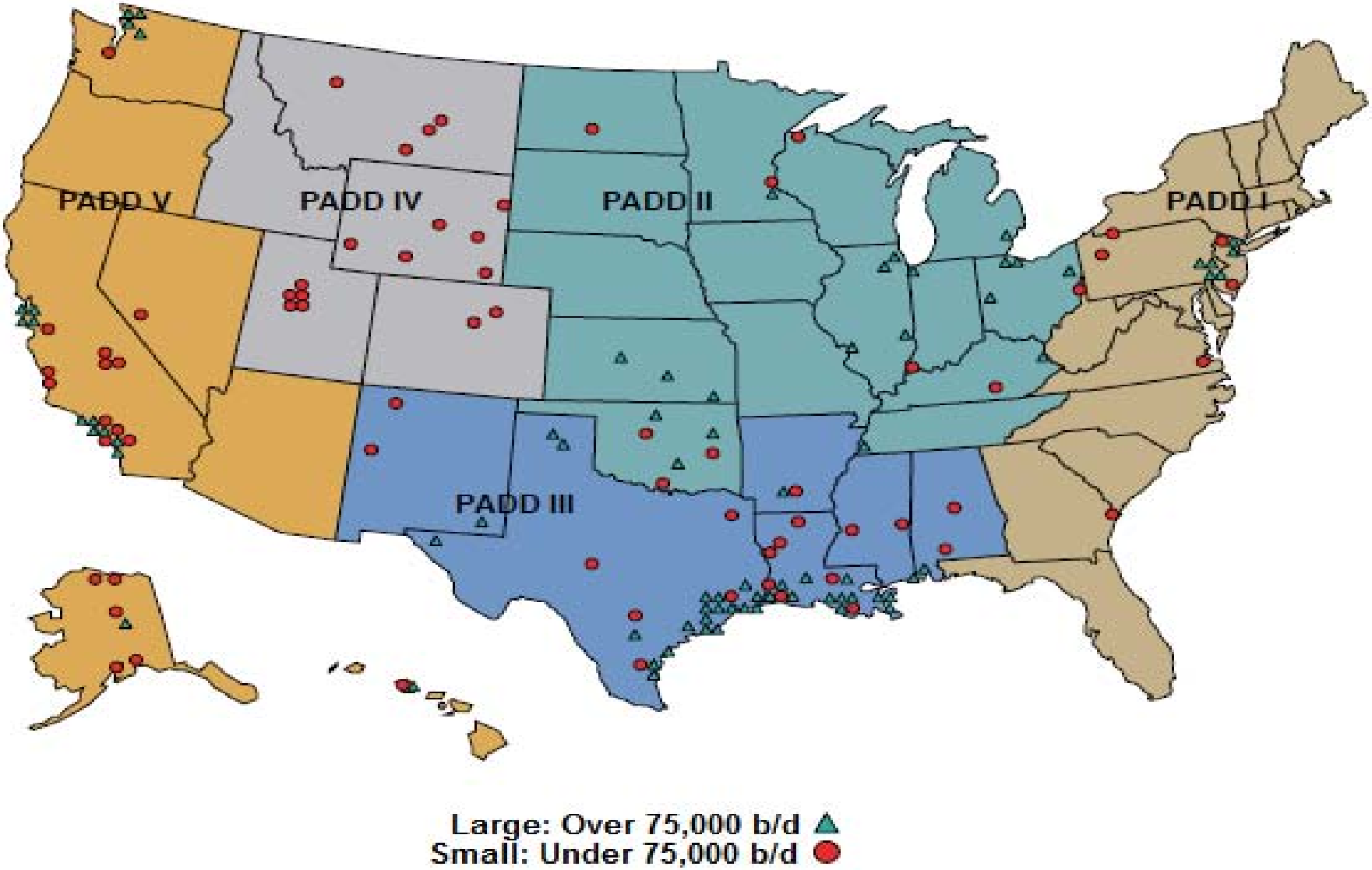
Refinery Upgrading of Hydropyrolysis Oil

PROJECT TEAM



- Currently finalizing contracts with partners

US Oil Refineries

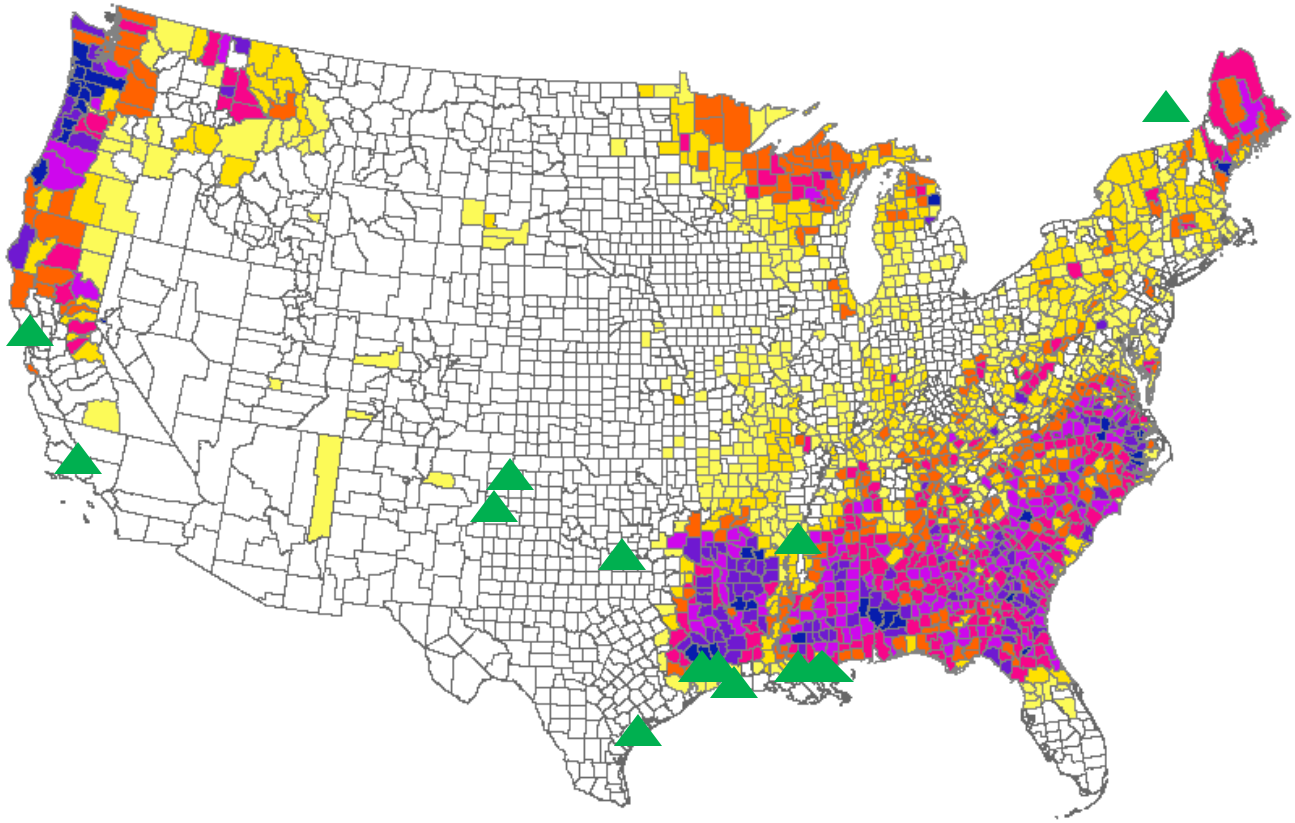


U.S. Timber Production by County (2007)

Board feet per hectare

WORLD RESOURCES INSTITUTE

Less than 0.2	0.6 - 1.0	1.7 - 2.3	3.4 - 4.9
0.3 - 0.5	1.1 - 1.6	2.4 - 3.3	5.0 - 10.9

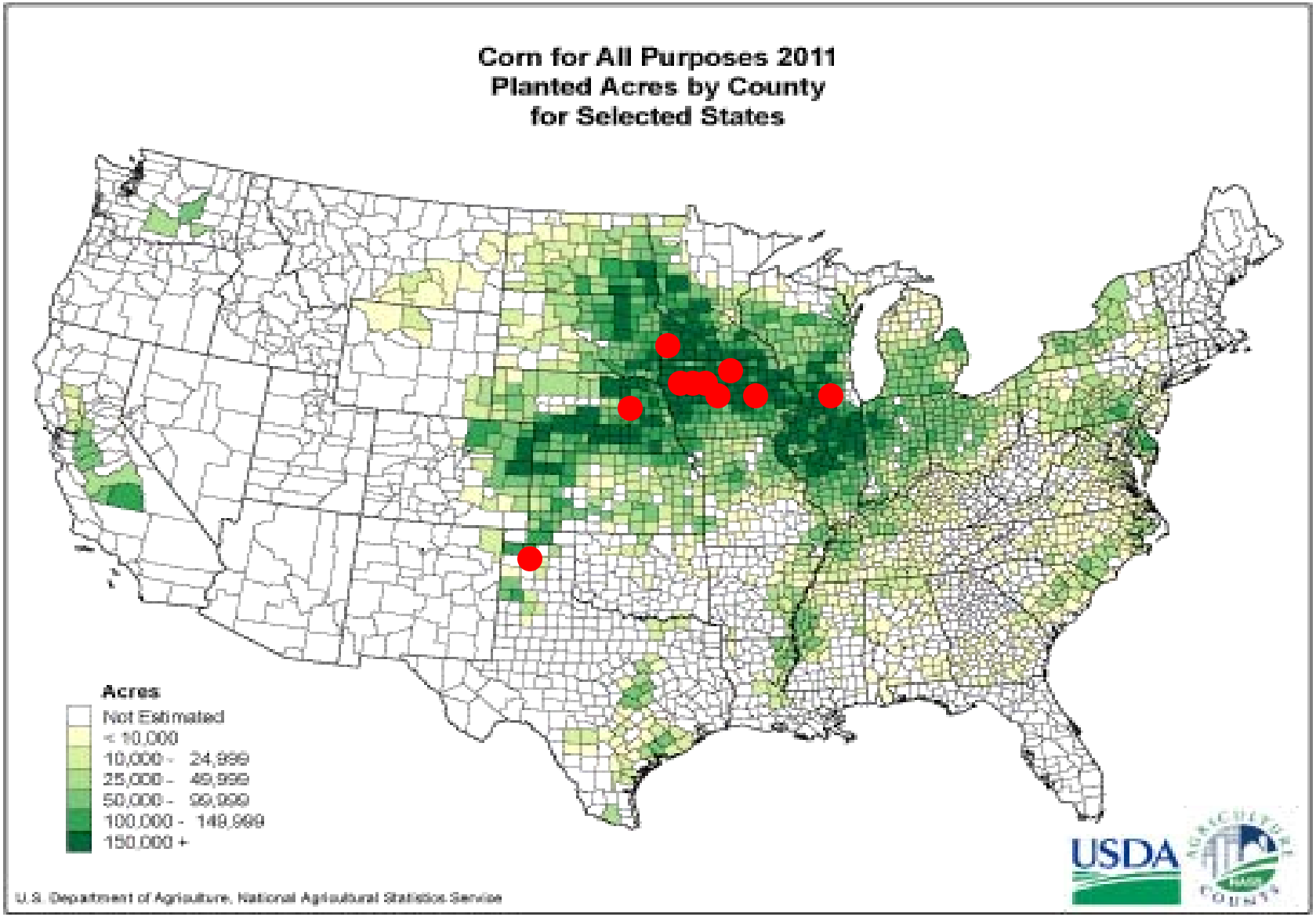


Sources: WRI analysis on national timber production (Johnson et al., 2009), administrative boundaries (ESRI Data and Maps 9.3.1, ESRI, 2008).

0 100 200 400 600 800 Miles

N

▲Valero Refineries

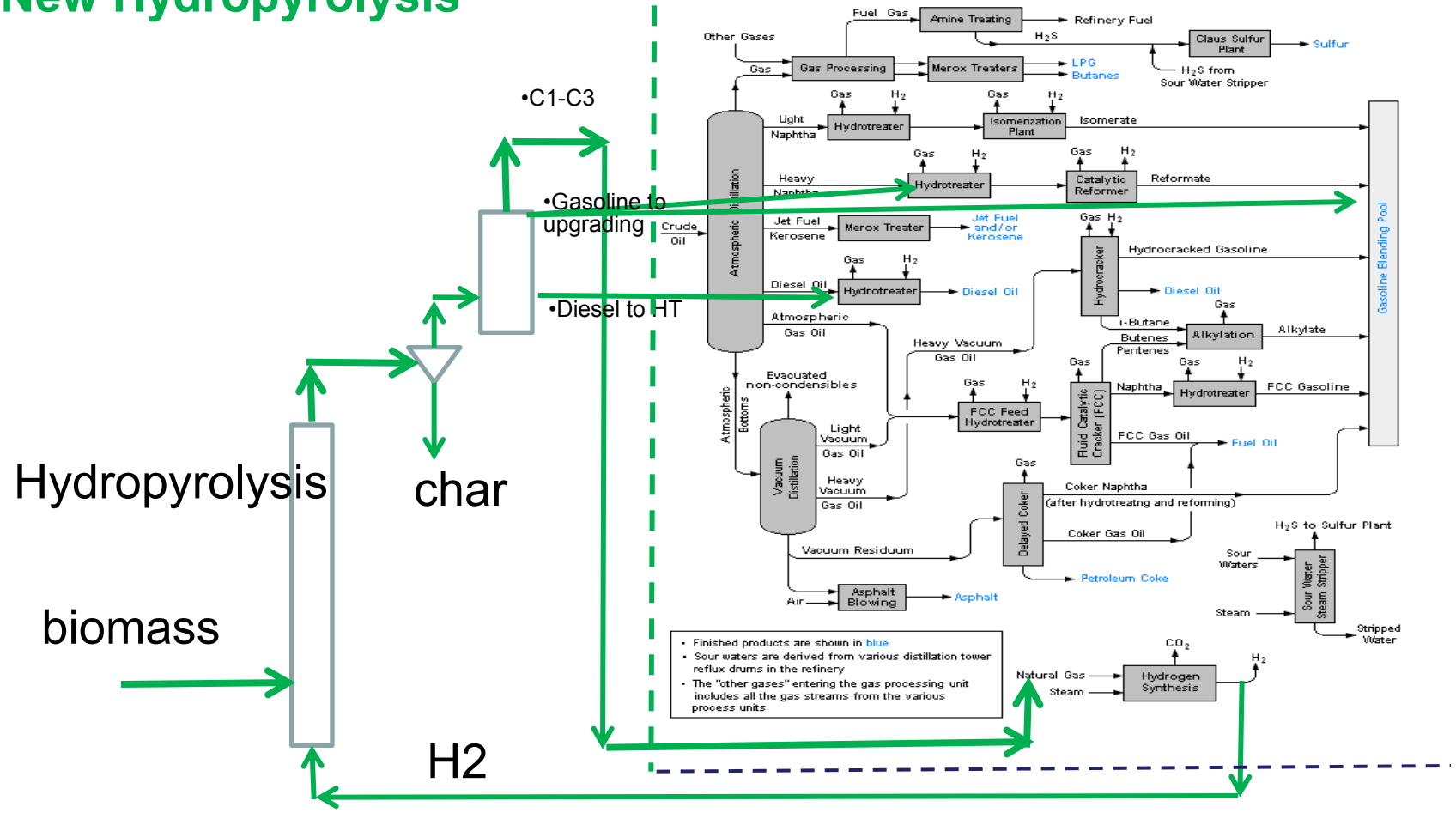


● Valero – Corn Ethanol Plants

Adjacent Hydropyrolysis Integration With a Refinery

New Hydropyrolysis

Existing refinery

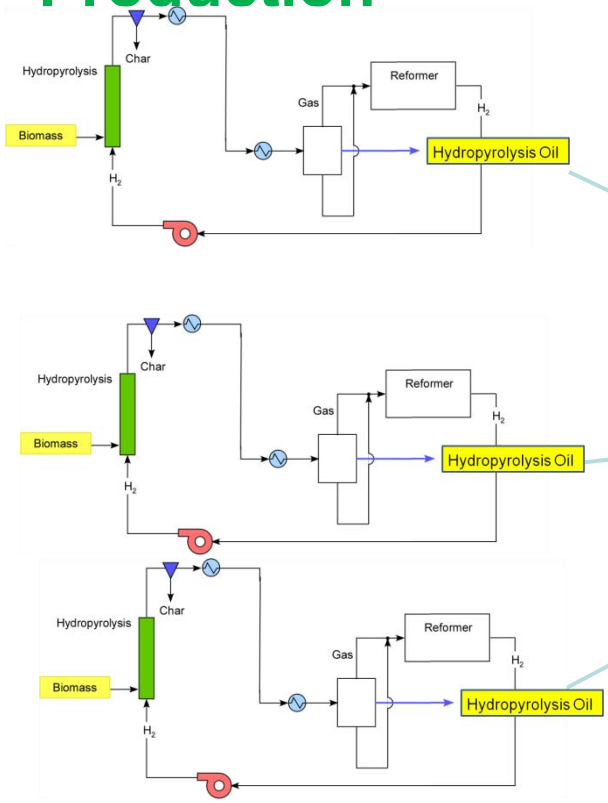


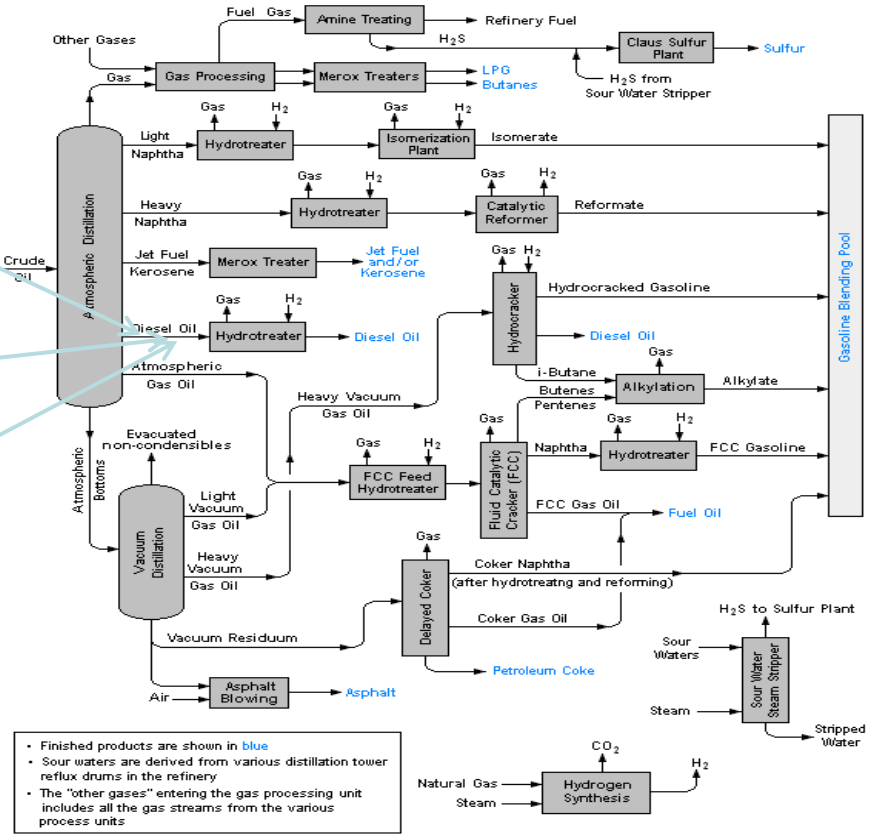
•Best Integration system depends on Oil Refinery specifics-Hydropyrolysis products have low TAN's and can be blended into Refinery streams – Capital cost could be <$50MM for 2000 t/d of biomass feed

Distributed Hydropyrolysis Sites Feeding an Existing Refinery

Multiple Hydropyrolysis Sites Integrated with Corn Ethanol Production

Existing Refinery





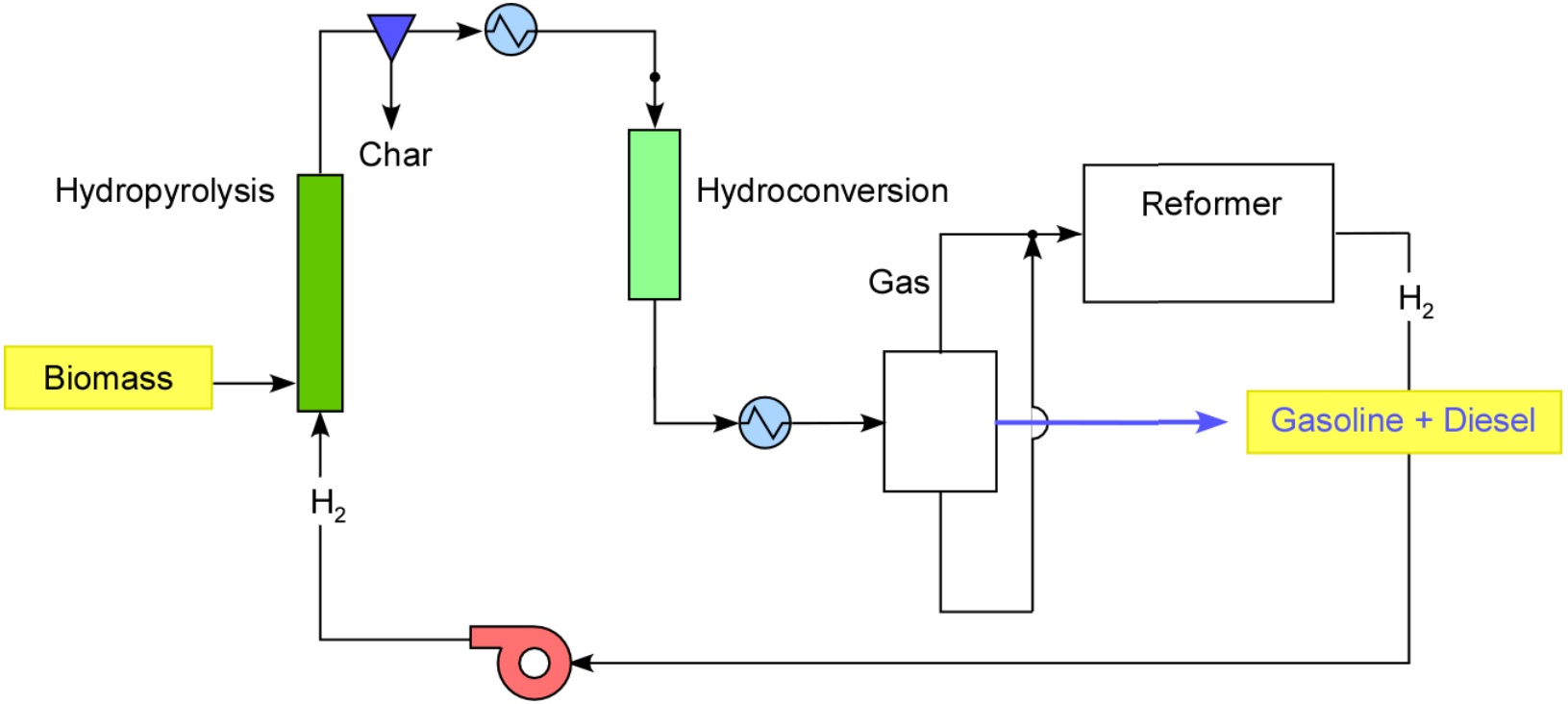
Hydropyrolysis products sent for further upgrading in existing refinery hydrotreaters

Advantages of Hydropyrolysis Oil versus Pyrolysis Oil

	Hydropyrolysis Oil from small batch tests	Pyrolysis Oil	Typical Partially Upgraded Pyrolysis Oil	Typical Catalytic Pyrolysis Oil
% Oxygen	<3	50	8-10	6-10
% Water	<0.5	20	2-3	2-3
Molecular weight	150-200	500-750	na	na
TAN	<2	100	5-20	5-20

- A more upgraded bio-oil fits in refineries better and presents less risk

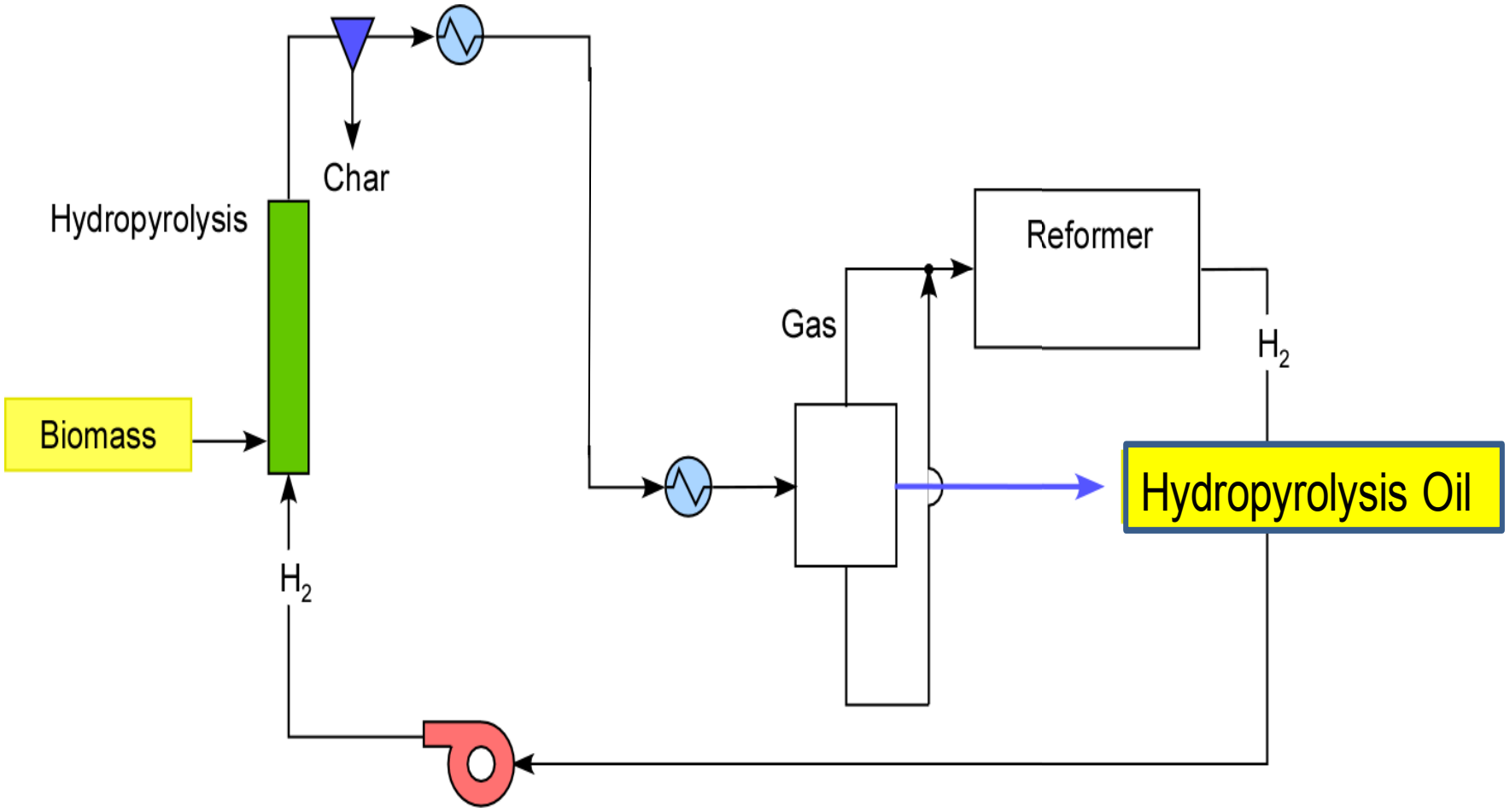
Integrated Hydropyrolysis and Hydroconversion (IH^2)



- Directly make desired products
- Run all steps at moderate hydrogen pressure (200-500 psi)
- Utilize C_1-C_3 gas to make all hydrogen required
- Avoid making "bad stuff" made in pyrolysis – PNA, free radicals

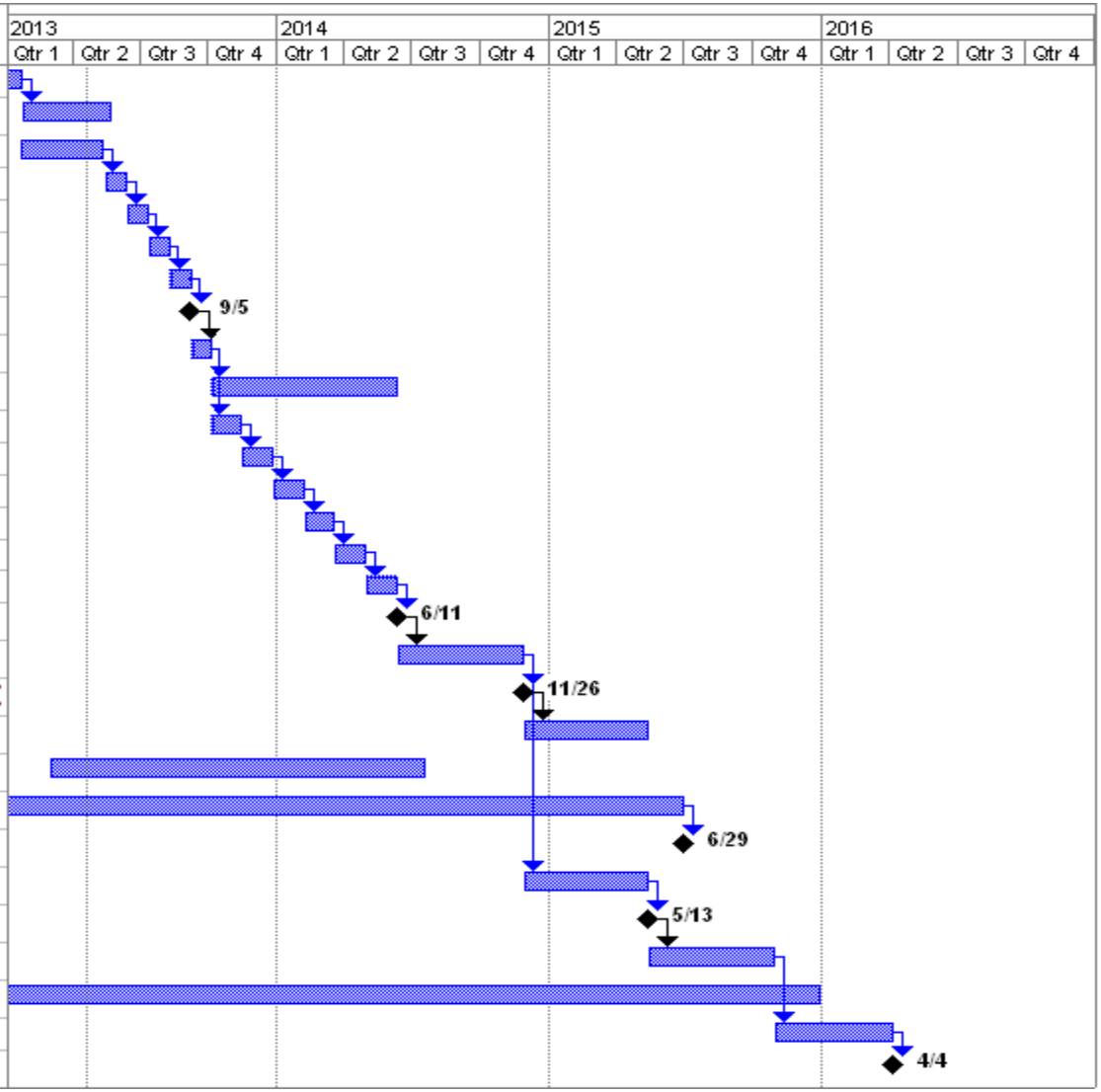
gti

Integrated Hydropyrolysis and Reformer System



Upgrading Hydropyrolysis Oil In a Refinery

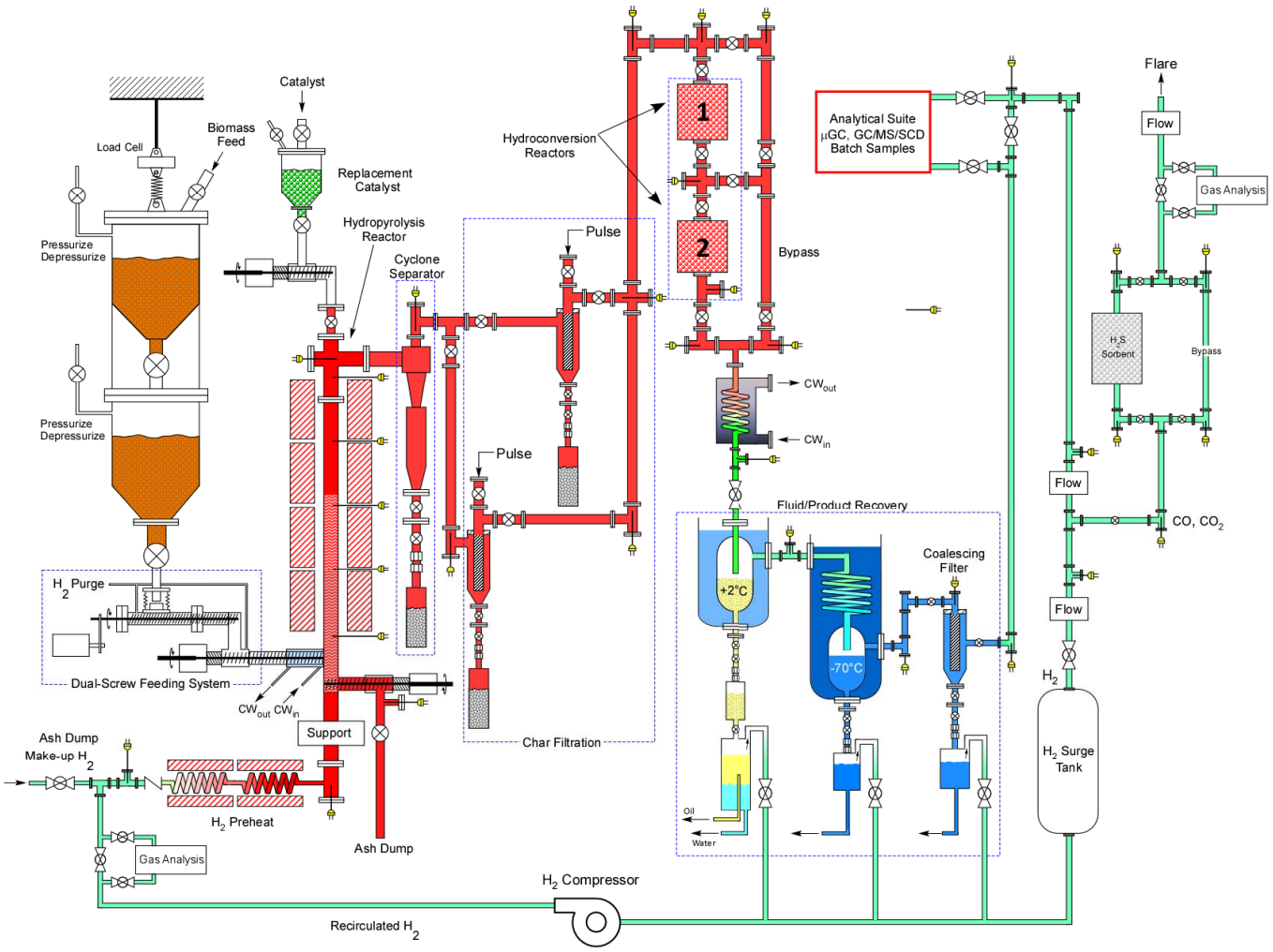
ID	Task Name
1	FEEDSTOCK PROCUREMENT
2	**Prepare Hydropyrolysis Oil**
3	Restart Plant
4	Prepare 25 L of Hydropyrolysis Oil from wood
5	Prepare 25L of Hydropyrysis Oil from cornstover
6	Prepare 25 L of IH2 oil from wood
7	Prepare 25L of IH2 oil from cornstover
8	**HYDROPYROLYSIS OIL PREPARED**
9	**Fractionate diesel and Gasoline cuts**
10	**Hydrotreat oils**
11	Hydrotreat diesel cut from Hydropyrolysis oil from wood
12	hydrotreat diesle cut from hydropyrolysis oil from cornstover
13	hydrotreat gasoline cu from hydropyrolysis oil from wood
14	hydrotreat gasoline cut from hydropyrolysis oil from wood
15	hydrotreat diesel cut for IH2 of wood
16	Hydrotreat diesel cut for Ih2 of conrstover
17	**HYDROTREATING COMPLETE**
18	**Refinery Integration Analysis**
19	**RISK ANALYSIS-OPTIMAL DESIGN REPC**
20	**RIN ANALYSIS**
21	**Feedtock Supply Logistics**
22	**LCA Analysis**
23	**LCA REPORT COMPLETE**
24	**Engineering**
25	**ENGINEERING DESIGN PACKAGE**
26	**Technoeconomic Analysis**
27	**Project Management**
28	Final report
29	**FINAL REPORT COMPLETE**



IH² 50 kg/d Continuous Pilot Plant

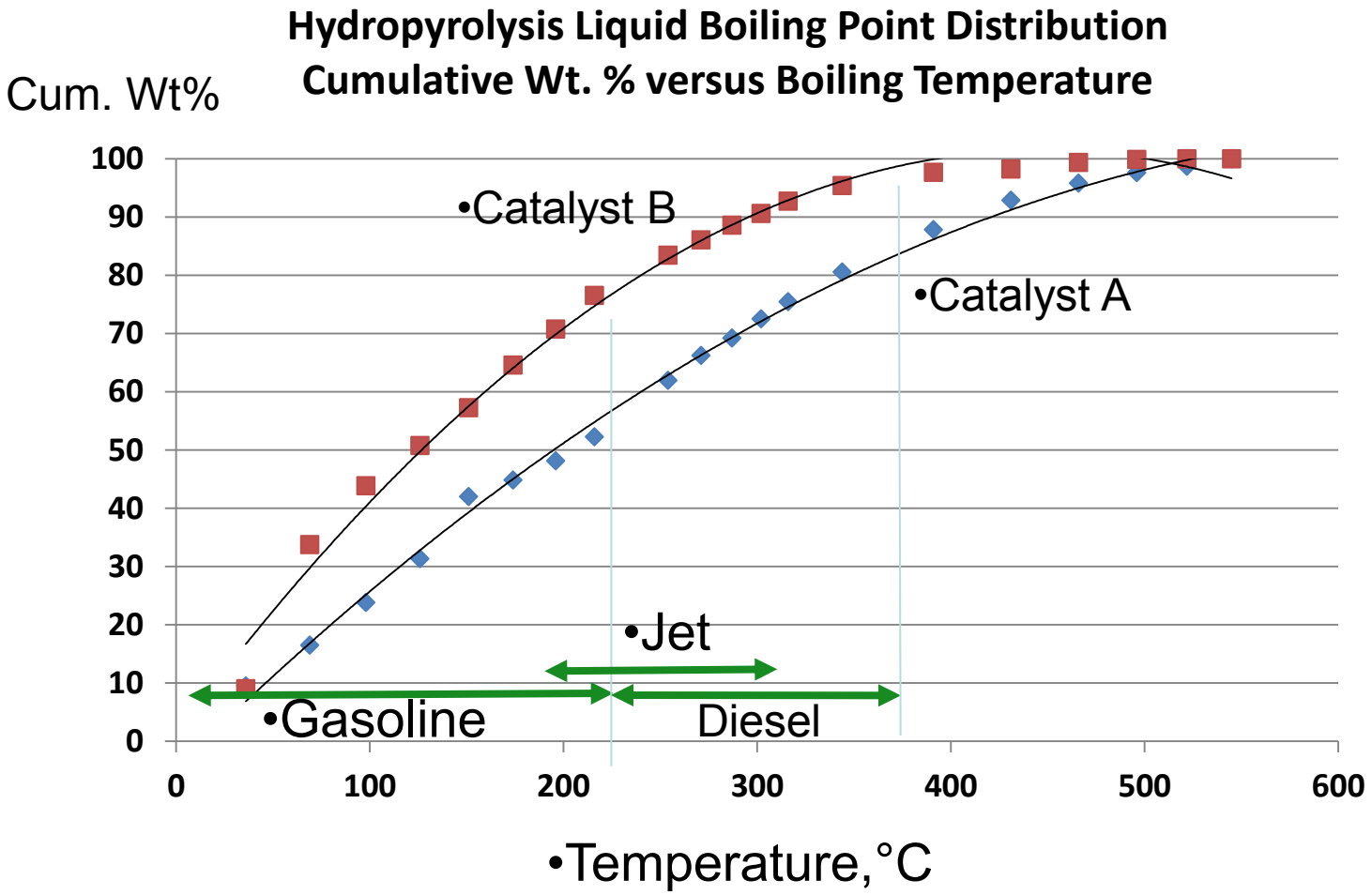
- Only Continuous IH² Pilot Plant in the world

Schematic Diagram of Continuous IH² Process Unit



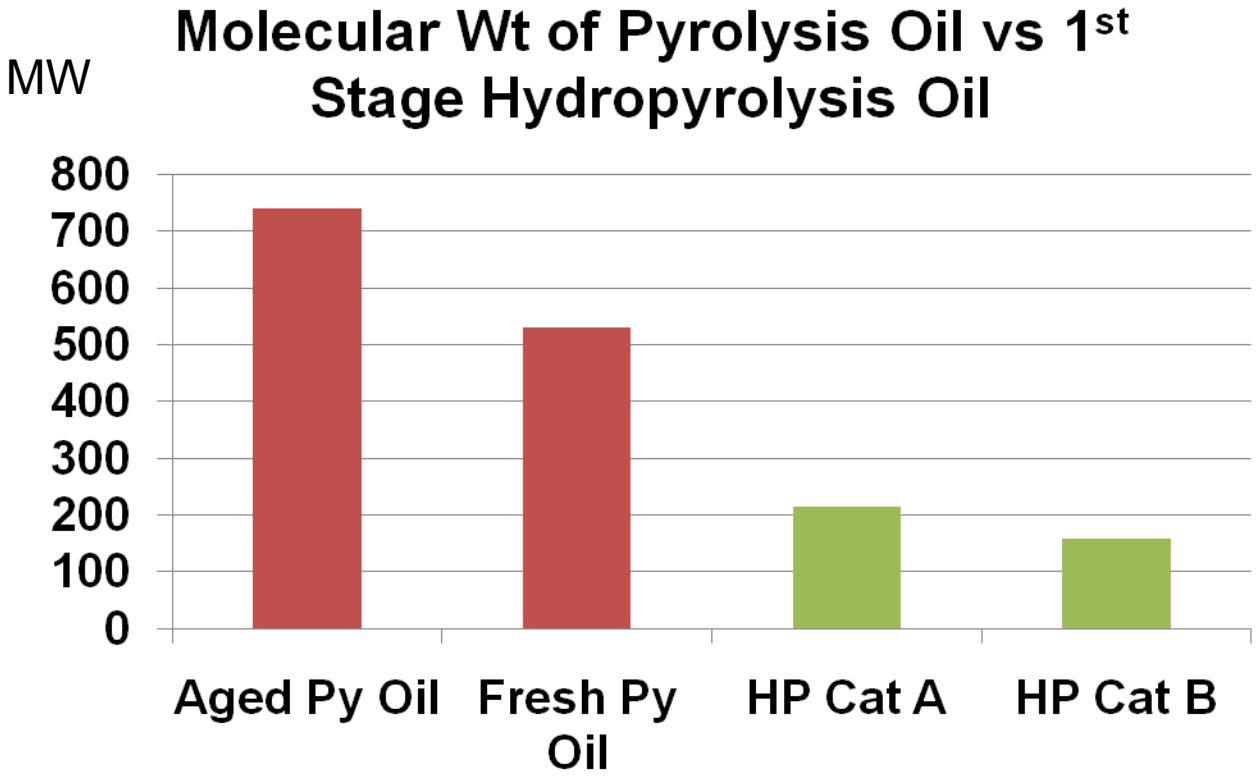
- 2 kg/hr of biomass feed
- Continuous char-catalyst separation
- Continuous operation

First Stage Hydropyrolysis Liquid Boiling Point Distribution from Small Batch tests

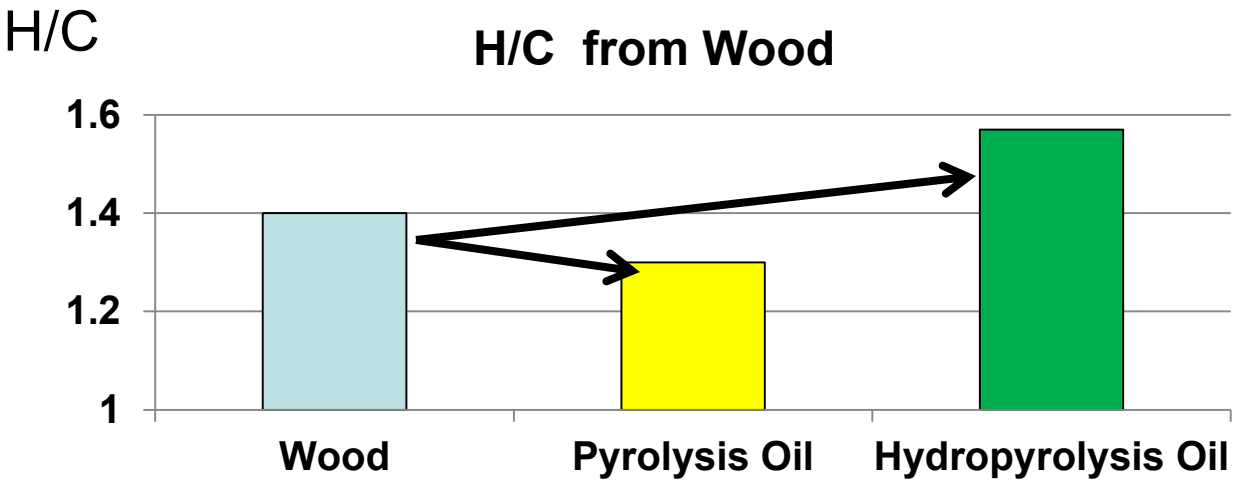


•First stage Hydropyrolysis Liquids have smooth boiling point distribution and are primarily gasoline, jet and diesel

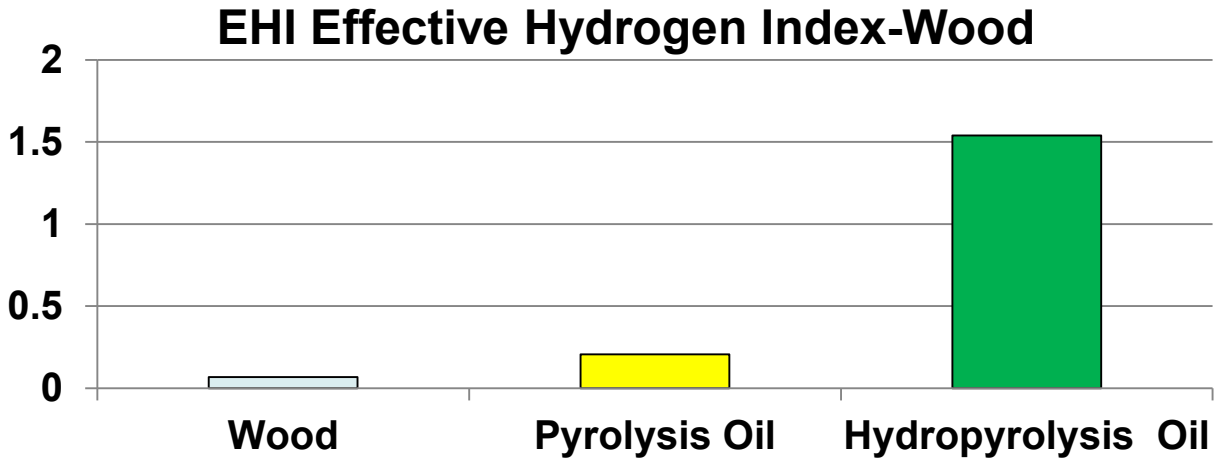
Average Molecular Weight of 1st Stage Hydropyrolysis Oil compared to Pyrolysis Oil



Advantages of Hydropyrolysis vs Pyrolysis



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



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

Conclusions and Future Work

- **Project will look at refinery integration to minimize cost for biomass conversion to gasoline and diesel**
  - **Goal is to work closely with Valero and develop the best possible process integration for refiners**
  - **Project also enables study of hydropyrolysis step alone in IH^2 – very important for hydropyrolysis design**
  - **Project enables continuous testing of hydropyrolysis and IH^2 for cornstover**
  - **Will gather important comparison of risk for IH^2 versus hydropyrolysis from a refiners point of view**
  - **Expect excellent LCA and economics of production (estimated <$2/gallon minimum selling cost)**
- **Remaining work to be done**
  - **Project has just begun so bulk of work remains**
  - **Hydropyrolysis Pilot plant testing to produce hydropyrolysis oil just beginning**