U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Catalytic Conversion of Cellulosic or Algal Biomass plus Methane to Drop-in Hydrocarbon fuels and Chemicals

3/9/2017

Thermochemical Conversion

Terry Marker

GTI

Project Description and Goal

TRL 2 → TRL 4

Bioenergy Technology Incubator Project (DE-FOA-0000974)to improve hydrocarbon liquid yields of Catalytic Pyrolysis and Hydropyrolysis of Biomass through the use of Methane as a fluidizing gas

- Show that Methane plus a hydrogen transfer catalyst can positively influence biomass pyrolysis reactions
- Project Goals: Show that Methane with hydrogen transfer Catalyst can
    - Impact reactions of model compounds
    - Increase hydrocarbon liquid yields in pyrolysis and hydropyrolysis of biomass
    - Reduce hydrogen requirement in biomass and hydropyrolysis
    - Develop a new process which incorporates a methane + hydrogen transfer catalyst and evaluate the technoeconomics of the new process
    - Develop a LCA for the new process

Quad Chart Overview

Timeline

- 4/1/15- 6/15/16 Phase 1
- 11/15/16- 12/31/17 Phase 2
- Percent complete 67%

Budget

	Total Costs FY 12 –FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date)
DOE Funded	0	$564K	$436	$500K
Project Cost Share	0	$141K	$109	$125K

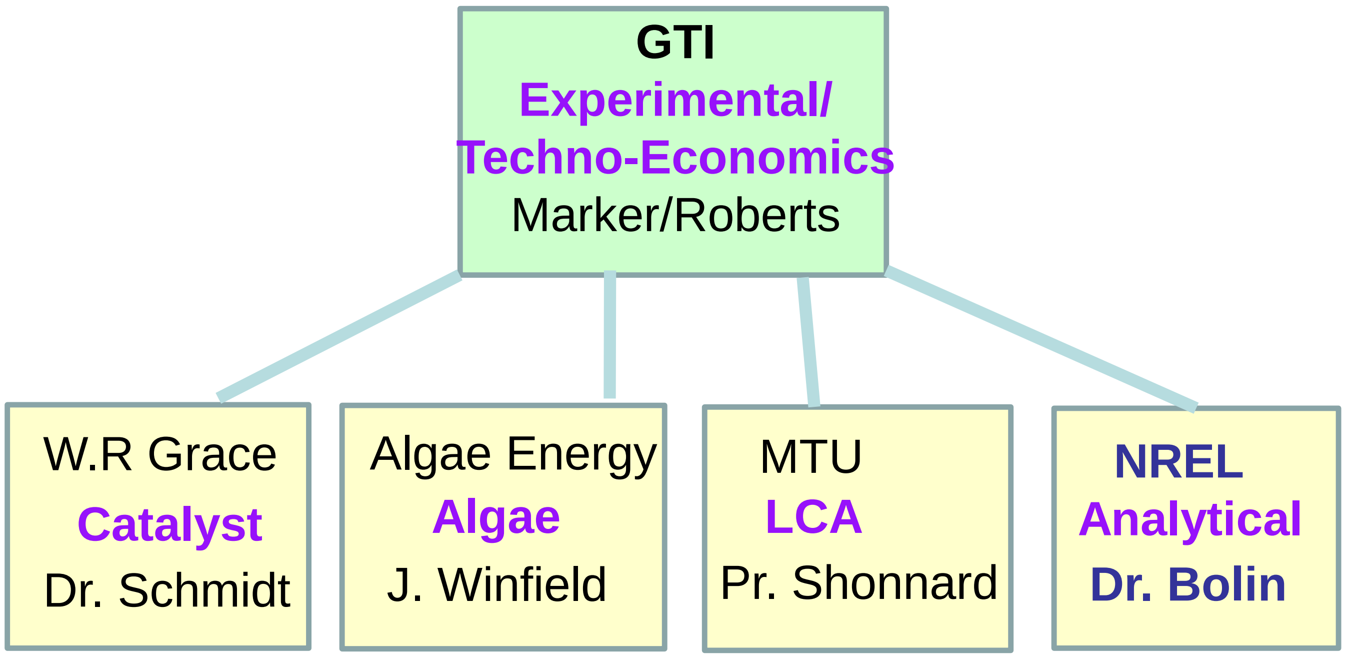
Barriers

- Ct-F Efficient high temperature deconstruction to Bio Oil Intermediates
  - Need for higher yield of biooil
  - Need for improved understanding of tradeoffs of producing high quality biooil or higher yields
  - Need for improved understanding of the impact of feedstock characteristics on biooil yield and quality

Partners

- **GTI**
- **Grace Catalyst**
- **Algae Energy**
- **MTU**
- **NREL**

1- Project Overview
Bioincubator Project Team



1- Project Overview - Technical Background

- **Choudary reported 29-36% methane conversion at 500-600°C with light olefins and paraffins over Ga-ZSM-6 catalyst (strong H2 transfer catalyst)**

  $2CH_4 + 2C_nH_{2n} \rightarrow 2C_nH_{2n+2} + C_2H_4$

  $2C_nH_{2n+2} \rightarrow 2C_nH_{2n} + 2H_2$

  C2-C4 alkenes → C6-C10 olefins → aromatics

- **Steinberg reported that for biomass pyrolysis there is a difference in products for non-catalytic pyrolysis of biomass with methane as fluidizing gas, instead of nitrogen. More ethylene, benzene, and CO is produced when methane is used instead of nitrogen as fluidizing gas. Steinberg concludes free radicals produced from the devolatilization reacted with the methane.**

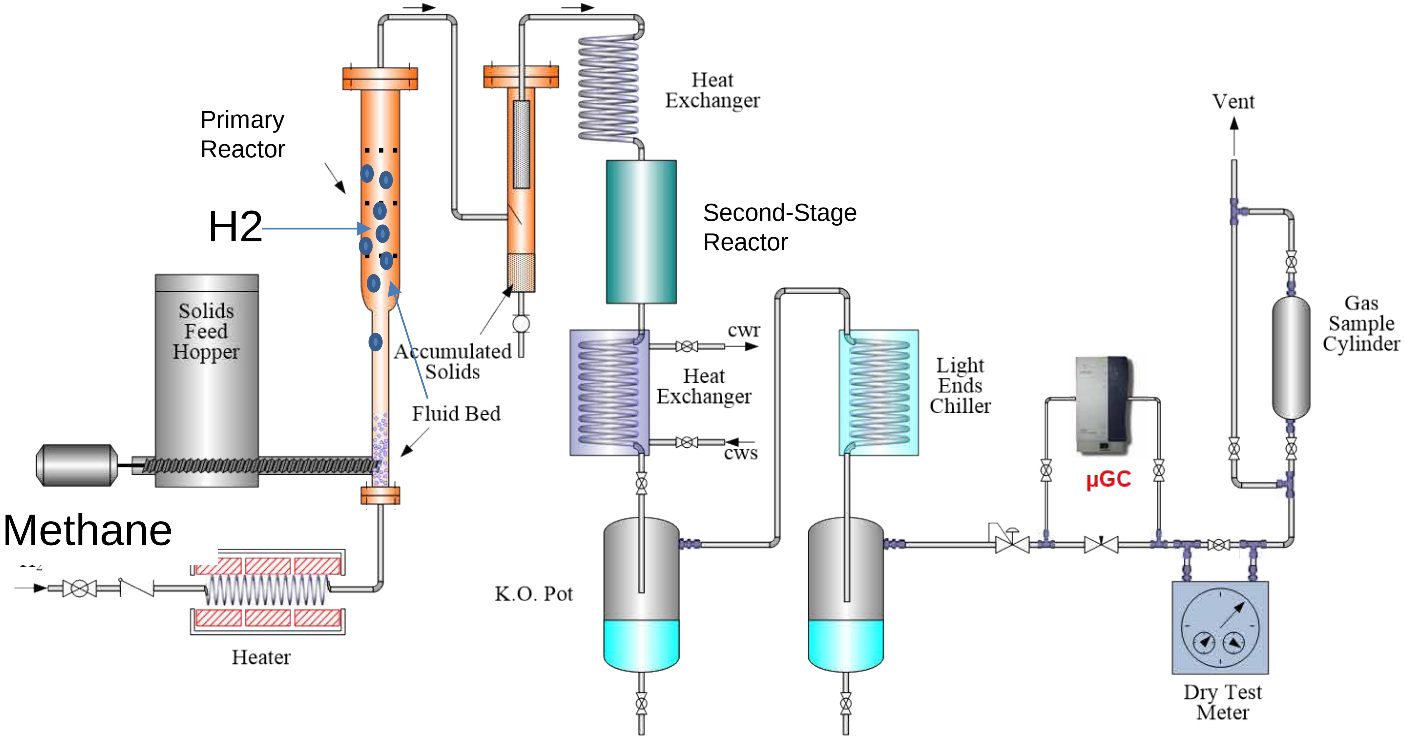
Can we duplicate these results and show improvements in pyrolysis and hydropyrolysis yields or a reduction in hydrogen use when methane is used as a fluidizing gas with a strong hydrogen transfer catalyst ?

2 – Approach

- **Pilot plant tests to study pure component reactions (methane and olefins) with high hydrogen transfer catalysts**
- **Pilot Plant Tests to study catalytic conversion of biomass in methane and methane plus hydrogen**
- **Detailed Analysis of Liquids produced via NREL (newly added part of phase 2)**
- **Technoeconomic analysis of process improvements**
- **LCA of process improvements**

2- Approach – Equipment Utilized

Semi-Continuous Lab Unit



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

Dedicated laboratory unit for process testing.

2 – Approach - Potential Challenges

- Methane is difficult to activate- can it be used to effect reactions with the right catalyst
- Finding the best catalyst to utilize the methane
- Developing a viable commercial approach which significantly improves hydropyrolysis, or catalytic pyrolysis through the use of methane plus hydrogen transfer catalysts

2 – Approach – Critical Success Factors

- Increase hydrocarbon liquid yields
- or Improve hydrocarbon liquid quality
- or Decrease Hydrogen requirements
- or Decrease Reformer costs

Note: This project had just started as of 2015 peer review,

3-Technical Accomplishments/ Progress/Results

- Modified Bench Scale equipment to go to higher temperature and run a variety of feed gases
- Obtained wood and algae feeds for testing
- Obtained high hydrogen transfer catalyst (Ga-ZSM-5 and hydrocracking catalyst)
- Completed pure component testing of methane with ethylene, ethane and propane
- Completed some wood –methane tests in pyrolysis and hydropyrolysis

•Key Milestones

- Demonstrated that Methane can donate H2 to olefins when hydrogen transfer catalyst is present
- Demonstrated increased deoxygenation, improved liquid product quality, reduced char yields for Catalytic methane enhanced pyrolysis
- Demonstrated 16% increase in hydrocarbon liquid yield for IH2 through temperature increase

3- Technical Accomplishments

Comparison to Choudhary

	Choudhary	Choudhary	GTI
Feed	1:1 CH_4:C2=	1:1 CH_4:C2=	1:1CH_4:C2=
Catalyst	Ga-Zsm-5	Ga-Zsm-5	Ga-Zsm-5
Temperature, °C	550	600	570
Pressure, psia	15	15	20
% C2= conversion to aromatics	94	99	40
% methane conversion to aromatics	29	36	-7.2
% methane produced			7.2

At these conditions, methane is actually made from ethylene and **NOT** consumed as reported by Choudhary

3 Technical Accomplishment -Effect of Excess Methane on Ethylene Reaction (400C,400psi, NiW catalyst)

Feed	11:1 N2/C2=	11:1 CH4/C2=	11:1 H2/C2=
% hydrogen	2.6	1.3	0
% methane	2.8	-1.0 to -5.0 (methane consumed)	24.9
% ethylene	8.6	44.0	0
% ethane	15.7	30.6	80.4
% propane	4.5	1.3	0
% propylene	9.2	6.9	0
% C4 gas	16.5	7.7	0
% liquids	14.9	0	3.3
% coke	25.5	7.9	0
% H2 added	0	2.3	8.3

Shifted to lower temperature, higher pressure, different catalyst to get H2 transfer
Methane can actually transfer its H2 and behave like a hydrogen substitute

Wt% Products from Ethylene reaction in excess N_2 vs Methane using Ga-ZSM-5 Catalyst at 400C, 400 psi

Feed	11:1 N2/C2=	11:1 CH4/C2=	%difference
% hydrogen	1.4	1.0	
% methane	6.6	-1.2	
% ethylene	0.6	0	
% ethane	8.8	14.7	+ 67 %
% propane	16.3	24.1	+ 48 %
% propylene	0.9	0.3	
% C4 gas	9.2	7.9	
% liquids	56.5	51.5	
%coke	0	0	
% H2 added	0	0	

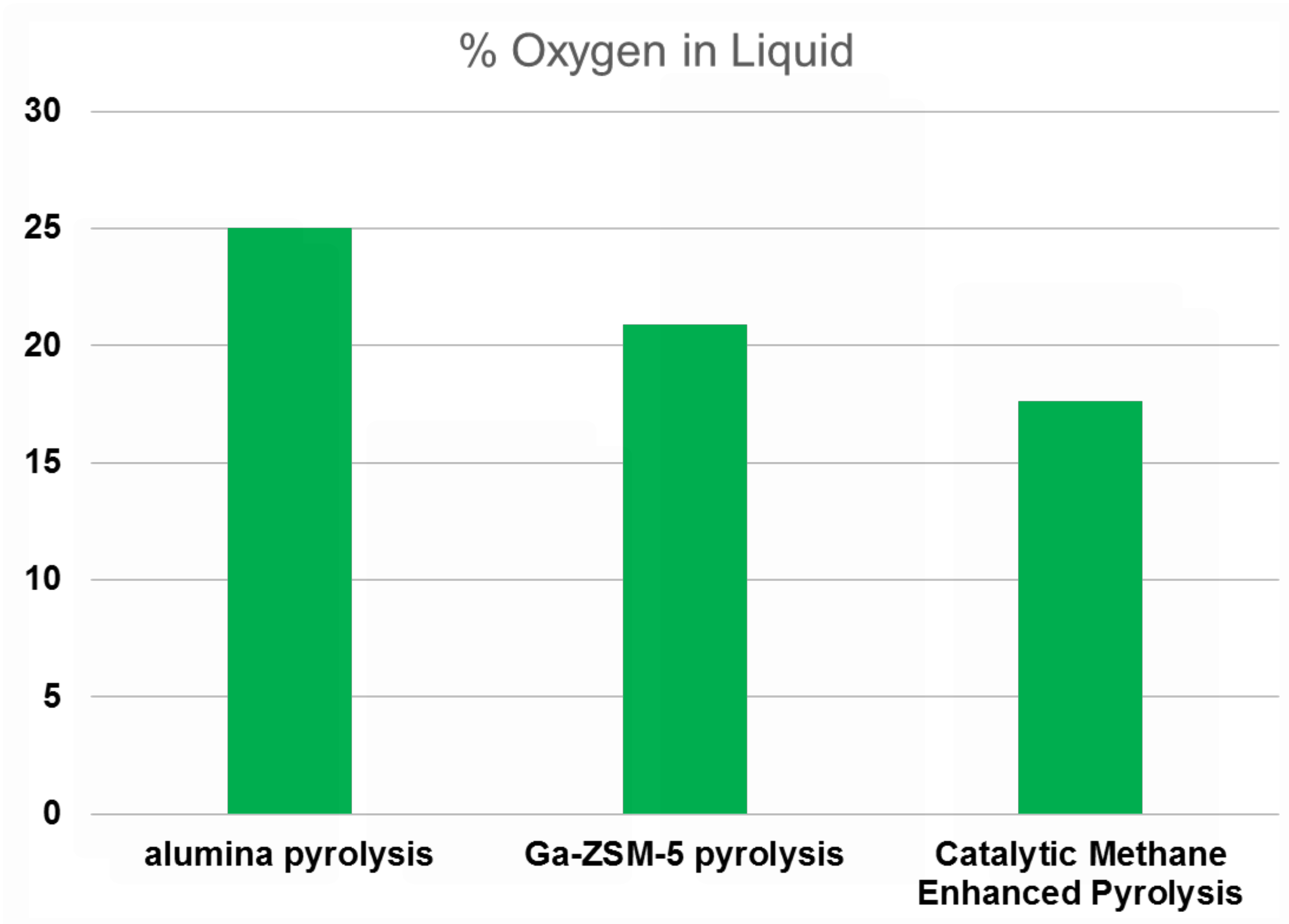
Methane atmosphere produces more saturates

Ga-ZSM-5 not as good at saturating as hydrocracking catalyst

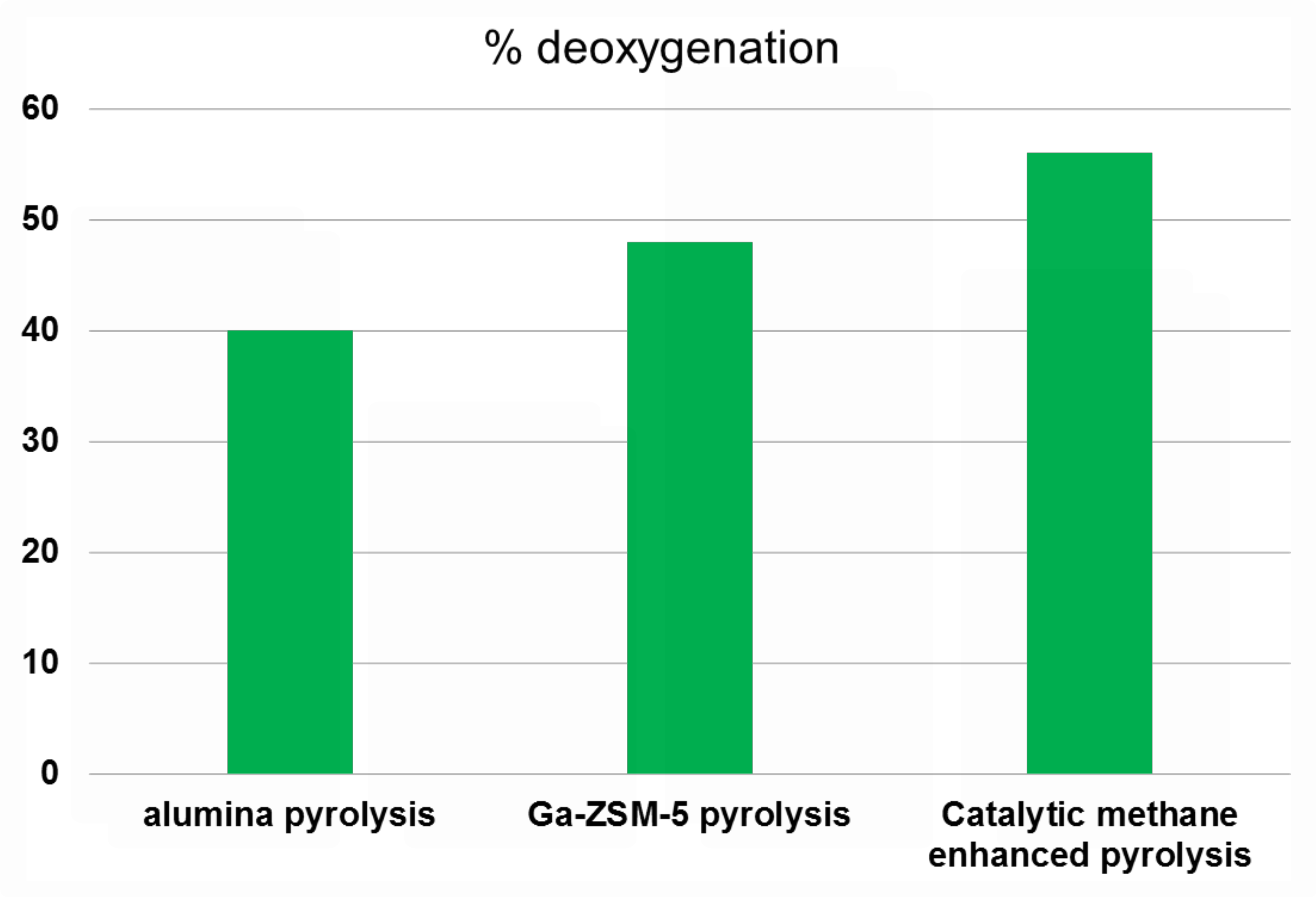
3-Wood Biomass Conversion - Comparison of Catalytic Pyrolysis and Catalytic Methane Enhanced Pyrolysis

	Catalytic Pyrolysis alumina	Catalytic Pyrolysis Ga-ZSM-5	Catalytic (Ga-ZSM-5) Methane Enhanced Pyrolysis
Catalyst	Alumina	Ga-ZSM-5	Ga-ZSM-5
Fluidizing gas	Nitrogen	Nitrogen	Methane
filter pressure problem	P increase	no	no
Wt% C4+HC Liquid Yield	21.9	18.7	18.7
Wt % O in liquid	25.0	20.9	17.6
Wt % Water in liquid	10.6	6.6	5.5
% deoxygenation	40	48	56
% biogenic liquid	100	100	100
Wt % C1-C3 HC gases	1.1	19.4	7.3
Wt % CO+CO2	15.5	14.2	29.8
Wt % water (phase)	34.9	27.4	31.8
Wt% C in water	15.8	11.4	10.2
Wt % char	26.6	19.5	12.4

Oxygen Reduction in Hydrocarbon Liquid Phase with Catalytic Methane Enhanced Pyrolysis



% Deoxygenation with Catalytic Methane Enhanced Pyrolysis



3 Technical Accomplishments - Demonstrated Improved Yields in IH^2® by Raising Temperature

	IH^2 ® Base Case	Improved Yield Case	% change
Temperature, C	400	482	
pressure, psia	325	325	
fluidizing gas	H2	H2	
Wt% Hydrocarbon Liquid Yield	25.8	**30.0**	+16%
Wt % Yield increase from base	BASE	16.3	
Wt %O in liquid	**<0.4**	**<0.4**	
Wt % methane +ethane +propane	14.5	15.4	
Wt %CO+CO2	13.9	13.6	
Wt % water	37.0	36.8	
Wt % char	13.4	9.8	
Wt % H2 added	4.6	5.5	

Nice improvement for IH ® if it doesn't increase rate of catalyst deactivation

3 Technical accomplishment -Ga-ZSM-5 in IH^2® 2nd stage Increases % Diesel in Hydrocarbon Liquid Product

	Improved Yield Case	Ga-ZSM-5 in 2nd stage +HT catalyst
Temperature, F	900-950	900-950
pressure, psa	325	325
Fluidizing gas	H2	H2
Wt% Hydrocarbon Liquid Yield	30.0	26.4
Wt % Yield increase from base	16.3	2
Wt %O in liquid	<0.4	<0.4
HC liquid density	.815	.835
% diesel in liquid product (the rest is gasoline)	**16.8**	**23.6**
Wt % methane +ethane +propane	15.4	15.7
Wt %CO+CO2	13.6	13.9
Wt % water	36.8	39.6
Wt % char	9.8	9.7
Wt % H2 added	5.5	5.3

Added Ga-ZSM-5 (more acidic catalyst) to second stage increased aromatics, diesel fraction. Catalyst acid= more polymerization

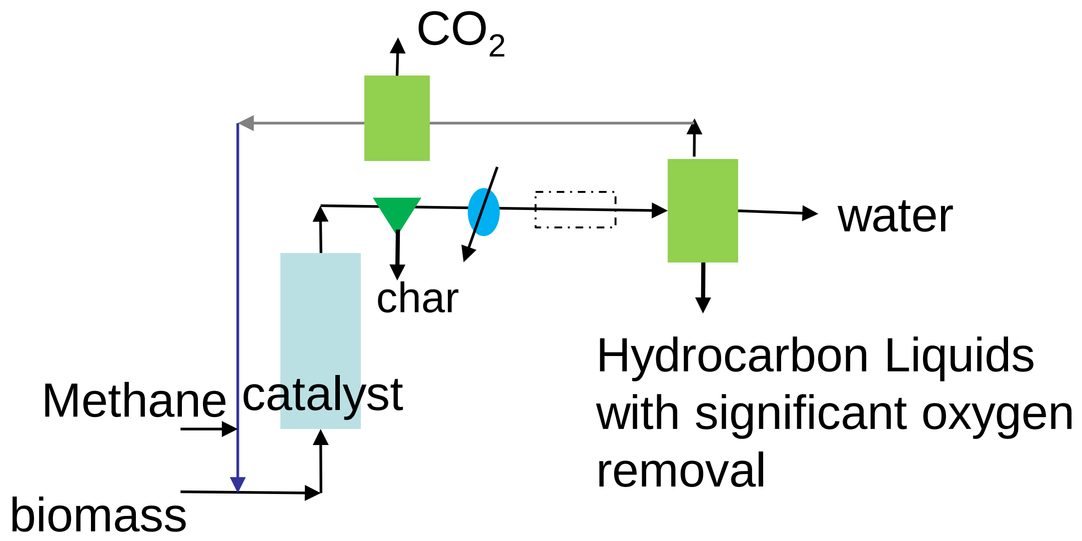
3 Technical Accomplishment- Showed methane can be recycled with hydrogen- Simpler reformer possible

	Ga-ZSM-5 in 2nd stage +HT catalyst	Ga-ZSM-5 in 2nd stage + methane+ higher pressure	Ga-ZSM-5 in 2nd stage +methane
Temperature, F	900	900	900
pressure, psa	325	408	325
fluidizing gas	H2	H2 +CH4(20%)	H2+CH4(20%)
Wt% Hydrocarbon Liquid Yield	26.4	26.2	24.5
Wt %O in liquid	<0.4	<0.4	<0.4
HC liquid density	.835	.837	.833
% diesel in liquid product (rest is gasoline)	23.6	22.9	22.4
Wt % methane +ethane +propane	15.7	16.4	20.2
Wt %CO+CO2	13.9	15.4	18.2
Wt % water	39.6	38.1	36.0
Wt % char	9.7	9.0	9.0
Wt % H2 added	5.3	5.1	5.1

Adding methane to H2 in IH^2® didn't have a large effect – means substantial methane could be recycled.

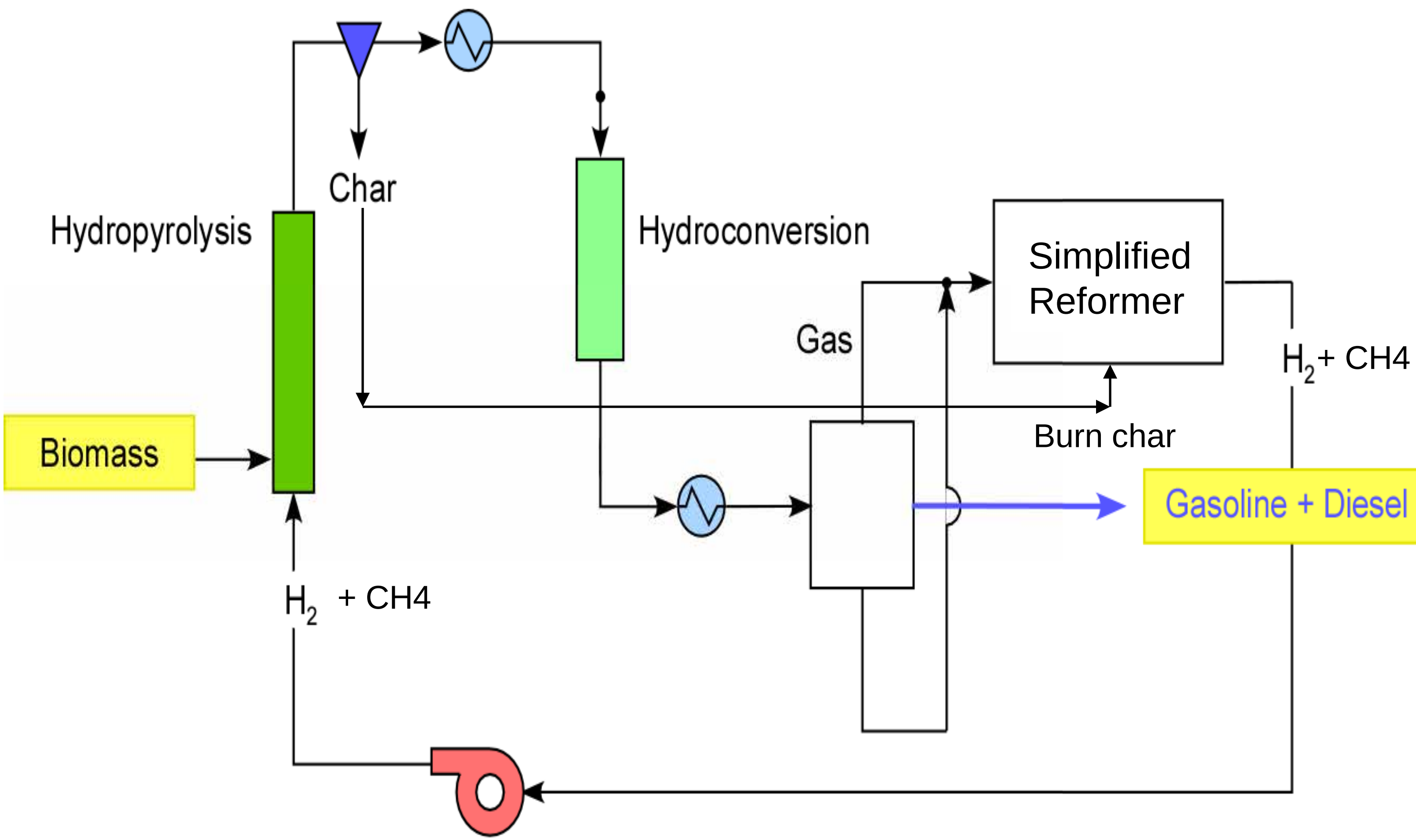
New Vision 1

Catalytic Methane Enhanced Pyrolysis



- Significantly upgraded hydrocarbon liquids with lower char yield and easier upgrading
- High hydrogen transfer catalyst uses hydrogen from methane to upgrade liquids avoid need for hydrogen plant – Transport to refinery for final polishing
- Best for small modular, mobile systems – low cost easy system

New Vision 2 – Methane Enhanced IH²®



Lower Capital- Simplified Reformer which recycles some methane

TEA of modified reformer currently under study

4-Relevance

- Directly supports BETO mission:
  - “Develop and Transform our biorenewable biomass resource into commercially viable high performance biofuels”
- **Directly addresses BETO’s 2017 target for Bio-Oils Pathways R&D of a conversion cost of $1.83 per gallon of total blendstocks**
  - Showed higher deoxygenation in catalytic pyrolysis with methane than catalytic pyrolysis without methane
  - Showed higher yields of drop in hydrocarbon liquids
  - Showed increased flexibility to make more diesel products
  - Will show lower capital for IH^2® reformer step- Expect to cut reformer costs in half
  - Some improvement directly transferable to IH^2®.
  - Some improvements directly transferable to catalytic pyrolysis

Future Work

- **Additional experiments** to optimize Catalytic Methane Enhanced Pyrolysis/Hydropyrolysis
  - Goal of higher Hydrocarbon liquid yields with lower Oxygen content
- **Enhanced Analytical** on hydrocarbon liquids from Catalytic Methane Enhanced Pyrolysis
- **TEA** to quantitate value of all improvements
- **LCA** to quantitate environmental benefits of all improvements

Summary

- Methane can change the distribution of products from olefin polymerization-donating hydrogen when H2 transfer catalyst used
- **Catalytic Methane Enhanced Pyrolysis of Biomass has benefits, of more upgraded hydrocarbon liquids**, possibly slower catalyst deactivation in a mobile, compact, low cost system

- **Showed significant levels of methane can be recycled with no problem in IH^2® – ie simpler reformer possible**
- **Increased IH^2® drop-in liquid yields to 30% by increasing temperature**
- **Showed we can adjust toward more diesel in IH^2® by using a more acid catalyst – product slate can be controlled with catalyst/conditions in IH^2®**

- Results will be published – Choudary's results not duplicable but some effects of methane + catalyst evident

UPDATE ON IH²® DEMONSTRATION UNIT

- 5 t/day Demonstration IH²® plant
- Funded by CRI Catalyst, a division of Shell
- IH²® plant Built by Zeton
- Hydro-Chem providing small integrated H2 plant
- Arrived and will be installed at Shell R&D facility in Bangalore, India
- Expected to be operational by July 2017
- Wood feed to start
- Once operational, several commercial IH²® plants expected

IH² ® 5t/day Demonstration Plant

DOE funding helped develop IH²®

UPDATE ON IH^2® DEMONSTRATION UNIT

IH2® 5ton/day being assembled in Bangalore, India, at Shell Research Center
Feb 2017

Additional Slides

3. Pure Component Results Summary
Reactions of methane with olefins and light paraffins

- GTI could not duplicate Choudhary results which showed 36% conversion of methane to aromatics over Ga-ZSM-5 catalyst when reacted with ethylene at 500-600C. We believe Choudhary results/data are in error

- GTI did find that when ethylene is reacted over hydrocracking catalyst when excess methane present, hydrogen is donated from the methane and a small amount of methane is consumed. The products of ethylene conversion when methane is present have **less coke, and the gases and hydrcocarbon liquids contain more hydrogen than those produced in a nitrogen atmosphere.**

- Ga-ZSM-5 is also good at converting light paraffins to aromatics

- **Conclusion : Methane isn't as reactive as Choudhary reported, but can donate hydrogen to olefins when used with a strong hydrogen transfer catalyst.**

Experimental Plans for Phase II

	Catalytic Methane Enhanced Pyrolysis
Higher pressure	X
Hydrocracking Catalyst	X
Increased temperature	X
Second stage	X
Algae testing	X

- New Process around Catalytic Methane Enhanced Pyrolysis
- In process of filing provisional patents for CMEP
- TEA and LCA

Simpler Steam - Methane, Ethane and Propane - Reformer

- **Use special very active sulfur tolerant catalyst**
- **Burn char to provide heat**
- **Run at 1200F**
- **No clean up required – reduces pots and pans**