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

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Executive Summary

The goal of this Bioincubator Project was to improve the pyrolysis of biomass through the use of methane. Our initial concept was to use methane as a fluidizing gas with a hydrogen transfer catalyst. The results of the experiments did show that methane as a fluidizing gas, with a hydrogen transfer catalyst, does enhance catalytic pyrolysis over that which is achieved with an inert fluidizing gas. Using methane as a fluidizing gas, with a hydrogen transfer catalyst, consistently produced better products with lower oxygen content than the products produced when an inert gas was used. These improvements were also consistent with the results obtained through pure component testing as well.

However, the improvement was too small to justify any significant expense. The addition of hydrogen with a hydrogen transfer catalyst consistently showed a much greater, more significant effect than methane. This indicates that hydropyrolysis is a more effective approach to improved catalytic pyrolysis than methane addition.

During the course of this project, another way to significantly increase biogenic liquid yields from pyrolysis through the use of methane was discovered. We discovered a remarkably stable CO_2/steam reforming catalyst which directly makes a 2:1 H_2/CO synthesis gas from the CO, CO_2, methane, ethane and propane product gas from integrated hydropyrolysis and hydroconversion (IH$^{2®}$). The biogenic synthesis gas can then be converted to liquid hydrocarbons using Fischer Tropsch. The hydrogen for the IH^2 unit would then be provided through the use of added methane. By utilizing the biogenic gas to make liquids, 40% more biogenic liquid hydrocarbons can be made from wood, thereby increasing liquid yields from IH^2 from 86GPT to 126GPT. It also simplifies the hydrogen plant since no CO or CO_2 removal is required. Figure 1 shows the new IH^2 high yield system

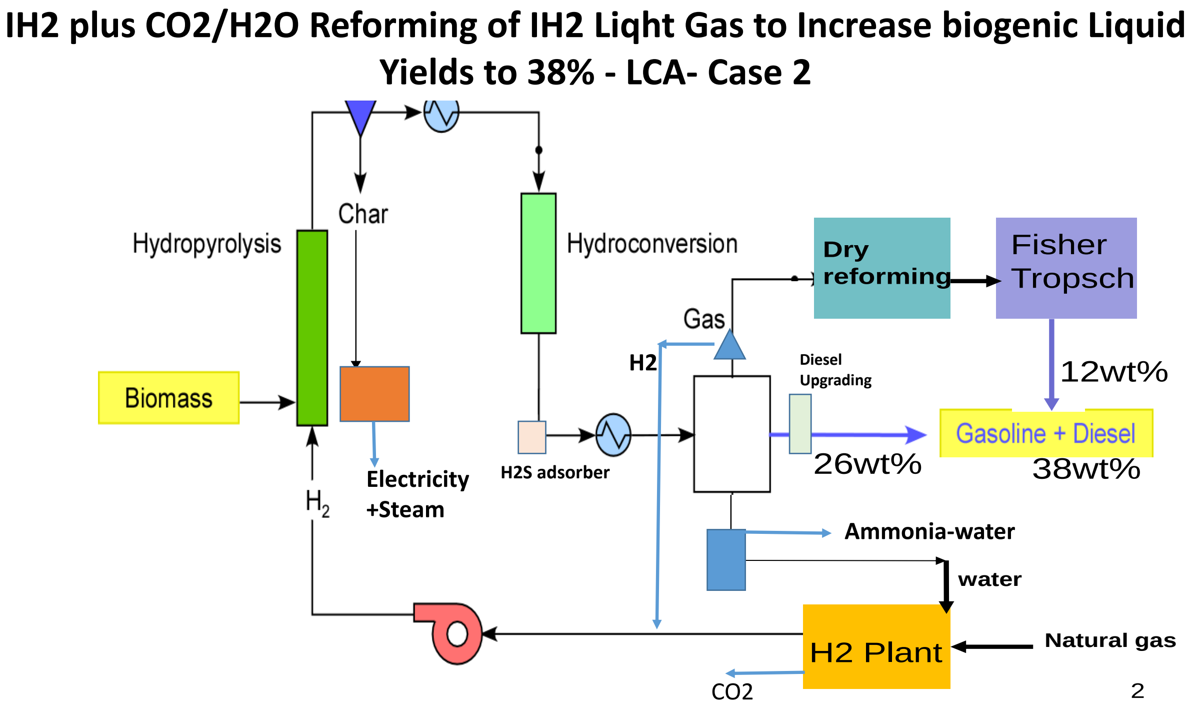

IH2 plus CO2/H2O Reforming of IH2 Liqht Gas to Increase biogenic Liquid Yields to 38% - LCA- Case 2

Figure 1- IH^2 plus Cool GTL to increase biogenic Liquid Yields from wood

This new catalyst discovery allowed us to develop a unique low cost method of converting CO_2 or CO containing methane, ethane, and propane gases to liquids. GTI has named this new gas to liquid (GTL) process “Cool GTL.” Cool GTL has multiple applications for the conversion of biogases and also CO_2

containing natural gas to liquids. Detailed development of this new GTL process was done using internal GTI follow-on funding, but the results from these tests are included in this report because the stable CO_2/steam reforming catalyst was discovered during this project. This new approach also met the original objectives of the project to increase biomass liquid yields through the use of methane. Therefore; this discovery turned the project from a mild success to a step change improvement in total hydrocarbon liquid yield.

Project Objectives

The goal of this Bioincubator Project was to improve the pyrolysis and hydropyrolysis of Biomass through the use methane. Our specific plan was to try to improve catalytic pyrolysis by using methane as a fluidizing gas, with a strong hydrogen transfer catalyst to improve liquid yields and quality.

The project objectives are a methane plus hydrogen transfer catalyst can:

1. Impact reactions of model compounds
2. Increase liquid yields in biomass pyrolysis and hydropyrolysis
3. Reduce hydrogen requirement in biomass and hydropyrolysis
4. Develop a new process which incorporates methane + hydrogen transfer catalyst and evaluate technoeconomics of the new process
5. Develop lifecycle analysis (LCA) for new process

As such, the goal of the project is to take the methane enhanced pyrolysis or hydropyrolysis from a TRL-2 to a TRL-4- i.e. to take the process from a concept stage to a bench stage. This is shown in Figure 2.

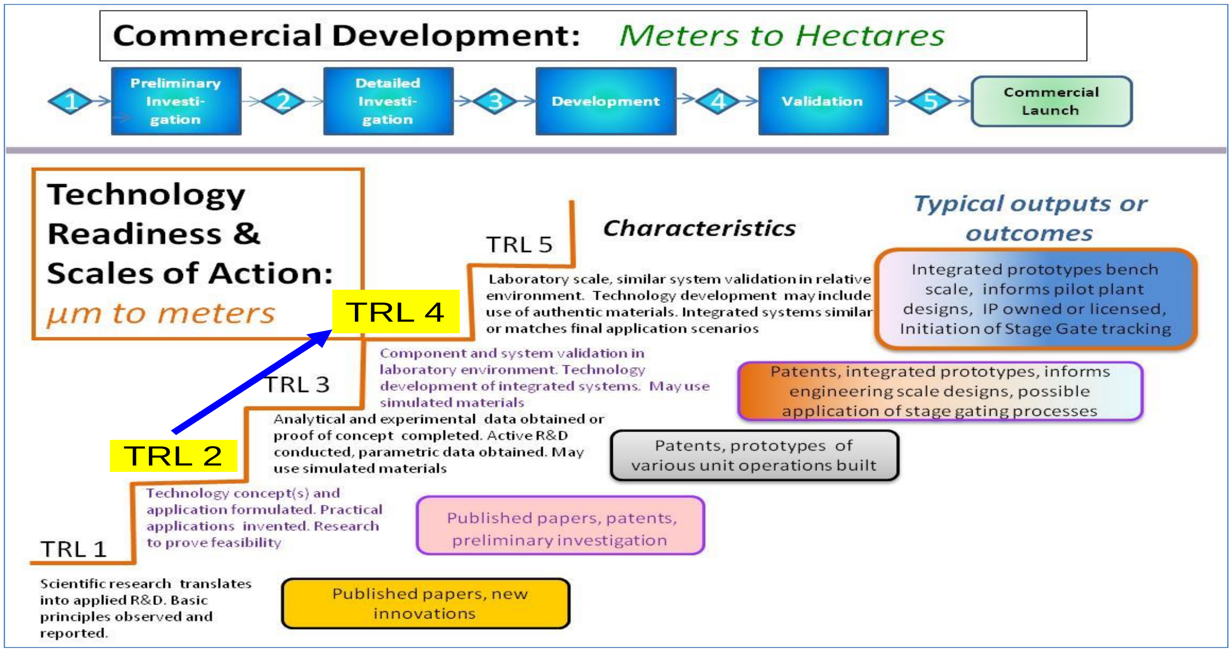


Figure 2- TRL-2 to TRL 4

Background:

There have been several studies, which have shown methane can be catalytically activated at pyrolysis conditions and that pyrolysis with methane yields different products than either pyrolysis with hydrogen or with inert gas. The use of methane to convert biomass in a high pressure (200-400 psi) catalytic fluidized bed has never before been tested, making this a totally novel approach.

Choudhary reported that methane may become activated at pyrolysis temperature when olefins and hydrogen transfer catalysts are present. Choudhary[1] reported per pass conversion of methane to aromatics of 45% when 50 mole % butene was present at 500°C with H-Galloaluminasilicate (Ga ZSM-5) catalyst. The key reactions are as follows:

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

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

C2-C4 alkenes→C6-C10 olefins→aromatics

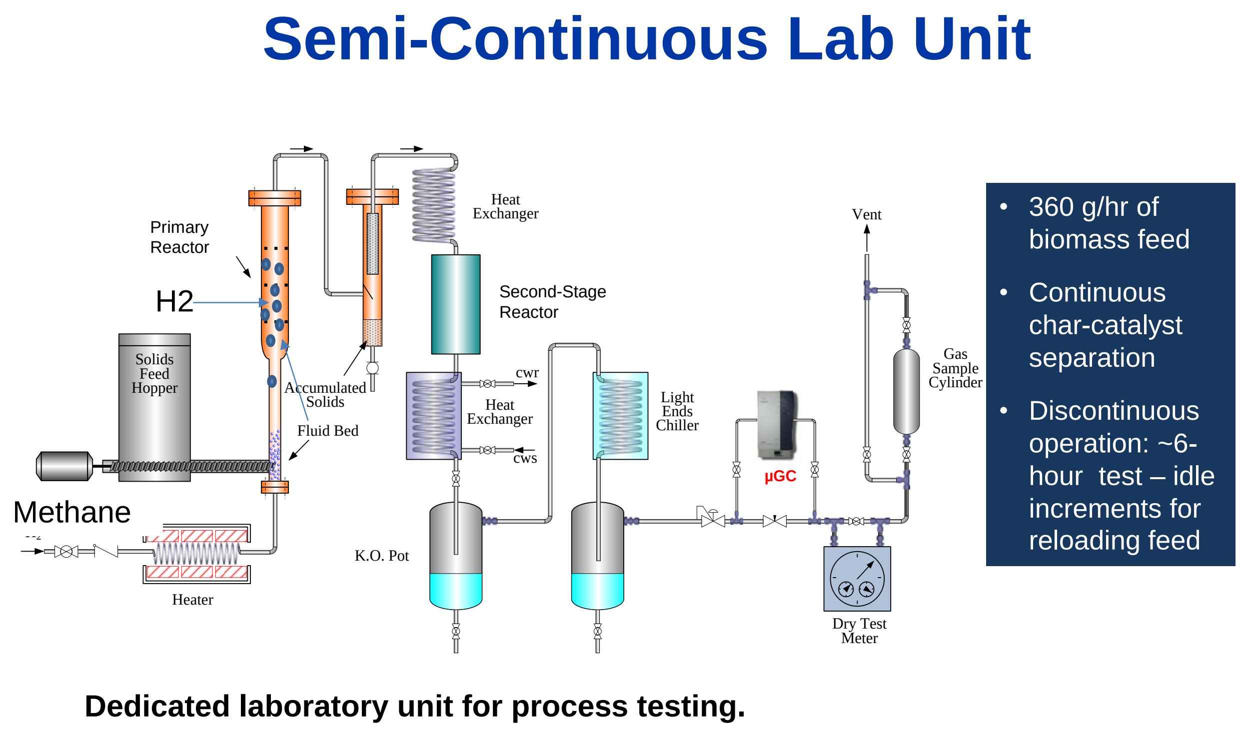
According to Choudhary, the methane is used to donate its hydrogen to saturate the olefin and then reacts further to produce additional olefins and aromatics.

Choudhary postulated that methane activation in the presence of alkene over the H-GaZSM-5 zeolite occurs over the non-framework Ga-oxide species. The C-H bond cleavage takes place by hydride transfer from the partially activated methane to the carbonium ion. The methylinium ion (CH_3+) formed in this reaction is rapidly decomposed and releases the proton and CH_2 radical and then the CH_2 radical rapidly dimerizes to ethene. The presence of the carbonium ion is therefore essential for the cleavage of the C-H bond. Because of the very large change in free energy that would be involved, the direct formation of benzene from methane at less than <600°C is thermodynamically impossible without the olefin additives. The thermodynamic barrier is reduced or eliminated by the addition of alkenes or higher alkanes. The Gibbs free energy approaches zero, or even becomes negative depending on the additive and its concentration relative to methane. For example, for an n-butene/methane ratio of 1.0, the Gibbs free energy is -4.1kcal/mole at 500°C and -10.6kcl/mole at 600°C.

A non-catalytic, high temperature (650°C-1000°C) study by Steinberg[2] of biomass flash pyrolysis showed different products were formed from woody biomass when inert gas, methane, or hydrogen were used as the fluidized gas during pyrolysis. When hydrogen was used, mostly methane, water, and CO was produced. When methane was used, mostly ethylene, benzene, and CO was produced. Pyrolysis of biomass with methane fluidizing gas produced 2-7 times more ethylene than when a nitrogen or helium inert fluidizing gas was used. Steinberg concluded that the free radicals produced from the devolatilization of wood interacted with the methane. Likewise, it has been shown in heavy crude upgrading with methane[3,4], that the methane was actually incorporated into the liquid produced. Furthermore, it has been shown by Calkins[5], that coal flash pyrolysis in the presence of methane produces more lower molecular weight hydrocarbons than flash pyrolysis of coal in the presence of nitrogen.

Experimental equipment:

The experimental equipment used for this project was the semi-continuous laboratory unit shown below, modified to allow the use of multiple gases.



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.

Figure 3-Dedicated Laboratory Mini Bench Unit (MBU) for Process testing

Model Compound Testing:

The initial goal of the project was to reproduce and confirm the results of Choudhary. Choudhary reported 29-36% methane conversion to liquids at 500-600ºC with light olefins and paraffin over Ga-ZSM-6 catalyst (strong hydroden transfer catalyst). Experiments were done at the same conditions used by Choudhary with methane and ethylene, ethane or propane at 500-600ºC. A few experiments were done to vary the Si/Al ratio of the Ga-ZSM-5 to see if that could have an effect. Unfortunately at these conditions, we consistently made methane from the light paraffin and did not convert the methane to liquids. Typical results are shown in Table 1.

Table 1- Experimental Results for Conversion of 1:1 Methane + Ethylene over Ga-ZSM-5 at 5 psig at 600ºC - Choudhary vs GTI

	Choudhary	Choudhary	GTI
% C2= conversion to aromatics	94	99	40
% methane conversion to aromatics	29	36	-7.2
% methane produced			7.2

Additional data is shown in Table 2. Again methane is actually produced and not consumed when reacted with propane over Ga-ZSM-5 catalyst.

Table 2- Experimental Results for Conversion of 1:1 Methane + propane over Ga-ZSM-5 at 600ºC Choudhary vs GTI

	Choudhary	GTI
Methane conversion, per pass wt.%	12	-5.9
Propane to Liquid yields per pass wt.%	91.1	25

Our conclusion, after completing these experiments, is that the Choudhary results were in error since in every case, in the GTI experiments, methane is produced and not consumed at the conditions used by Choudhary. GTI also did a blank experiment with no catalyst to make sure the metal reactor walls were not catalyzing methane production. No methane production or composition changes were seen in the blank experiment showing that the reactor was inert with no catalyst present.

Next the ethylene reaction was studied using hydrocracking catalyst at milder temperatures and higher pressures. The reaction of ethylene under a methane atmosphere was compared to the reaction of ethylene in a nitrogen atmosphere and ethylene in a hydrogen atmosphere at 400ºC and 400 psi pressure. In this approach, methane is used as a substitute for hydrogen. The hydrocracking catalyst is a NiMoW zeolite catalyst. The results are shown in Table 3.

Table 3- Experiments with Hydrocracking Catalyst, Ethylene and Excess Nitrogen or Methane at 400ºC and 400 psi, 0.3 Weight Hourly Space Velocity (WHSV)

Feed (molar ratio)	11:1 N_2/C2=	11:1 CH_4/C2=	11:1 H_2/C2=
WHSV. g ethylene/g cat/hr.	0.3	0.3	0.3
Methane consumption	NO	1-5(est)	No
Methane production from ethylene wt.%	2.8	NO	24.9
Hydrogen yield from ethylene wt.%	2.6	1.3	0
Ethylene remaining unconverted	8.6	44.0	0
Ethylene to ethane wt.%	15.7	30.6	80.4
Ethylene to liquid yields wt.%	14.9	0	3.3
Ethylene conversion to C3+ gas wt.%	30.0	16.0	0
Ethylene conversion to coke wt.%	25.5	7.9	0
Ethylene selectivity to methane, wt.%	3.1	0	22.9
Ethylene selectivity to ethane, wt.%	16.8	66.5	73.8
Ethylene selectivity to C2 gas+liquid+H_2, wt.%	69.4	85.8	76.9
% Hydrogen added	0	2.3	8.3

In the experiments with excess methane at 400ºC, and 400 psi, there were clear indications that small amounts (1-5%) of methane were being consumed based on a reduction in the methane to nitrogen (tracer) ratio. In contrast, in the case where only nitrogen and ethylene were present, with the hydrocracking catalyst, 3% methane was produced from cracking the ethylene. In the case where excess hydrogen was present at the same conditions, very high levels of methane were produced.

Moreover with hydrocracking catalyst, the product slate produced, when excess methane was present with the ethylene, showed a significant difference from the product slate produced when only excess nitrogen was present with the ethylene. In the case where only nitrogen and ethylene were present, more coke and hydrogen were made from the ethylene than when excess methane was present. The reaction selectivity to coke was also affected by the presence of methane. With excess methane present with the ethylene, the selectivity of ethylene to coke was much lower, and the selectivity of ethylene to ethane was much higher, than when excess nitrogen was present with the ethylene. When excess hydrogen was present the catalyst produced primarily ethane and methane.

Based on these experiments, we can state that the methane was **not** behaving as an inert compound, like nitrogen, under these conditions, with the hydrocracking catalyst. For these experiments, *the methane was actively involved in the ethylene reactions* but was not as active as hydrogen.

Table 4- Experiments with Ga-ZSM-5 Catalyst, Ethylene and either excess Nitrogen or Methane at 400ºC and 400 psi, 0.3WHSV

Feed (molar ratio)	11:1 N_2/C2=	8:1 CH_4/C2=	% difference
Methane consumption wt.%	-	1.2 (est)	
Methane production from ethylene wt.%	6.6	NO	
Hydrogen yield from ethylene wt.%	1.4	1.0	
Ethylene remaining unconverted	0.6	0	
Ethane yield wt.%	8.8	14.7	67
Propane yield wt.%	16.3	24.1	48
Propylene yield wt.%	0.9	0.3	
C4+ gas yield wt.%	9.2	7.9	
liquid yields wt.%	56.5	51.5	
Coke yield wt.%	0	0	
% H_2 added	0	0	

Table 4 summarizes the experiments completed with Ga-ZSM-5 catalyst at 400 psi and 400ºC and excess methane. With the nitrogen present, methane was produced not consumed, while with methane present, small amounts of methane were consumed. Once again the presence of methane affected the products produced. But in the case of the Ga-ZSM-5, no hydrogen was added to the products showing that the Ga-ZSM-5 was less effective than the hydrocracking catalyst at transferring hydrogen.

Overall these experiments show that excess methane at 400 psi combined with hydrogen transfer catalysts are able to significantly reduce the amount of coke and methane produced from olefin reactions. The hydrocracking catalyst was more active than the Ga-ZSM-5.

Biomass Conversion

The MBU pilot plant system was converted back to biomass conversion and then it was used to reproduce the base IH^2 (hydropyrolysis) results with wood. Our base case wood IH^2 liquid yield is 26 wt. % liquid containing less than <0.4% oxygen. The IH^2 liquids are drop in quality gasoline and diesel blending components. The comparison of these results and results from 5.5 years ago is shown in Table 5. The replicate case compared well with work completed 5.5 years ago.

Table 5- IH^2 base Case and Referenced Case

	IH^2 Base Case	IH^2 BASE CASE rechecked
Date	8/23/2010	4/5/2016
Feed	Wood	Wood
Feed Size, mm	0.4-1.0	0.4-1.0
Pressure, psig	325	320
Wt.% Liquid yield	**25.8**	**27.3**
Wt. % Yield increase from base	**BASE**	
Wt. % O in liquid	< 0.4	< 0.4
Wt. % methane +ethane +propane	14.5	13.9
Wt. % $CO+CO_2$	13.9	14.7
Wt. % water	37.0	35.2
Wt. % char	13.4	13.5
Wt. % H_2 added	4.6	4.7
Wt.% recovery	106	99

Wt.% C recovery	101	98

Initial testing of pyrolysis in the presence of excess methane with a strong hydrogen transfer catalyst was done next. We have termed pyrolysis in the presence of excess methane with a strong hydrogen transfer catalyst, catalytic methane enhanced pyrolysis (CMEP). This is the same as normal pyrolysis, except methane is used as a fluidizing gas and a strong hydrogen transfer catalyst is used. Initial CMEP testing showed the use of methane with a high hydrogen transfer catalyst could improve the quality of liquid products and reduce the char make. Results of the initial testing is shown in Table 6.

Table 6- Comparison of Catalytic Pyrolysis and CMEP for Wood Biomass Conversion (435ºC, 15-20 psig)

	Catalytic Pyrolysis	Catalytic Pyrolysis	Catalytic Methane Enhance Pyrolysis
Catalyst	alumina	Ga-ZSM-5	Ga-ZSM-5
Fluidizing gas	Nitrogen	Nitrogen	Methane
Wt. % O in hydrocarbon Liquid	25.0	20.9	17.6
Wt. % Deoxygenation	40	48	56
Wt. % biogenic liquid	100	100	100
% water in hydrocarbon phase	10.6	6.6	5.5
Wt.% yield C4+ hydrocarbon liquid	21.9	18.7	18.7
Wt. % yield C1-C3 HC gases	1.1	19.4	7.3
Wt. % yield CO+CO_2	15.5	14.2	29.8
Wt. % yield water (phase)	34.9	27.4	31.8
Wt. % C in water phase	15.8	11.4	10.2
Wt. % char	26.6	19.5	12.4

Figure 4 and 5 also illustrate these effects.

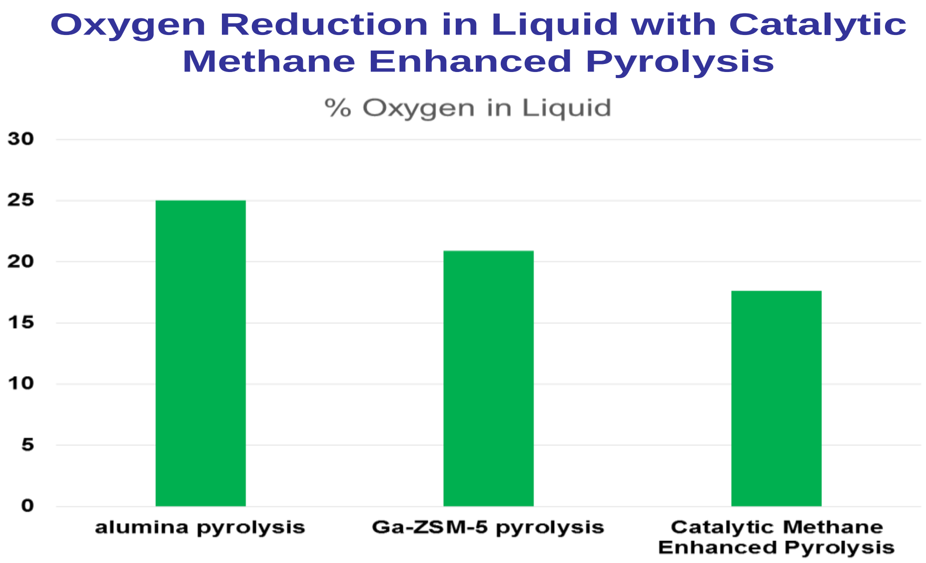


Figure 4- Oxygen Reduction in Liquid with CMEP

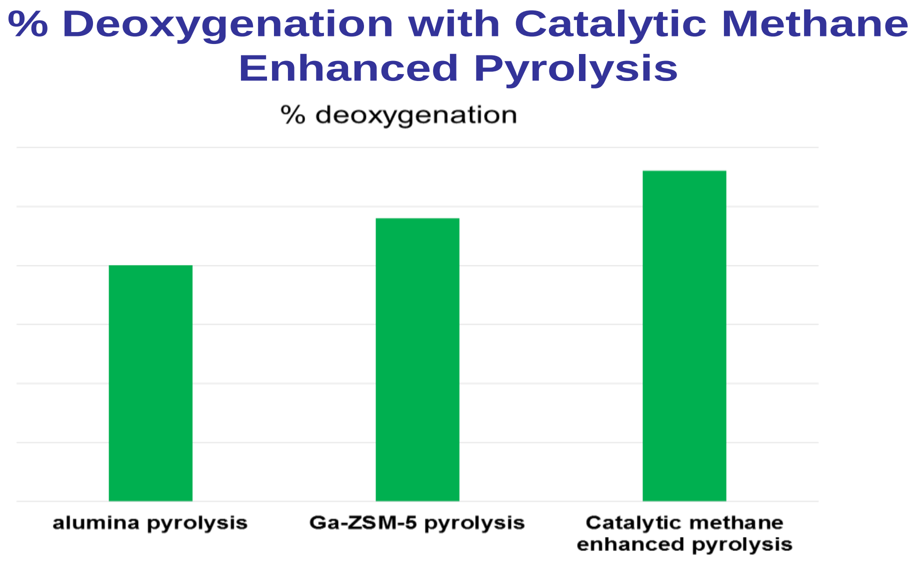


Figure 5- % Deoxygenation with CMEP

CMEP was envisioned to work best as a process in remote locations where hydrogen is not available. It can eliminate the expense of the hydrogen plant which is typically about 40% of the costs. Some experiments were also completed in hydropyrolysis and IH^2. By raising the hydropyrolysis temperature from 400 to 482ºC, it was found that IH^2 liquid yields increased from 25.8wt% to 30wt%, an increase of 16%. However, long term tests will be needed to confirm whether the catalyst can avoid excessive deactivation over long periods of time at these higher temperature conditions

Table 7 - Improved Yield in IH^2 in Hydrogen Atmosphere by Raising Hydropyrolysis Temperature

	IH^2 Base Case	IH^2 Improved Yield Case	% change
Hydropyrolysis Temperature, C	400	482	
Pressure, psig	325	325	
Wt.% Liquid Yield	25.8	30.0	16%
Wt.% Yield from Base	BASE	16.3%	
Wt.% O in Liquid	<0.4	<0.4	
Wt.% yield Hydrocarbon gas	14.5	15.4	
Wt.% yield $CO+CO_2$	13.9	13.6	
Wt.% yield water	37.0	36.8	
Wt.% yield char	13.4	9.8	
Wt.% Hydrogen added	4.6	5.5	

Additional tests were run to determine if the use of high hydrogen transfer catalyst could improve IH^2 yield above 30%. First the effect of Ga-ZSM-5 catalyst, by itself, was tested. The Ga-ZSM-5 catalyst was tested by replacing 19% of the normal IH^2 hydrotreating catalyst, in the hydrotreating stage, with Ga-ZSM-5 catalyst in a layer before the normal hydrotreating catalyst. In Table 8, the effects of the Ga-ZSM-5 are shown. The use of Ga-ZSM-5 catalyst in the second stage, slightly decreased liquid yield. Ga ZSM-5 catalyst is more acidic than the standard catalyst used in IH^2, which led to more cracking and less hydrogen addition. The Ga-ZSM-5 catalyst did produce more diesel and less gasoline than typical. This experiment suggests the Ga-ZSM-5 catalyzed more polymerization because of its increased acidity. This experiment also suggests that the use of more acidic catalyst in IH^2 can be used as a ways to shift the product slate toward diesel.

Table 8 - Effect of 19% Ga-ZSM-5 in Second Stage of IH^2 on IH^2 Yields, (HP temperature =482ºC, Pressure =325 psig, hydrogen fluidizing gas)

	IH^2 at higher temperature	Second stage containing Ga-ZSM-5 and hydrotreating catalyst
Wt.% Yield hydrocarbon liquid	30	26.4
Wt.% O in liquid	<0.4	<0.4
Hydrocarbon Liquid density	0.815	0.835
Wt.% diesel in liquid	16.8	23.6
Wt.% Yield Hydrocarbon gas	15.4	15.7
Wt.% Yield $CO+CO_2$	13.6	13.9
Wt.% Yield water	36.8	39.6
Wt.% Yield char	9.8	9.7
Wt.% Hydrogen added	5.5	5.33

Then tests were done to study the use of methane plus hydrogen as a fluidizing gas in IH^2. For these tests, 20% methane was added to the hydrogen fluidizing gas. The addition of 20% methane was chosen since it significantly effects the hydrogen partial pressure, but still insures plenty of hydrogen is present to avoid coking. As shown in Table 9, the use of 20% methane with hydrogen in IH^2 had little effect on liquid yields or other properties.

Table 9- IH^2- with Ga-ZSM-5 catalyst in second stage with varying levels of methane (Temperature 482ºC)

	Second stage containing Ga-ZSM-5 and hydrotreating Catalyst	Second stage containing Ga-ZSM-5 and hydrotreating Catalyst + Methane + Higher pressure	Second stage containing Ga-ZSM-5 and hydrotreating Catalyst + Methane
Pressure, psia	325	408	325
Fluidizing Gas	Hydrogen	80% Hydrogen +20% methane	80% Hydrogen +20% methane
Wt.% Yield hydrocarbon liquid	26.4	26.2	24.5
Wt. % O in liquid	<0.4	<0.4	<0.4
HC Liquid density	0.835	0.837	0.833
Wt.% Diesel in liquid	23.6	22.9	22.4
Wt.% Yield, methane + ethane + propane	15.7	16.4	20.2
Wt.% Yield $CO+CO_2$	13.9	15.4	18.2
Wt.% Yield water	39.6	38.1	36.0
Wt.% Yield char	9.7	9.0	9.0
Wt. % Hydrogen added	5.3	5.1	5.1

For the test in which the hydrogen partial pressure was kept high by increasing total pressure, the yields were about the same. For the test in which the hydrogen partial pressure dropped, the liquid yield slightly dropped.

As a result of these tests, it was concluded methane plus hydrogen transfer catalyst could improve pyrolysis but was not be very helpful for IH^2 situations where hydrogen and hydropyrolysis catalyst is available. Biomass yields are highest with the addition of hydrogen, so IH^2 catalyst with hydrogen is the best way to add hydrogen to the biomass fragments and results in the highest yields. The Ga-ZSM-5 catalyst, because of its acidity, did have the ability to shift the liquid products toward diesel and this or other types of acidic catalyst can help produce more diesel in IH^2.

In Phase 2, more tests were run on catalytic pyrolysis, methane enhanced catalytic pyrolysis and also IH^2 with methane. One goal was to run higher pressure tests with methane as a fluidizing gas, but these were unsuccessful, because apparently too much coking in the bed occurred at high pressure under methane. Methane reduces coking compared to nitrogen, but clearly not as much as hydrogen. In each case when higher pressure methane was used, without hydrogen, the bed rapidly coked and defluidized, making it impossible to run more than a few minutes. Higher pressure tests are possible and preferred when hydrogen is the fluidizing gas but simply do not work with methane as a fluidizing gas because of excessive coking.

The CMEP experiments did show that the use of methane can improve oxygen removal when it is used with the correct type of catalyst. However; the effects were much smaller than the effects of hydrogen. Table 10 shows the base case of catalytic pyrolysis with nitrogen and alumina catalyst

Table 10- Catalytic Pyrolysis – with Nitrogen + Alumina Catalyst

Test	5/25/2016	2/22/2017
Fluidizing gas	Pure Nitrogen	Pure Nitrogen
Catalyst	Crushed Porous Alumina 1/16" Adsorbent Spheres	Crushed Porous Alumina 1/16" Adsorbent Spheres
Filter	Sintered Metal	Wound Fiberglass
Fluidized bed temperature, °C	434	431
WHSV	1.43	1.38
Pressure, psig	325	325
Time biomass fed. hr.	1.83	2.33
Recovery and Yield		
Wt.% Recovery (relative to biomass)	81.9	93.9
% C Recovery	76.7	92.6
Wt.% C_4+ Liquid yield (MAF*, normalized)	21.9	20.3
Wt.% char yield (MAF, normalized)	26.6	25.6
Wt.% water yield(MAF, normalized)	34.9	27.5
Wt.% CO (MAF, normalized)	7.0	11.0
Wt.% CO_2 (MAF, normalized)	8.5	13.8
Wt.% methane (MAF, normalized)	0.5	1.0
Wt.% ethane (MAF, normalized)	0.1	0.2
Wt.% ethylene (MAF, normalized)	0.1	0.2
Wt.% propane (MAF, normalized)	0.0	0.1
Wt.% propylene (MAF, normalized)	0.3	0.3
Hydrocarbon Liquid Analyses		
Wt.% Oxygen	29.7	23.6
Wt.% Fischer water	10.6	9.34
Wt.% Organic oxygen	20.3	15.4
Wt.% Carbon	60.37	65.29
Wt.% Hydrogen	7.42	7.06
Wt.% Nitrogen	<0.5	<0.5
Wt.% Sulfur	0.02	0.03
Density, gm/cc	1.21	1.11
% Gasoline C_4-345°F	23.1	17.8
% Diesel 345°F +	76.8	83.2
TAN (total acid number)	124.70	103.24
H/C	1.5	1.3

Water Analysis		
pH	2	2
% Carbon	15.2700	12.7184

- MAF= Moisture ash free

Table 11 shows the results for catalytic pyrolysis with nitrogen fluidizing gas and Ga-ZSM-5 Catalyst. Table 12 shows the results with methane as the fluidizing gas and Ga-ZSM-5 catalyst. Table 13 shows the results with methane as a fluidizing gas and NiW catalyst. Table 14 shows the results of IH^2 testing with hydrogen and also with additional methane added.

Table 11-Catalytic Pyrolysis with Nitrogen and Ga-ZSM-5 catalyst

Test	5/19/2016	2/6/2017	2/13/2017
Fluidizing gas	Pure Nitrogen	Pure Nitrogen	Pure Nitrogen
Catalyst	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh
Filter	Sintered Metal	Sintered Metal	Wound Fiberglass
Fluidized bed temperature, °C	432	426	428
1st stage WHSV	1.34	1.39	1.36
Pressure, bar	2.2	2.2	2.2
Time biomass fed. hr.	2.33	2.33	2.33
Recovery and Yield			
Wt.% Recovery (relative to biomass)	95.1	96.4	95.9
% C Recovery	95.9	97.5	97.0
Wt.% C_4+ liquid yield (MAF, normalized)	19.7	22.0	23.6
Wt.% char yield (MAF, normalized)	21.5	22.2	21.6
Wt.% water yield (MAF, normalized)	29.0	27.3	26.3
Wt.% CO (MAF, normalized)	8.4	14.8	14.6
Wt.% CO_2 (MAF, normalized)	6.6	11.6	11.6
Wt.% methane (MAF, normalized)	14.0	0.7	0.8
Wt.% ethane (MAF, normalized)	0.1	0.1	0.1
Wt.% ethylene (MAF, normalized)	0.2	0.5	0.5
Wt.% propane (MAF, normalized)	0.0	0.1	0.1
Wt.% propylene (MAF, normalized)	0.5	0.7	0.7
Hydrocarbon Liquid Analyses			
Wt.% Oxygen	23.4	21.1	18.2
Wt.% Fischer water	6.6	7.2	4.3
Wt.% Organic oxygen	17.5	14.7	14.4
Wt.% Carbon	68.27	66.81	71.22
Wt.% Hydrogen	7.67	7.26	7.33
Wt.% Nitrogen	<0.5	<0.5	<0.5
Wt.% Sulfur	0.03	0.03	0.02
Density, gm/cc	1.08	1.10	1.04
% Gasoline C_4-345°F	25.2	21.0	32.1
% Diesel 345°F +	74.9	79.0	68.4
TAN (total acid number)	69.50	78.60	49.28
H/C	1.3	1.3	1.2
Water Analysis			
pH	2	2	2
% Carbon	11.0100	15.2363	11.4146

Table 12-Catalytic Pyrolysis with Methane and Ga-ZSM-5 catalyst

Test	5/13/2016	1/6/2017	1/12/2017	1/18/2017	1/23/2017	2/17/2017	3/8/2017
Fluidizing gas	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen	80% Methane, 20% Nitrogen
Catalyst	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh	1% Ga-H-ZSM5, Fresh
Filter	Sintered Metal	Sintered Metal	Sintered Metal	Sintered Metal	Sintered Metal	Wound Fiberglass	400 mesh 316 SS wire cloth
Fluidized bed temperature, °C	433	431	496	425	432	432	432
First stage WHSV	1.29	1.49	1.32	1.39	1.41	1.40	1.35
Pressure, bar	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Time biomass fed. Hr.	2.33	2.33	2.33	2.00	2.33	2.33	2.33
Recovery and Yield							
Wt.% Recovery (relative to biomass)	94.4	98.2	99.2	95.3	93.6	95.8	94.9
% C Recovery	80.3	101.9	99.2	93.5	93.6	94.2	94.7
Wt.% C_4+ liquid yield (MAF, normalized)	18.7	24.5	19.9	21.7	21.3	23.0	20.7
Wt.% char yield (MAF, normalized)	12.4	22.2	19.2	22.0	23.6	23.1	22.1
Wt.% water yield (MAF, normalized)	31.8	24.8	22.1	26.7	27.6	25.2	26.6
Wt.% CO (MAF, normalized)	16.6	13.6	19.7	14.6	13.6	14.4	16.1
Wt.% CO_2 (MAF, normalized)	13.2	12.5	13.8	12.4	11.5	12.0	12.0
Wt.% methane (MAF, normalized)	5.4	0.8	1.9	0.9	1.0	0.8	0.7
Wt.% ethane (MAF, normalized)	0.1	0.1	0.3	0.1	0.2	0.1	0.1
Wt.% ethylene (MAF, normalized)	0.6	0.5	1.4	0.6	0.4	0.5	0.7
Wt.% propane (MAF, normalized)	0.1	0.1	0.2	0.1	0.1	0.1	0.1
Wt.% propylene (MAF, normalized)	1.2	0.8	1.7	0.9	0.8	0.7	0.9
Hydrocarbon liquid analyses							
Wt.% Oxygen	19.5	22.5	13.0	17.5	19.4	19.4	20.2
Wt.% Fischer water	5.5	8.5	2.9	4.7	5.8	5.5	5.5
Wt.% Organic oxygen	14.6	14.9	10.4	13.3	14.2	14.5	15.3
Wt.% Carbon	70.52	65.19	77.15	71.65	69.60	71.46	69.60
Wt.% Hydrogen	7.70	7.52	7.69	7.59	7.36	7.29	7.42
Wt.% Nitrogen	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Wt.% Sulfur	0.04	0.04	0.03	0.03	0.01	0.02	0.01
Density, gm/cc	1.08	1.11	1.04	1.06	1.08	1.07	1.08
% Gasoline C_4-345°F	22.0	23.8	32.5	26.1	23.4	25.7	24.3
% Diesel 345°F +	78.0	76.2	67.5	74.5	76.6	84.3	75.7
TAN (total acid number)	79.54	68.50	13.58	47.70	66.09	43.70	84.24
H/C	1.3	1.4	1.2	1.3	1.3	1.2	1.3
Water Analysis							
pH	2	2	2	2	2	2	2
% Carbon	9.8400	16.9054	5.1670	8.0390	10.4000	10.4854	12.5847

Table 13-Methane Catalytic Pyrolysis with NiW catalyst

Test	12/16/2016	12/28/2016	2/27/2017	3/2/2017
Fluidizing gas	79% Methane 21% Nitrogen	80% Methane 20% Nitrogen	80% Methane 20% Nitrogen	50% Hydrogen 30% Methane 20% Nitrogen
Catalyst	Regenerated NiW	Regenerated NiW	Fresh NiW	Fresh NiW
Filter	Sintered Metal	Sintered Metal	Wound Fiberglass	Wound Fiberglass
Fluidized bed temperature, °C	397	427	432	434
First stage WHSV	1.50	1.64	1.35	1.35
Pressure, bar	2.2	2.2	2.2	2.2
Time biomass fed. hr.	1.32	1.25	2.33	2.33
Recovery and Yield				
Wt.% Recovery (relative to biomass)	94.5	96.2	95.5	96.1
%C Recovery	94.6	95.7	95.2	97.7
Wt.% C_4+ Liquid yield (MAF, normalized)	14.3	18.4	15.7	20.5
Wt.% char yield (MAF, normalized)	33.6	26.7	29.4	25.8
Wt.% water yield (MAF, normalized)	27.9	29.1	29.2	29.2
Wt.% CO (MAF, normalized)	9.1	11.7	11.1	11.1
Wt.% CO_2 (MAF, normalized)	13.0	12.3	12.6	10.9
Wt.% methane (MAF, normalized)	1.4	0.9	1.1	1.5
Wt.% ethane (MAF, normalized)	0.2	0.1	0.2	0.2
Wt.% ethylene (MAF, normalized)	0.1	0.2	0.2	0.3
Wt.% propane (MAF, normalized)	0.0	0.0	0.1	0.1
Wt.% propylene (MAF, normalized)	0.2	0.5	0.4	0.5
Hydrocarbon Liquid Analyses				
Wt.% Oxygen	25.9	24.8	23.1	21.0
Wt.% Fischer water	9.19	11.17	8.2	6.0
Wt.% Organic oxygen	17.73	14.9	15.9	15.6
Wt.% Carbon	64.75	61.85	65.14	68.60
Wt.% Hydrogen	7.01	7.12	7.70	7.48
Wt.% Nitrogen	<0.5	<0.5	<0.5	<0.5
Wt.% Sulfur	0.01	0.02	0.02	0.00
Density, gm/cc	1.12	1.11	1.07	1.07
% Gasoline C_4-345°F	16.6	20.0	27.1	20.1
% Diesel 345°F +	83.4	80.1	73.0	80.0
TAN (total acid number)	80.30	90.30	69.41	51.61
H/C	1.3	1.4	1.4	1.3
Water Analysis				
pH	2	2	2	2
% Carbon	10.5779	15.3623	12.1569	12.7953

Table 14-IH^2 testing with various amounts of hydrogen and methane

Test	3/21/2017	3/24/2017	3/30/2017
Fluidizing gas	Pure Hydrogen	Pure Hydrogen	50/50 Hydrogen/Methane
First stage Catalyst	HP Base catalyst	NiW	NiW
Filter	Sintered Metal	Sintered Metal	Sintered Metal
Fluidized bed temperature, °C	420	411	426
First stage WHSV	1.45	1.41	1.40
Pressure, bar	22	22	22
Second stage temperature	732	694	706
Second stage catalyst	HT Base catalyst	HT Base Catalyst	HT Base Catalyst
Second stage WHSV	0.36	0.35	0.35
Time biomass fed. hr.	1.00	2.33	2.33
Recovery & Yield			
Wt.% Recovery (relative to biomass)	110.0	108.8	103.2
%C Recovery	98.5	107.2	102.5
Wt.% C_4+ Liquid yield (MAF, normalized)	26.3	23.6	21.7
Wt.% char yield (MAF, normalized)	10.8	18.3	20.1
Wt.% water yield (MAF, normalized)	36.2	35.0	33.7
Wt.% CO (MAF, normalized)	7.9	6.0	6.4
Wt.% CO_2 (MAF, normalized)	6.0	7.1	9.9
Wt.% methane (MAF, normalized)	4.3	2.0	1.5
Wt.% ethane (MAF, normalized)	4.9	4.1	3.0
Wt.% ethylene (MAF, normalized)	0.0	0.0	0.0
Wt.% propane (MAF, normalized)	3.6	4.0	3.6
Wt.% propylene (MAF, normalized)	0.0	0.0	0.0
Hydrocarbon Liquid Analyses			
Wt.% Oxygen	BDL, <0.5	BDL, <0.5	BDL, <0.5
Wt.% Fischer water	0.1	0.1	0.1
Wt.% Organic oxygen	0	0	0
Wt.% Carbon	83.66	86.49	88.65
Wt.% Hydrogen	9.79	10.43	9.23
Wt.% Nitrogen	BDL <0.5	BDL <0.5	BDL <0.5
Wt.% Sulfur	0.01	0.01	0.00
Density, gm/cc	0.83	0.84	0.90
% Gasoline C_4-345°F	60.6	59.1	42.8
% Diesel 345°F +	39.5	41.0	57.2
TAN (total acid number)	BDL <0.05	<0.05	<0.05
H/C	1.4	1.4	1.2
Water Analysis			
pH	6	7	7
% Carbon	0.3100	0.3100	0.1900

Figure 6 shows that liquid yields are similar for nitrogen with alumina catalyst, nitrogen with Gallium ZSM-5 catalyst, and methane with Gallium ZSM-5 catalyst. The % oxygen in the liquid is less with methane and Gallium ZSM-5 than N2 and alumina or with N2 and Ga-ZSM-5 catalyst. The IH^2 case which uses hydrogen as a fluidizing gas has the best liquid yields and no measurable oxygen and is shown for comparison.

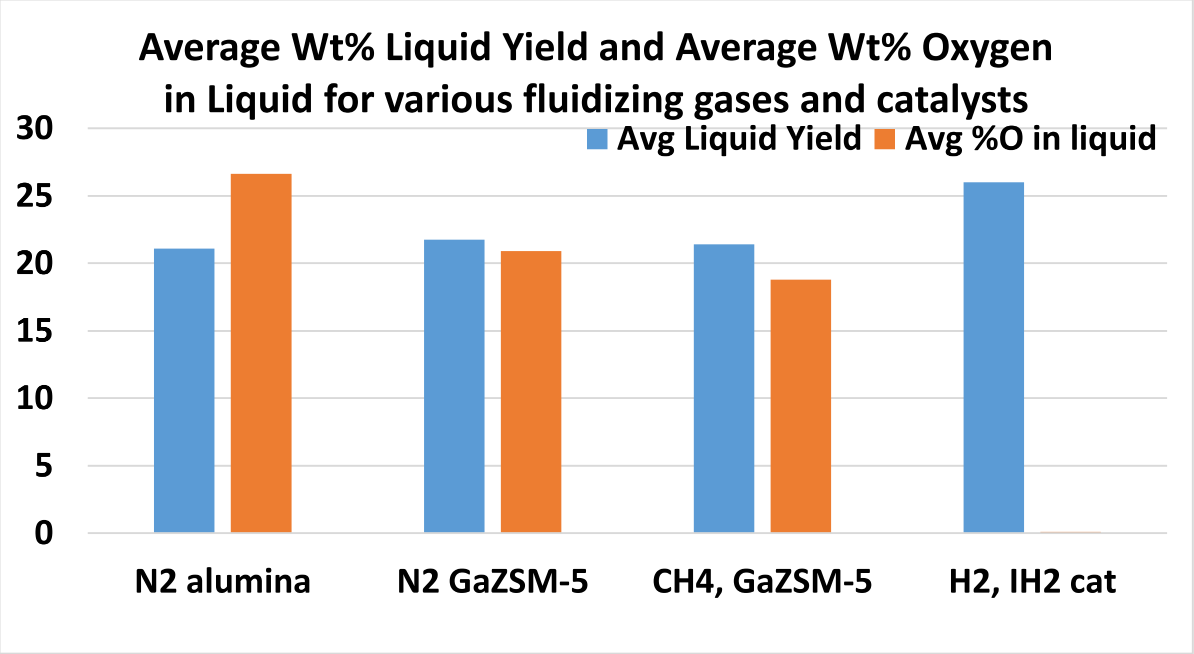


Figure 6- Effect of Fluidizing gas and Catalyst on Liquid Yields and Quality

Figure 7 compares the average Wt.% char yield and the average liquid TAN for various fluidizing gases and catalyst. The methane Gallium- ZSM-5 is lower in TAN than the nitrogen cases. However, the hydrogen, IH^2 system is a step change better than the catalytic pyrolysis systems.

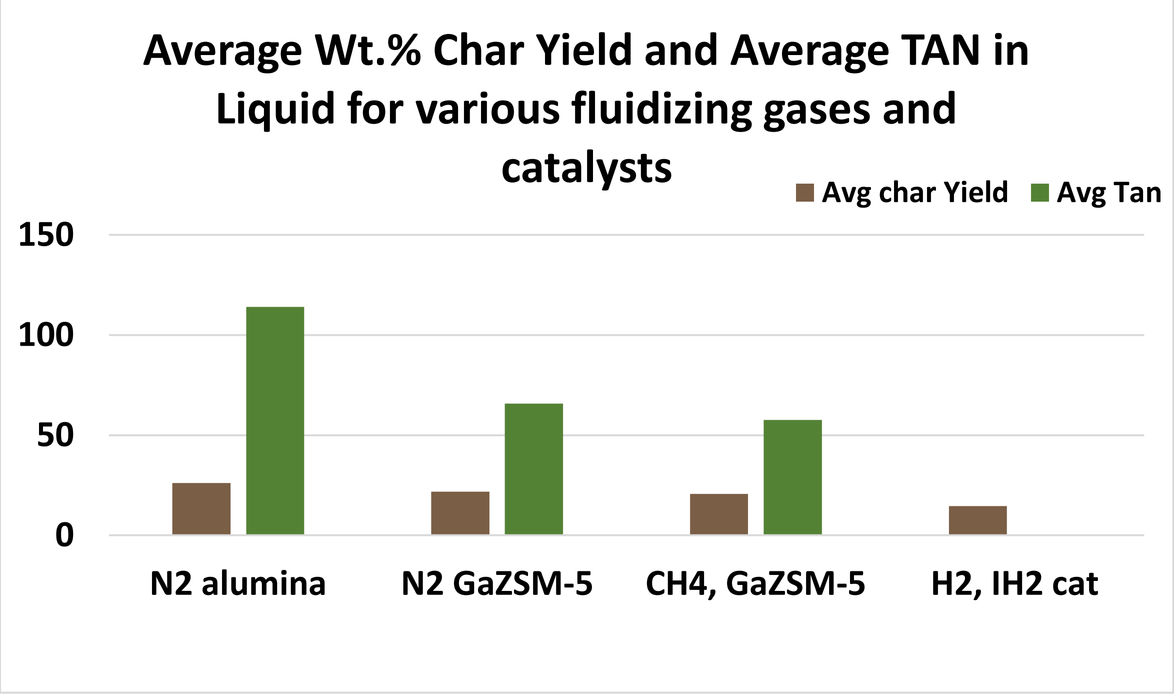


Figure 7- Average Wt. % Char yield and Average TAN for various fluidizing gases and catalysts

The NiW catalyst always gave lower liquid yields than the Ga-ZSM-5 catalyst in methane enhanced catalytic pyrolysis so we can conclude Ga-ZSM-5 is a better catalyst than NiW for this application.

Detailed analysis of the liquids obtained from catalytic pyrolysis testing were completed by NREL using their detailed component comparison technique (7). These results are shown in Table 15 and Table 16 and compared to typical fast pyrolysis oil. Note that typical fast pyrolysis oil is diluted with roughly 25% water whereas the oils produced from catalytic pyrolysis or IH^2 contained little water. The NREL detailed analysis are consistent with the overall results. All catalytic pyrolysis liquids show a decrease in carbonyl content, aliphatic OH content, and carboxylic OH acid content compared to fast pyrolysis oil. The IH^2 liquids oxygenate contents are generally less than 1% those for typical starting fast pyrolysis oil which shows the step change improvement attained in IH^2 technology. For carbonyl, aliphatic OH, and carboxylic OH, the pyrolysis oil has the highest oxygenate content, the oil produced using N2+ alumina the next highest content, the oil produced from N2 and Ga-ZSM-5 was next, the oil produced with methane and Ga ZSM-5 catalyst was next, and the IH^2 product had the lowest oxygenate content. The phenolic OH content was the exception. This type of oxygenate actually increased using catalytic pyrolysis, except in the case of IH^2 oil which still had only 12% of the phenolic oxygenate content of the starting pyrolysis oil. Overall, the liquids produced from catalytic pyrolysis of wood using methane fluidizing gas and a Gallium ZSM-5 catalyst had lower carbonyl content, lower aliphatic OH and lower carboxylic content that the liquids produced from wood using a nitrogen fluidizing gas with gallium ZSM-5 or a nitrogen fluidizing gas with alumina catalyst. However the hydrogen system of IH^2 produced liquid which was one to two orders of magnitude lower in oxygen than any other system. The conclusion, is that although the presence of methane as a fluidizing gas, with a hydrogen transfer catalyst does improve the liquid product quality, compared to standard catalytic pyrolysis, the hydrogen system of IH^2 is one to two orders of magnitude better at reducing product oxygen content than any others system.

Table 15- NREL Analysis of Carbonyl Content of Selected Samples

Description	Carbonyl Content mole carbonyl/kg bio-oil
IH^2 (H_2+ IH^2 cat)	0.0336
Methane + GaZSM-5	2.54
N_2 + GaZSM-5	2.74
N_2 + Alumina	3.22
Typical Fast Pyrolysis oil (oak) (7)	3.87

Table 16– NREL Analysis of mmol Aliphatic, Phenolic and Carboxylic OH/g biooil

Description	mmol aliphatic OH	mmol phenolic OH	mmol carboxylic OH
IH^2 (H_2 + IH^2 cat)	0.02	0.27	0.01
Methane + GaZSM-5	0.41	3.92	0.68
N_2 + GaZSM-5	0.54	3.80	0.76
N_2 + Alumina	0.69	3.60	0.95
Typical Fast Pyrolysis oil (oak) (7)	5.09	2.34	1.23

The detailed NREL report is shown in Appendix A

The CMEP experiments did show that the use of methane can improve oxygen removal when it is used with a strong hydrogen transfer catalyst. However, the effects were much smaller than the effects of hydrogen. Our conclusion from these tests is that although the methane can improve product quality in catalytic pyrolysis of biomass, the effect is not large enough to justify the added expense of using methane. By contrast, hydrogen use in IH^2 shows dramatic improvements of yields and quality and is therefore the better choice.

Cool GTL

The goal of the Bioincubator Project was to improve the pyrolysis of biomass through the use of added methane. The use of methane is economically attractive since methane is low priced in the U.S. because of recent fracking advances. Another way to achieve this goal, aside from the use of methane as a fluidizing gas, is to utilize the biogenic gas produced in the IH^2 process to make more liquids and use additional methane to produce the required hydrogen.

It is very desirable to convert the biogenic gas from IH^2 to biogenic liquids. The conversion of IH^2 biogenic gas enables a substantial increase in biogenic liquid production per ton of biomass feed. The conversion of IH^2 biogenic gas to liquids has a strong economic driver as well since high quality biogenic gasoline and diesel is worth much more than biogenic gas. The conversion of IH^2 gas to gasoline and diesel also simplifies the hydrogen plant in IH^2. Currently the hydrogen plants used in the IH^2 process requires complex IH^2 gas cleanup which adds significant cost. In particular, in IH^2, the standard commercial hydrogen plant vendors required the CO and CO_2 to be removed from the hydrogen plant feed. By instead utilizing this CO and CO_2 to make more liquids, and using methane to make the H2, these gas cleanup costs are avoiding and the hydrogen plant is less costly.

Therefore, as part of the bioincubator project, a few tests were run to look at the potential to use IH^2 biogenic gas to directly make 2:1 H_2/CO synthesis gas which could then be converted into gasoline and diesel using Fischer Tropsch (FT). Through these tests, GTI discovered a new CO_2-steam reforming catalyst with unusual stability. This discovery enabled us to separately develop a new process for converting CO_2 containing methane, ethane, and propane to liquids that we have named Cool GTL (developed under GTI internal funding). The key elements of the Cool GTL process were experimentally tested. The long term catalyst stability of the first stage reformer catalyst was tested, showing that this catalyst lasted 500 hours with no deactivation. The FT section was also experimentally tested showing good per pass yields. The entire integrated system with recycle was modeled based on the results of these experimental tests.

Based on experimental data and modeling, Cool GTL can produce 126 GPT of biogenic liquids from wood (and external methane) instead of 86 GPT. Figure 8 shows the new combined process.

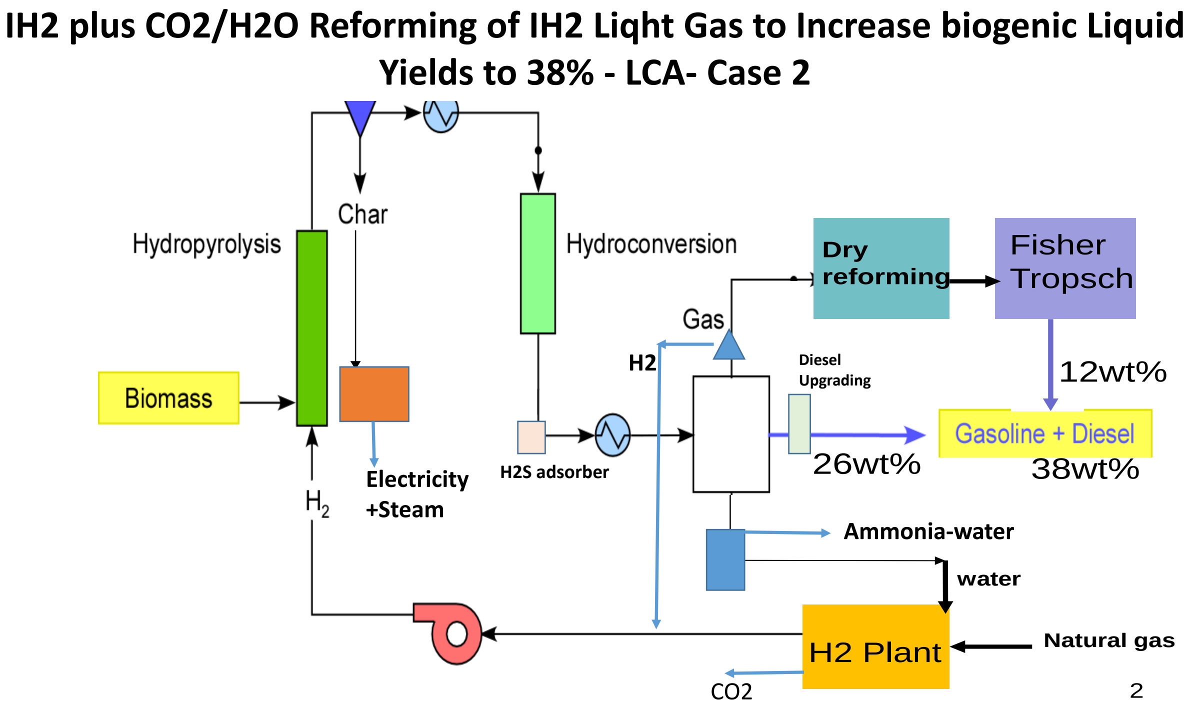


Figure 8- Cool GTL addition to IH2 to increase liquid yields

Although the addition of Cool GTL means that the IH^2 process would now require a natural gas feed to produce hydrogen, it also means that 40% more biogenic liquid product can be made from wood. GTL using CO/CO$_2$ reforming has multiple applications including the conversion of biogas from digestion processes to liquid and the conversion of natural gas with high levels of CO$_2$ present to liquids.

Because initial tests of the CO$_2$/natural gas reforming catalyst were very encouraging, GTI went further to develop the entire Cool GTL technology based on internal GTI funding. The economics for the Cool GTL process are very favorable.in this and numerous other GTL applications.

A summary of some of the Cool GTL results are included here. A process diagram of the entire Cool GTL system is shown in Figure 9.

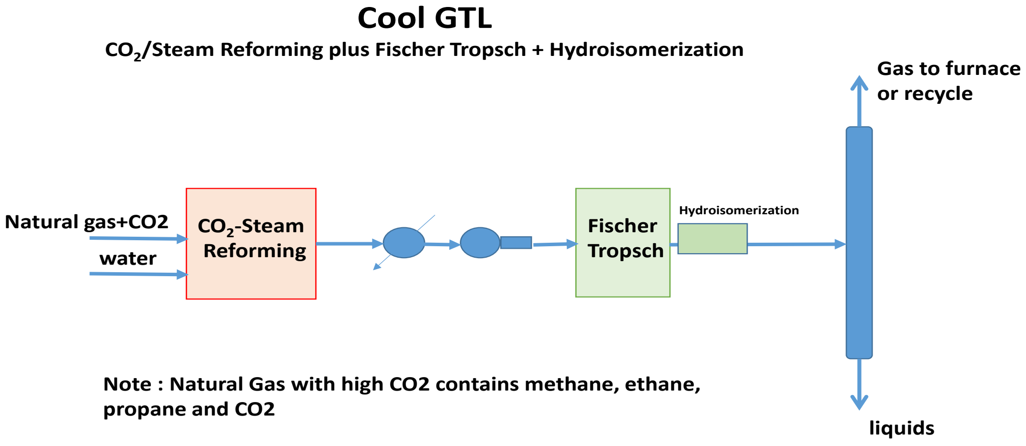


Figure 9 - The Cool GTL Process

The Cool GTL process should be a very simple skid mounted unit. It includes the reformer, Fischer Tropsch reactor and integrated hydroisomerization/hydrocracking step so that no wax is produced. As envisioned, gas goes in and liquid comes out.

The main problem with CO_2 reforming is that catalyst deactivation is typically rapid. However, GTI has discovered a catalyst which is very stable for CO_2/steam reforming. The product analysis from a long 500 hour test for this catalyst is shown in Figure 10 and 11.

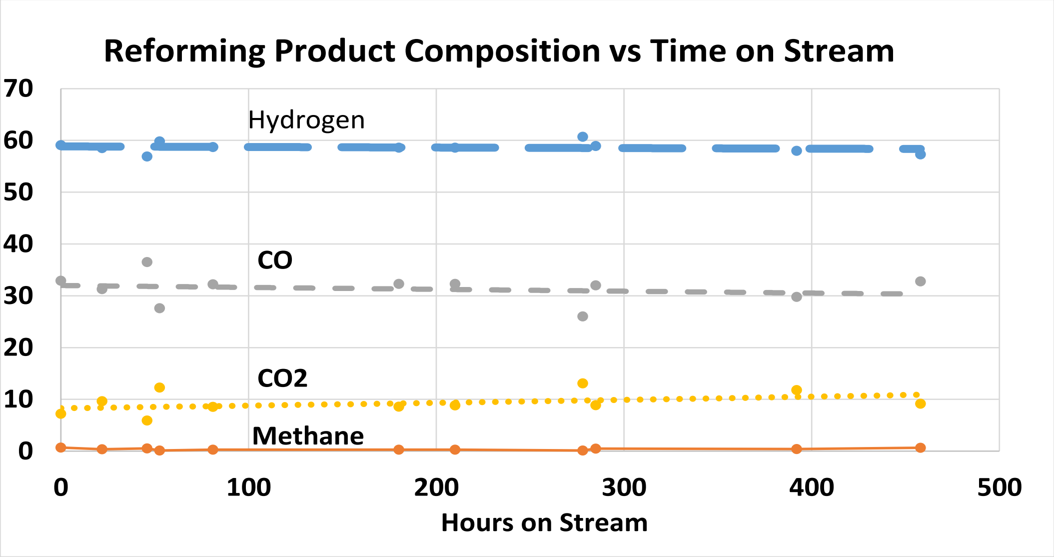


Figure 10- Reforming Product Composition versus Time on Stream

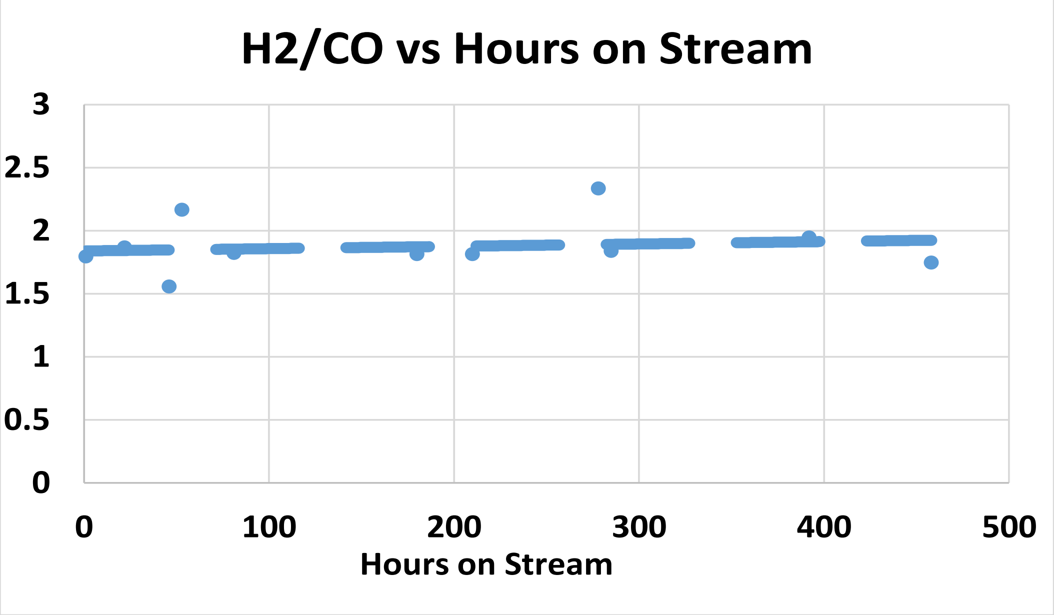


Figure 11- Reformer Product Hydrogen/CO vs Time on Stream

In addition, testing was done with the Fischer Tropsch section to show the effect of the integrated Hydroisomerization/hydrocracking stage using a proprietary catalyst. This data is shown in Table 17.

These tests showed that integrated wax cracking can be done to totally eliminate wax with only a small increase in C1-C3 gas production.

Table 17- Effects of Integrated Wax Cracking on Fischer Tropsch

	Base Case Fischer Tropsch	Fischer Tropsch plus Wax Cracking Step
Fischer Tropsch Temperature ºF	420	420
Pressure (units)	300	300
HI/HC temperature	NA	500
Wt.% Recovery	96	100
% C Recovery	95	96
% CO Conversion	56	53
% C selectivity to C1-C3	36	40
% C selectivity to C4+ liquids	26	60
% C selectivity to wax	39	0

Products from our testing are shown in Figure 11. They are water white.

Figure 12- Cool GTL Process Liquids

Cool GTL looks very favorable from an economic standpoint although more testing is needed to fully develop the process.

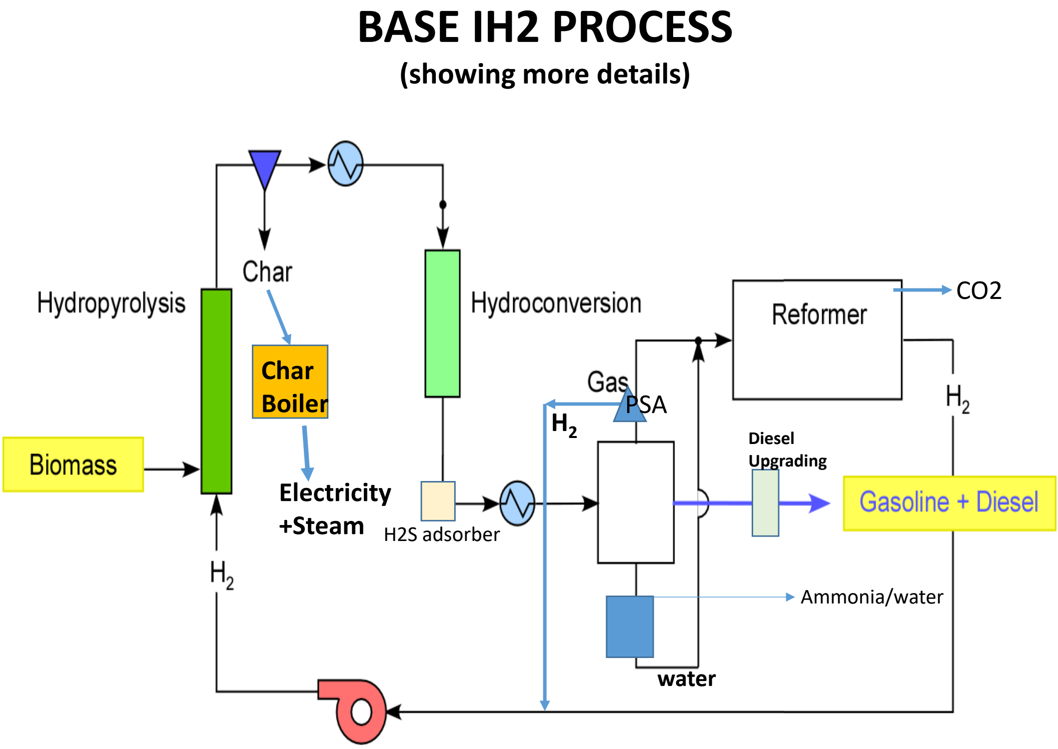
Table 18-Cool GTL Economics for IH^2 Application

	IH^2 type (500 t/d biomass)
liquid product bbl./d	434
Value of product	\$2.5/gal (as refined biogenic liquid)
Product value/year \$	15,960,000
Value of feed gas	\$3/MMBTU for C1-C3 hydrocarbon
Overall incentive \$ Million/year	12.9
Modular capital estimate from Zeton \$ Million	29.9
Estimated erected costs \$ Million	35.4
Estimated footprint	60 ft x 150 ft.
Years to simple payback	2.7

Life Cycle Analysis

Michigan Technical University (MTU) completed a life cycle analysis to look at the effect of the Cool GTL addition to IH^2.

The focus of the LCA was to compare case 1 shown in Figure 1 and Case 2 shown in Figure 2. Case 1 is the base IH^2 case. Case 2 is the IH^2 case where the hydrogen is made from natural gas and the IH^2 gas is used to make more biogenic liquid. These cases are shown in Figure 13 and 14.


BASE IH2 PROCESS

(showing more details)

Figure 13- Base IH^2 process

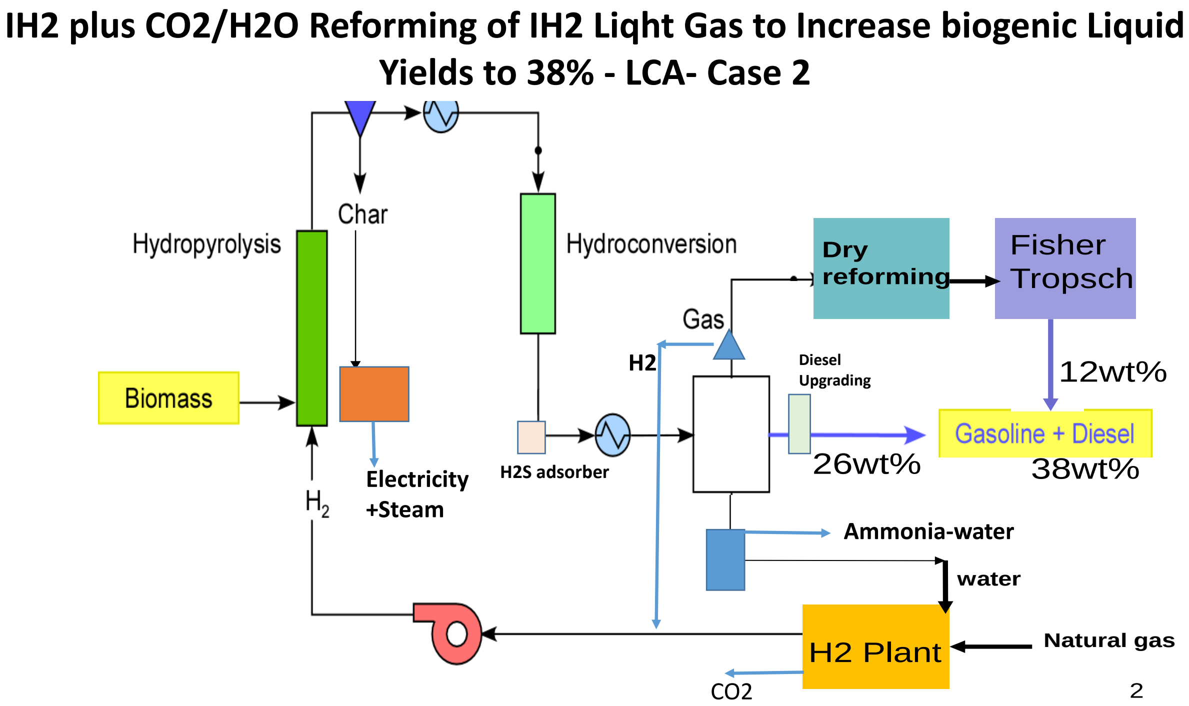


Figure 14- IH^2 + Light Gas Conversion to Increase Biogenic Liquid Yields

Then similar LCA cases were completed for algae feeds, in case 3 and case 4. The case 2a is of particular interest because that is the case where 120 GPT of biogenic liquid is produced from wood. From Figure 3 it can be seen that addition of the Cool GTL process to IH^2 still has more than a 60% reduction of greenhouse gases (GHG) despite the fact that the hydrogen is now produced from natural gas.

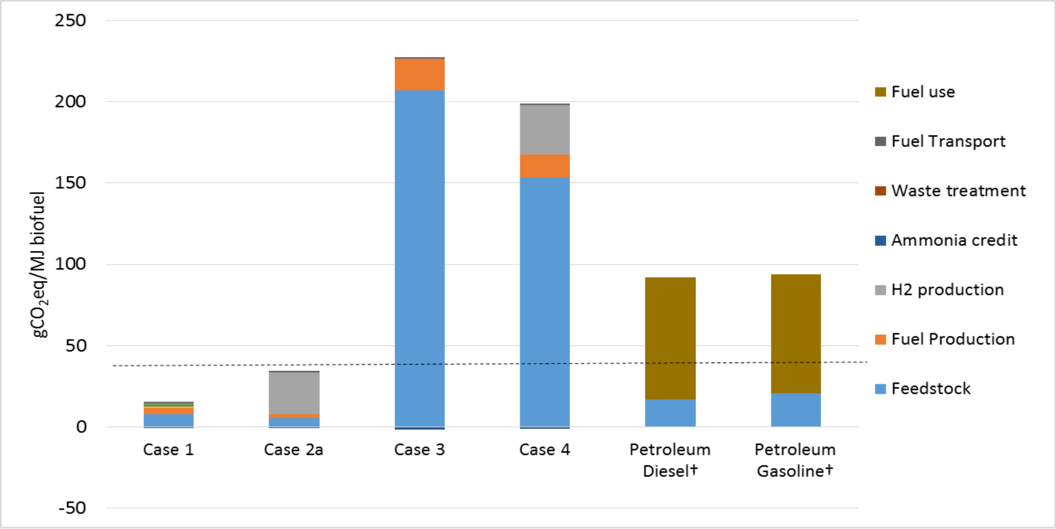


Figure 15: Life-cycle GHG emissions of IH^2 and IH^2 Plus fuel blends. Dashed line represents a 60% reduction in GHG emissions from Petroleum Gasoline. Petroleum fuel data from Elgowainy et al. (2014)

Case 3 and 4, which are the algae cases, have very high greenhouses gas production although the case which makes more liquids is better than the algae base IH^2 case. More improvements need to be made in algae harvesting and drying, according to this analysis, in order to improve the algae feed LCA.

Conclusion

Experimental testing showed that methane is a more effective background gas for use during wood catalytic pyrolysis, with a strong hydrogen transfer catalyst, than nitrogen. Use of a methane background gas is able to decrease the liquid product oxygen content in catalytic pyrolysis while producing the same level of liquid yield as nitrogen background gas. This finding is consistent with pure component tests, as well, which showed that more hydrogen transfer occurred, with hydrogen transfer catalysts, when methane is present as a background gas than when nitrogen is present as a background gas.

However, the reduction in oxygen content for the liquid products made with methane present was only 10%, which is too small to justify any significant expense. The addition of hydrogen with a hydrogen transfer catalyst consistently showed a huge improvement in deoxygenation and yield compared to methane, showing, once again, that hydropyrolysis is a more effective approach to oxygen removal than catalytic pyrolysis. Hydrogen also allows higher pressure operation, easier product recovery, longer catalyst life, and complete deoxygenation.

During the course of this project, another way to significantly increase biogenic liquid yields from pyrolysis, through the use of methane, was discovered. GTI discovered a remarkably stable CO_2/steam reforming catalyst which directly makes a 2:1 H_2/CO synthesis gas from IH^2 CO, CO_2, methane, ethane and propane off-gas. This synthesis gas can then be converted to liquid hydrocarbons using Fischer Tropsch + inline dewaxing. GTI has named this process for converting mixtures of CO_2, CO, methane, ethane, and propane to liquids, Cool GTL, and filed several patents on it. When Cool GTL is used to convert the biogenic gases from IH^2 to liquids, the hydrogen for the IH^2 unit would be provided by using natural gas to feed the hydrogen plant. By utilizing the biogenic gas to make hydrocarbon liquids, 40% more biogenic liquids with no detectable oxygen content can be made from wood, thereby increasing hydrocarbon liquid yields from IH^2 from 86 GPT to 126 GPT. Adding the Cool GTL step improves the IH^2 economics and simplifies the required hydrogen plant, since in this case the H_2 plant feed requires no pretreatment, and no prereformer. Therefore, the hydrogen plant in this case is lower cost. The LCA of this case reveals that this configuration, in which the biogenic gases from IH^2 are upgraded to biogenic liquids, should still be able to meet the requirements for GHG reduction, so that the products can receive RIN credits in the US. This new Cool GTL system also has application in many other areas including conversion of biogas and conversion of CO_2 rich natural gas streams to liquids.

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Appendix A –NREL Detailed Liquid Analysis Report

NOTE: PO-041117 is IH^2 liquids, PO-012317 is catalytic pyrolysis liquid produced using methane fluidizing gas and Ga-ZSM-5 catalyst, PO-022217 is catalytic pyrolysis liquid produced using N2 fluidizing gas and Ga-ZSM-5 catalyst and PO-044117 is catalytic pyrolysis liquid produced using N2 fluidizing gas with alumina catalyst.

Summary

Four samples were received from GTI in the spring of 2017: PO-012317, PO-020617, PO-022217, and PO-041117. These four samples were analyzed using carbonyl titration, carboxylic acid titration, ^{31}P nuclear magnetic resonance (NMR), and gas chromatography (GC) standard methods. These four standard analytical methods represent the first examples of standard chemical characterization methods for pyrolysis bio-oils. All analyses were performed in triplicate, and errors are reported as relative standard deviations (RSD) between the triplicate samples. Samples PO-012317, PO-020617, and PO-022217 all gave reliable results using the standard methods, which were developed for raw pyrolysis bio-oils. These three samples appeared to be similar to a partially upgraded pyrolysis bio-oil, such as a catalytic fast pyrolysis (CFP) bio-oil with ~20 wt% oxygen content. Sample PO-041117 appeared to be similar to a hydrotreated pyrolysis bio-oil with very low oxygen content. Given this, sample PO-041117 was near the lower detection limit for several methods, and subsequently exhibited much higher variabilities than the other three samples. Due to the apparent highly upgraded nature of sample PO-041117, several additional GC-based methods (including detailed hydrocarbon analysis using ASTM D6729) were utilized to further elucidate the nature of PO-041117.

Carbonyl Titration

In the past several years, a new method for quantification of total carbonyl content has been developed for pyrolysis bio-oils.[1-4] This method reports carbonyl content as the sum of aldehyde and ketone functional groups; aldehydes and ketones are not individually quantified, and therefore only the sum of these two functional groups is quantified. Carbonyl titration results for the GTI samples are shown below:

Sample	**Average Carbonyl Content** (mol carbonyl/kg bio-oil)	**Standard Deviation** (mol carbonyl/kg bio-oil)	**Relative Standard Deviation** (% RSD)
PO-012317	2.54	0.02	0.9
PO-020617	2.74	0.09	3.1
PO-022217	3.22	0.24	7.3
PO-041117	0.04	0.02	62.8

Samples PO-012317, PO-020617, and PO-022217 all show variabilities of lower than 8 %RSD. Errors on this order are to be expected for bio-oil samples using this method. Sample PO-041117 shows a significantly higher variability of 62.8 %RSD. Given the very low carbonyl content of 0.03 mol/kg, this sample is near the lower detection limit for this method. Given this, a variability of this magnitude is not unreasonable, as there are simply very few carbonyl groups present in this sample.

Phosphorus NMR

^{31}P NMR has recently been developed into a standard analytical method for the analysis for pyrolysis bio-oils. [4-6] This method quantifies three hydroxyl (OH) functional groups: aliphatic hydroxyl groups, phenolic hydroxyl groups, and carboxylic hydroxyl groups. ^{31}P NMR results for the GTI samples are shown below.

Aliphatic Hydroxyl Groups:

Sample	**Average Aliphatic Hydroxyl Content** (mol aliphatic OH groups/kg bio-oil)	**Standard Deviation** (mol aliphatic OH groups/kg bio-oil)	**Relative Standard Deviation** (% RSD)
PO-012317	0.41	0.04	8.8
PO-020617	0.54	0.02	3.1
PO-022217	0.69	0.05	7.7
PO-041117	0.02	0.01	56.9

Phenolic Hydroxyl Groups:

Sample	**Average Phenolic Hydroxyl Content** (mol phenolic OH groups/kg bio-oil)	**Standard Deviation** (mol phenolic OH groups/kg bio-oil)	**Relative Standard Deviation** (% RSD)
PO-012317	3.92	0.10	2.6
PO-020617	3.80	0.09	2.4
PO-022217	3.60	0.08	2.1
PO-041117	0.27	0.05	16.8

Carboxylic Hydroxyl Groups:

Sample	**Average Carboxylic Hydroxyl Content** (mol carboxylic OH groups/kg bio-oil)	**Standard Deviation** (mol carboxylic OH groups/kg bio-oil)	**Relative Standard Deviation** (% RSD)
PO-012317	0.68	0.05	7.2
PO-020617	0.76	0.07	9.3
PO-022217	0.95	0.01	1.2
PO-041117	0.01	0.01	76.6

As seen above, samples PO-012317, PO-020617, and PO-022217 all show variabilities of lower than 10 %RSD for all three functional groups quantified. These are very typical results for pyrolysis bio-oils using this standard method. In contrast, sample PO-041117 showed significantly higher variabilities for all three functional groups. Similarly to the carbonyl titration method, this is because there are very few hydroxyl functional groups in sample PO-041117, and the hydroxyl quantities present in the sample are near the lower detection limit for this method. As with all data in this report, the absolute value of the hydroxyl quantities for sample PO-041117 should be considered only alongside the variability. For example, the average phenolic hydroxyl content for sample PO-041117 is 0.27 ± 0.05 mol/kg. Thus the range in phenolic hydroxyl content is 0.22 to 0.32 mol/kg. In this context, it is clear that there are very few aliphatic or carboxylic hydroxyl groups remaining. However, there is a relatively higher amount of phenolic hydroxyl groups present in sample PO-041117.

Carboxylic Acid Titration

While carboxylic acid titration has been commonly-used for pyrolysis bio-oils for several decades, only recently has an analytical method been validated for these samples, and subsequently published as a standard analytical method.[4,7] This standard method is slightly different than the commonly-used ASTM D664 method, and uses both a different titrant (tetrabutyl ammonium hydroxide or TBAOH) and pH electrode electrolyte (tetraethyl ammonium bromide or TEABr). During method development, it was noted that these changes not only resulted in higher accuracy and precision for carboxylic acid content, but also allowed for quantification of weaker acidic components such as phenolics. This standard method quantifies both carboxylic acids (via a carboxylic acid number or CAN) and total acidic content (via a total acid number or TAN). Using this method, the difference between TAN and CAN represents the phenolic contribution to the total acid content. Therefore, this difference is often called a phenolic acid number (PhAN) where PhAN = TAN – CAN. Finally, it should be noted that even though this method uses a TBAOH titrant, results are still reported in terms of mg KOH/g of sample, as this is the accepted unit for this measurement. Acid titration results are shown below. Sample PO-041117 did not show any acid value using this method, and is therefore not included with the results.

Sample	**Average CAN** (mg KOH/g bio-oil)	**CAN Standard Deviation** (mg KOH/g bio-oil)	**CAN Relative Standard Deviation** (%RSD)	**Average TAN** (mg KOH/g bio-oil)	**Average PhAN** (mg KOH/g bio-oil)	**PhAN Standard Deviation** (mg KOH/g bio-oil)	**PhAN Relative Standard Deviation** (% RSD)
PO-012317	41.3	0.9	2.1	214.9	173.5	0.2	0.1
PO-020617	49.8	0.1	0.2	231.0	181.2	0.7	0.4
PO-022217	59.3	1.2	2.0	235.7	176.4	2.1	1.2

As seen above, all acid titration results showed very low variabilities, with all relative standard deviations below 3%. Compared to raw fast pyrolysis bio-oils, these samples showed lower carboxylic acid content, and relatively higher phenolic acid numbers.[4] While all three samples showed similar phenolic acid contents, sample PO-022217 showed a slightly higher carboxylic acid content as compared to samples PO-012317 and PO-020617.

Gas Chromatography Methods

A gas chromatography – mass spectrometry (GC-MS) method developed for catalytic fast pyrolysis bio-oils was used for samples PO-012317, PO-020617, and PO-022217. This was the most appropriate GC-MS method available, as these samples have an intermediate oxygen content (~20 wt%) which is very similar to CFP bio-oils. Details of the analytical method used can be found in the following reference.[8] Over 60 compounds were identified for each sample, the results have been grouped by compound type, including 1, 2, and 3-ring hydrocarbons and 6 different classes of oxygenates. Finally, it is well-known that GC methods are only able to quantify volatile species. Given that bio-oils contain many heavy and non-volatile species, GC methods are unable to quantify all compounds present in the sample. Solely based on volatility, we have previously found that GC methods can quantify up to 55 wt% of a CFP bio-oil sample, and we expect a similar limit to samples PO-012317, PO-020617, and PO-022217. GC-MS results for these three samples are shown below, including the portion of the sample that was quantified, which was between 40-46 wt% for these samples.

PO-012317	**Average** (wt%)	**Standard Deviation** (wt%)	**Relative Standard Deviation** (%RSD)
Total Mass % Accounted	46.0	0.42	0.9
Mass % Oxygen Accounted	8.5	0.21	2.5
Mass % Carbon Accounted	34.1	0.19	0.6
Hydrocarbon	**12.9**	**0.15**	**1.1**
1-Ring	**6.4**	**0.06**	**0.9**
Benzene	<0.2	NA	NA
Other 1-Rings	2.2	0.03	1.3
Toluene	1.3	0.00	0.1
Xylenes	2.9	0.03	1.0
2-Ring	**6.5**	**0.09**	**1.4**
Alkyl Naphthalene	2.5	0.03	1.0
Indanes/Indenes	3.3	0.05	1.7
Naphthalene	0.7	0.01	1.2
3-Ring	**<0.3**	**NA**	**NA**
Phenanthrenes/Anthracenes	<0.3	NA	NA
Oxygenates	**33.2**	**0.30**	**0.9**
Furans/Benzofurans	**2.6**	**0.04**	**1.6**
Benzofurans	0.5	0.01	2.2
Furans	2.1	0.03	1.5
Indenols/Naphthols	**1.1**	**0.04**	**3.4**
Indenols	0.2	0.02	11.5
Naphthols	0.9	0.02	2.3
Light Oxygenates	**8.1**	**0.04**	**0.5**
Caboxylic Acids	3.2	0.03	0.8
Ketones	4.8	0.05	1.0
Methoxybenzenes	**3.4**	**0.29**	**8.5**
Methoxybenzenes	3.4	0.29	8.5
Methoxyphenols	**9.6**	**0.38**	**3.9**
with additional O groups	1.3	0.31	23.2
without additional O groups	8.3	0.09	1.1
Phenols	**8.3**	**0.19**	**2.3**
Alkyl Phenol	3.2	0.06	1.8
Catechols	3.8	0.14	3.6
Phenol	1.3	0.01	1.0

PO-020617	**Average** (wt%)	**Standard Deviation** (wt%)	**Relative Standard Deviation** (%RSD)
Total Mass % Accounted	43.6	0.31	0.7
Mass % Oxygen Accounted	9.0	0.18	2.0
Mass % Carbon Accounted	31.4	0.15	0.5
Hydrocarbons	**8.9**	**0.09**	**1.0**
1-Ring	**<0.2**	**NA**	**NA**
Benzene	4.2	0.03	0.8
Other 1-Rings	1.6	0.01	0.5
Toluene	0.8	0.01	1.0
Xylenes	1.8	0.02	1.0
2-Ring	**4.7**	**0.06**	**1.2**
Alkyl Naphthalene	1.6	0.05	2.9
Indanes/Indenes	2.6	0.01	0.4
Naphthalene	0.5	0.00	0.4
3-Ring	**<0.3**	**NA**	**NA**
Phenanthrenes/Anthracenes	<0.3	NA	NA
Oxygenates	34.7	0.22	0.6
Furans/Benzofurans	**2.3**	**0.10**	**4.1**
Benzofurans	0.3	0.09	32.1
Furans	2.0	0.02	0.8
Indenols/Naphthols	**0.9**	**0.01**	**1.1**
Indenols	0.2	0.01	3.2
Naphthols	0.7	0.01	1.7
Light Oxygenates	**9.0**	**0.01**	**0.1**
Caboxylic Acids	4.2	0.03	0.8
Ketones	4.8	0.04	0.8
Methoxybenzenes	**4.1**	**0.03**	**0.8**
Methoxybenzenes	4.1	0.03	0.8
Methoxyphenols	**11.7**	**0.08**	**0.7**
with additional O groups	2.1	0.04	1.8
without additional O groups	9.6	0.06	0.7
Phenols	**6.7**	**0.05**	**0.7**
Alkyl Phenol	2.2	0.02	1.1
Catechols	3.5	0.03	0.8
Phenol	0.9	0.01	0.8

PO-022217	**Average** (wt%)	**Standard Deviation**	**Relative Standard**

		(wt%)	**Deviation** (%RSD)
Total Mass % Accounted	40.5	0.61	1.5
Mass % Oygen Accounted	11.2	0.18	1.6
Mass % Carbon Accounted	26.4	0.39	1.5
Hydrocarbon	**0.8**	**0.01**	**1.5**
1-Ring	**0.5**	**0.01**	**1.2**
Benzene	<0.2	NA	NA
Other 1-Rings	<0.2	NA	NA
Toluene	0.4	0.01	1.8
Xylenes	0.2	0.00	0.7
2-Ring	**0.2**	**0.01**	**2.2**
Alkyl Naphthalene	0.2	0.01	2.2
Indanes/Indenes	<0.2	NA	NA
Naphthalene	<0.2	NA	NA
3-Ring	**<0.3**	**NA**	**NA**
Phenanthrenes/Anthracenes	<0.3	NA	NA
Oxygenate	39.8	0.60	1.5
Furans/Benzofurans	**4.2**	**0.03**	**0.7**
Benzofurans	<0.2	NA	NA
Furans	4.2	0.03	0.7
Indenols/Naphthols	**<0.2**	**NA**	**NA**
Indenols	<0.2	NA	NA
Naphthols	<0.2	NA	NA
Light Oxygenates	**15.2**	**0.24**	**1.6**
Caboxylic Acids	4.6	0.10	2.2
Ketones	10.6	0.15	1.4
Methoxybenzenes	**3.2**	**0.06**	**2.0**
Methoxybenzenes	3.2	0.06	2.0
Methoxyphenols	**10.4**	**0.18**	**1.8**
with additional O groups	1.7	0.06	3.7
without additional O groups	8.8	0.12	1.4
Phenols	**6.8**	**0.09**	**1.3**
Alkyl Phenol	0.9	0.01	1.1
Catechols	5.4	0.08	1.5
Phenol	0.5	0.01	1.2

Given the very low oxygen content of sample PO-041117, a detailed hydrocarbon analysis (DHA) method using GC-FID was the most appropriate method. The DHA method used was ASTM D6729.[9] Roughly 200 compounds were identified in sample PO-041117, and these compounds have been grouped into the following groups: paraffins, iso-paraffins, aromatics, naphthenes, olefins, and oxygenates. 90.1 wt% of the sample was quantified using this method, leaving only 9.9 wt% unidentified. Results are shown below:

PO-041117			
GROUP	**Average** (wt%)	**Standard Deviation** (wt%)	**Relative Standard Deviation** (%RSD)
Paraffin	19.2	0.24	1.3
I-Paraffins	2.7	0.05	2.0
Aromatics	21.6	0.06	0.3
Mono-Aromatics	14.5	0.21	1.5
Naphthalenes	1.3	0.02	1.2
Naphtheno/Olefino-Benzs	3.8	0.08	2.1
Indenes	2.0	0.08	3.8
Naphthenes	41.6	0.68	1.6
Mono-Naphthenes	40.6	0.67	1.6
Di/Bicyclo-Naphthenes	0.9	0.02	1.7
Olefins	3.0	0.08	2.6
n-Olefins	0.5	0.02	3.3
Iso-Olefins	0.2	0.00	1.6
Naphtheno-Olefins	2.4	0.06	2.6
Di-Olefins	NA	NA	NA
Oxygenates	2.1	0.02	1.0
Unidentified	9.9	1.10	11.0

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Appendix B –MTU Life Cycle Analysis Report

Life Cycle Carbon Footprint of $IH^{2®}$ Biofuel from Woody Biomass and Algae: Effects of Enhanced Yield

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Executive Summary

Gas Technology Institute (GTI) has developed a range of promising technologies for the conversion of biomass feedstocks into renewable fuels and chemicals, and is interested in understanding the environmental implications of different process configurations and biomass feedstocks, in order to guide new research and development initiatives. In this study, a life cycle assessment (LCA) framework has been employed to evaluate greenhouse gas (GHG) emissions through the production of gasoline and diesel from the entire GTI IH^2 process. The renewable fuels industry benefits by comparing the environmental impacts of different fuel production configurations against one another using a life cycle framework.

Two feedstocks were considered in this study: woody biomass, including forest logging residues, unmarketable roundwood, and mill residues, and microalgae. The inputs for production of woody biomass were obtained from a supply chain study performed by Mr. John Gephart (North Shore Forest Products, Duluth, MN) and Johnson Timber Company (JTC, Park Falls, WI), which were also used in a prior study involving GTI biofuels development (2015 Final Report). Algae production data were provided by Mr. James Winfield (Algae Energy, Cumming, GA.). Inputs for the IH^2 and related conversion processes were provided by GTI. The scope of this study encompasses the entire life cycle of IH^2 renewable fuel blend, including feedstock collection, transport and processing (size reduction and drying), renewable fuel blend production, and final use in vehicles. The functional unit for this LCA is the quantity of renewable biofuel blend equal to one megajoule (MJ) of energy content. This is a suitable functional unit because transportation vehicle performance is largely based on energy content of fuel. Inventory data for all of the inputs to the life cycle reside in the ecoinvent version 3 database within the software used for this LCA, SimaPro 8.0. For this LCA, co-products such as electricity and ammonia were dealt with using the system expansion (displacement) method, the EPA-recommended method as per the Renewable Fuels Standard 2. For GHG emissions, the results are given in grams of CO_2 equivalents (CO_{2eq}) emitted per MJ of fuel by using global warming potentials for all greenhouse gases in the IPCC 2013 GWP 100a method.

Several cases were assessed to explore the environmental impacts of different process configurations. Case 1 represents an IH^2 facility using woody biomass from TN, with required H_2 produced internally from steam reforming of the C1-C3 co-products from the IH^2 process. Case 2 represents the use of woody biomass from TN with an improved IH^2 process by adding Cool GTL (referred to collectively as IH^2 Plus) to boost the yield of renewable liquid fuel, while H_2 is generated from a steam methane reforming (SMR) facility relying on imported fossil natural gas. Case 3 assumes algae is used as a biomass feedstock in the IH^2 process, similar to Case 1, while Case 4 involves algae feedstock and the IH^2 Plus processing system to increase yield and use natural gas for H_2 production. In Cases 1 and 2 with woody biomass, char produced in the IH^2 and IH^2 Plus processes is combusted for internal production of heat and power. GHG savings of GTI renewable fuels are compared to the petroleum fuel counterparts (gasoline and diesel), which were obtained from an Argonne National Lab study (Elgowainy et al., 2014).

GHG emissions of IH^2 fuel blend are summarized in Table ES.1. IH^2 fuel from woody biomass has life cycle GHG emissions of between 12.4 and 41.5 g CO_{2eq} / MJ, representing emission reductions of between 57-87% compared to fossil gasoline, depending on the processing configuration. Case 1 shows the most favorable results because of its low impacts from woody biomass procurement, reasonable fuel yield and avoidance of fossil methane inputs for H_2 production. IH^2 fuel blend from algae show an increase in GHG emissions compared to fossil gasoline, due largely to the large impacts associated with cultivating algae. Several alternate scenarios are described in the report which elaborate on these basic findings. For example an optimized scenario for Case 2 which utilizes waste energy in the process exhibits GHG emission savings of 63% compared to fossil gasoline and diesel.

Table ES.1: Life cycle GHG emissions of IH^2 renewable fuel blend

g CO_{2eq}/MJ	Case 1 Wood IH^2	Case 2a Wood IH^2 Plus	Case 3 - Algae IH^2	Case 4 – Algae IH^2 Plus	Petroleum Diesel	Petroleum Gasoline
Feedstock	7.96	5.45	206.77	153.04	17.00	20.80
Fuel production	3.65	2.49	19.57	14.49	--	--
H_2 production	0.00	25.72	0.00	30.51	--	--
Ammonia credit	-0.08	-0.05	-1.63	-1.21	--	--
Waste treatment	0.04	0.04	0.06	0.06	--	--
Fuel transport	0.85	0.85	0.85	0.85	--	--
Fuel use	0.00	0.00	0.00	0.00	75.00	73.20
Total	**12.42**	**34.50**	**225.63**	**197.75**	**92.00**	**94.00**
GHG reduction	**86.8%**	**63.30%**	**-140.0%**	**-110.4%**		

*all scenarios performed considering a feedstock input rate of 500 dry short tons per day

1. Introduction

Anthropogenic GHG emissions are one of the major concerns facing the world today. Biofuel production with lower amounts of associated GHG emissions could help to address issues associated with climate change in a sustainable manner, if pursued wisely (Brownbridge, 2013).

Increased demand for biofuels is a response to concerns of reliance on imported petroleum, increasing fuel costs, domestic job creation, and a strong interest in reducing the impacts of human-caused global climate change. This trend in increased biofuels production is being supported at the highest levels of national governments, particularly in the most developed nations. For example, the Energy Independence and Security Act (EISA) of 2007 mandates renewable fuel production targets through the year 2022, at which time 36 billion gallons should be produced annually (U.S. EPA, 2010). This quantity would represent about 25% of current annual gasoline consumption in the U.S. (EPA, 2010). A report by the U.S. Department of Energy (U.S. DOE, 2011) estimated that over 1 billion dry metric tons of biomass is available for collection per year in the U.S. within sustainability constraints and for a price less than $60/dry ton (2011 basis). The majority of this biomass from the domestic “billion ton vision” is woody (lignocellulosic) as opposed to the current biomass feedstocks for biofuels, corn starch, and plant oils. Anticipated conversion technologies for lignocellulosic biomass are either biochemical, including hydrolysis for production of sugars and fermentation production of biofuels, or thermochemical, which includes gasification, pyrolysis, or hydropyrolysis, plus a catalytic upgrading step to convert intermediate synthesis gas or pyrolysis oil to hydrocarbon “drop-in” biofuels (Brodeur-Campbell, 2012).

The IH^2 process developed by Gas Technology Institute (GTI) (Marker, 2012) is a thermochemical process for the conversion of a broad range of biomass types into liquid hydrocarbon biofuels spanning the range of gasoline and diesel. The process is carried out in two sequential yet integrated stages at moderate pressure (250–500 psi) and temperature ranging between 350 and 450°C. The first step involves exothermic catalytic fast hydropyrolysis and hydrodeoxygenation reactions carried out in a fluidized bed reactor at moderate hydrogen pressure. The product vapors from the first step are carried to the second conversion step, an exothermic polishing hydrodeoxygenation and hydroconversion fixed-bed reactor operating at essentially the same pressure as the first reactor. The hydrogen required for the IH^2 process can be either imported from an external source such as a steam methane reformer, or can be produced in a reformer using internally produced short chain (C1-C3) co-products. Other co-products from the process are solid char, high pressure steam, and ammonia/ammonium sulfate. Solid char can be combusted internally to provide heat for feedstock drying and process start-up, and electricity for internal use within the process. Ammonia and hydrogen sulfide in the process condensate from the separator are stripped and oxidized to make an aqueous ammonia/ammonium sulfate product, which can be used as a fertilizer.

The IH^2 Plus process was also recently developed by GTI as an improvement to the base IH^2 process, and this modification aims to increase the yield of liquid hydrocarbon transportation biofuel (Marker, 2012). Instead of utilizing the C1 – C3 gas co-products for the production of required hydrogen, the gas stream is sent directly to a dry reforming system that uses CO_2 and steam to generate synthesis gas in the IH^2 Plus process. The synthesis gas is then processed in an integrated Fischer Tropsch system to produce additional hydrocarbon liquid biofuels resulting in an increase in the yield of hydrocarbon biofuels from 26% (IH^2) to 38% (IH^2 Plus). Because the C1-C3 stream is used to generate additional liquid biofuel in the IH^2 Plus process, hydrogen required in the IH^2 Plus system is instead produced from the steam reforming of natural gas from external sources.

The purpose of this LCA is to evaluate the life cycle GHG emissions of renewable fuel blends (gasoline and diesel) produced by the IH^2 and IH^2 Plus processes utilizing woody biomass (forest residues, unmarketable roundwood, and mill residues) and algae as feedstock, under several processing scenarios. In this LCA study, the system boundary is cradle-to-grave, including feedstock collection and transportation, feedstock processing (size reduction and drying), fuel production, waste treatment, transportation and use of final fuel product. The functional unit of the study is 1 MJ of final fuel blend used, and all the inventory data were normalized based on this functional unit. The inputs of woody biomass were obtained from a supply chain analysis by Mr. John Gephart (North Shore Forest Products, Duluth, MN) and Johnson Timber Company (JTC, Park Falls, WI). Algae production data are provided from personal communication with Mr. James Winfield (Algae Energy, Cumming, GA.) Inputs and outputs from the IH^2 and IH^2 Plus processes were provided by GTI.

2. Study Methods

2.1 Feedstock

2.1.1. Woody biomass

A forest feedstock supply study undertaken by John Gephart to understand the economic feasibility of supplying woody biomass to an IH^2 processing facility next to an existing refiner determined the Valero Memphis Tennessee location as a suitable location for the IH^2 facility. A plant size of 500 bone dry tons per day was evaluated for the Memphis Tennessee location. The feedstock includes forest residues, unmarketable roundwood, and mill residues. Forest residues are collected using conventional logging equipment, converted roadside into chips, and hauled to the receiving location. Roundwood is processed into 8' and tree length logs using conventional logging equipment, transported to the receiving facility, and then converted into chips. Mill residues are collected in a sawmill facility, which include bark from round logs and pulpwood, sawdust and sawmill chips, and slabs. All feedstock is delivered to Memphis where they are processed and dried. The hauling distances vary from 70 to 82 miles depending on the feedstock source. The inputs of woody biomass feedstock supply are tabulated in Table 1.

Table 1: Inputs for woody biomass collection, transport and processing (Basis: 500 dry short tons per day feedstock input)

Processing Stage	Item	Input Amount (In gallons unless otherwise noted)
Raw material processing in woods	Diesel	1,284
	Lubricating oil	10
	Hydraulic fluid	11
	Grease	29
	Gasoline	29
Trucking (round trip)	Diesel	1,106
	Lubricating oil	2
	Grease	1
Yard equipment	Diesel	182
	Lubricating oil	8
	Hydraulic fluid	8
	Grease (4 oz tubes)	21
Feedstock processing and drying (TN electricity grid)	Energy in kWh (size reduction)	14,920
	Energy in kWh (drying) *	12,757

*feedstock drying uses excess heat from the IH^2 process, so these values do not represent actual inputs

2.1.2. Algae

There are two basic ways to cultivate algae on a commercial scale: open pond systems and enclosed photobioreactor (PBR) systems. PBRs are closed systems with controlled environments and typically facilitate higher growth rates of algae. One of the advantages of using closed systems is that it is easier to define optimal growth requirements of algae (e.g., nutrient supply, water supply, temperature, light, density, pH, and mixing rate) and control accordingly.

Algae Energy PBR cultivation technology is based a series of acrylic rectangular boxes, stacked side by side to cultivate algae. Between each PBR unit there is an LED light panel that runs the entire height of the PBR to shine light on each PBR. The PBRs are run in parallel and the modules have two distinct sides to offer the capacity to grow two types of algae at once, as well as prevent total collapse if one side has issues. High efficiency LEDs are used that provide a complete wavelength spectrum (White), along with bonus light in red and blue wavelengths that algae are particularly attuned to use. The algae cultivation medium is supplemented by nutrients which have been added to meet the stoichiometric requirements of the algae, using a standard f/2 medium method (Guillard and Ryther in 1962, Guillard 1975).

After cultivation, algae must be harvested and subsequently dewatered before further processing. Harvesting and dewatering are next stages of the process. A hollow fiber membrane filter system is used to separate the algae, followed by two sequential centrifuge steps to bring the water content below 20%. Algae biomass is then crushed in a bead mill and dried in a rack dryer down to a moisture content of less than 10%.

Algae often has a high lipid content, and these algae oils may be isolated for use as fuel precursors, chemical feedstocks, or food ingredients. If oil extraction is required, that may be accomplished while the algae is still largely in an aqueous environment, depending on the technique used. Chemical oil extraction is the most common method, using a solvent like hexane to attract the lipids after cell disruption. In this study, whole algae biomass is used for the GTI process, although potential variations on that scenario are discussed in later sections of the report. Table 2 presents more details of the inputs and outputs of algae cultivation and processing.

Table 2: Inputs and outputs of algae cultivation and processing

(Basis: 500 dry short tons per day feedstock input)

Process Stage	Item	Amount
Cultivation	Electricity (pumping, lighting) in kWh	2.11×10^6
	Water in MT	3.83×10^2
	CO2-containing gas stream in MT	1.20×10^3
	Nutrients* in MT	5.47×10^1
	Salt in %	2.4
Processing	Electricity in kWh (hollow fiber membrane filter)	4.26×10^4
	Electricity in kWh (Centrifuge)	3.20×10^5
	Electricity in kWh (Rack dryer)	6.40×10^4
Outputs	Algae (dry wt) in ton	500
	Oil content	50%

*Nutrients are based on f/2 medium (Guillard and Ryther in 1962, Guillard 1975), MT is metric tons. GA electricity grid is assumed.

2.2 IH^2 processing

The IH^2 processing data was provided by GTI. The case analyzed assumes a stand-alone integrated IH^2 facility, where H_2 is produced internally using C1-C3 co-products made in the process. The IH^2 process is used in this study for Cases 1 and 3 to convert woody and algae biomass to fuel, respectively. Integrated hydropyrolysis and hydroconversion steps convert the biomass to an IH^2 fuel blend of gasoline and diesel. C1-C3 products from the process are reformed with steam to produce the hydrogen required in the process. The char produced from the process is used internally to produce steam and electricity. Electricity from the grid is used to supplement electricity demand not met by the internally generated electricity. The system flow diagram of IH^2 process for biomass (woody and algae) conversion to fuel is illustrated in Figure 1.

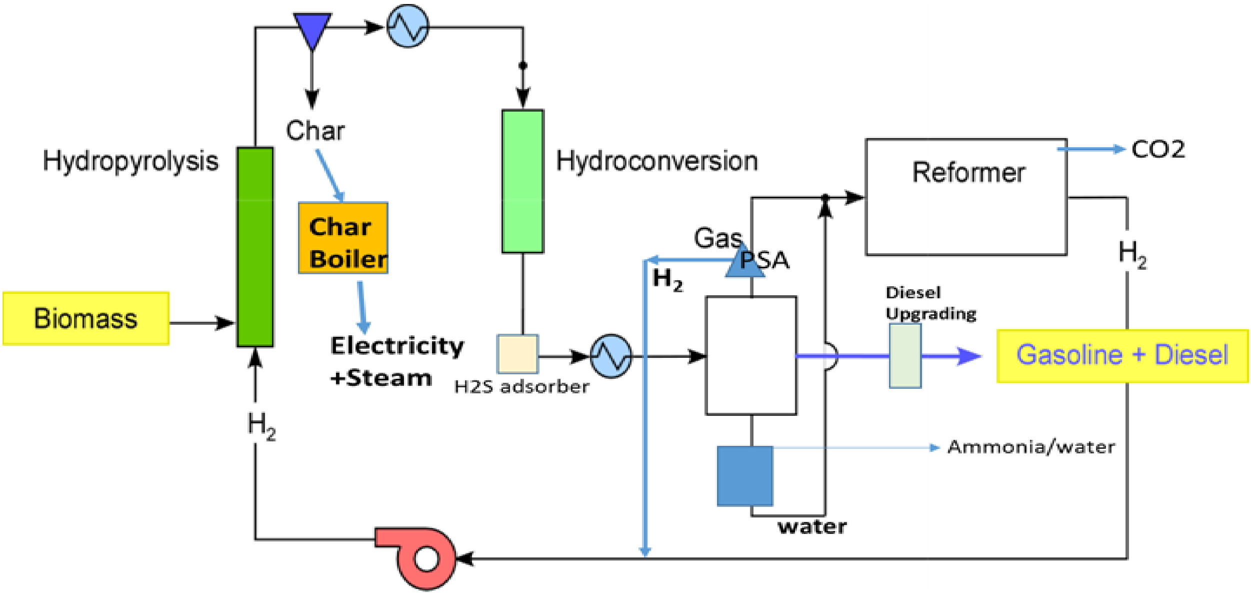

Figure 1: Schematic of IH^2 process (provided by GTI)

2.3 IH^2 Plus processing

The IH^2 Plus processing data was provided by GTI. The H_2 required in the IH^2 Plus process is generated from a steam methane reforming (SMR) unit. This is because unlike the base IH^2 process, C1-C3 co-products made in the IH^2 Plus are treated in a dry reformer system with steam and CO_2 to produce synthesis gas. The synthesis gas is then processed through a Fischer Tropsch system to produce additional fungible fuel. With this configuration, the yield of the fuel is boosted from 26% obtained in the base IH^2 process to 38%. Similar to the IH^2 process, the char produced from the process is used internally to produce steam and electricity while unmet electricity demand is satisfied from external electricity from the grid. The system flow diagrams of IH^2 Plus process for biomass conversion to fuel is illustrated in Figure 2

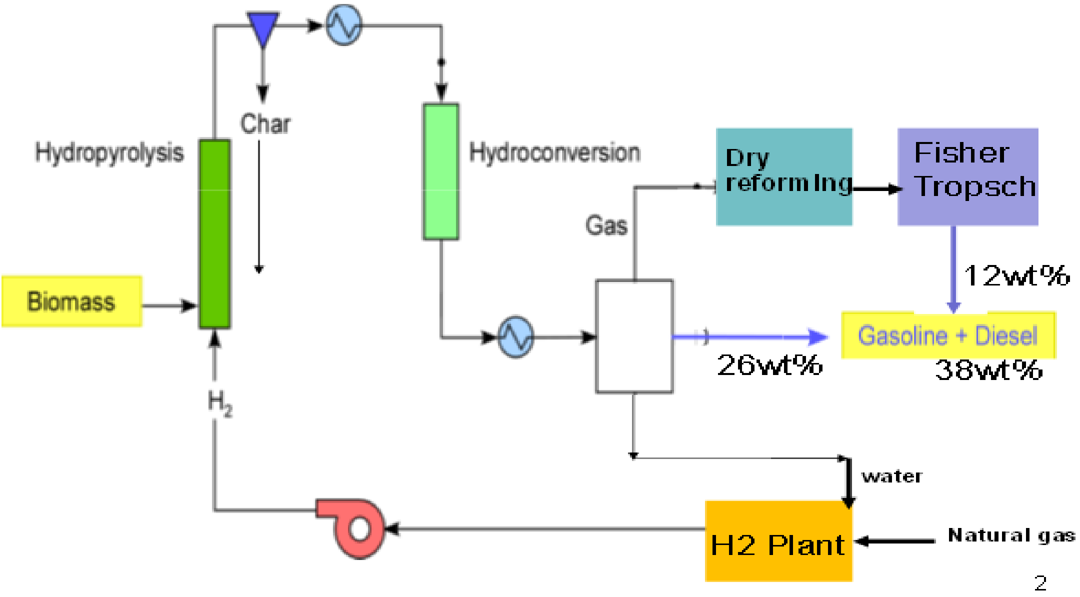

Figure 2: Schematic of IH^2 Plus process (provided by GTI)

To illustrate the potential differences in GHG emissions associated with different feedstocks and different processing platforms, the four primary Cases in this study were designed to reflect this range of options, and are outlined in Table 3.

Table 3: Summary of primary Cases in LCA study

	Case 1	Case 2	Case 3	Case 4
Feedstock	Woody biomass	Woody biomass	Algae	Algae
Conversion Technology	IH^2	IH^2 Plus	IH^2	IH^2 Plus

Many other processing decisions or assumptions surrounding the process may have an impact on the final LCA results, and several additional scenarios were investigated to address the impacts of those assumptions. Case 2a evaluates how optimizing the IH^2 process affects the GHG emissions from the IH^2 Plus process relative to the unoptimized baseline Case 2. Compared to the base Case 2 where the heat for the H_2 plant is generated by burning some of the feed methane, in Case 2a, waste gas from the Fischer Tropsch process is utilized to provide some of the heat. As a result, Case 2a results in lower methane requirement for process heat and also lower fossil-derived CO_2 from the combustion of the imported fossil resource.

Case 2b investigates how increasing the yield of diesel while reducing the yield of gasoline from the IH^2 Plus process affects the GHG emissions. Though the yield of diesel and gasoline changes in this case, the overall yield of fungible fuel is the same as the yield obtained in the base Case 2. The change in yields of diesel and gasoline examined in this case can be achieved by catalyst modifications.

Case 2c examines how lower yield of fuel relative to the base case (roughly 7% yield reduction) affects the GHG emissions. The main reason for the lower yield here can be as a result of any potential inefficiency of the IH^2 Plus process. In this scenario, reduction in liquid fuel blend is not compensated for with increases in either char or other co-products containing carbon. Therefore, this is only a “first order” scenario analysis that measures sensitivity of the LCA result with change in one process variable. In Case 2d, the effect of higher electricity demand from the TN grid was examined; electricity input rate increase from 2 MW to 4 MW. The higher electricity demand can result from the use of electric heaters in the IH^2 process instead of heat exchangers. Additional scenarios involving woody biomass feedstock are summarized in Table 4. These same scenario ideas presented for woody biomass in Cases 2a-2d were also tested for the algae feedstock, and those Cases, labeled 4a-d in a similar fashion, are summarized in Table 5.

Table 4: Summary of sensitivity analysis scenarios for Case 2

	Case 2a	Case 2b	Case 2c	Case 2d
Feedstock	Woody biomass	Woody biomass	Woody biomass	Woody biomass
Conversion technology	IH^2 Plus	IH^2 Plus	IH^2 Plus	IH^2 Plus
Other changes	Lower natural gas input	More diesel, less gasoline	Lower yield	More electricity required

Table 5: Summary of sensitivity analysis scenarios for Case 4

	Case 4a	Case 4b	Case 4c	Case 4d
Feedstock	Algae	Algae	Algae	Algae
Conversion technology	IH^2 Plus	IH^2 Plus	IH^2 Plus	IH^2 Plus
Other changes	Lower natural gas input	More gasoline, less diesel	Lower yield	More electricity required

For this study, the Tennessee (TN) and Georgia (GA) electricity mix profile present in the ecoinvent database was updated using more recent literature data based on electricity generation statistics from 2014, the most recent available year (U.S. EPA eGRID 2017). The inventory inputs are tabulated in Table 6. Sulfur hexafluoride is used in the electric power industry as a dielectric and insulating material. It is an input to the electricity generation mix in table 6 for the electricity externally supplied from the electricity grid. Ultimately, it is a very small contribution to the overall GHG emissions.

Table 6: Inventory inputs of TN and GA electricity generation mix

Electricity mix	TN	GA	
Electricity production, hard coal	45.1	36	%
Electricity production, oil	0.2	0.3	%
Electricity production, nuclear	34.8	25.9	%
Electricity production, hydro	10.6	1.8	%
Electricity production, biomass	1.3	3.3	%
Electricity production, natural gas,	7.8	32.6	%
Electricity production, wind	0.1	0	%
Electricity production, solar	0.0	0.1	%
Transmission network, electricity, high voltage	3.24×10^{-8}	3.24×10^{-8}	km/kWh
Sulfur hexafluoride, liquid	7.48×10^{-8}	7.48×10^{-8}	kg/kWh

Table 7 presents the comparison of collected inputs and outputs of all Cases at the fuel production stage. All scenarios were developed using a basis of 500 dry short tons per day of feedstock input. Utilities required for processing algae biomass are expected to be about the same as the woody biomass processing, except the amounts of electricity required from external sources differ between the two feedstocks due to the amount of electricity that can be produced internally from char in each situation. The electricity generated internally in all the four Cases through the combustion of char was not sufficient to fully offset the electricity required by the processes, therefore unmet electricity demands were satisfied by external electricity from the grid.

Table 7: Comparison of selected inputs and outputs in primary Cases

	Case 1	Case 2	Case 3	Case 4
Input/Outputs				
Input. Wood Dry tons (t/d)	500	500	500	500
Input, oxygen in air (used to combust char and in H2 plant furnace) (t/d)	317	458	138	125
Input Natural gas (t/d)	0	70	0	70
Output t/d				
Gasoline t/d (Mgal/yr)	90	120	112.5	152
diesel t/d (Mgal/yr)	40	70	112.5	152
Total Fuel Product Created	130	190	225	304
ammonia t/d in sour water t/d	0.25	0.25	9.06	9.06
ash t/d	1.5	1.5	66.5	66
water, process t/d	12	12	76	66
water, burning char + reformer gas	103	103	82	82
Water, burning FT waste gas	0	78	0	28
water total t/d	115	193	194	176
CO_2 (from IH^2 process) t/d	95	0	74	0
CO_2 (from H_2 plant reformer process) t/d	171	171	171	171
CO_2 (from H_2 plant reformer burning) t/d	53	53	53	53
CO_2 (from FT process) t/d	0	100	0	7
CO_2 (from FT waste gas burning) t/d	0	66	0	100
CO_2 (from char burning) t/d	257	257	37	29
CO_2 total t/d	576	647	335	360
Utilities				
Electricity, MW	2	2	11	11
Raw Makeup water, l/s	17.9	17.9	17.9	17.9
Wastewater out, l/s	7.1	7.1	7.1	7.1
Nitrogen, kg/hr	2.2	2.5	2.5	2.5

Woody biomass is transported between 70-82 mi one way to the GTI processing facility, depending on the biomass source. It was assumed that algae would basically be processed in the same place it was cultivated, in Georgia, and transportation requirements are negligible. The final fuel products (renewable diesel and gasoline blend) are assumed to be distributed to the adjacent Valero fuel terminal at Memphis, which are to be blended with fossil gasoline and diesel. We assume similar fuel transport requirements for all Cases at this time. Although that could be changed to more accurately model the fuel life cycles in each case, we will see that fuel distribution likely has a minimal impact compared to other items.

The IH^2 and IH^2 Plus processes also produces a water-ammonia stream, which is sold as N fertilizer. Energy and GHG credits were assigned to this water-ammonia stream based on the environmental burden of synthetic N fertilizer. Ash is trucked and disposed of. Ash content is approximately 0.5% in woody biomass. Cooling tower blowdown and storm/oily water are treated at the refinery wastewater treatment plant. GHG emissions of waste treatment are estimated in SimaPro as well.

LCA results were calculated in SimaPro using the IPCC 2013 GWP 100a method to tabulate GHG emissions for climate-active gases, most notably CO_2, CH_4, and N_2O. Net CO_2 emissions of renewable fuel blend at the combustion stage are considered carbon neutral because CO_2 is sequestered by photosynthesis during the growth of biomass. Thus, only fossil CO_2 is accounted for in this life cycle C footprint analysis. GHG savings of GTI renewable fuels are compared to the petroleum fuel counterparts (gasoline and diesel), which were obtained from a study from Argonne National Lab (Elgowainy et al., 2014).

3. Results and Discussion

GHG emissions from the four Cases investigated and petroleum derived diesel and gasoline, are illustrated in Figure 3. From the figure, it can be observed that Cases 1 and 2 utilizing woody biomass feedstock in the IH^2 and IH^2 Plus processes, respectively, resulted in lower GHG emissions relative to petroleum derived diesel and gasoline.
The IH^2 Plus (Case 2) resulted in higher GHG emissions (41.52 g CO_{2eq}/MJ) relative to the IH^2 process (Case 1) (12.42 g CO_{2eq}/MJ) for woody feedstock. This is mainly due to the anthropogenic CO_2 emissions from the reforming of natural gas to produce the hydrogen in IH^2 Plus process relative to the biogenic CO_2 from the same step for the IH^2 process where hydrogen was produced by reforming the C1-C3 co-products from process. Though the increase in yield of fungible fuel obtained from IH^2 Plus process by processing the C1-C3 co-products resulted in lower GHG emission for the feedstock

stage for the IH^2 Plus process in comparison to the IH^2 process as seen in Figure 3 and Table 8, the lower emission was not enough to offset the emission from utilizing natural gas for hydrogen production.

Cases 3 and 4 using algae feedstock for the IH^2 and IH^2 Plus processes, respectively, resulted in higher GHG emissions relative to the petroleum derived fuels. For the algae feedstock cases (3 and 4) the major contributor to the GHG emissions is the feedstock cultivation stage. This is due to the high electricity consumption during the algae cultivation process for pumping, lighting, and dewatering unit operations. The opposite trend is observed in the algae cases, where the increase in fuel yield offered through the IH^2 Plus process (Case 4) more than made up for the burdens imposed by the requirements for external natural gas-H_2. Because the impacts associated with producing each unit of algae was so high, it was worth the extra H_2 burden to reduce the requirement for algae biomass to achieve the same functional unit of 1 MJ of fuel product.

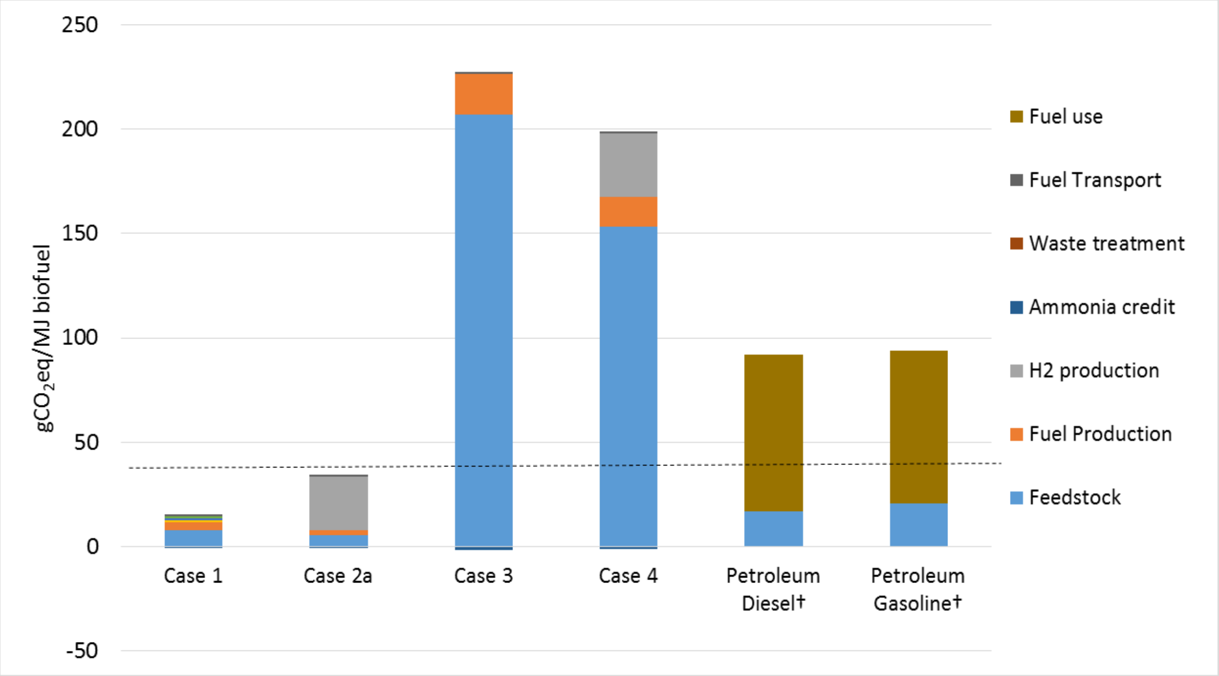

Figure 3: Life-cycle GHG emissions of IH^2 and IH^2 Plus fuel blends. Dashed line represents a 60% reduction in GHG emissions from Petroleum Gasoline. Petroleum fuel data from Elgowainy et al. (2014)

Table 8: Life cycle GHG emissions of IH^2 renewable fuel blend

g CO_{2eq}/MJ	Case 1 Wood IH^2	Case 2a Wood IH^2 Plus	Case 3 Algae IH^2	Case 4 Algae IH^2 Plus	Petroleum Diesel	Petroleum Gasoline
Feedstock	7.96	5.45	206.77	153.04	17.00	20.80
Fuel production	3.65	2.49	19.57	14.49	--	--
H_2 production	0.00	25.72	0.00	30.51	--	--
Ammonia credit	-0.08	-0.05	-1.63	-1.21	--	--
Waste treatment	0.04	0.04	0.06	0.06	--	--
Fuel transport	0.85	0.85	0.85	0.85	--	--
Fuel use	0.00	0.00	0.00	0.00	75.00	73.20
Total	12.42	34.50	225.63	197.75	92.00	94.00
GHG reduction*	86.8%	63.30%	-140.0%	-110.4%		

* GHG reductions are compared to petroleum gasoline

Life cycle GHG emissions sensitivity analysis of IH^2 Plus renewable fuel blend for woody biomass Cases 2a-d and algae Cases 4a-d are presented in Figures 4 and 5, respectively. In the woody biomass scenarios presented in Figure 4, it is observed that Case 2a with optimized use of gases within the system can achieve a lower life cycle GHG emissions value compared to the baseline Case 2 (34.5 vs 41.52 g CO_{2eq}/MJ, respectively). This improvement is enough to make the IH^2 Plus processing platform achieve a 63% GHG emissions reduction compared to fossil gasoline, which exceeds the 60% threshold to qualify this biofuel as a 'cellulosic biofuel' under EPA standards (EPA 2010). Case 2b results in a nearly identical result to Case 2a, because the overall distribution of fuel products does not significantly alter the environmental impacts when normalized to a per MJ basis. Case 2c, representing a ~7% lower yield of fuel per unit input of biomass, resulted in a slightly higher life cycle GHG emissions value compared to the Case 2 baseline (44.51 vs 41.52 g CO_{2eq}/MJ, respectively). Increasing electricity requirements in Case 2d resulted in an increase of roughly 4 g CO_{2eq}/MJ compared to Case 2a, which illustrates the importance of power usage at the fuel conversion stage. Similar trends can be observed in Figure 5 for algae Cases.

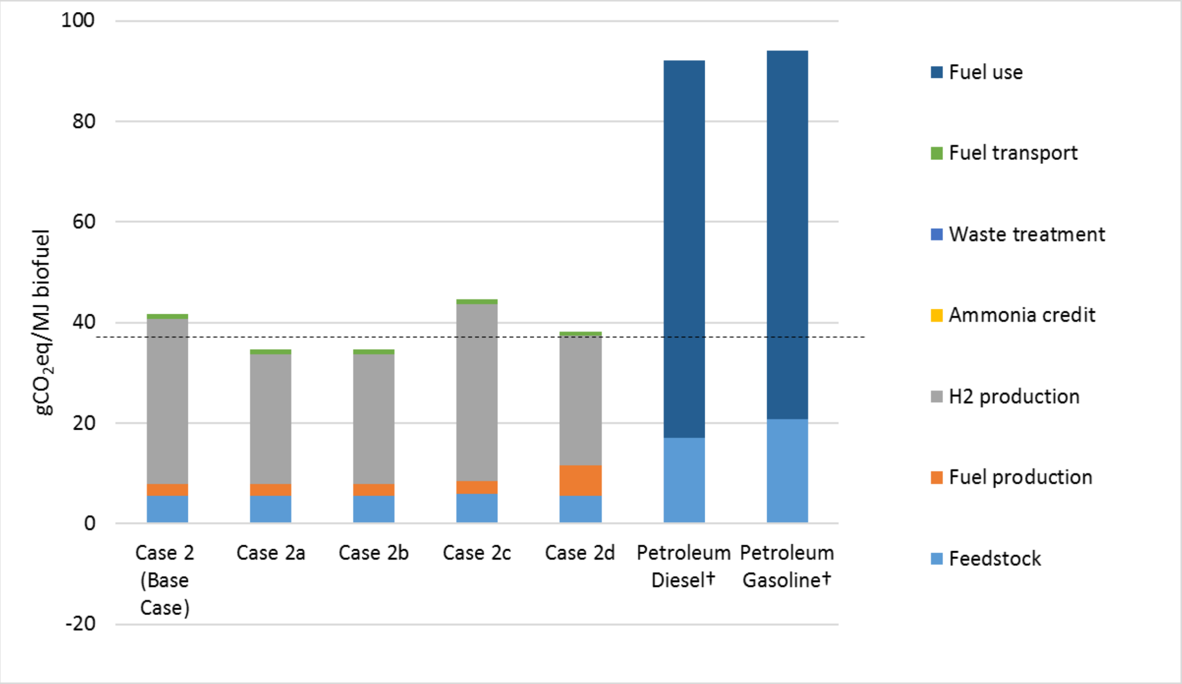

Figure 4: Life cycle GHG emissions sensitivity analysis of IH^2 Plus renewable fuel blend for woody biomass (Case 2). Petroleum fuel data from Elgowainy et al. (2014)

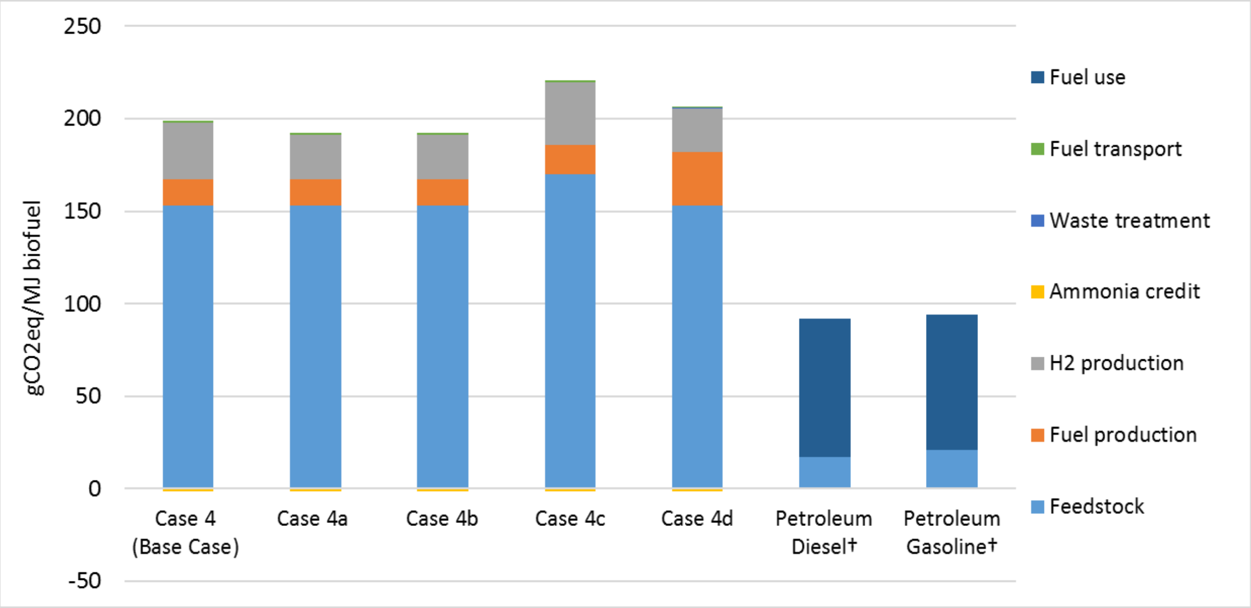

Figure 5. Life cycle GHG emissions sensitivity analysis of IH^2 Plus renewable fuel blend for algae biomass (Case 4). Petroleum fuel data from Elgowainy et al. (2014)

One topic worthy of mention is the issue of sustainable practices for biomass feedstock procurement of woody biomass and algae. This discussion will focus on issues that may affect the carbon footprint analysis in these forest landscapes and algae. One of the first concepts to acknowledge is that biomass carbon in and on soils is connected to atmospheric carbon (CO_2) through rapid cycles of photosynthesis and mineralization. Therefore, if C in biomass increases on the landscape and in soils then this increase corresponds to a proportional decrease of C (CO_2) in the atmosphere. Likewise, if landscape biomass C decreases, possibly due to unsustainable biomass collection practices, then C in the atmosphere will increase in a proportional manner. This could lead to an increase in greenhouse gas emissions from biofuels production systems. Most forest-based biofuels systems assume that land-use change impacts on GHG emissions are minimal, but this assumes a sustainable harvest level and a relatively unchanged amount of forested land base as a result of new biofuels use. In forest landscapes where logging residues are collected, the depletion of C from the landscape may cause a delay of several decades for the benefits of biofuels displacing fossil fuels to be felt (Mckechnie, 2011). It is feasible to estimate these landscape effects through the use of appropriate carbon budget models in agricultural settings using the DAYCENT or iEPIC models and in forest landscapes using a model such as the Carbon Budget Model of the Canadian Forest System (CBM-CFS). In this LCA report, we have assumed that biomass collection for IH^2 biofuel production using and forest residue collection would remain within sustainability constraints.

Algae has the potential to utilize waste CO_2 from industrial sources and convert this carbon into rapidly growing algae biomass, which makes it a promising feedstock worthy of future study. Previous research has shown that improper siting of algae cultivation facilities may lead to direct land use change impacts from cleared lands (Handler et al. 2017), but this is less likely to be an issue with a PBR cultivation system which should use much less land than an open pond system.

Current LCA Cases involving algae assume that all algae that is cultivated in the PBR system is subsequently sent to a GTI fuel production facility, but that may not be the best assumption to use when thinking about how this opportunity may develop in the near term. Companies that are developing algae cultivation systems are often finding markets for algae oil in cosmetics or nutraceuticals or food applications that are much more lucrative than current opportunities in the renewable fuels sector. It is reasonable to assume that algae cultivation would continue to prioritize those opportunities for algae oil as long as the markets were still favorable. However, the non-lipid biomass that is being cultivated also represents a potential opportunity for fuel production, and thermochemical systems like GTI IH^2 are not dependent on the oil fraction of algae to generate high yields - in fact, comparable yields in the IH^2 process have been achieved using algae with markedly different oil contents. If the lipid-extracted algae (LEA) fraction of algae biomass was sent to a GTI processing system for upgrading to fuels, which the algae oil was sent to traditional market opportunities, it would be worth considering how to allocate the admittedly large environmental impacts associated with algae cultivation between these two products. As an example, if algae is produced at a 25% oil content, 3 kg of non-lipid LEA would be produced for every kg of oil. If we assume market values of $5/kg for LEA, and $50/kg for algae oil, then an economic allocation of impacts for algae cultivation between LEA and oil would result in over 75% of the impacts associated with cultivation being attributed to the oil, while less than 25% would be attributed to the LEA fraction. There are a few more complexities that would result from imagining the algae biomass feedstock opportunity in this fashion, as the co-product of a more lucrative algae industry, but clearly this potential to drastically reduce the impacts associated with algae cultivation would result in biofuels with a more favorable environmental profile. Future scenarios to more thoroughly explore this opportunity will be considered.

4. Conclusion

IH^2 renewable fuels produced from woody biomass show considerable GHG savings compared to their fossil fuel counterparts. Depending on the H_2 sources and other processing assumptions, IH^2 fuel blends from woody biomass would achieve 55-87% reductions in life cycle GHG emissions compared to fossil fuels. On the other hand, IH^2 renewable fuels produced from algae appear to have a GHG emissions profile that is not currently favorable, compared to fossil fuels. There are potential opportunities to explore how algae cultivation could be performed in a manner that produces lower GHG emissions per MJ of fuel produced, but the current operational assumptions do not appear to produce a satisfactory result.

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