Hydrothermal Processing of Wood for Electricity

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Hydrothermal Processing

- **Advanced process efficiently converts wet organic matter to biofuels and clean water**
  - Can produce bio-crude oil, methane gas, or both
  - App. 99% of organic matter is converted
- **Process perfected by US Department of Energy at PNNL over 40-year period with extensive testing**
- **Process has recently been documented under two major US DOE programs costing USD $100 million**
  - NABC for wood
  - NAABB for algae

Terminology and Acronyms

- **Hydrothermal Processing = HTP**
- **Hydrothermal Liquefaction = HTL**
- **Catalytic Hydrothermal Gasification = CHG**
- **All of these processes use temperature (350°C) and pressure (200 bar) to convert organic material (biomass or organic chemicals) to hydrocarbon fuels**
- **Process uses wet materials**
  - Must be wet—water is part of reactions
  - Material is processed as slurry with 15% to 30% solids

Avoiding Confusion

- **HTP is different than pyrolysis—it is a liquid process, not a dry process**
- **CHG is not "gasification" as generally used**
  - General use almost always means pyrolysis
- **Output of pyrolysis is syngas, which is mostly a mix of hydrogen and carbon monoxide**
  - Energy content HHV = 280 BTU/scf
- **Output of HTP is methane and carbon dioxide**
  - Energy content HHV = 620 BTU/scf

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Process Concepts

- **Process is similar to fossil fuel formation, but faster**
  - 30 minutes instead of 30 million years
- **Best technology available for converting wet organics to true hydrocarbon fuels (not esters)**
- **Equipment is compact and scalable**
- **Tested on more than 100 feedstocks with thousands of hours of runtime**
- **Liquid fuels refined from the bio-crude are replacements for fossil fuels; methane is methane**
  - Gasoline, jet, diesel

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Partial List of Tested Feedstocks

Waste	Dairy Manure, Poultry Manure, Pig Manure, Municipal Solid Waste, Pulp and Paper Mill Waste, Plastic Bottles
Aquatic	Water Hyacinths, Kelp (Marine), Red Algae (Marine), Green Algae (Brackish), Green Algae (Marine), Green Algae (Fresh), Diatoms, Cyanobacteria
Ligno-Cellulosic	Wood Slash, Sawdust, Corn Stover, Poplar Fermentation Residuals, Wood Gasification Residuals, Cellulosic Fermentation Residuals
Herbaceous	Napier Grass, Sorghum, Sunflowers, Corn Stover, Marigolds
Food Processing	Potato Waste, Corn Ethanol Bottoms (DWG), Grape Pomace (Wine Making), Cranberry Pomace, Digester Sludge, Kraft Paper Black Liquor, Cheese Whey, Coffee Grounds, Spent Distillers Grain, Vinegar, Olive Wash Water, Chicken Processing Waste, Fish Processing Waste, Gelatin Mfg. Waste, Rum Vinasse, Soda Pulp Wastewater, Soft Drink Factory Waste, Potato Processing Crumbs, Shrimp Waste, Potato Peels, Dairy Waste, Onions, Corn Canning DAF, Apple Pomace, Beer Waste
Chemical Waste	Nylon Wastewater, Acrylonitrile Wastewater, Fatty Acid Waste, Metal Chelate Solution, Sodium Cyanide Waste, Polyol Wastewater, Vitamin Fermentation Broth, Paint Booth Wash, Methyl Ethyl Ketone, Propylene Glycol, Carbon Tetrachloride, many other chemical compounds

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Process Details

- **HTP uses only pressurized hot water--no solvents**
- **Wet feedstock is made into water slurry with 15% to 35% dry equivalent solids**
- **Process is NOT supercritical, which is important to the overall economics and success of HTP**
- **Continuous process converts more than 99% of the feedstock organic content in 30-45 minutes**
- **Process is efficient--uses 15% of energy (85% free) when system is designed with heat integration**
- **Material of construction is Stainless Steel 316L**

The Specific Case for Wood

- **How does wood compare to other feedstocks?**
- **Algae may be the easiest of all biomass to process—converts efficiently and is generally easy to process**
  – But there are no large algae farms
  – Algae is still far too expensive to use for fuels
- **Wood is harder to process but still converts well**
  – The difficulty is getting the wood into slurry form
  – When heated in water and pressure it liquefies quickly

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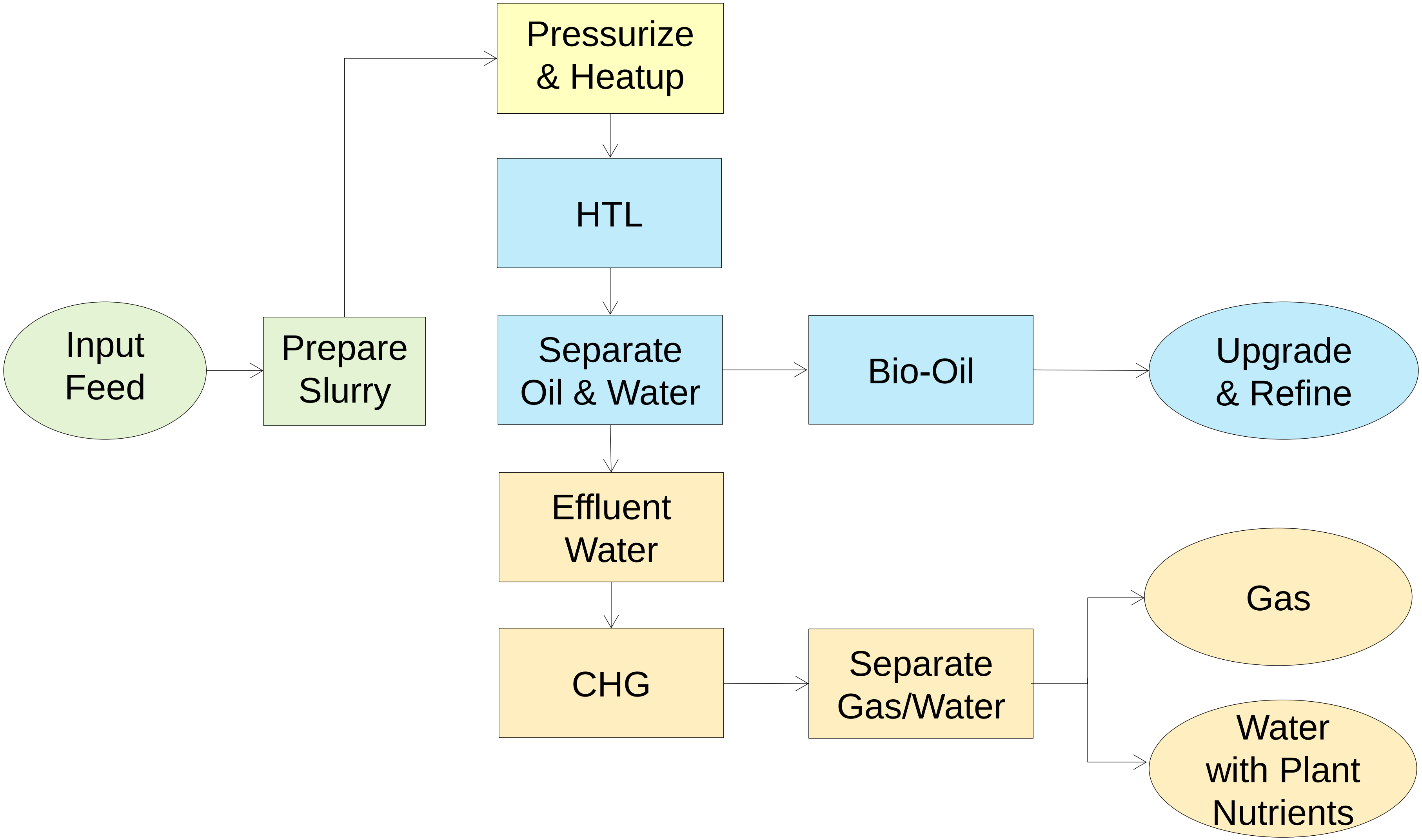
Setup for Wood

- **Wood generally produces acidic conditions**
- **Acid is corrosive to the stainless steel used in system**
  - Acid also produces unwanted molecular forms and promotes polymerization of products
  - pH may be raised by addition of small amount of alkali to the wood slurry, preferably no lower than 6.0
- **Size of wood particles depends on size of system**
  - Size of particle no more than 25% of piping ID to prevent bridging--Bigger pipes mean less size reduction
  - So we want to get to bigger systems for wood

Combined Oil-Gas Hydrothermal Process Flow



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Products

- **Bio-crude can be upgraded to refined fuels in a conventional refinery**
  - May need pre-treater depending on refinery
- **Methane can be used several ways**
  - Use as fuel for generator to make electricity and heat
  - Remove CO_2 , then inject into natural gas pipeline or use locally as CNG
  - Gas is clean (no sulfur, phosphorus, siloxanes)
- **Most feedstocks produce fuels and power which are eligible for renewable incentives internationally**

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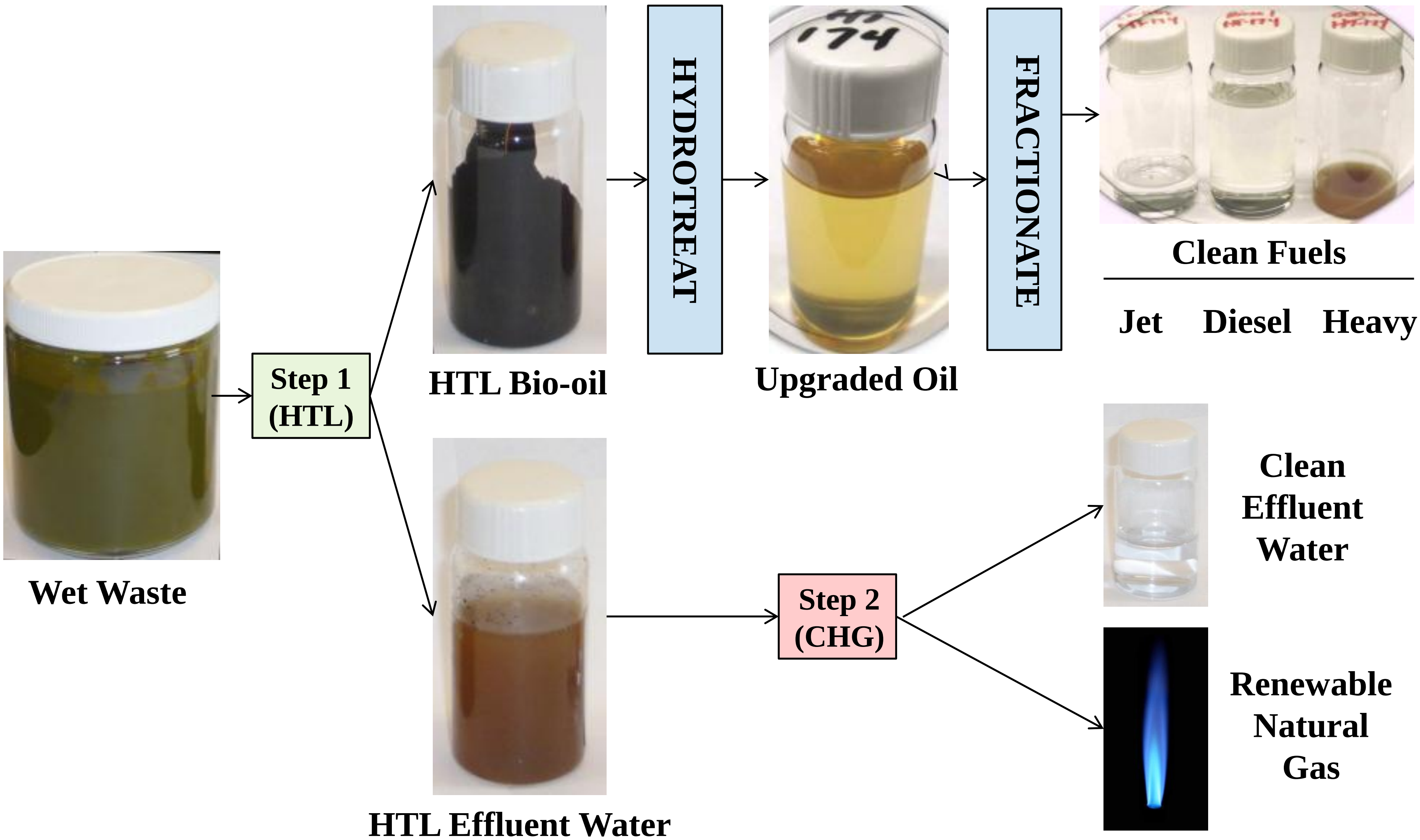
Products are Crude Oil, Methane Gas, or Both



van Krevelen chart for HTL Oil

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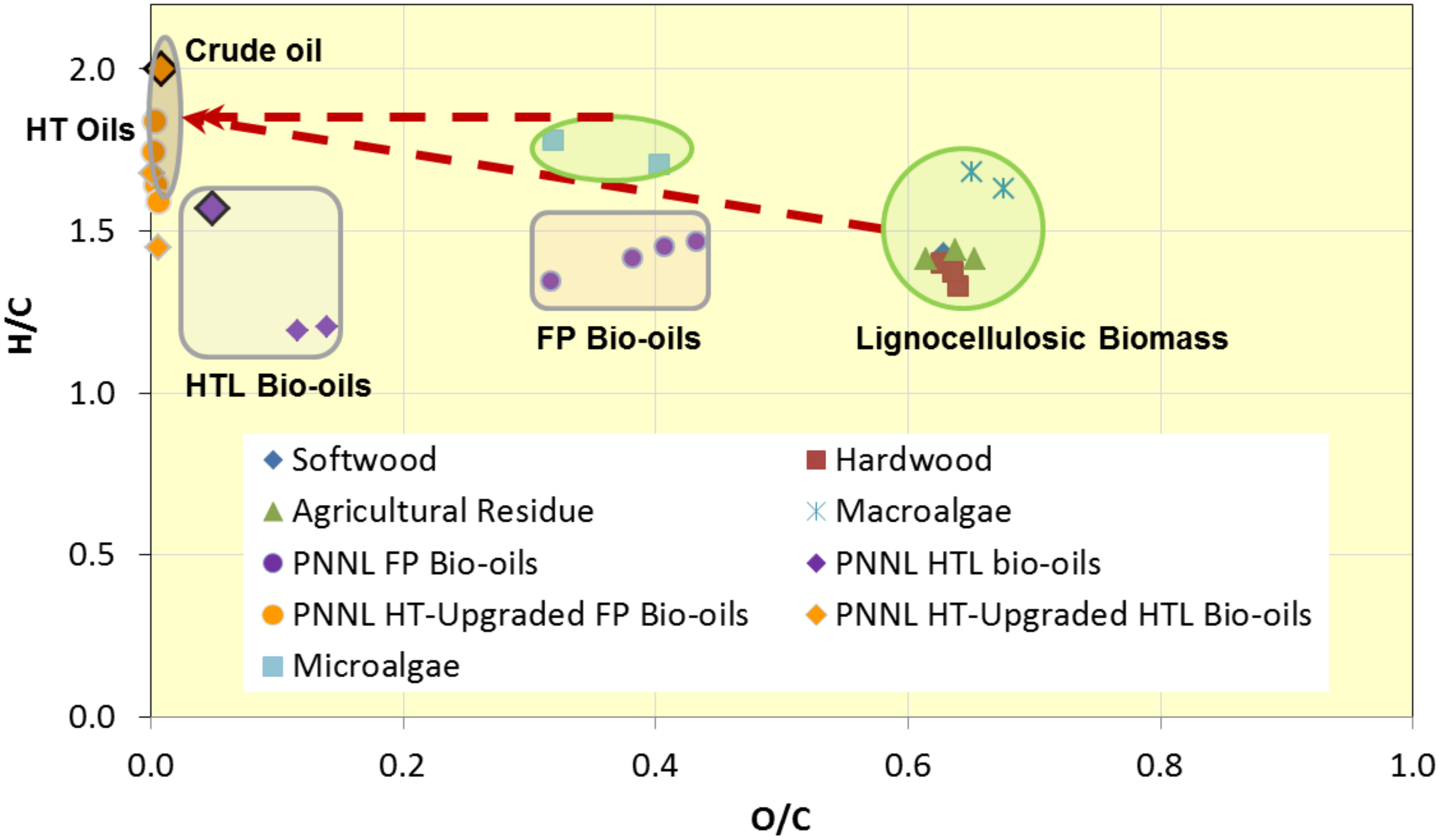

- ❑ Type of feedstock has an effect on the properties of the liquids produced.
- ❑ The type of liquefaction processing also has an effect

Water

- **HTL process converts 35 to 50% of the biomass to oil; remaining biomass is in the HTL effluent water**
- **Effluent water from the HTL process will have COD in range of 50,000 to 100,000**
  - Appearance is brownish water without visible solids
- **This water can be further processed with CHG to extract remaining energy and clean the water**
- **After CHG water is sterile and clear with COD in range of 200 to 400; usually meets discharge standards**

Water (cont.)

- **Water will contain all plant nutrients in original biomass except phosphorus,**
- **Phosphorus is recovered earlier in the process as a wet solid which can be processed into fertilizer in the same way as phosphate ore**
- **Nitrogen will be in the form of ammonia**
- **Following chart shows water analysis from a high-potassium algae species**

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Analysis for CHG Effluent Water

Element	Algae 4 composite water sample
K 766.490	718.6
Na 589.592	364.2
B 249.772	13.75
Si 251.611	11.03
Al 396.153	5.561
S 180.669	1.534
Ca 317.933	0.505
Ba 233.527	0.087
Cu 327.393	0.066
Sn 189.927	0.052
P 213.617	0.041
Mg 285.213	0.041
Fe 238.204	0.018
Mo 202.031	0.014
Zn 206.200	0.014
Ni 231.604	0.018
V 310.230	0.01
Mn 257.610	0.005
Ti 334.940	0.002
Cr 267.716	0.002
Pb 220.353	0.002
	green is below quantifiable level of 1

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Status: Pilot System in Final Tests

Description of the Pilot System

- **Pilot System capacity of 1 metric ton per day of wet algae slurry at 30% solids**
- **Will produce 1 barrel of oil per day**
- **Owner is a large oil refiner, who wants to test the system in a refinery environment**
  - System is heavily instrumented and designed like a refinery system, with remote operating capability
  - Formal HAZOP review like a refinery system—but it is not a hydrocarbon system, it is a water system
  - Cost is USD $2.3 million
- **A more typical system would be simpler and cheaper**

Other Biomass to Fuel Technologies

- **Anaerobic Digestion (AD) is most widely known**
  - Biological process, more than 2,000 years old
  - Slow and incomplete conversion--app. 45% in 20 days vs. 99% in 45 minutes for hydrothermal
- **Cellulosic ethanol production**
  - 35% of carbon goes to fuel, vs. 85% for hydrothermal
  - Alcohol lower value than hydrocarbon fuels
- **Another technology—high-temperature pyrolysis—is not practical for wet materials**
  - 40% of the energy is lost drying the material
  - Output oil is lower energy and higher cost to refine

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CHG Conversion Process

- **The feedstock can either be raw biomass or the residual after formation and removal of HTL oil**
- **CHG uses a catalyst to convert liquefied biomass to methane (HTL uses no catalyst)**
  - Catalyst is commercially available and produced in large quantities
  - Catalyst is pelletized in fixed bed in reactor pipes
- **Sulfur and phosphate removal is accomplished in liquid state in several steps before the catalyst bed**
- **CHG of raw biomass achieves carbon conversion from wood to methane = 65%**

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CHG (Gas) Chemistry

Partial equations:

$C_6H_{10}O_5 + H_2O \longrightarrow 6CO + 6H_2$ (steam reforming of carbohydrate)

$CO + 3H_2 \longrightarrow CH_4 + H_2O$ (methanation)

$CO + H_2O \longrightarrow CO_2 + H_2$ (water-gas shift)

The overall stoichiometry is then:

$$C_6H_{10}O_5 + H_2O \longrightarrow 3CH_4 + 3CO_2$$

Notes:

1. Starch is used as an example, but actual feedstocks will contain many molecular structures.
2. The gas product will usually contain a small amount (1-2%) of hydrogen and ethane in addition to methane and carbon dioxide.
3. In practice, the gas will be approximately 60% CH_4/40% CO_2, not 50/50 as shown because of feedstock differences

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Examples

System Data 10 t/d Dry Weight Wood

MEASURE	US UNITS	SI UNITS
Wood dry weight/day	11.0 tons per day	10 t/d
Wood dry weight/year	3,857 tons per year	3,500 t/y
Slurry wet weight	55.1 tons per day	50 t/d
Gas with 60% methane	254 MCF per day	7,200 m^3/d
Size of generator	875 kWe	875 kWe
Prime Mover Efficiency	NG IC Engine 40%	NG IC Engine 40%
Cost inc. genset	USD $12.8 million	CAD $14.4 million
Years to recover invest	28 Years	28 Years

System Data for 30 MWe System

MEASURE	US UNITS	SI UNITS
Wood dry weight/day	303 tons per day	275 t/d
Wood dry weight/year	106,067 tons per yr	96,250 t/y
Slurry wet weight	1,516 tons per day	1,375 t/d
Gas with 60% methane	6,989 MCF per day	198,000 m^3/d
Size of generator	30 MWe	30 MWe
Prime Mover Efficiency	CC Gas Turb 50%	CC Gas Turb 50%
Cost inc. genset	USD $109 million	CAD $122 million
Years to recover invest	4.2 years	4.2 years

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