Challenges and Opportunities for Biomass Pyrolysis in Washington State

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WASHINGTON STATE BIOENERGY RESEARCH SYMPOSIUM

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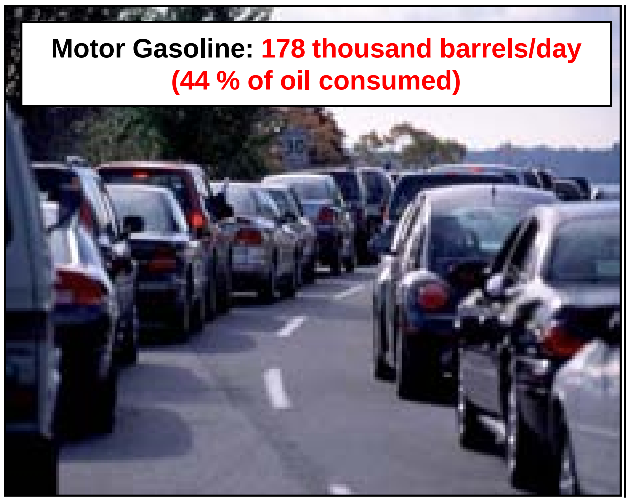
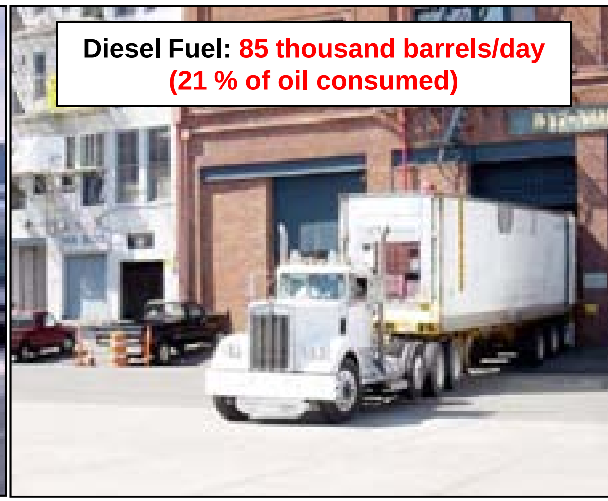
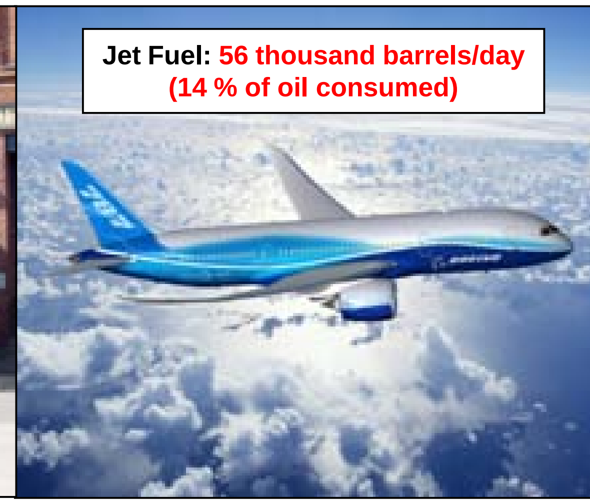
Introduction

Petroleum imports already supply more than *55 percent of the U.S. energy needs* and are expected to grow to more than *68 percent by 2025* as the *worldwide demand also continues to increase while domestic and global oil production continue to decline*.

Washington State consumes 405 thousand barrels of oil per day (60.4 barrels/day per 1000 people)







Washington State has no indigenous crude oil, some exploration has been carried out onshore and offshore, with no strong indications of important oil resources.

Introduction

The Unique Role of Biomass

While the growing need for a sustainable electric power can be met by other renewable resources …..

Biomass is our only renewable source of carbon-based fuels and chemicals.

Source: Pecheco M.A. The National Bioenergty Center and Biomass R&D; Overview. May 20, 2004. http://www.nrel.gov/docs/gen/fy04/36831c.pdf

OUTLINE

1.- Washington State Biomass Inventory

2.- Fast and Slow Pyrolysis Technologies

3.- Biomass Thermochemical Conversion Program at WSU

4.- Conclusions

Washington State Biomass Inventory

Washington State has large quantities of diverse and distributed biomass resources.

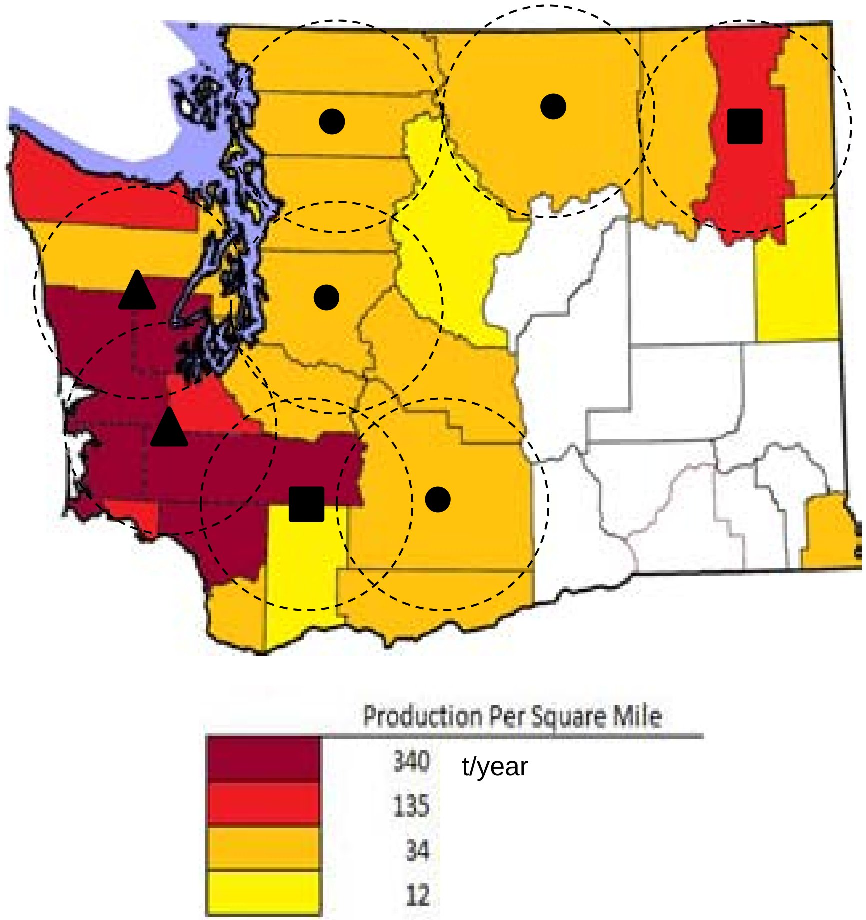
The **biomass inventory of the State of Washington,** funded by the **Department of Ecology**, was used as the primary source of information to evaluate the **potential of pyrolysis technologies to convert available forest and agricultural bio-resources into valuable products**.

Residue	Tons/Year
Agriculture →	**2,427,572**
Winter Wheat Straw	1,481,506
Spring Wheat Straw	283,579
Barley Straw	207,445
Corn Stover	334,371
Grass Seed Straw	111,760
Orchard Tear Out	8,911
Forest Residues →	**5,537,103**
Logging Residues	3,265,150
Forest Thinning Residues	505,665
Mill Residues (fuel)	1,588,288
Mill Resiues (total)	4,663,013
Construction Debris (Seattle)	150,000
Construction Debris (Spokane)	28,000

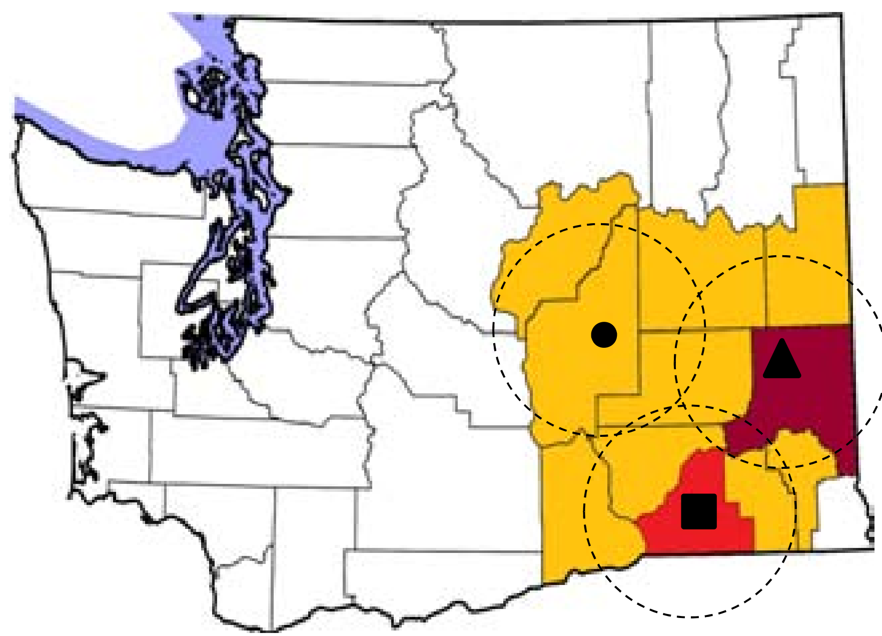
Washington State Biomass Inventory

Availability of Lignocellulosic Materials, potential size and location of Processing Facilities

Forest Residues



Agricultural Residues



Maximum Capacity of Biomass Processing Plant
(transportation radius **60 miles**)

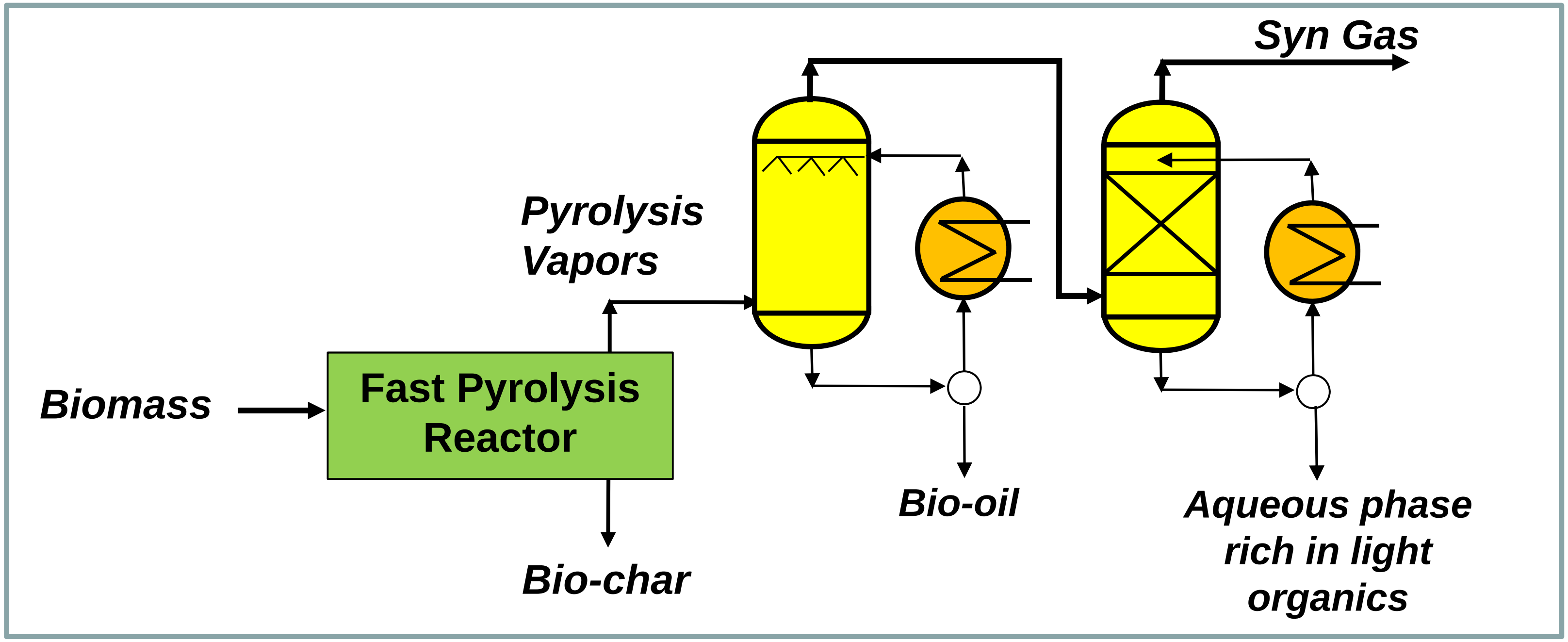
Marker	Size
★	100 TPD
●	500 TPD
■	2000 TPD
▲	4000 TPD

There is enough biomass within a 60 mile radius to build large processing facilities

Fast and Slow Pyrolysis Technologies

Fast Pyrolysis

Fast pyrolysis is a process in which very small biomass particles (less than 2 mm diameter) are heated at 450 – 600 °C in the absence of *air/oxygen to* produce high bio-oil yield (60-75 mass%).



Conditions	Liquid	Char	Gas
High heating rates, small particles, short residence time of vapors	60-75 %	12-20 %	13-20 %

Fast and Slow Pyrolysis Technologies

Mobile Units

Stationary Units

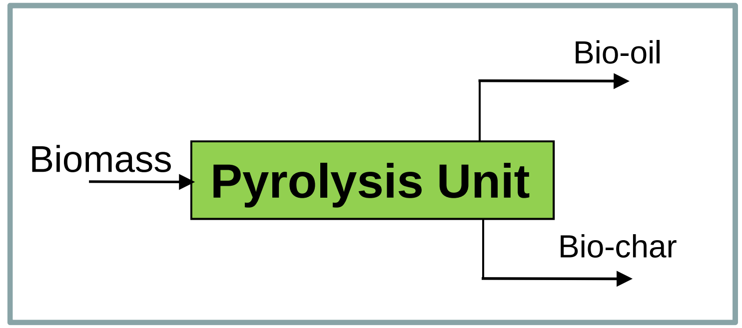
25-100 t/day

More than 100 t/day

Fast and Slow Pyrolysis Technologies

CONVERSION OF FOREST BIOMASS BY FAST PYROLYSIS
(LOW CONTENT OF ALKALINES)

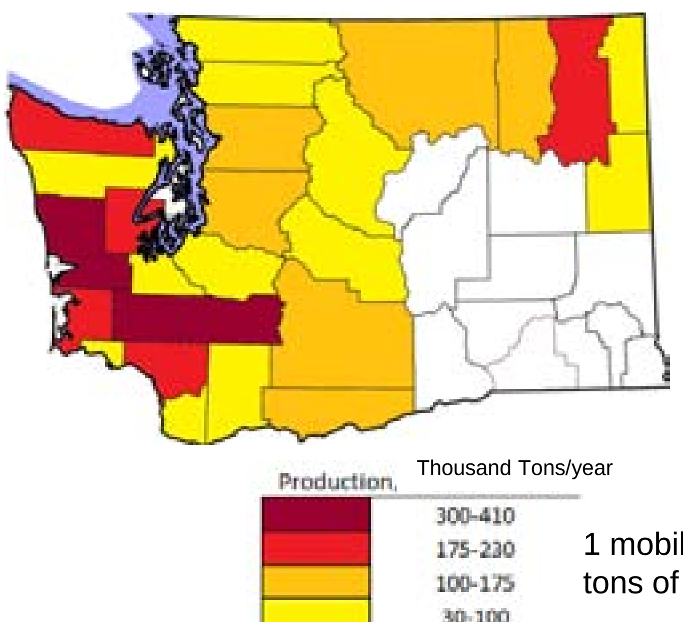
Fast Pyrolysis



Potential Crude Bio-oil production from forest wastes: **3.2 million t/year**

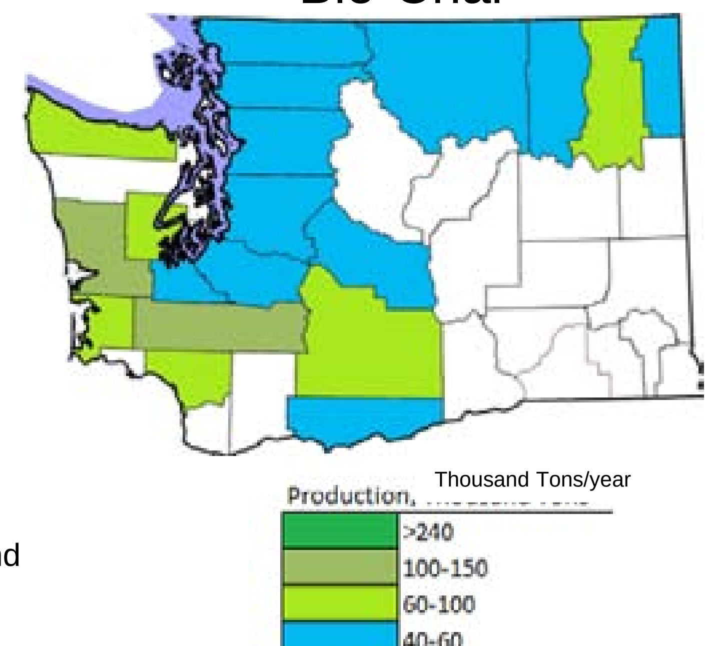
Potential Bio-char production from forest wastes: **0.8 million t/year**

Crude Bio-Oil



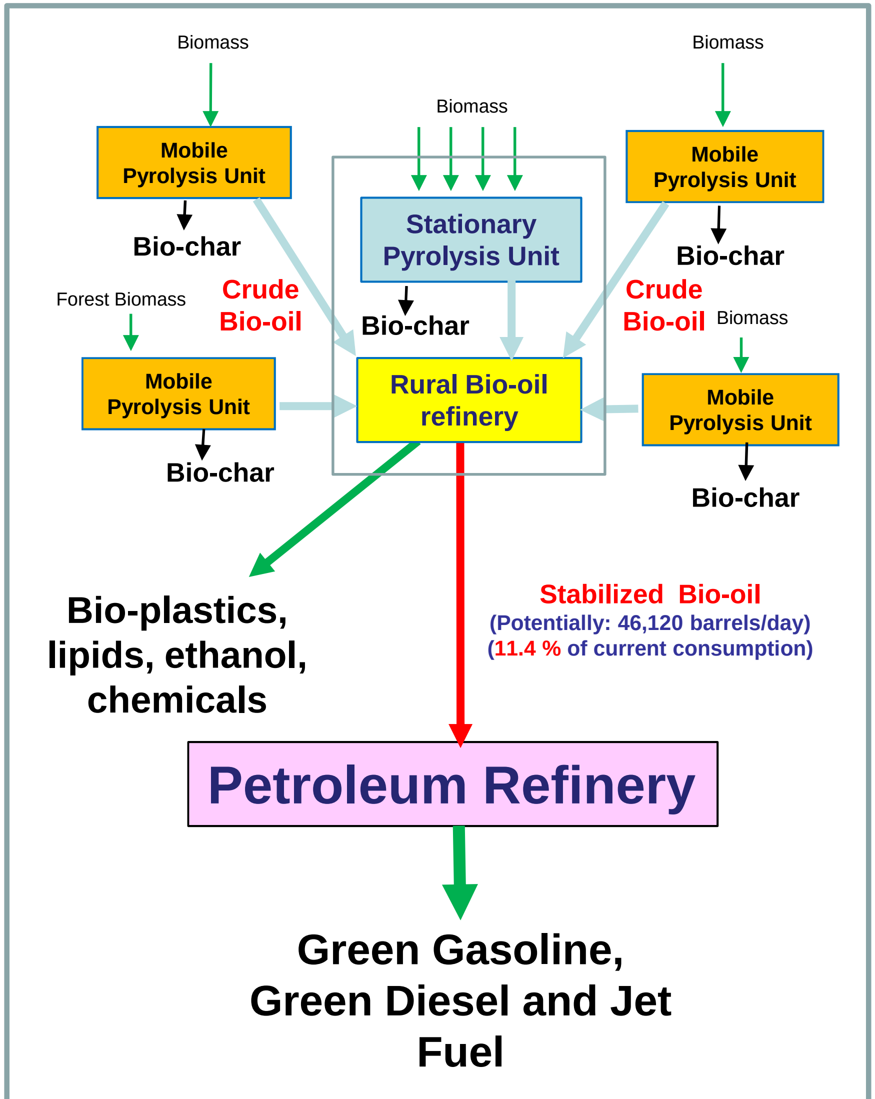
1 mobile unit: 5-22 thousand tons of bio-oil/year

Bio-Char

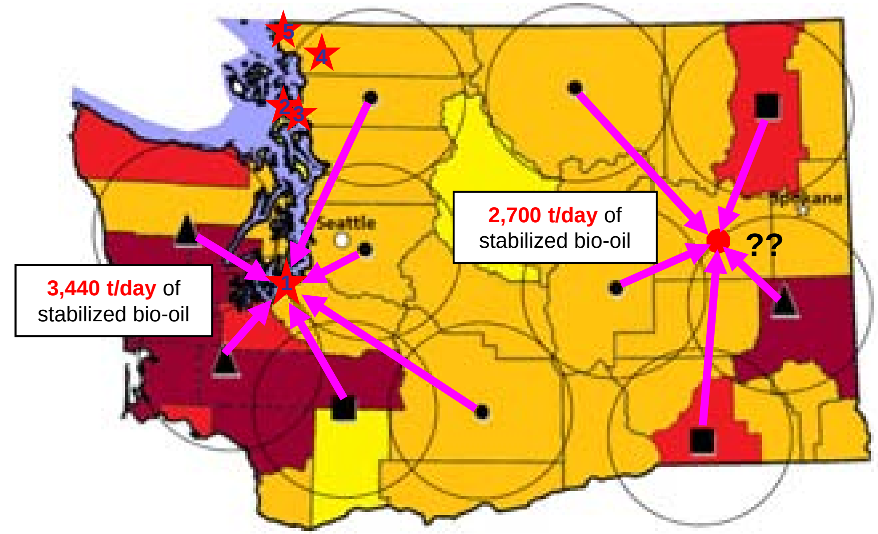


Fast and Slow Pyrolysis Technologies

Model of Biomass Economy Based on Pyrolysis and Rural Refineries



Potential Production (11.4 % of Current WA Oil Consumption)



★ Petroleum Refineries		Rural Bio-oil Refineries
1	Tacoma (Oil US): **4,600 t crude oil/day**	● 300 t crude bio-oil/day
2	Anacortes (Tesoro): 14,400 t crude oil/day	■ 1,200 t crude bio-oil/day
3	Anacortes (Shell): 19,000 t crude oil/day	▲ 2,400 t crude bio-oil/day
4	Ferndale (Conoco): 14,000 t crude oil/day	
5	Cherry Point (BP): 30,000 t crude oil/day	

Potential Production of Stabilized Bio-oil: 6,140 t/day (46,120 barrels/day)
Potential per-capita of Stabilized Bio-oil: 6.9 barrels per day/1000 people
Current WA per-capita consumption: 60.4 barrels per day/1000 people
World per capita consumption: 31.7 barrels per day/ 1000 people

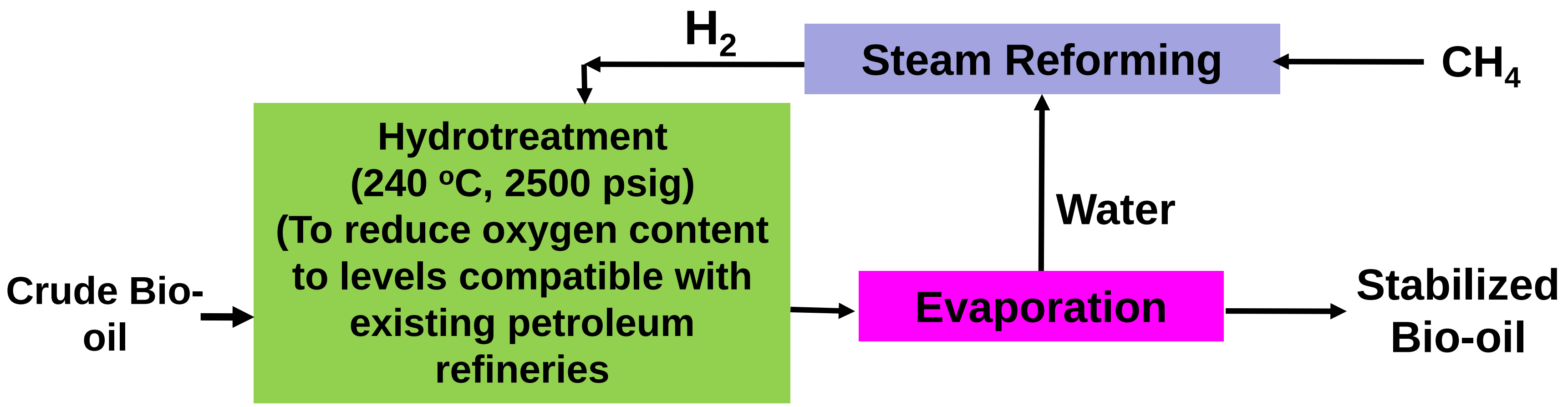
Assumptions: (1) Yield of crude bio-oil: 60 mass % of the biomass processed (2) Yield of stabilized bio-oils: 50 mass % of the crude bio-oil obtained

Fast and Slow Pyrolysis Technologies

Main Hurdle:

Lack of **Rural Refineries** to convert crude bio-oil into an stabilized oil compatible with existing petroleum refineries and high value products.

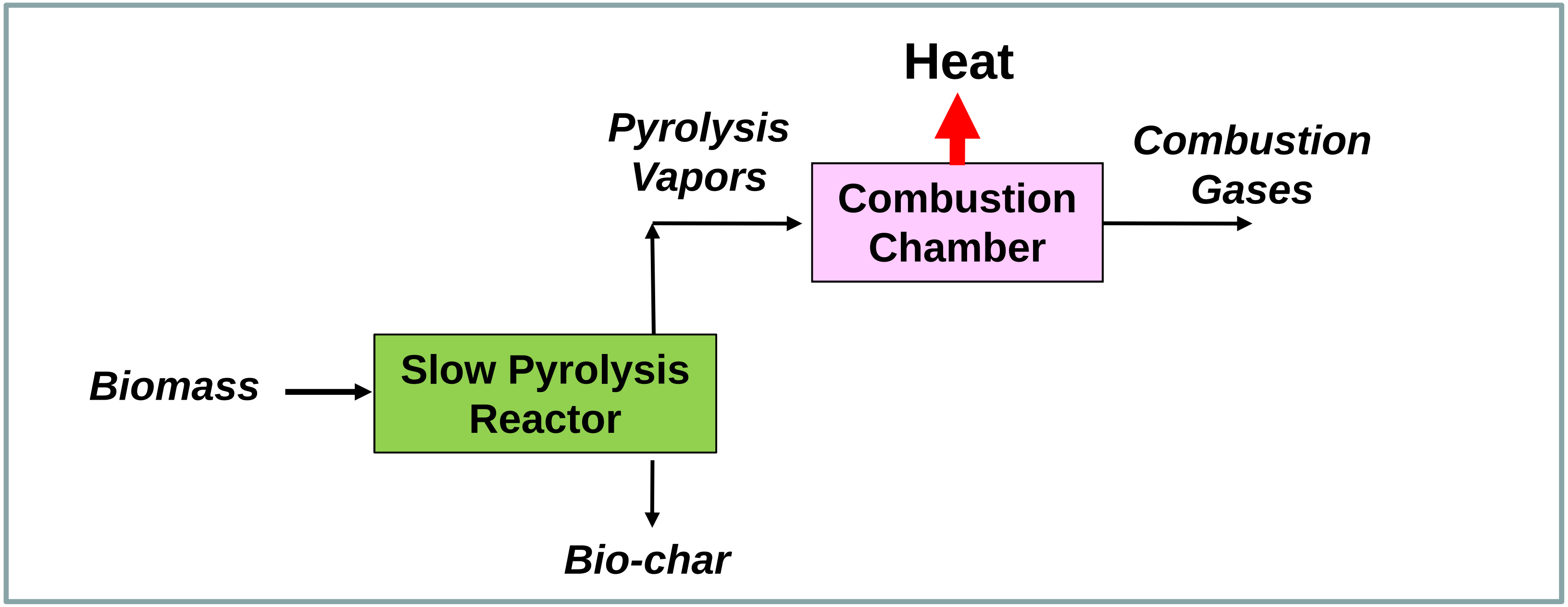
Rural Bio-oil Refinery (Looks like a modified Xylitol or Sorbitol Plant)



Fast and Slow Pyrolysis Technologies

Slow Pyrolysis

Slow pyrolysis is a process in which large biomass particles (more than 2 mm diameter) are heated at 450 – 600 °C in the absence of *air/oxygen to* produce high bio-char yield (25-35 mass %).

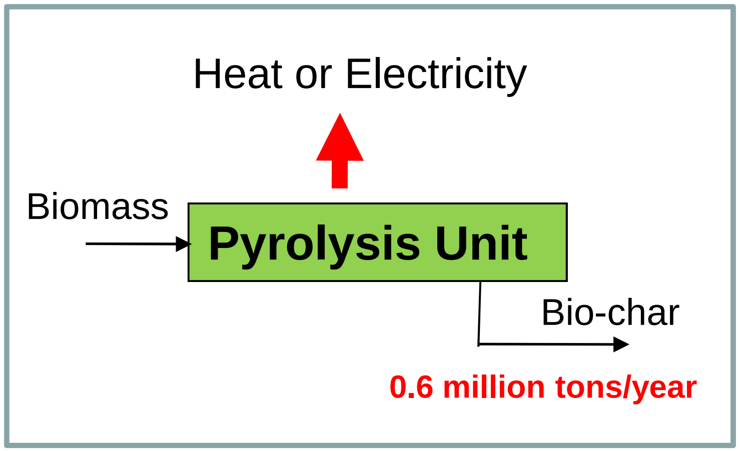


Conditions	**Liquid**	**Char**	**Gas**
Slow heating rates, large particles, large residence time of vapors	30 - 45 %	**25-35 %**	25-35 %

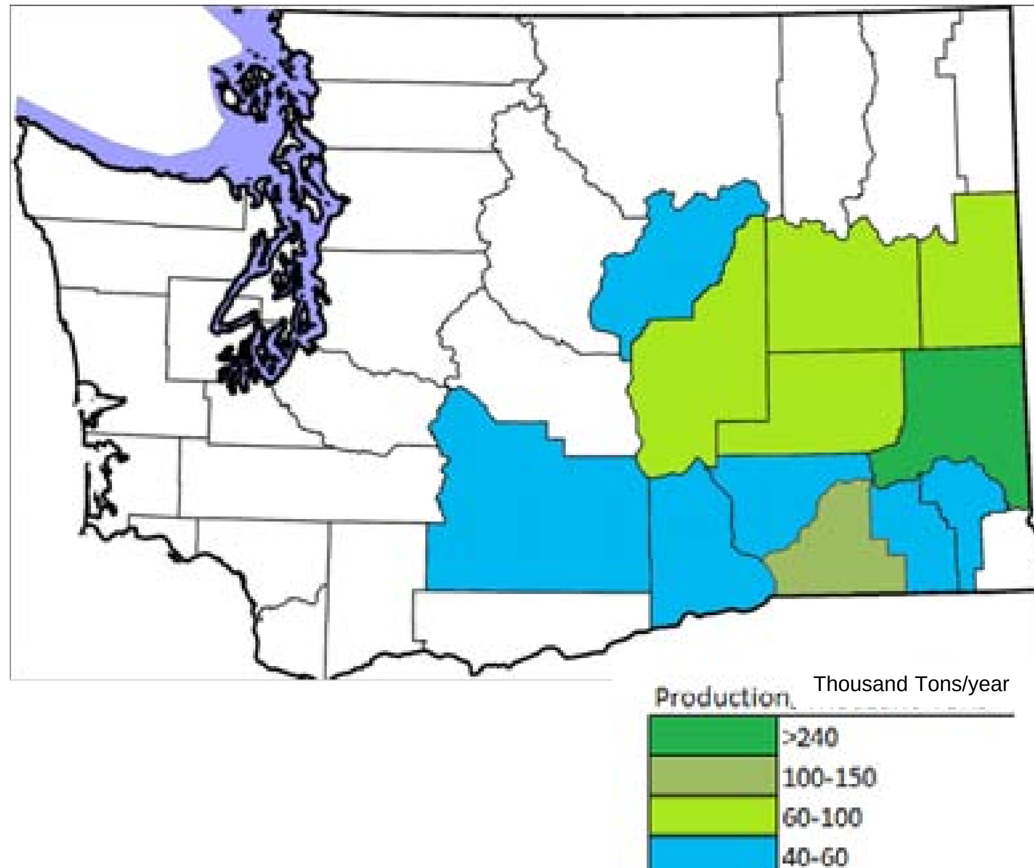
Fast and Slow Pyrolysis Technologies

CONVERSION OF AGRICULTURAL WASTES BY SLOW PYROLYSIS (HIGH CONTENT OF ALKALINES)

Slow Pyrolysis



Bio-Char



Companies producing bio-char can be found at: http://terrapreta.bioenergylists.org/company

Fast and Slow Pyrolysis Technologies

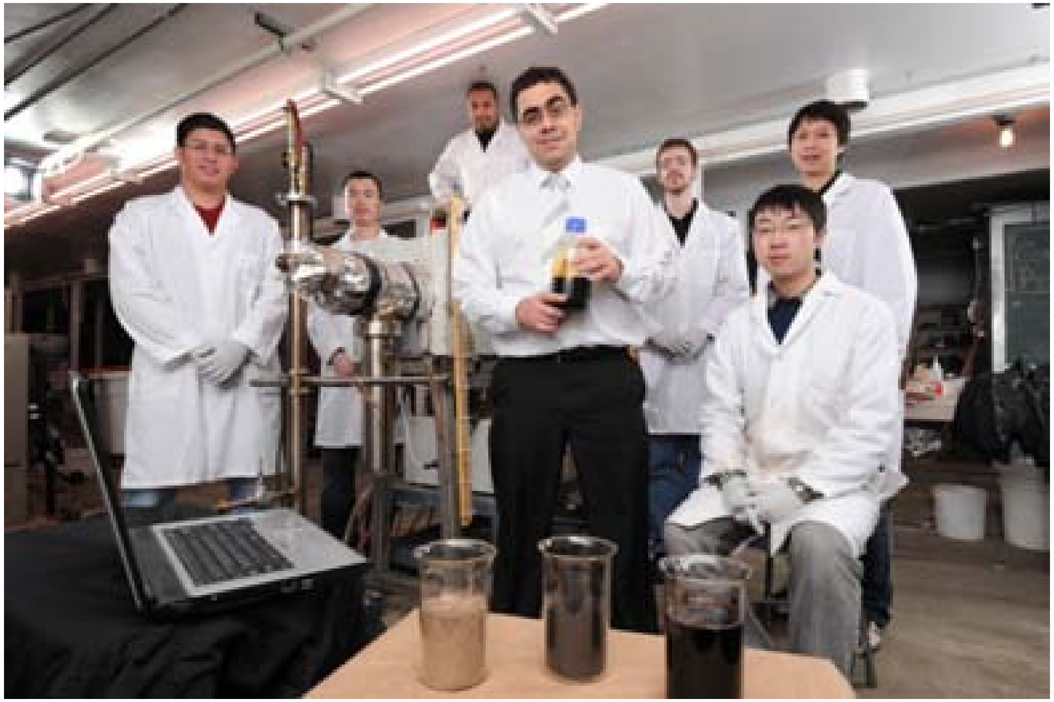
SLOW PYROLSYSIS is well suited for producing **bio-char and heat/electricity from the Agricultural Wastes with high contents of alkalines generated by the State.**

Main Hurdles:

Lack of environmentally friendly slow pyrolysis technologies able ***to produce heat and Bio-char***

Higher value products from Bio-char have to be developed

Biomass Thermochemical Program at WSU



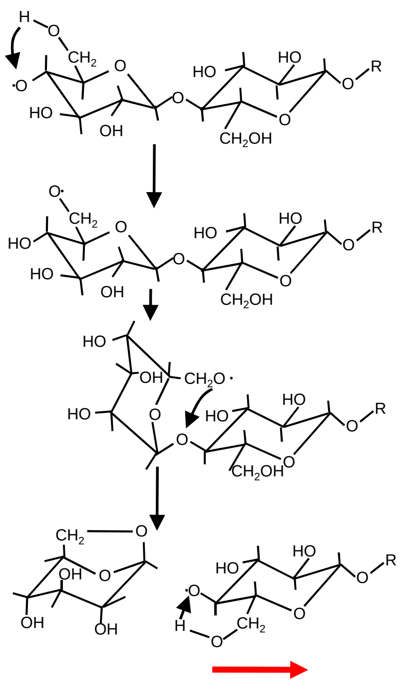
Process Development ⟷ **Product Development**

- Biomass → **PYROLYSIS**
  - **Crude Bio-oil**
    - *Ethanol*
    - *Lipids*
    - *Bio-plastics*
    - *Resins*
    - *Green Gasoline and Diesel, Bio-jet*
    - *Hydrogen*
  - **Bio-char**
    - *Advanced Soil Amendments*
    - *Construction Materials*

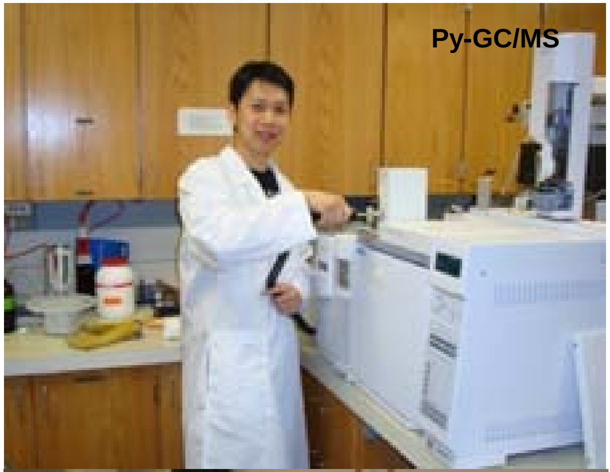
Biomass Thermochemical Program at WSU

*Fundamental studies on the **thermal degradation mechanisms of cellulose, hemicellulose, lignin** to enhance the selectivity of pyrolysis reactions towards the production of precursors of transportation and aviation fuels.*

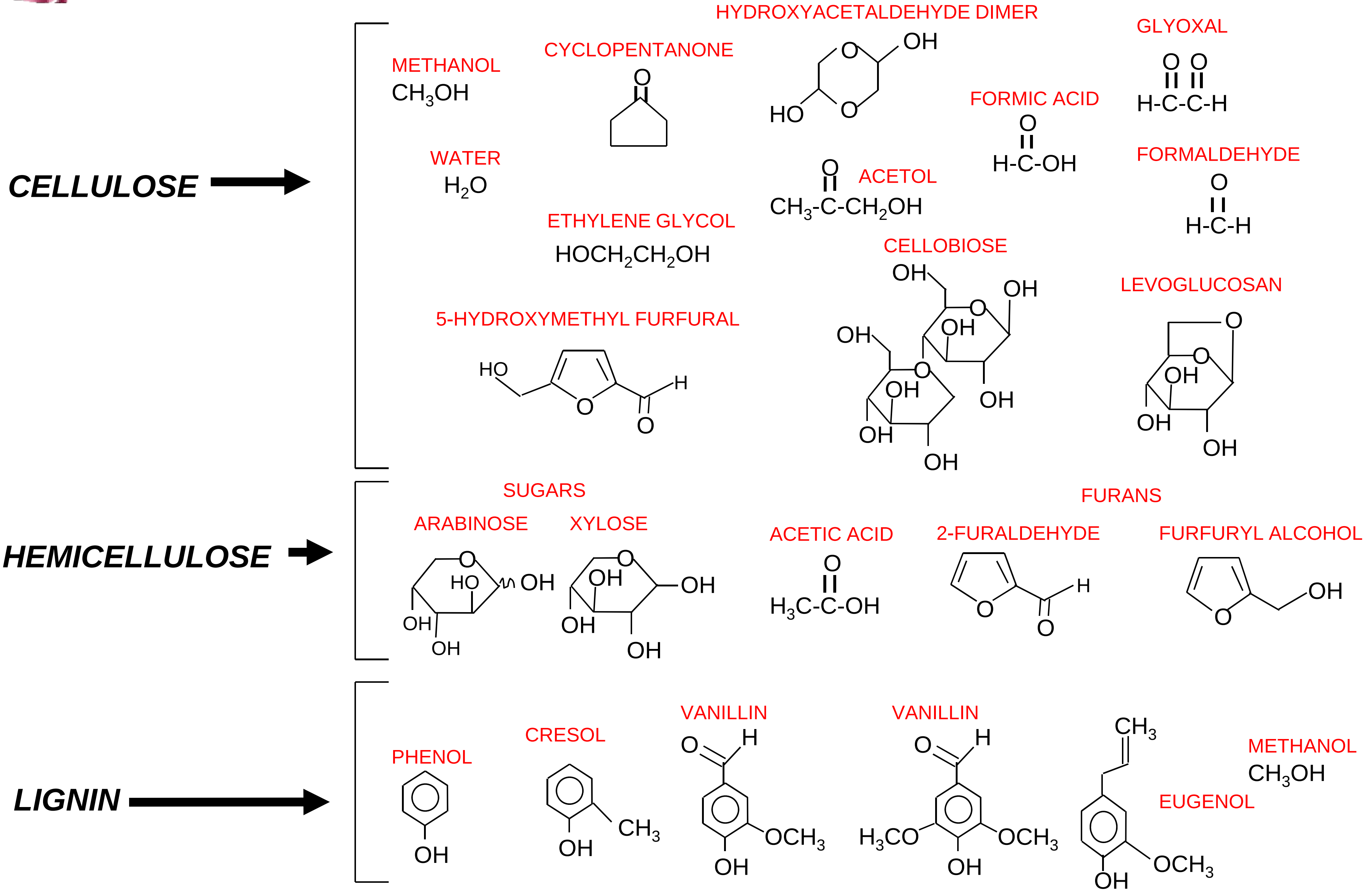
CELLULOSE DEPOLYMERIZATION (350-400 ºC)



UNZIPPING MECHANISM



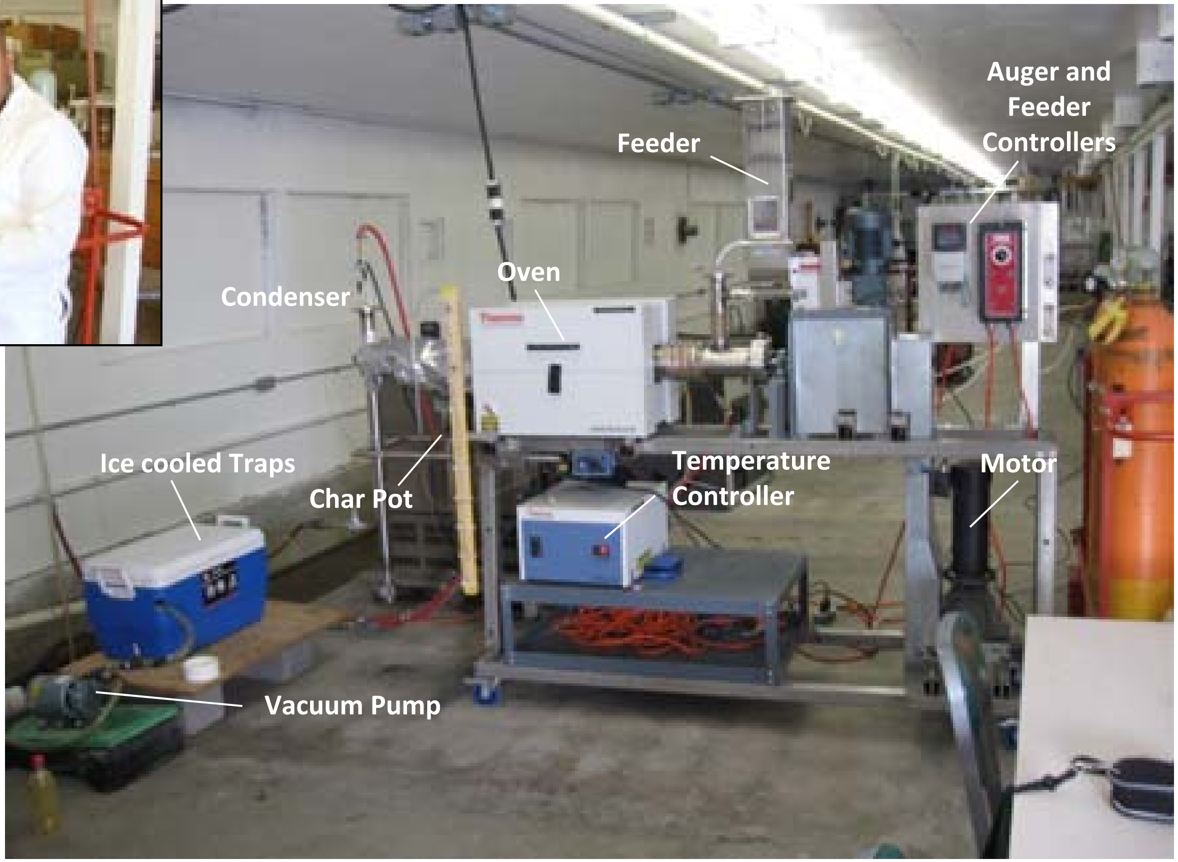
Biomass Thermochemical Program at WSU



Biomass Thermochemical Program at WSU

To develop and test **new types of thermochemical reactors**. **Mathematical modeling** of proposed concepts.

Auger Pyrolysis Reactor



EFFECT OF PYROLYSIS CONDITIONS ON THE YIELD OF TARGETED COMPOUNDS

Auger Reactor

(Washington State University)

Effect of Pyrolysis Temperature

Effect of Additives

Effect of Pretreatment Temperature

Fluidized Bed Reactor

(Curtin University of Technology (Australia))

Effect of Pyrolysis Temperature

Effect of Particle size

Effect of the content of alkalines

Effect of Additives

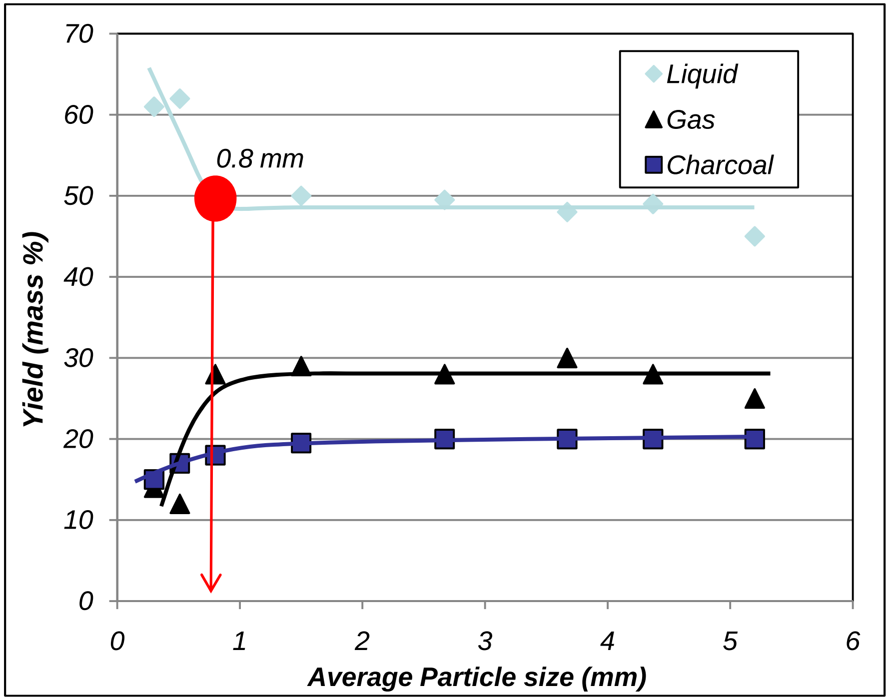
(University of Twente (Netherlands))

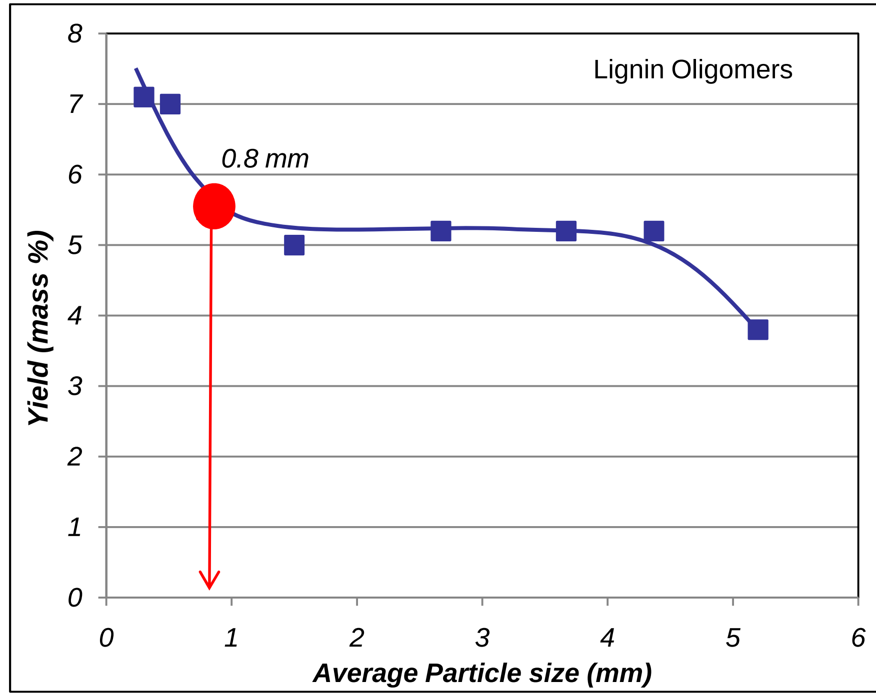
Effect of Pretreatment Temperature

Effect of Condenser Temperature

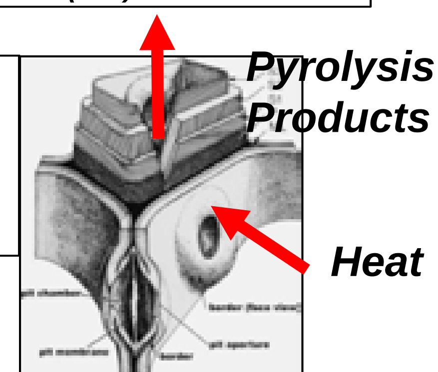
Biomass Thermochemical Program at WSU

Effect of Particle Size (Mallee- Fluidized bed pyrolysis reactor)





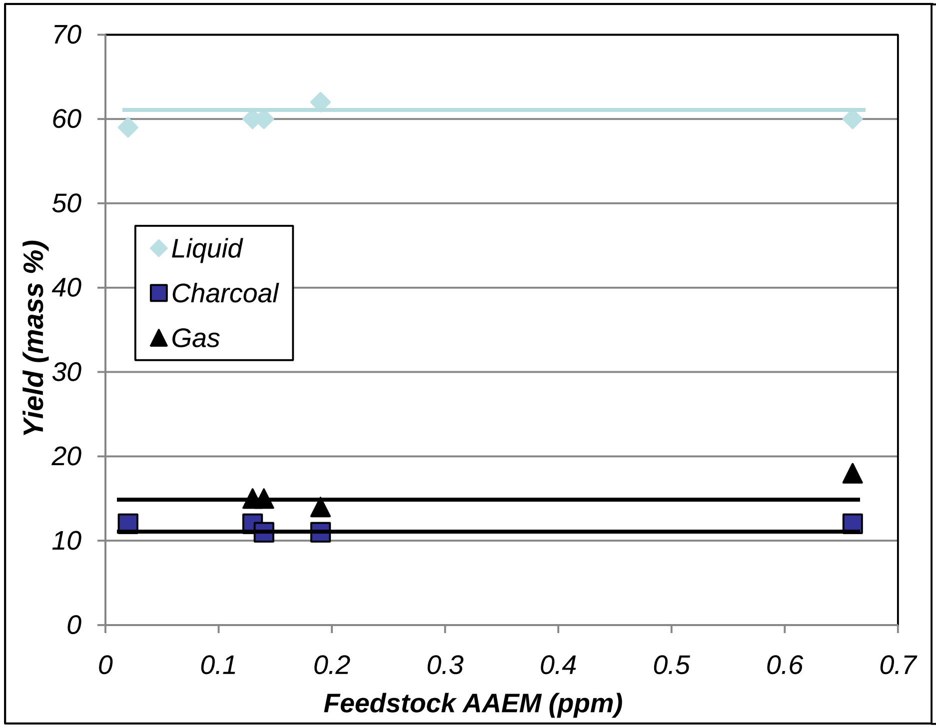
ACHIEVING FAST BIOMASS PARTICLE HEATING RATES AND THE FAST REMOVAL OF PYROLYSIS VAPORS OUT OF THE BIOMASS PARTICLES AND OUT OF THE REACTOR ARE NEEDED TO OBTAIN HIGH BIO-OIL YIELDS FROM THE PYROLYSIS OF LIGNO-CELLULOSIC MATERIALS.

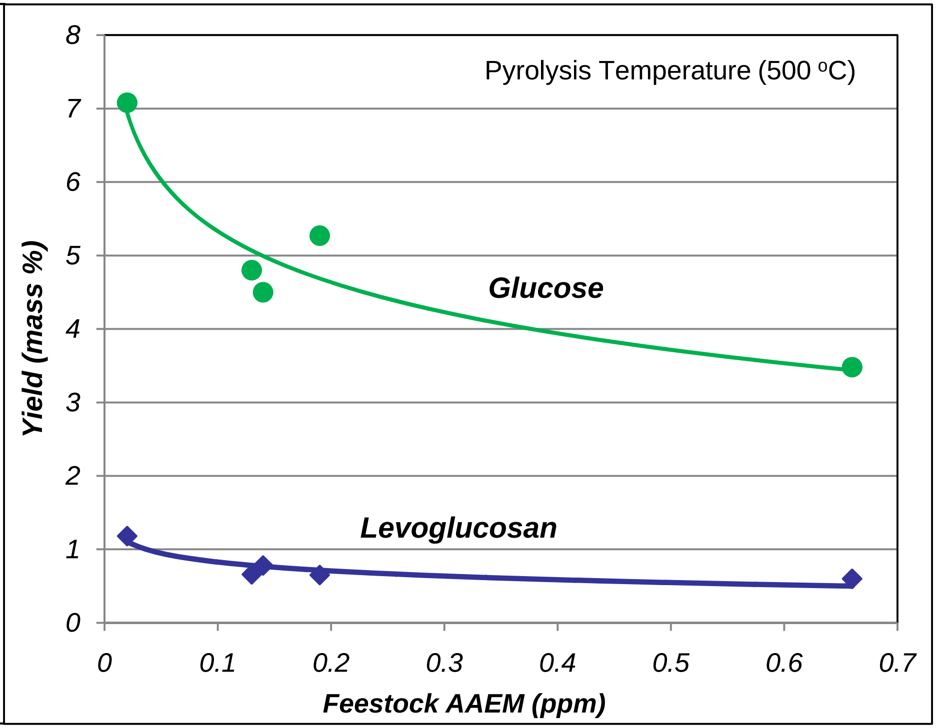


Shen J, Wang X-S, Garcia-Perez M, Mourant D, Rhodes M, Li C-Z: Effects of particle size on the fast pyrolysis of oil malee woody biomass. Fuel 88 (2009) 1810-1817

PRODUCTION OF PYROLYTIC SUGARS

Effect of Alkalines (Mallee- Fluidized bed pyrolysis reactors)

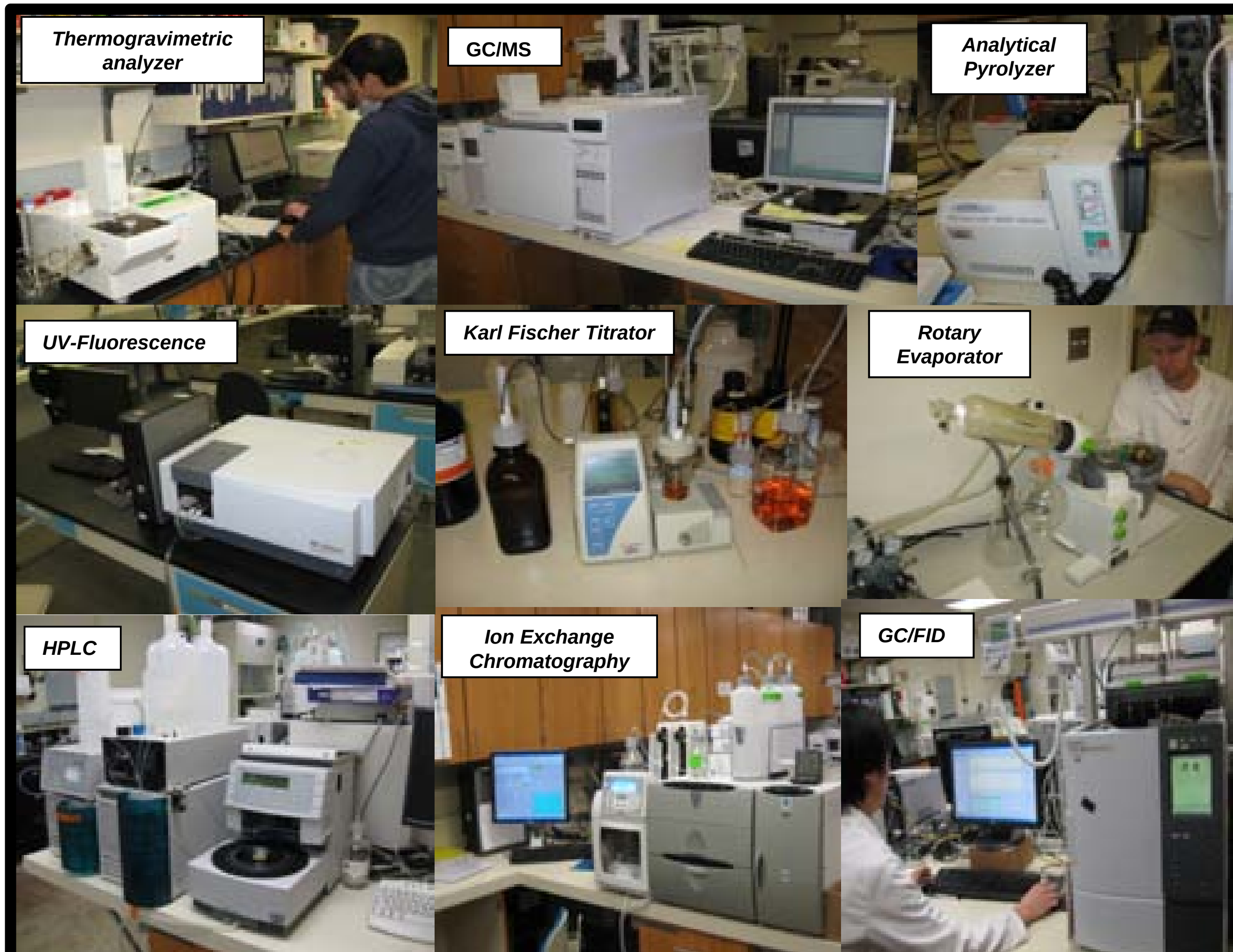




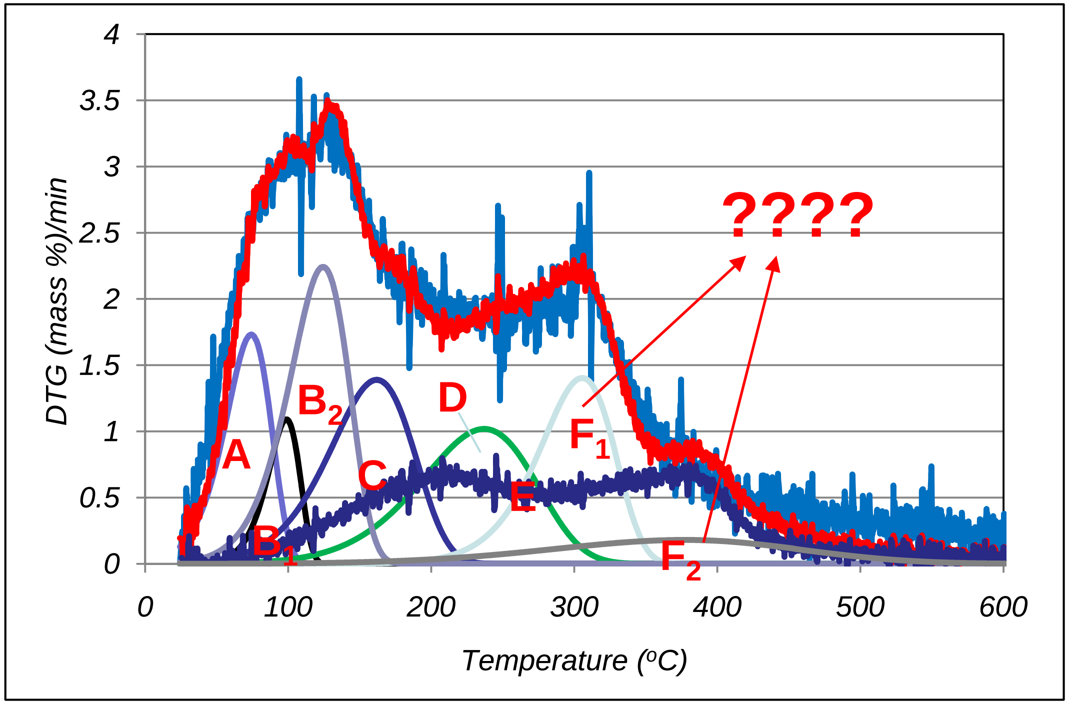
Mourant D, Garcia-Perez M, He M, Wang X-S, Wang Z, Li C-Z: Mallee Wood Fast Pyrolysis: Alkali and Alkaline Earth Metals Removal Impact on Product Yields and Bio-oil Composition (In Preparation)

Biomass Thermochemical Program at WSU

To develop ***new analytical methods*** *to* ***characterize the chemical composition of products from thermochemical reactions*** *(Bio-oil, Bio-char and Gases).*



Biomass Thermochemical Program at WSU

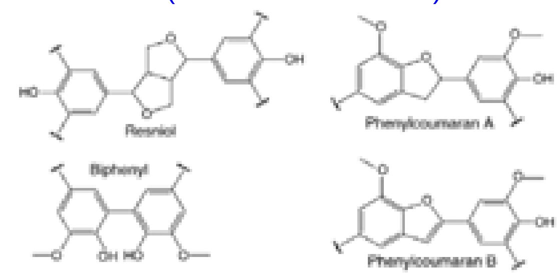


Characterization methods

Family A: GC-FID
Family B: K-F Titration and GC-FID
Family C: GC-MS
Family D: Acid Hydrolysis + IEC
Family E: Cold Water Precipitation
Family F: ???? ←

FAMILY E [1]

(LIGNIN OLIGOMERS)



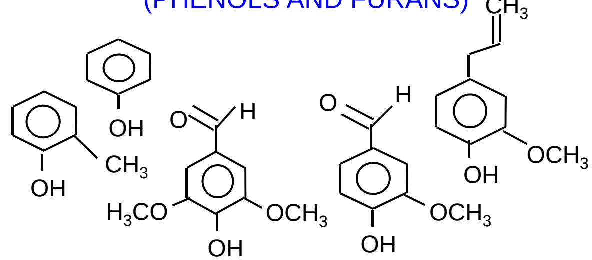
FAMILY A AND B

BOILING POINTS UNDER 150 °C

CH_3OH, $HOCH_2CH_2OH$, H-C(=O)-OH, H_2O, H-C(=O)-C(=O)-H, H-C(=O)-H, H_3C-C(=O)-OH, $HOCH_2CH_2OH$, CH_3-C(=O)-CH_2OH

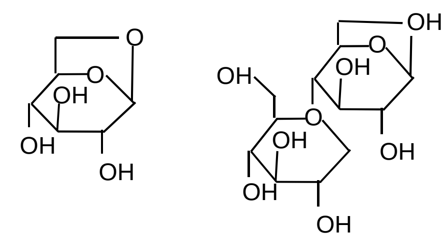
FAMILY C

(BOILING POINTS BETWEEN 100 AND 250 °C)
(PHENOLS AND FURANS)



FAMILY D

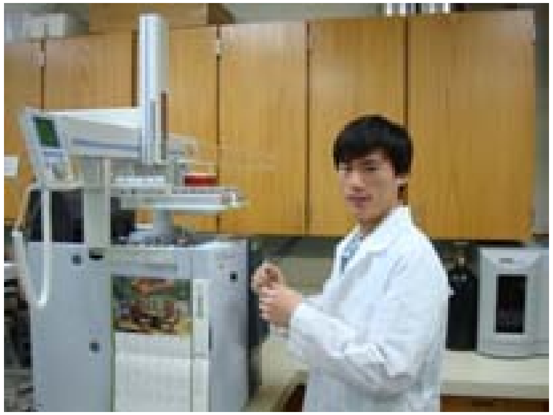
(BOILING POINTS BETWEEN 200 AND 300 °C)
(FERMENTABLE SUGARS)



[1]Bayerbach R, Nguyen VD, Schurr U, Meier D: Characterization of the water insoluble fraction from fast pyrolysis liquids (pyrolytic lignin). Part III: Molar mass characterizatics by SEC, MALDI-TOF-MS, LDI-TOF-MS and Py-FIMS. J. Anal. Appl. Pyrolysis 77, (2006), 95-101

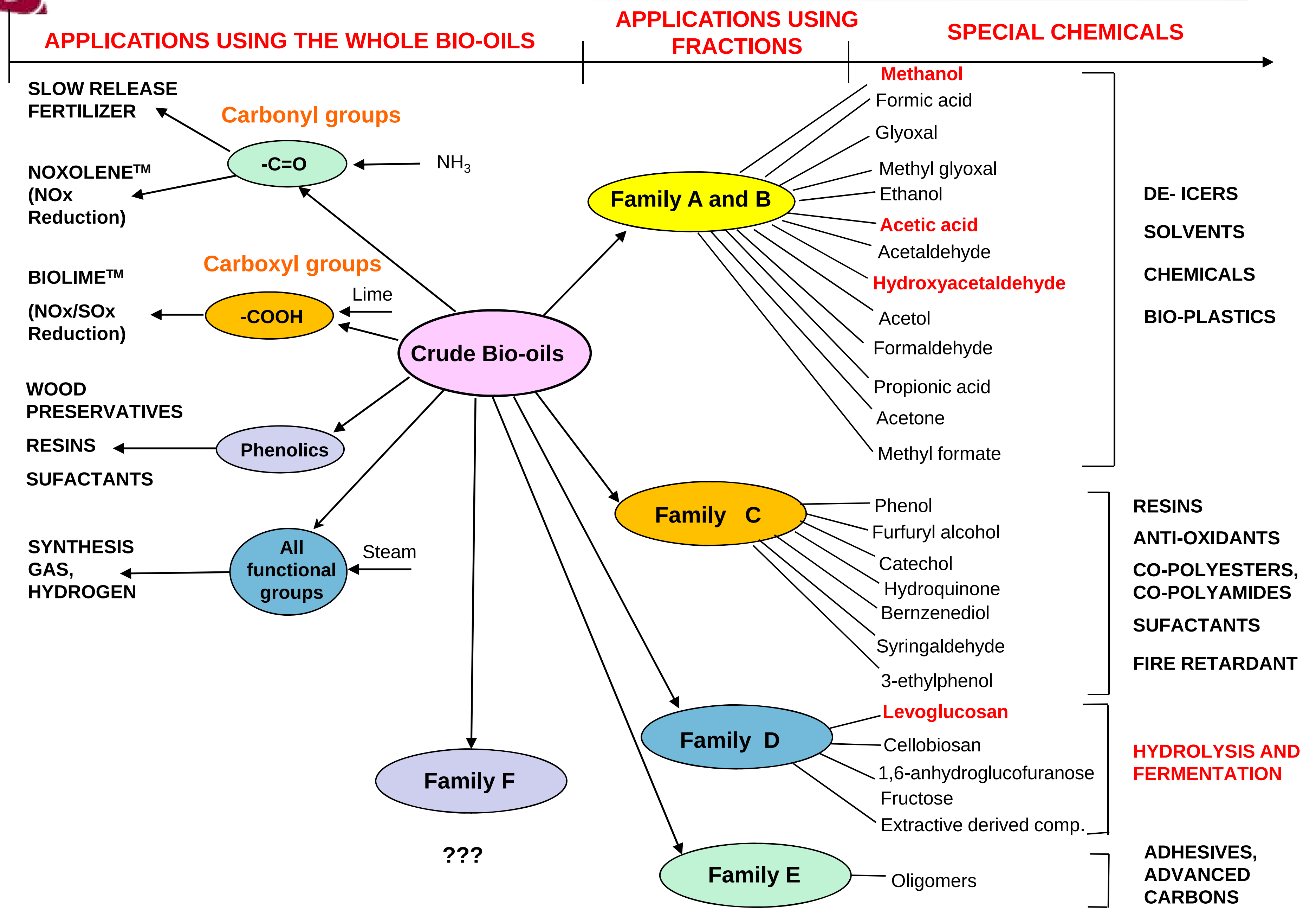
Biomass Thermochemical Program at WSU

To develop *new products from Bio-oils (Transportation fuels, jet fuels, resins and chemicals)*

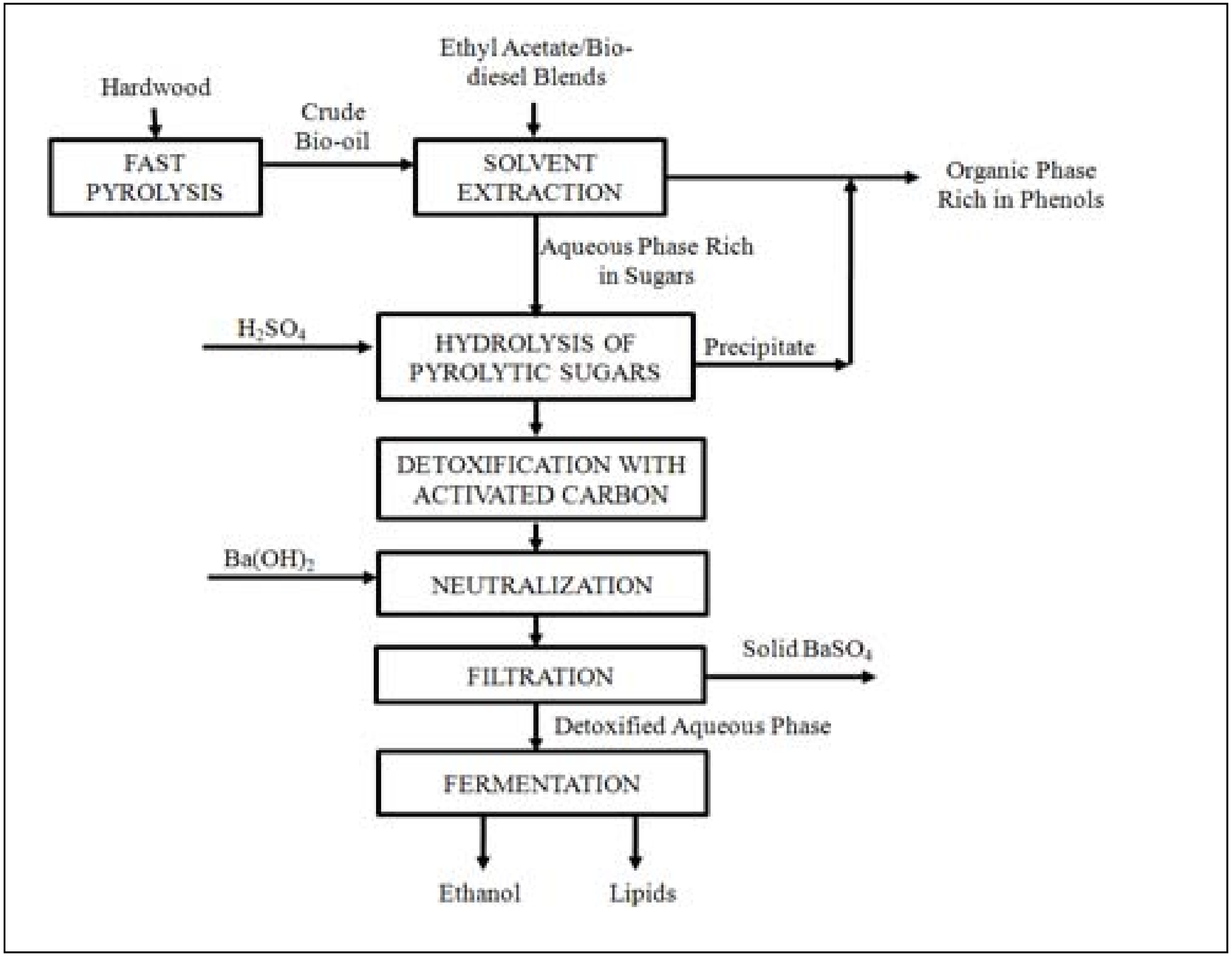




Bio-oil → Processes	Products
Hydrolysis of pyrolytic sugars, detoxification and fermentation	Ethanol Lipids Bio-plastics
Separation of mono and oligo-phenols	Resins
Hydrotreatment to produce stabilized bio-oils	Green Gasoline, jet fuel and Diesel
Steam Reforming	Hydrogen

Biomass Thermochemical Program at WSU

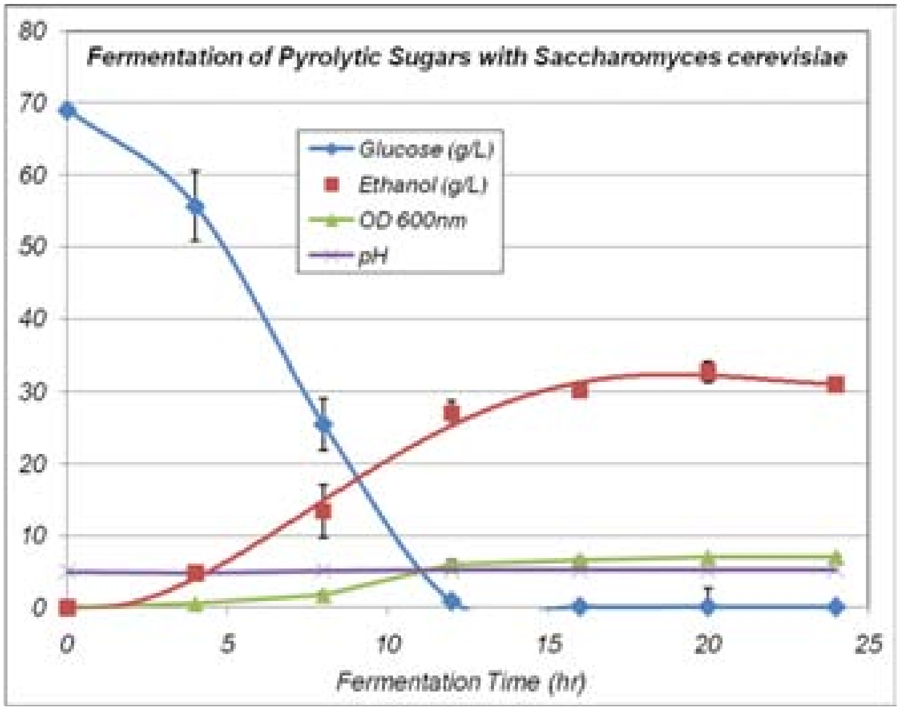


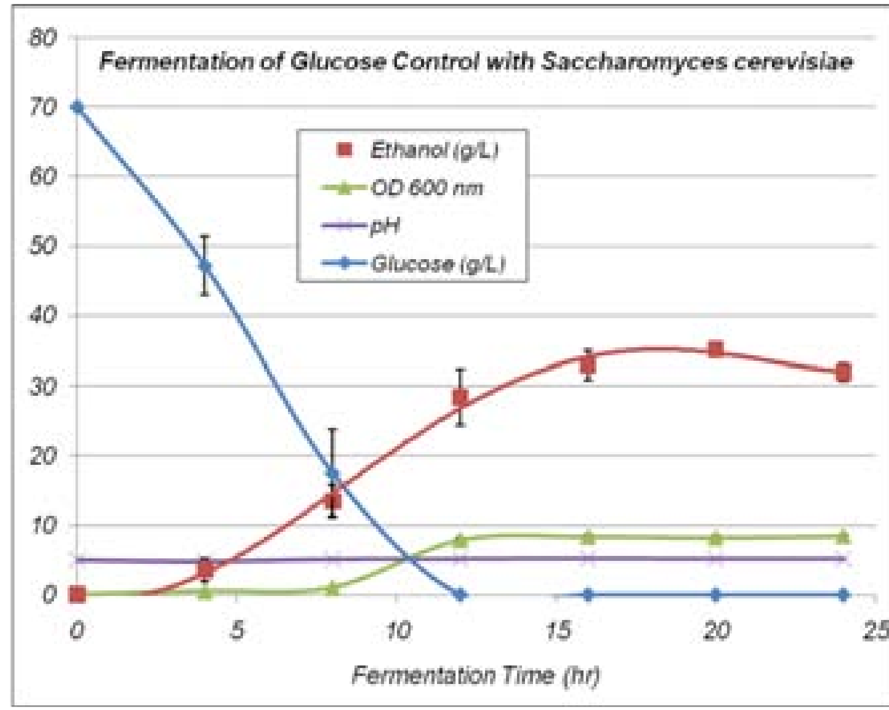
Biomass Thermochemical Program at WSU



Lian J, Chen S, Zhou S, Wang Z, O'Fallon, Li C-Z, Garcia-Perez M: Separation, Hydrolysis and Fermentation of Pyrolytic Sugars to Produce Ethanol and Lipids. Bio-resources Technologies. 101 (2010) 9688-9699

FERMENTATION OF PYROLYTIC SUGARS





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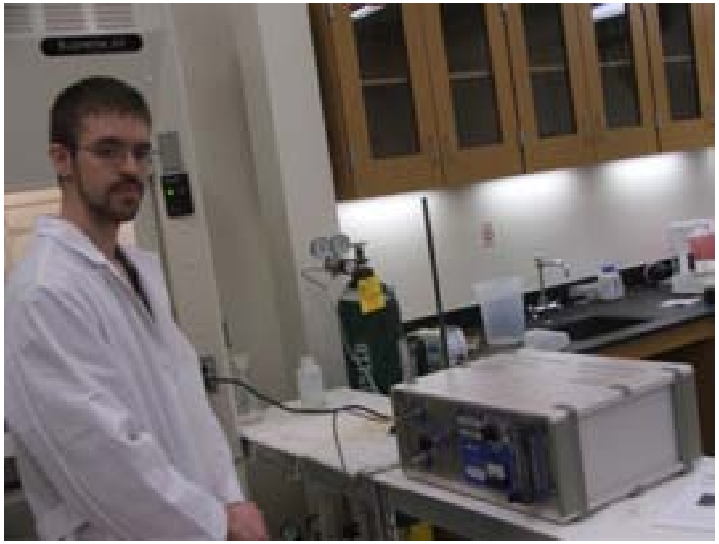
Biomass Thermochemical Program at WSU

To develop ***new products from bio-chars.***



Bio-char — ***Modifications of bio-char surface chemistry and the development of new Products***

- ***Advanced Soil Amendments for carbon sequestration***
- Construction materials
- Fuel to generate Electricity via gasification

FINAL REMARKS

Washington State produces enough biomass to support large scale pyrolysis units, however, the actual size of the pyrolysis unit that should be developed will depend on a **delicate balance of social, environmental and political considerations**.

Two types of Pyrolysis Technologies adapted to the conditions of the state should be developed ***(1)*** Slow Pyrolysis units to produce bio-char and heat (electricity, mostly from Agricultural wastes) ***(2)*** Fast Pyrolysis to produce bio-char and bio-oil (mostly from forest wastes).

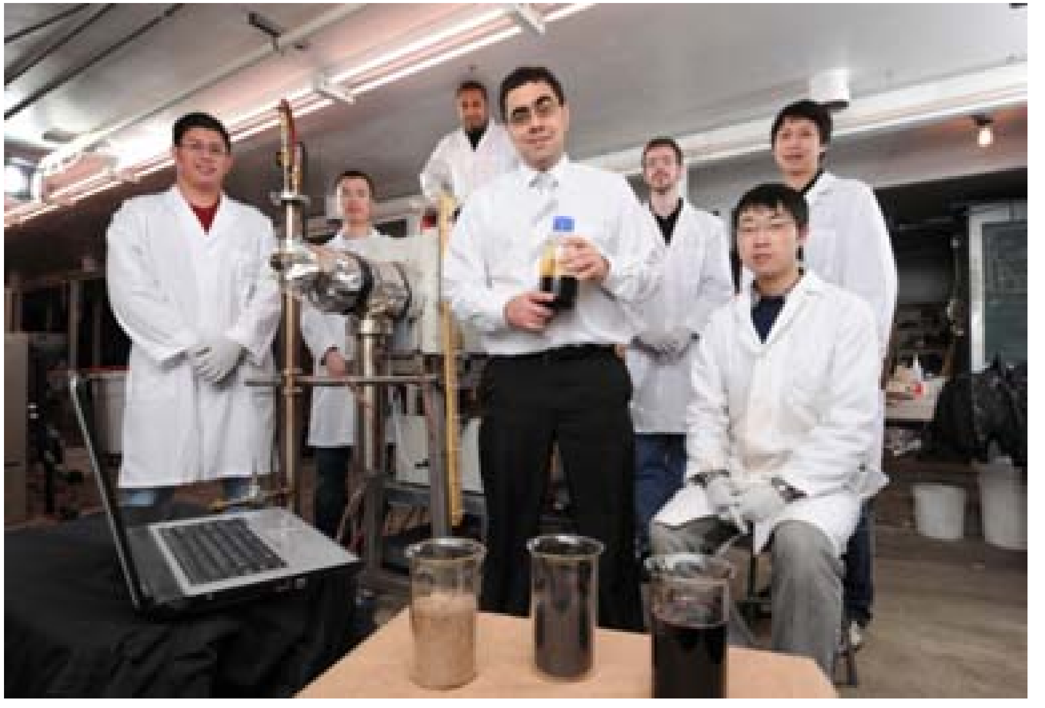
The **deployment of rural refineries** to convert crude bio-oil into a stabilized bio-oil compatible with existing petroleum refineries is the **main hurdle** to produce transportation fuels from bio-oils.

Using the **produced bio-char as a soil amendment is one of the most promising methods for carbon sequestration**. However, **high value bio-chars with enhanced agronomical functions must be developed in order for this to be economically viable**.

Using the current slow pyrolysis technologies to produce **bio-char and heat is the most viable short term option available**. With this in mind, it may be desirable to deploy pyrolysis units that **can produce heat and bio-char but can easily be modified to become fast pyrolysis units for when a technology to fully utilize the bio-oil is available**..

The development of **high value products** from **bio-oils** and **bio-char** is critical for the survival, development and economic viability of pyrolysis technologies.

AKNOWLEDGEMENT



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WASHINGTON STATE UNIVERSITY AGRICULTURAL RESEARCH CENTER

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WASHINGTON STATE DEPARTMENT OF AGRICULTURE

SUN GRANT INITIATIVE, U.S. DEPARTMENT OF TRANSPORTATION

U.S. NATIONAL SCIENCE FOUNDATION

U.S. DEPARTMENT OF ENERGY

QUESTIONS ?