Challenges and Opportunities of Biomass Pyrolysis to Produce Second Generation Bio-fuels and Chemicals

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Washington State University

Workshop on Lignocellulosic Bio-fuels Using Thermo-chemical Conversion

June 13, 2012 , Auburn University

THE PAST AND THE PRESENT

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

Milestones of Distilled Products from Pyrolysis

1658 - The acid called pyroligneous was identified as similar to the acid contained in vinager (**acetic acid**) **(SCIENCE)**

1792 - England commercialized **luminating gas** from wood **(MARKET)**

1819 - The first pyrolysis oven that transferred heat through its metal walls was designed by Reichenbach **(TECHNOLOGY)**

1835 - **Methyl alcohol**, an isolated product of crude wood-spirit, was discovered by Dumas and Peligot **(SCIENCE)**

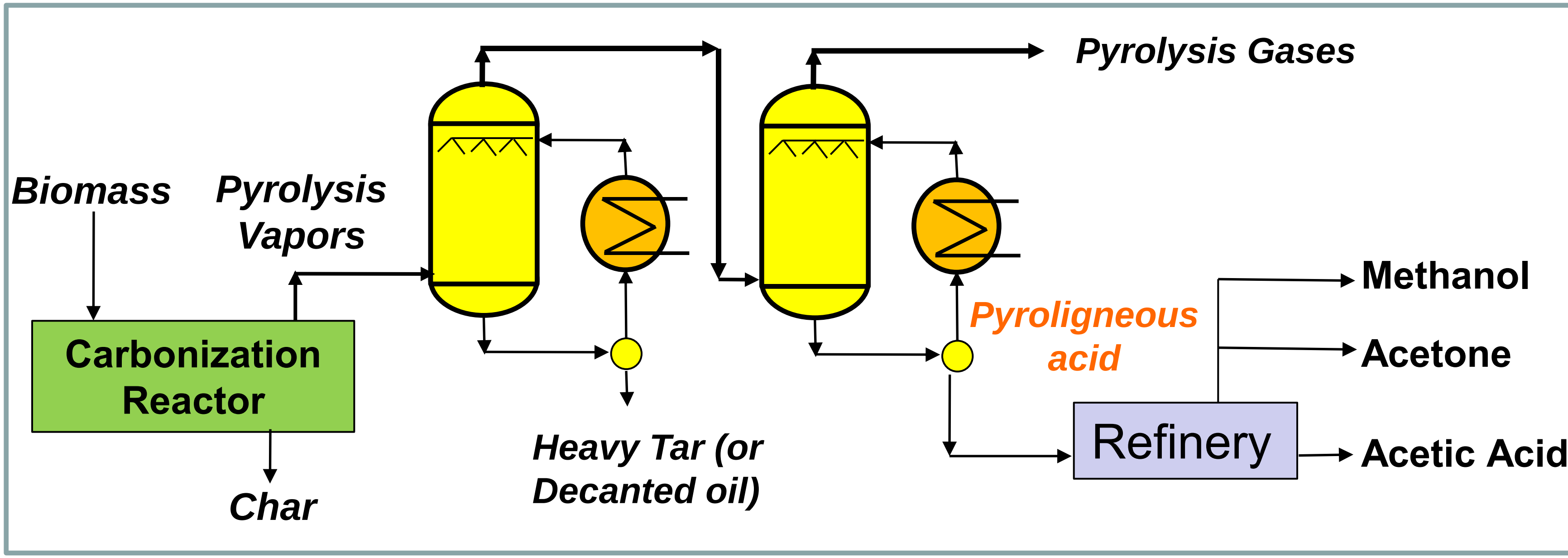
1856 - An increase in demand for **methyl alcohol** was a result of Sr. William H. Perkin's patent on aniline purple (first synthetic organic dye) **(MARKET)**

1870 - Early investigations done by Lowitz resulted in a new chemically **pure acetic acid** **(SCIENCE)**

1850 - The wood distillation industry began to expand **(PROGRESS)** **(SCIENCE+TECHNOLOGY+ MARKET)**

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

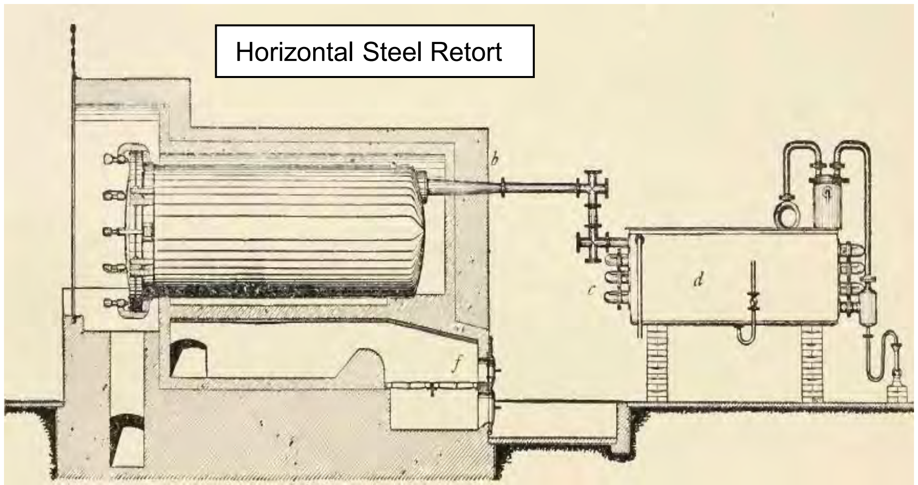
Carbonization (Slow Pyrolysis)

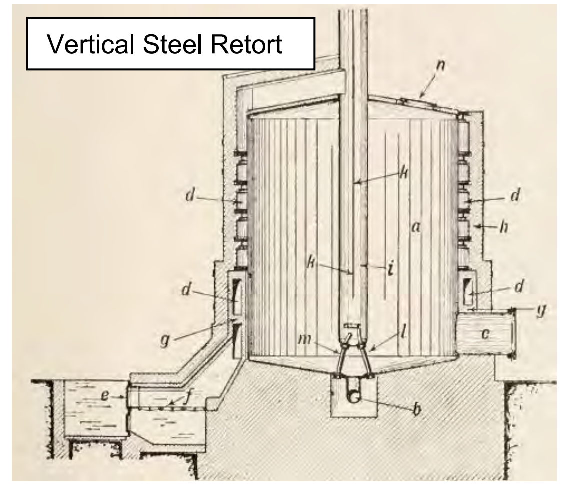


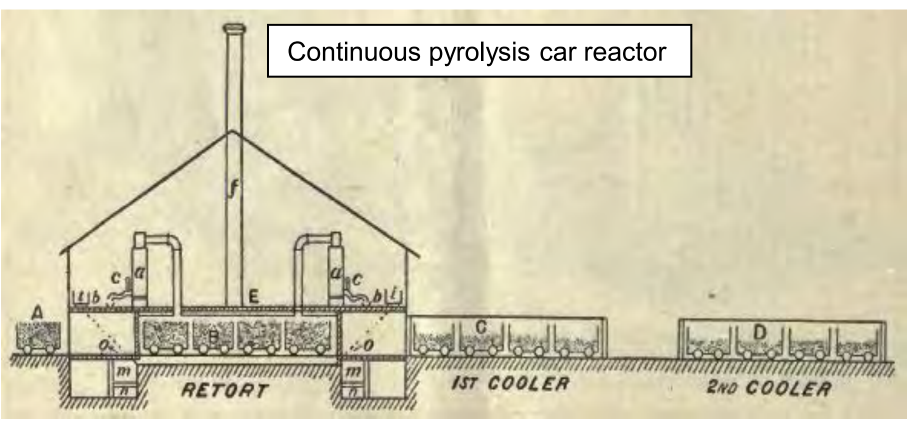
Conditions	Liquid	Char	Gas
Slow heating rates, large particles, large residence time of vapors	30 - 45 %	**25-35 %**	25-35 %

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

Wood Distillation Industry (Production of methanol, Acetone and Acetic Acid)

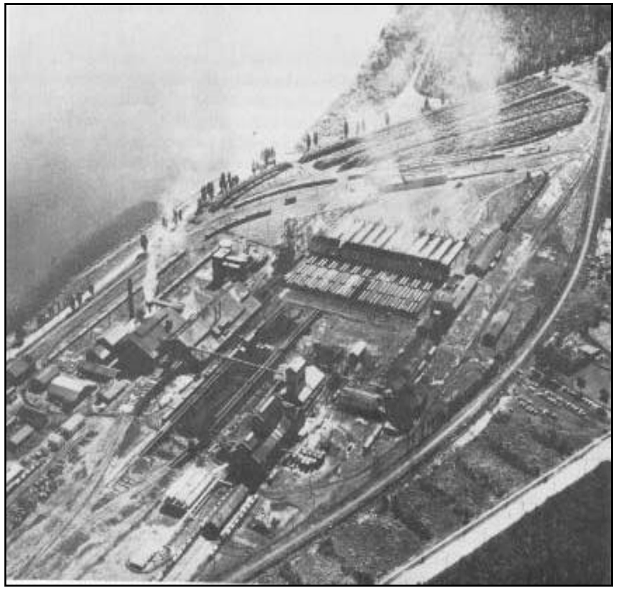


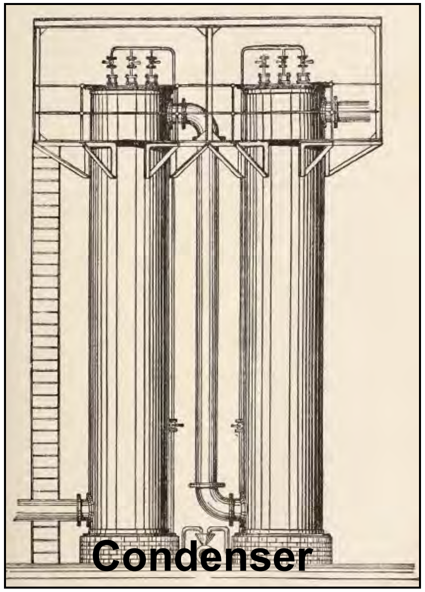


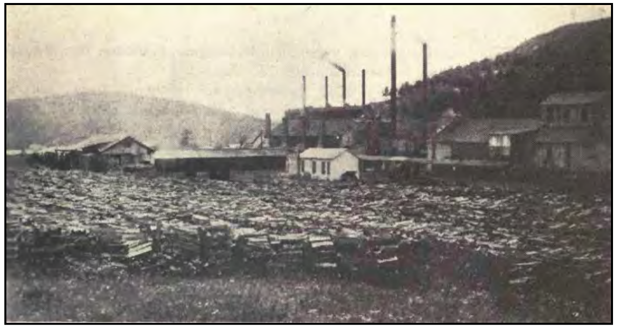


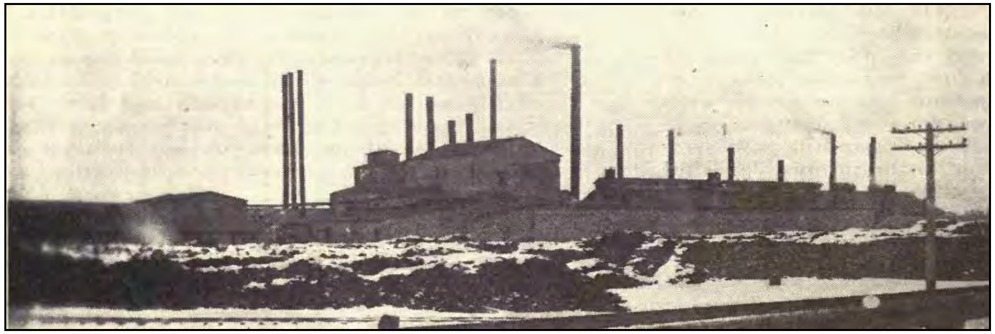
HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

Wood Distillation Industry (Production of methanol and Acetone)





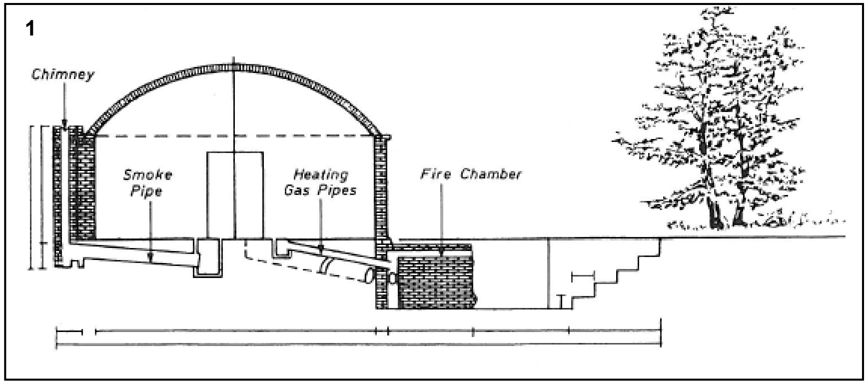


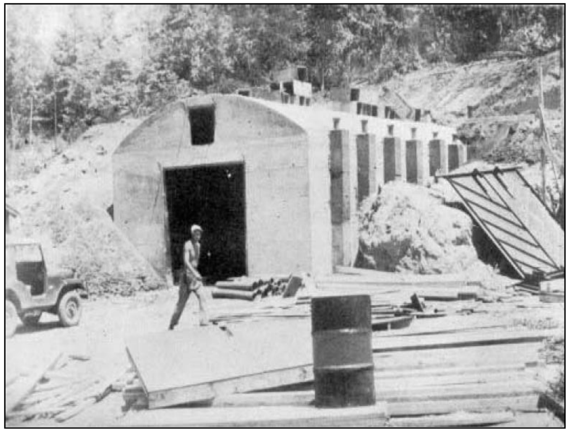


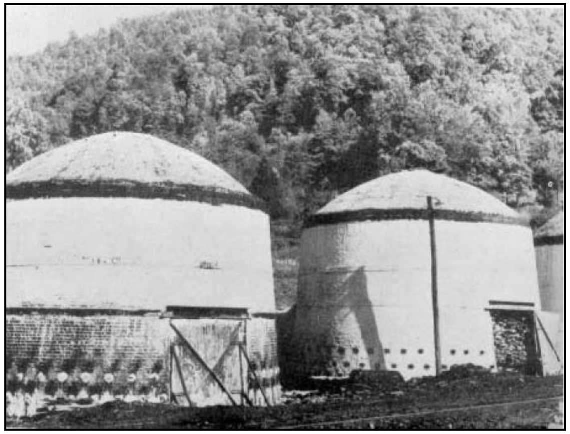
1920 - The rise of the **petroleum industry** caused a decline in the wood distillation **(MARKET)**

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

1920-60 Bio-char was produced in small ovens without liquid recovery. **MARKET: metallurgical applications and for cooking** (backyard home barbecues). Highly pollutant kilns without liquid product recovery.







[1] Emrich W: Handbook of Charcoal Making. The Traditional and Industrial Methods. Series Solar Energy R & D in the European Communities.

[2] http://www.fao.org/docrep/x5328e/x5328e0k.jpg

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

Milestones of Distilled Products from Pyrolysis

1960- Understanding the fundamentals of biomass pyrolysis reactions (**SCIENCE**)

1970 - Oil Crisis (**MARKET**)

1980 - The development of fast pyrolysis (**TECHNOLOGY**)

1980s - Several fast Pyrolysis Technologies reach commercial or near commercial status. Focus on bio-oil combustion studies (**TECHNOLOGY**)

1989 - Ensyn starts to commercialize **food flavors** (**MARKET**)

1990 - Bio-oil upgrading strategies (bio-oil micro-emulsions, hot vapor filtration, use of additives) began to be developed (**SCIENCE**)

1990 - Development of **new bio-oil derived products to replace products from the petroleum industry** (Bio-lime, Slow release fertilizers, Wood Preservatives, Glues, Sealing materials, hydrogen, phenol formaldehyde resins) (**SCIENCE** + **TECHNOLOGY**)

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

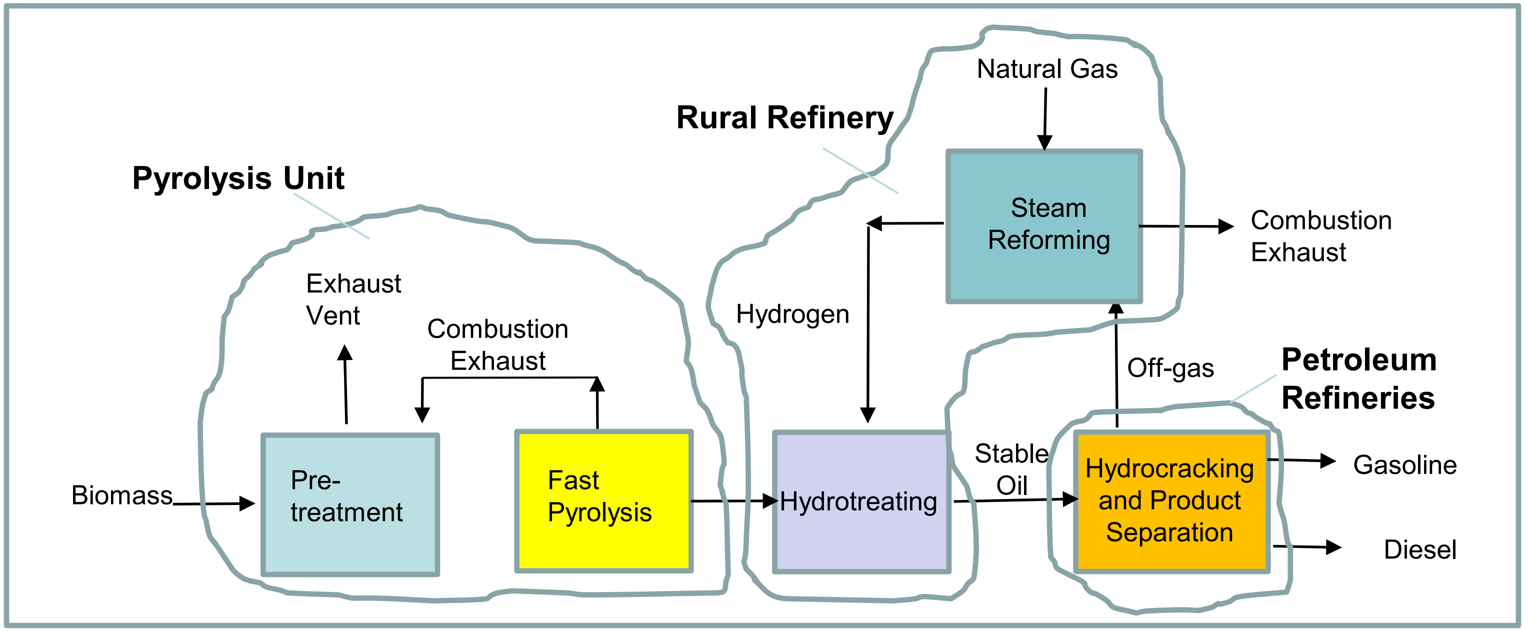
Milestones of Distilled Products from Pyrolysis

2000 - Pronounced increase in oil prices, global warming and first signs indicating the beginning of a steady decline of Petroleum Industry (**MARKET** + **SOCIAL PROBLEMS**)

2000 - New bio-oil based refinery concepts targeting the Production of Green Gasoline and Green Diesel began to be developed (**TECHNOLOGY**)

HISTORICAL DEVELOPMENTS OF PYROLYSIS TECHNOLOGIES

Bio-oil Refineries[1]:



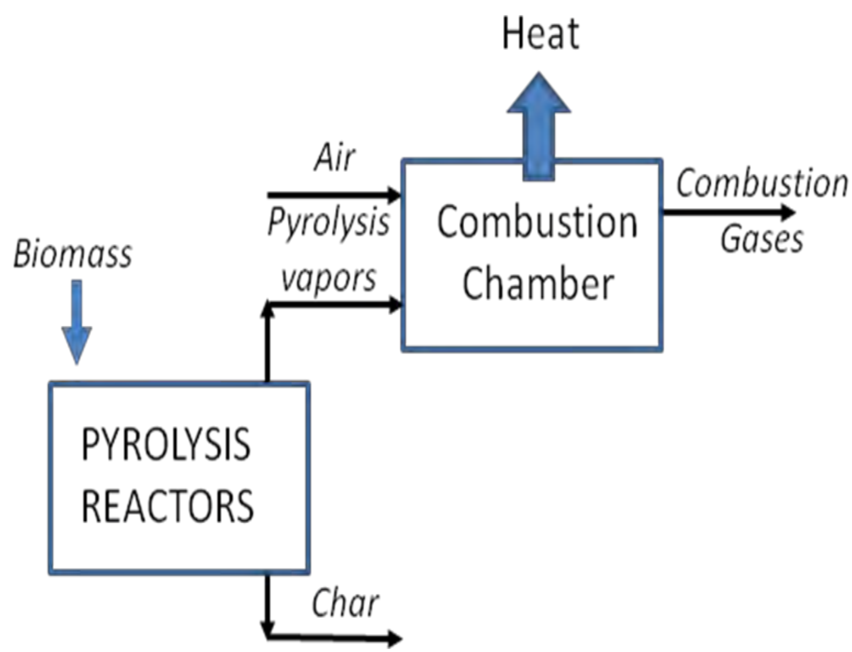
Demonstration Plant in Tesoro Corp. Refinery in Kapolei, Hawaii, expected to start in 2014 (34 mass %[2] of Biomass converted into Hydrocarbon)

[1] Jones SB, Holladay JE, Valkenburg C, Stevens DJ, Walton C, Kinchin C, Elliott DC, Czernik S: Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case. US Department of Energy, February 2009, **PNNL**-18284 Rev. 1. DE-AC05-76RL01830
[2] Elliott D, Advancement of Bio-oil utilization for Refining Feedstock. Presented at the Washington Bio-energy Research Symposium Nov. 8, 2010

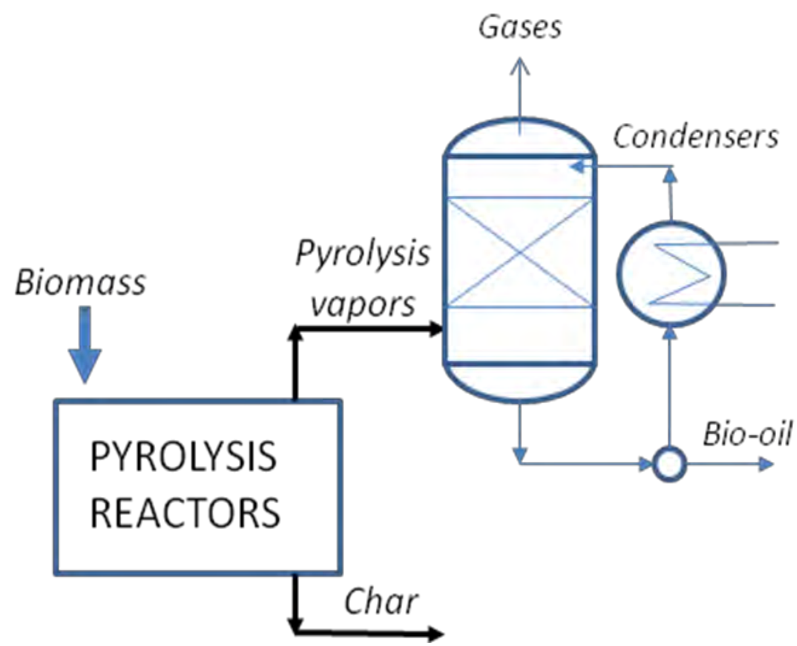
BUSINESS MODELS

BUSINESS MODELS

Pyrolysis Scheme to Produce Bio-char and Heat

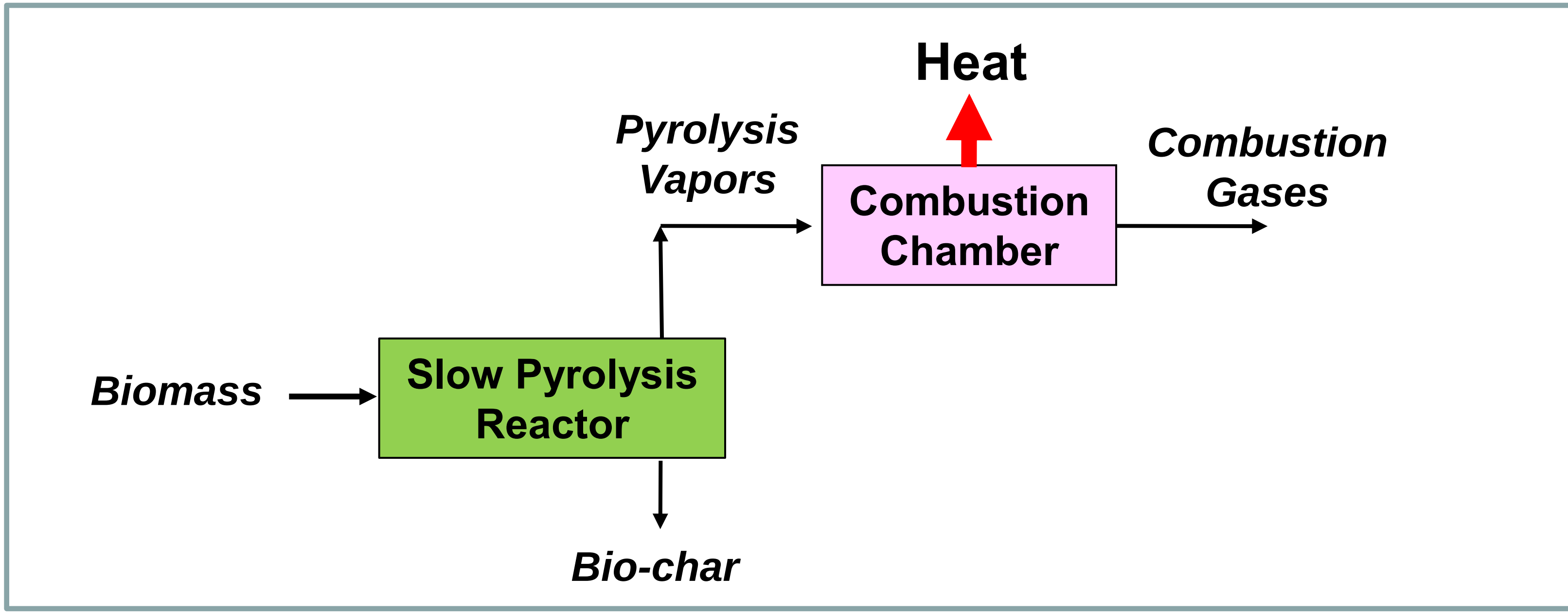


Pyrolysis Scheme to Produce Bio-char and bio-oil



BUSINESS MODELS

Concept 1: Slow Pyrolysis to produce heat and bio-char



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

BUSINESS MODELS

Despite the growing interest in producing bio-char and heat, the lack of available information on clean designs hinders those interested in developing this industry. **The inadequate flow of information for potential users forces the design of pyrolysis units to remain an art.**

Negative environmental impact of Pyrolysis technologies without heat recovery!

Garcia-Perez M, Lewis T: Feasibility Methods for Producing bio-char and advanced bio-fuels in the state of Washington. Report to the Washington State Department of Ecology, August 2010

BUSINESS MODELS

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

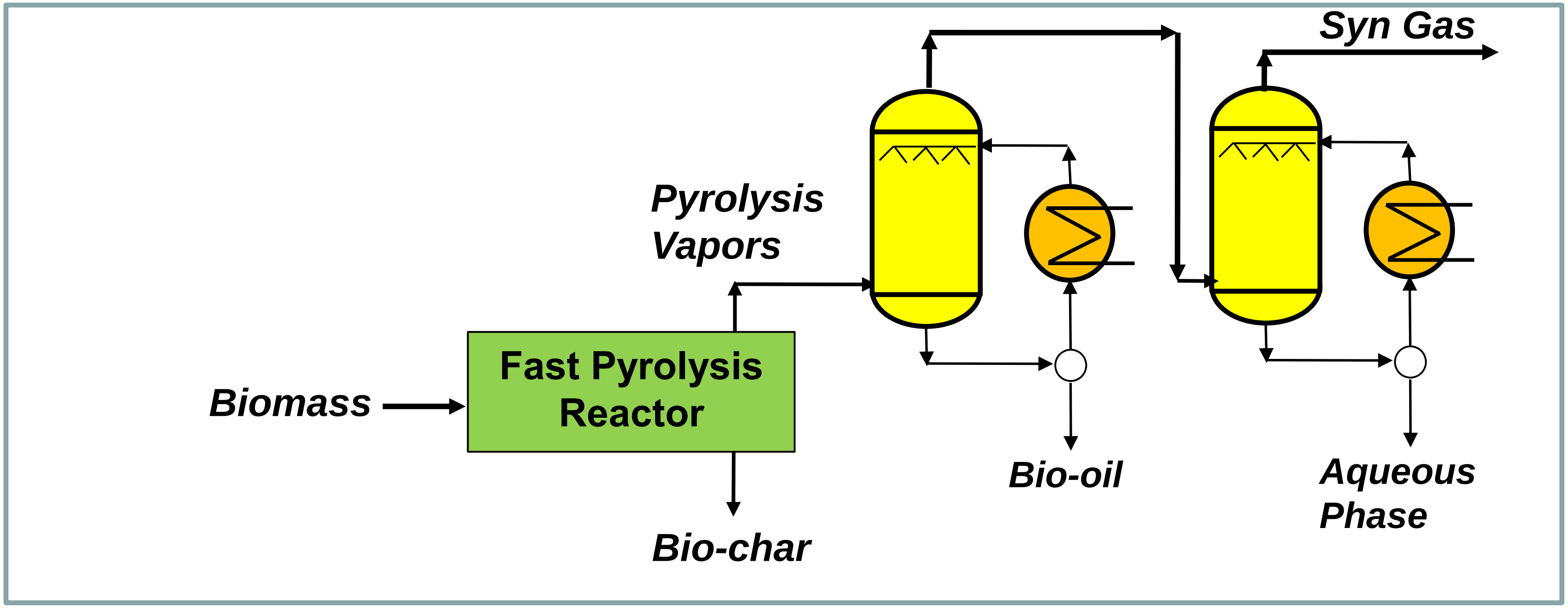
Main Hurdles: The deployment of environmentally friendly slow pyrolysis technologies able ***to produce heat and bio-char***

Higher value products from bio-char have to be developed

BUSINESS MODELS

Fast Pyrolysis

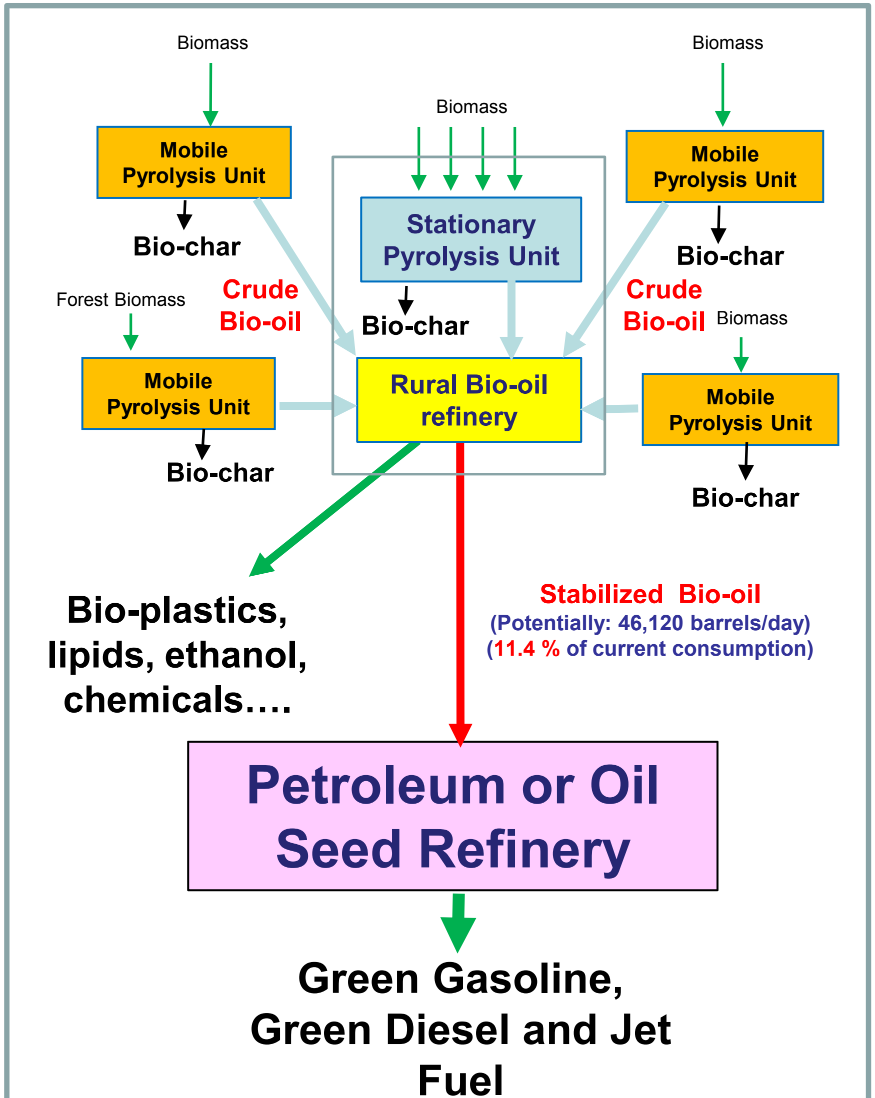
Fast pyrolysis is a process in which very small biomass particles (less than 2 mm diameter) are heated at 450 – 600 °C in the absence of *air/oxygen to* produce high bio-oil yield (60-75 mass%).



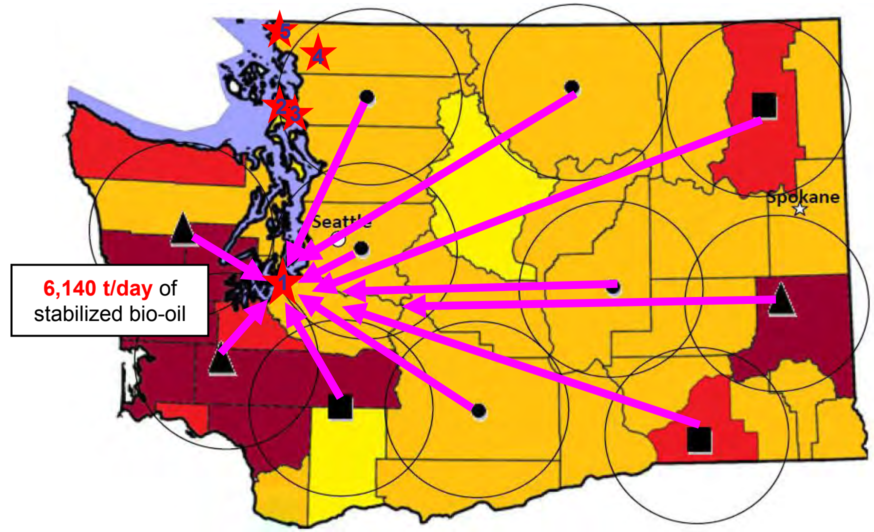
Conditions	Liquid	Char	Gas
High heating rates, small particles, short residence time of vapors	60-75 %	12-20 %	13-20 %

BUSINESS MODELS

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	

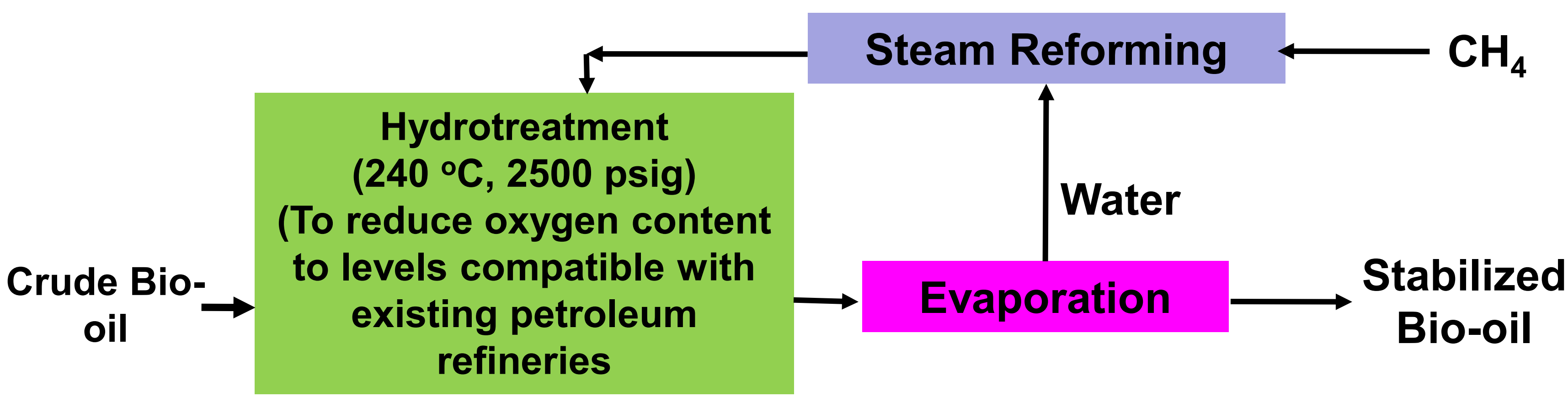
Potential Production of Stabilized Bio-oil: 6,140 t/day (46,120 barrels/day)
Potential per-capita of Stabilized Bio-oil: 6.9 barrels per day/1000 people
Current WA per-capita consumption: 60.4 barrels per day/1000 people
World per capita consumption: 31.7 barrels per day/ 1000 people

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

BUSINESS MODELS

Main Hurdle: Poor **Bio-oil Quality (need of selective pyrolysis reactors)** and lack of **Rural Refineries** to convert crude bio-oil into an stabilized oil compatible with existing petroleum refineries and **high value products from bio-oils**.

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



Jones SB, Holladay JE, Valkenburg C, Stevens DJ, Walton C, Kinchin C, Elliott DC, Czernik S: Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case. US Department of Energy, February 2009, PNNL-18284 Rev. 1. DE-AC05-76RL01830

AREAS OF RESEARCH

PYROLYSIS REACTIONS

Fundamentals of Biomass Thermo-chemical Reactions to develop more selective pyrolysis reactors (**produce bio-oil of better quality**)

Primary thermochemical reactions of cellulose, lignin and hemicellulose

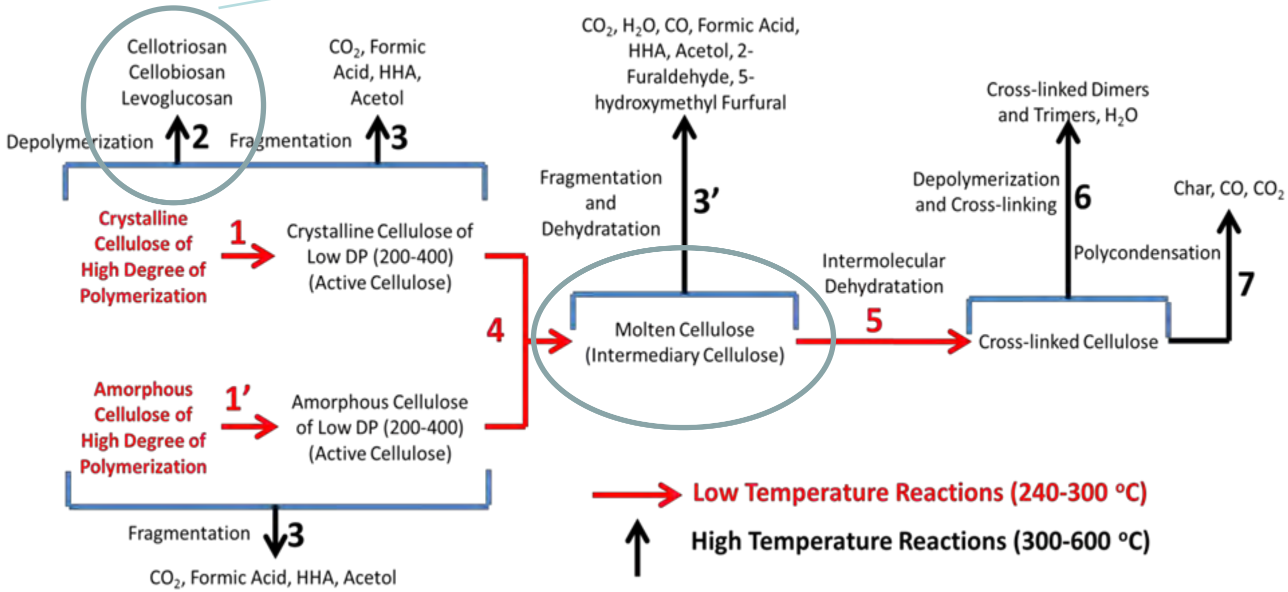
Cellulose-lignin, cellulose - alkalines, lignin – alkalines interactions during **primary thermochemical reactions**.

Homogeneous and Heterogeneous secondary reactions of cellulose, lignin and hemicellulose.

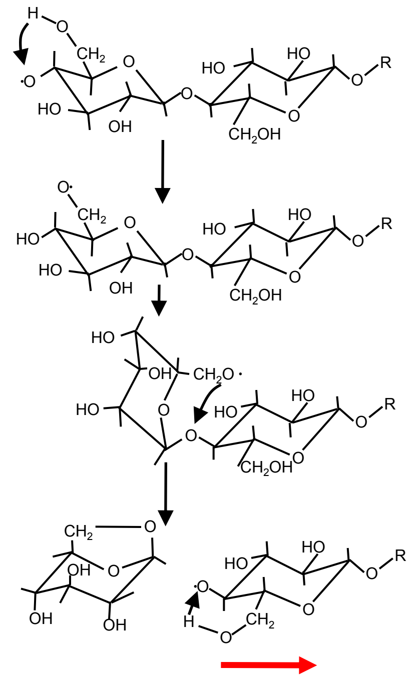
Cellulose - lignin **interactions** during homogeneous and heterogeneous **secondary reactions** .

PYROLYSIS REACTIONS

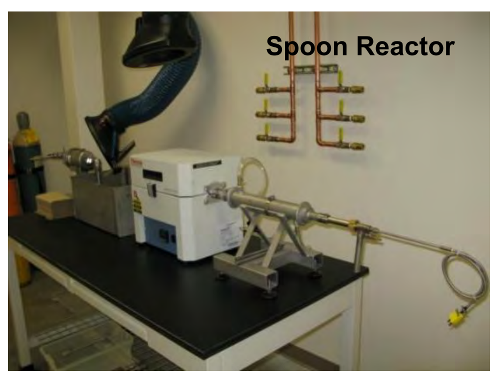
Cellulose Pyrolysis Reactions



CELLULOSE DEPOLYMERIZATION (350-400 °C)



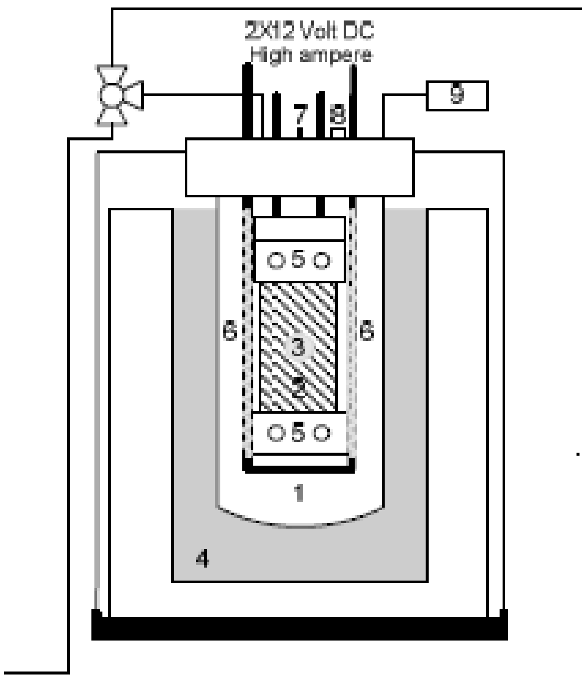
UNZIPPING MECHANISM



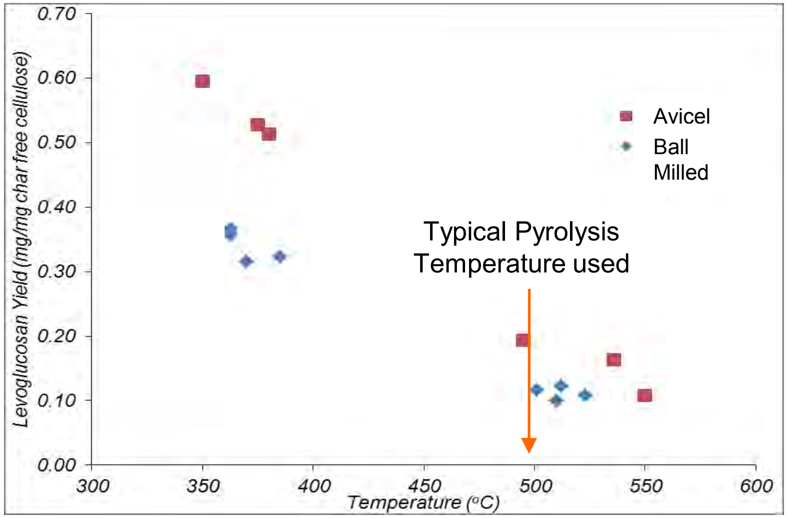
PYROLYSIS REACTIONS

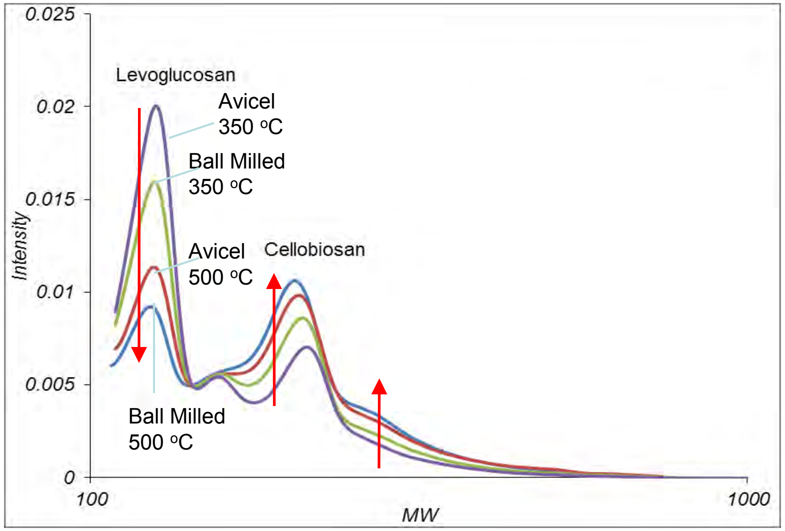
Cellulose Primary Reactions

Vacuum Mesh Reactor



In Collaboration with the University of Twente (Z. Wang, R. Westerhof and S. Kersten)



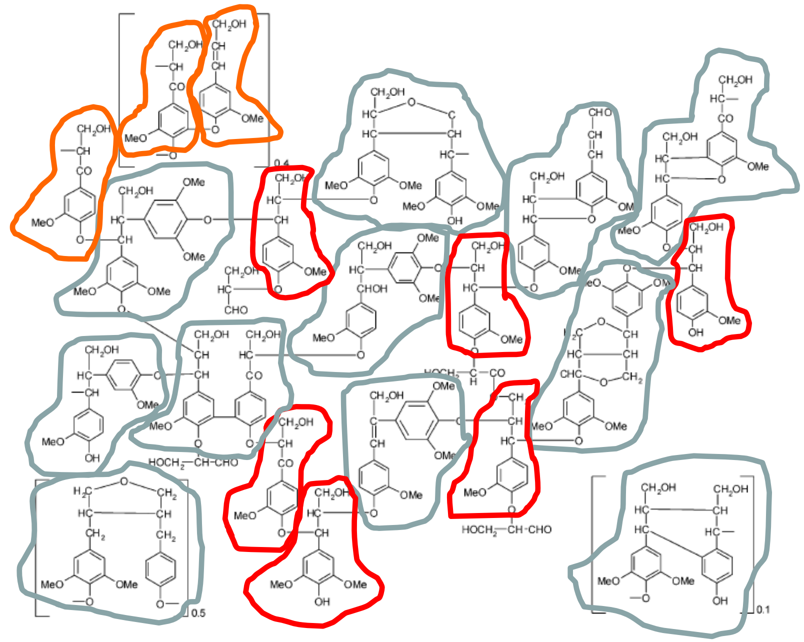


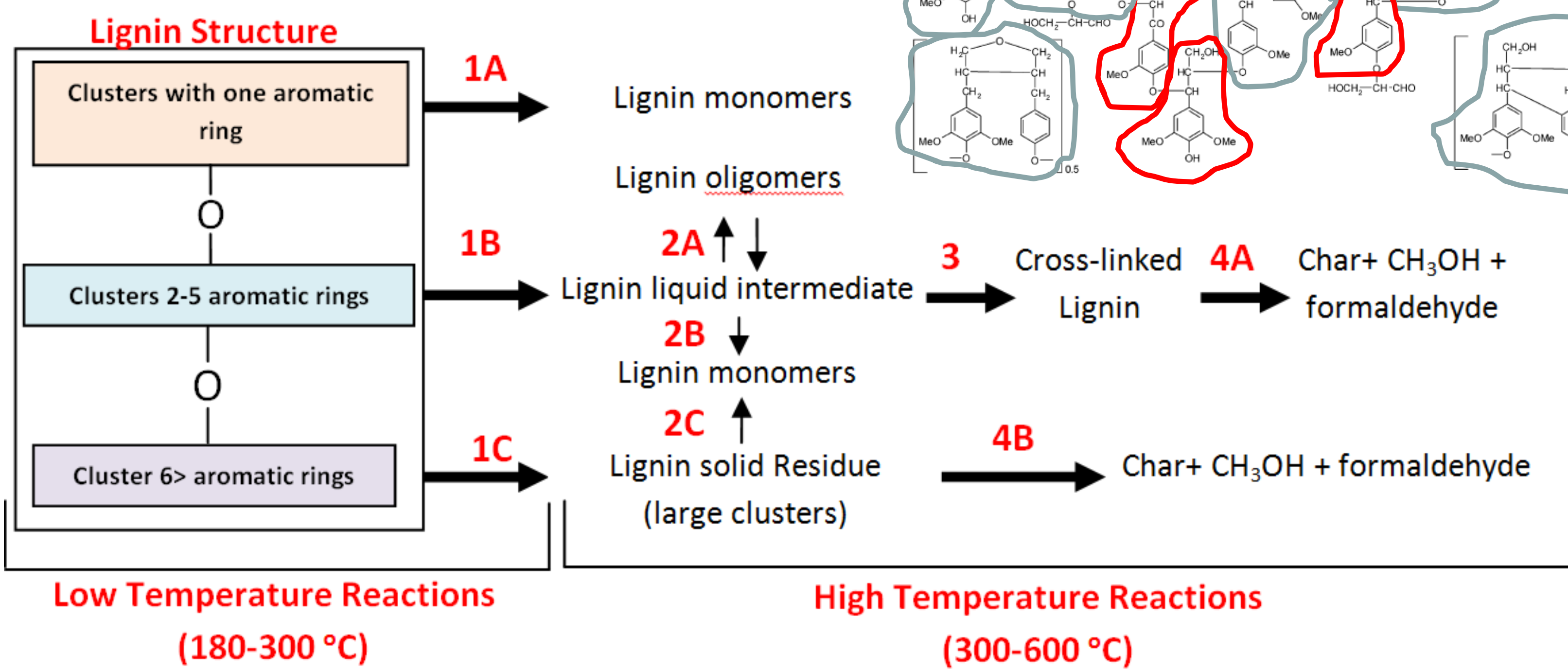
No Product of Fragmentation Reactions is observed

PYROLYSIS REACTIONS

Lignin Pyrolysis Reactions

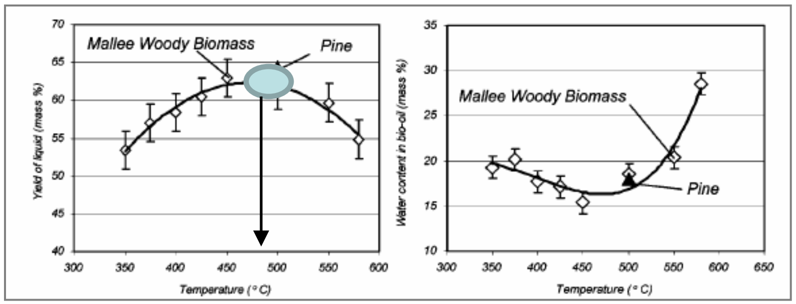
Lignin from Beech Wood

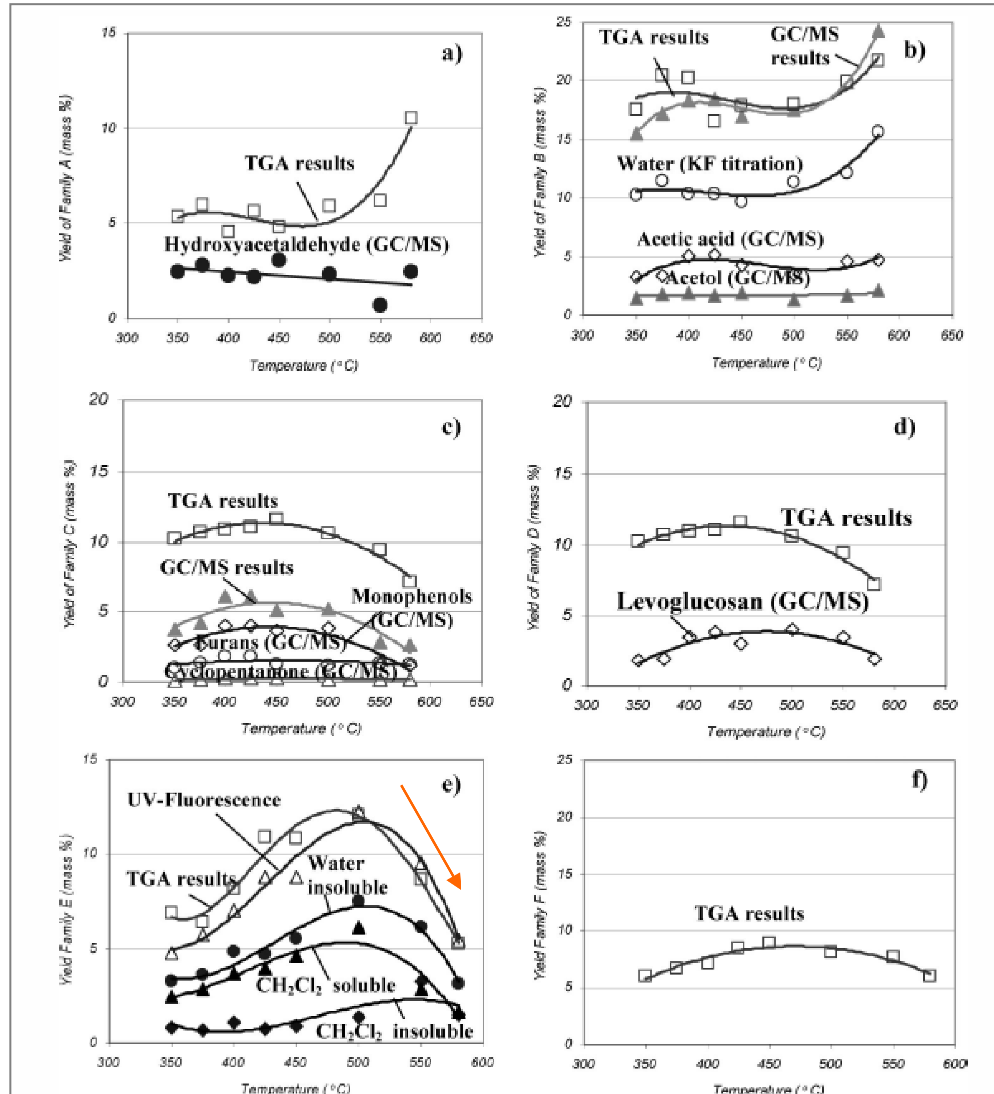




PYROLYSIS REACTIONS

EFFECT OF PYROLYSIS TEMPERATURE





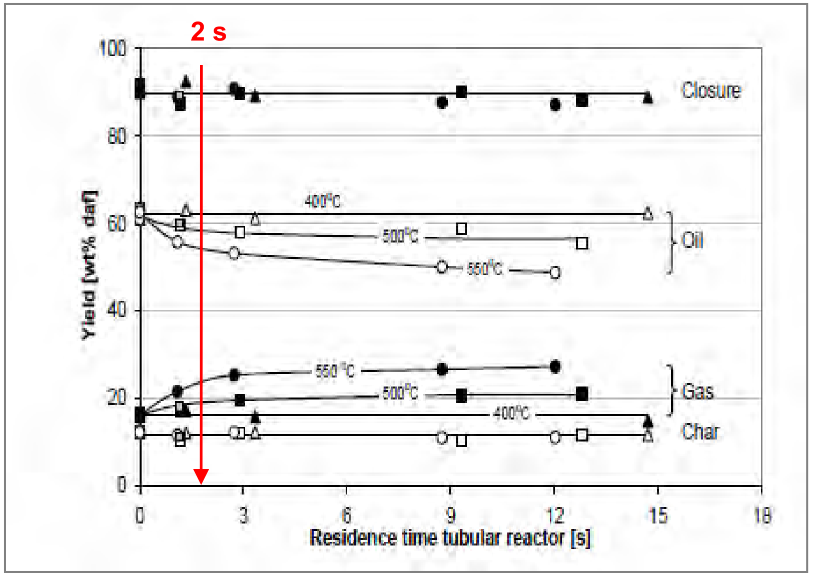
Families:

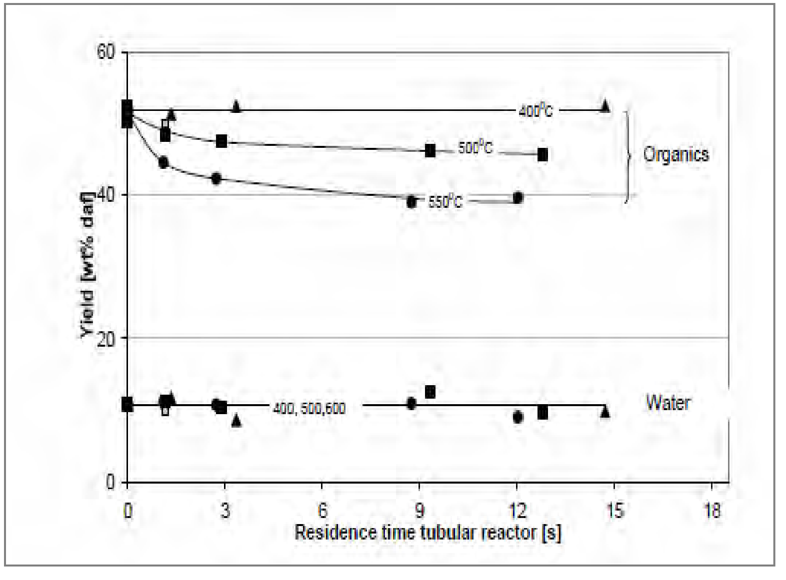
- A: Hydroxy-acetaldehyde, methanol, formic acid
- B: Water, Acetic Acid, Acetol
- C: Mono-phenols and furans
- D: Anhydrosugars (Levoglucosan)
- E: Lignin Oligomers
- F: Cross Linked Sugars???

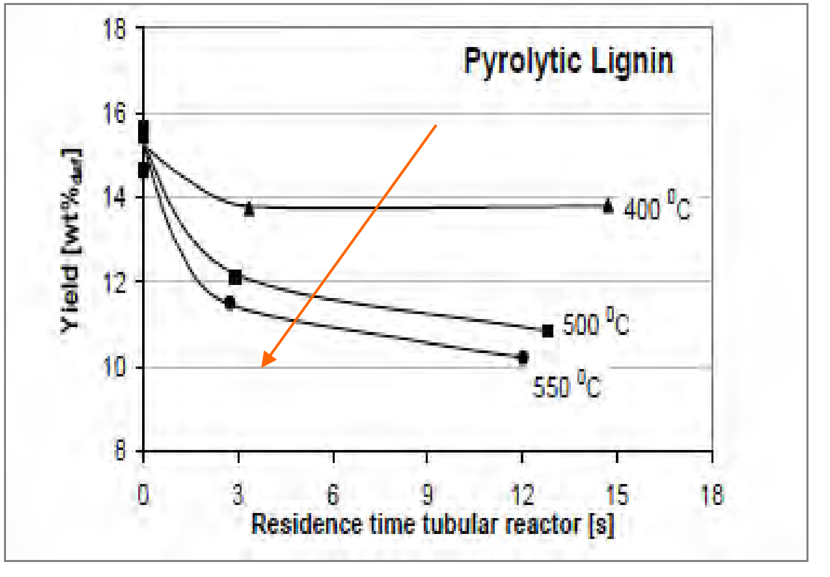
Garcia-Perez M, Wang S, Shen J, Rhodes M, Lee Woo L, Li C-Z: Effects of Temperature on the Formation of Lignin-Derived Oligomers during the Fast Pyrolysis of Malee Woody Biomass. Energy & Fuels 2008, 22, 2022-2032

PYROLYSIS REACTIONS

EFFECT OF VAPORS RESIDENCE TIME INSIDE THE PYROLYSIS REACTOR (University of Twente)



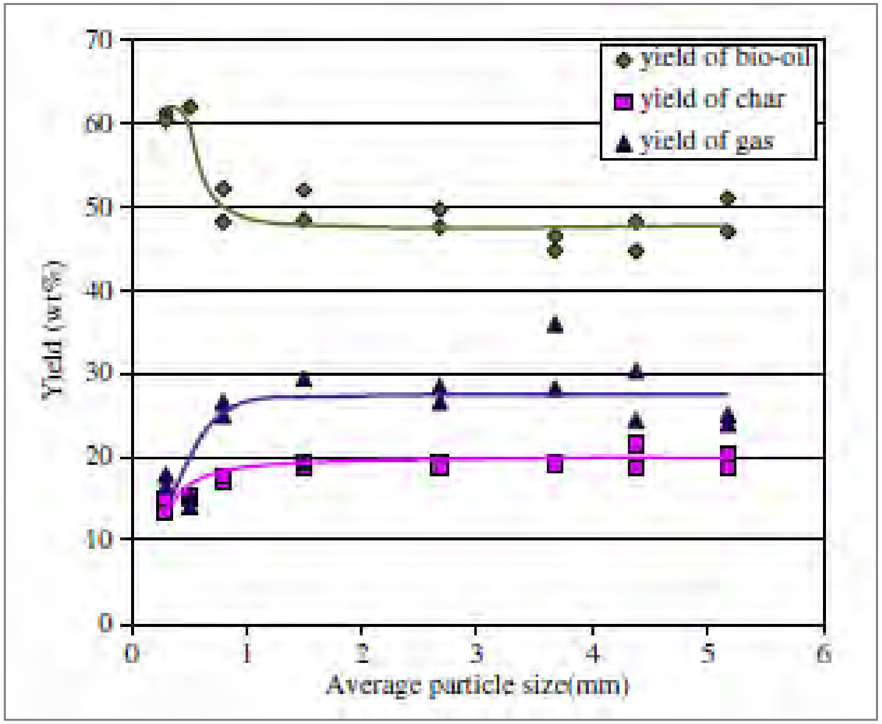


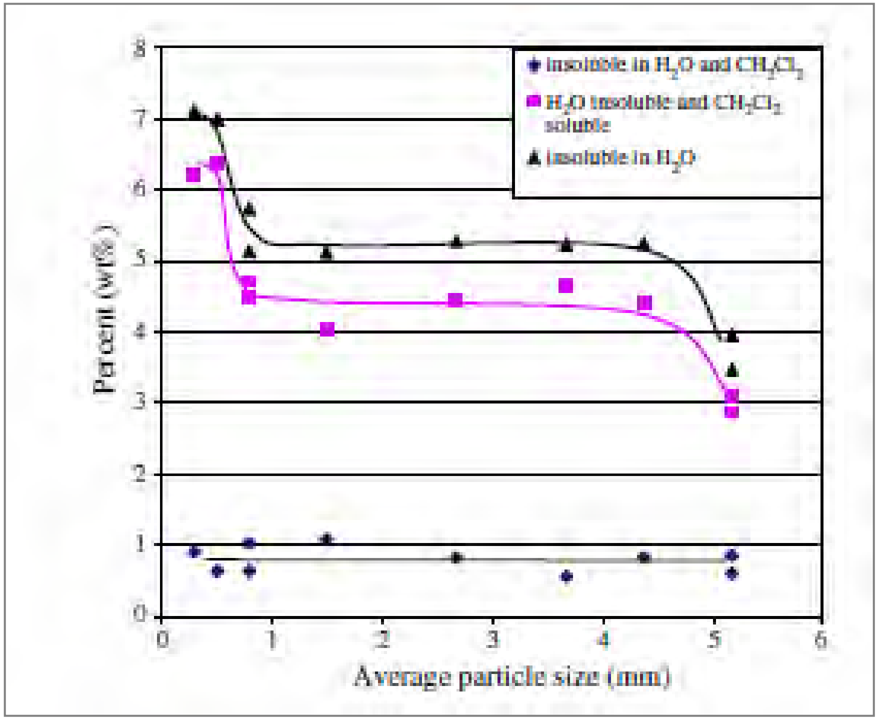


Roel JM Westerhof: Refining Fast Pyrolysis of Biomass. PhD Thesis University of Twente 2011

PYROLYSIS REACTIONS

EFFECT OF PARTICLE SIZE (C-Z Li, Monash University)

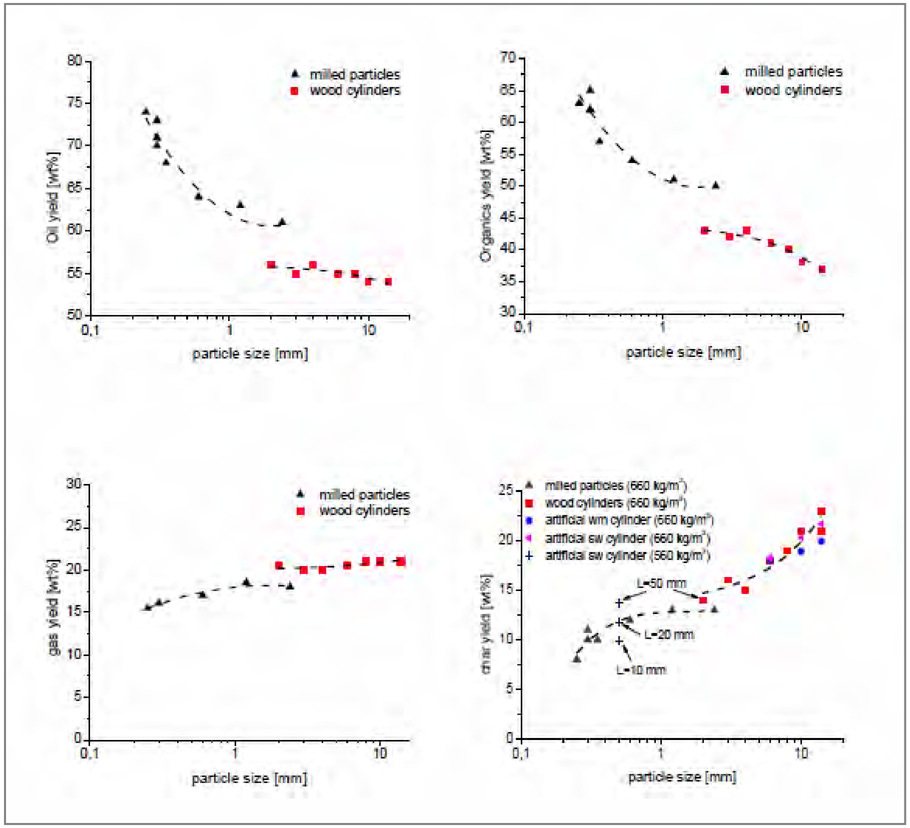


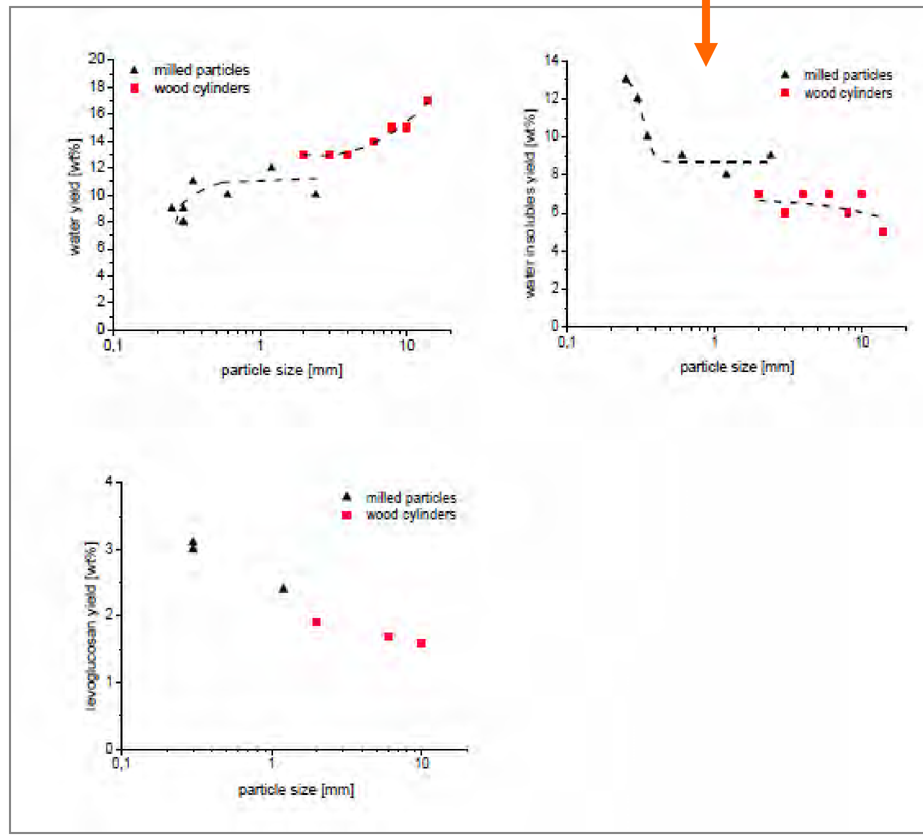


Shen J, Wang X-S, Garcia-Perez M, Mourant D, Rhodes MJ, Li C-Z: Effects of particle size on the fast pyrolysis of oil malee woody biomass. Fuel 88 (2009) 1810-1817

PYROLYSIS REACTIONS

EFFECT OF PARTICLE SIZE (University of Twente)



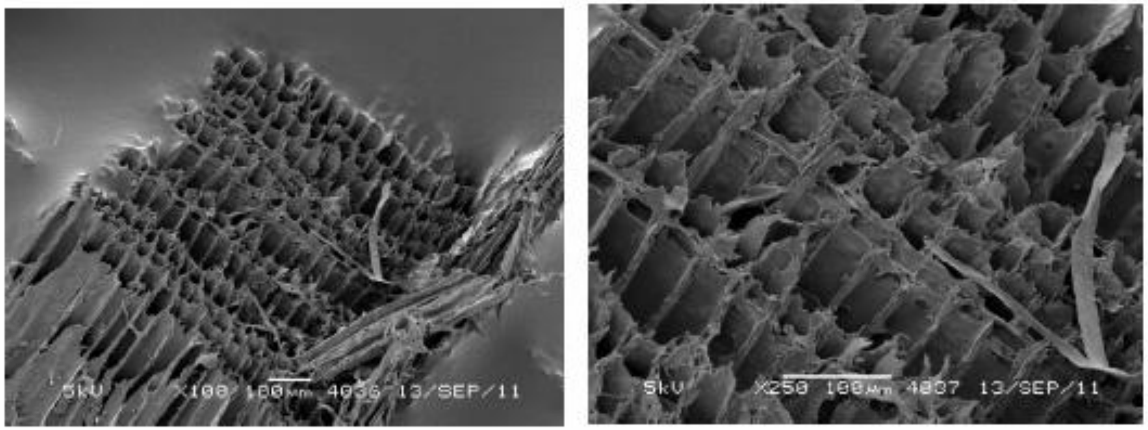


A fluidized bed reactor can result in bio-oil yields comparable to those of slow pyrolysis reactors if larger particle size are used.

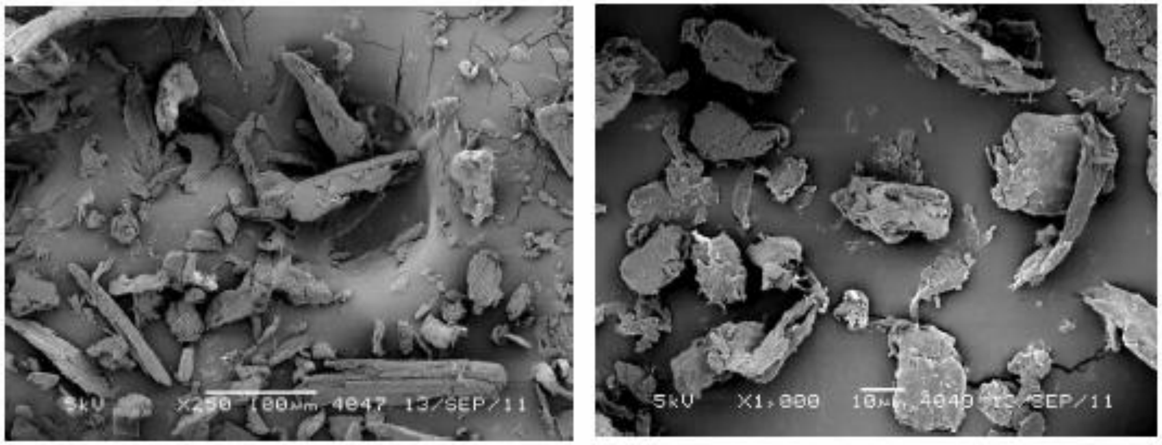
Roel JM Westerhof: Refining Fast Pyrolysis of Biomass. PhD Thesis University of Twente 2011

PYROLYSIS REACTIONS

EFFECT OF PARTICLE SIZE (University of Twente)



SEM Pictures of 1 mm beech wood particles

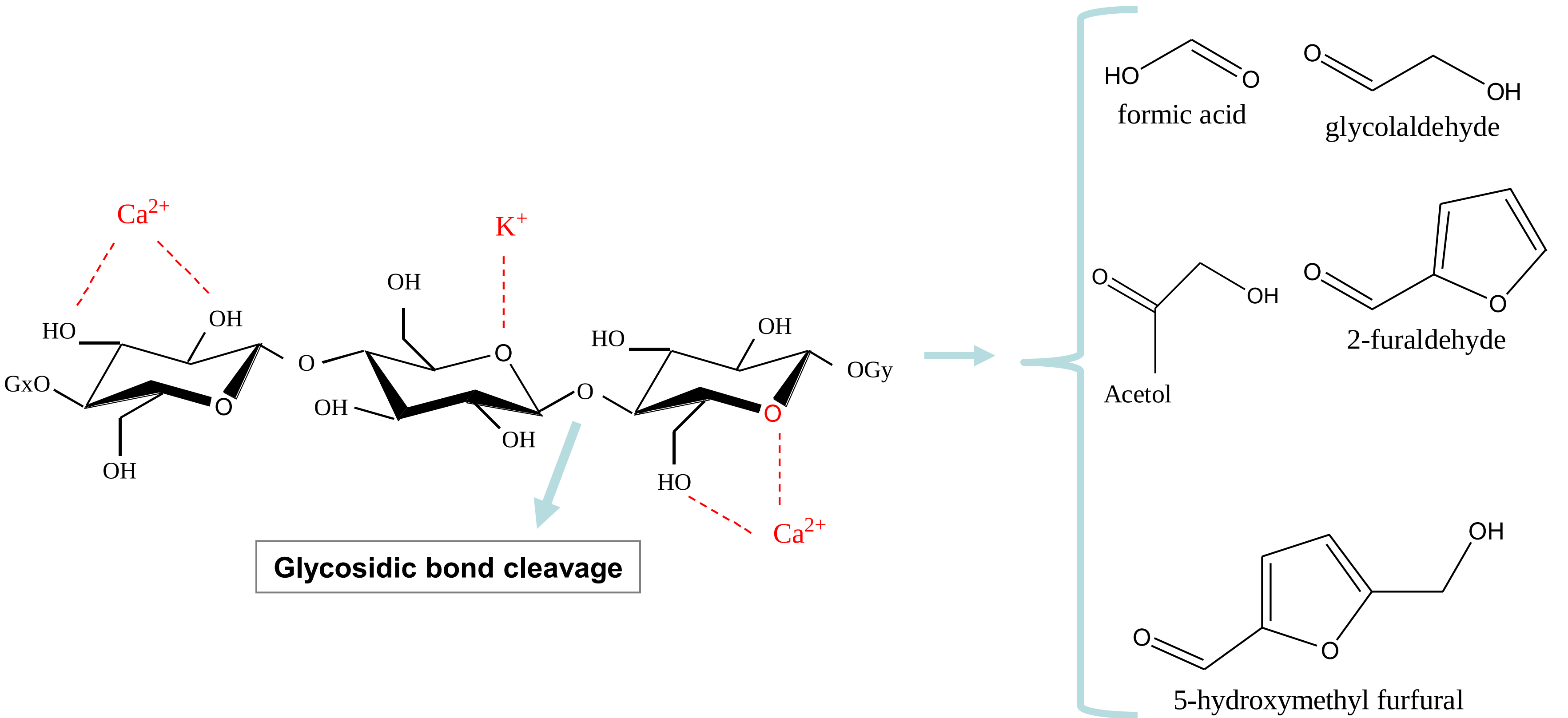


SEM Pictures of beech wood particles smaller than 80 micron

Roel JM Westerhof: Refining Fast Pyrolysis of Biomass. PhD Thesis University of Twente 2011

PYROLYSIS REACTIONS

Catalytic Effect of Alkalines



Brown RC: Prospects for a Thermolytic Sugar Platform. TC Biomass Conference. Chicago, IL, September 27-30, 2011

Use of Acid additives (H_2SO_4)

Product Yields (mass %) from the Pyrolysis of Various Cellulosic Substrates (Vacuum Pyrolysis) *(Shafizadeh and Stevenson 1982)*

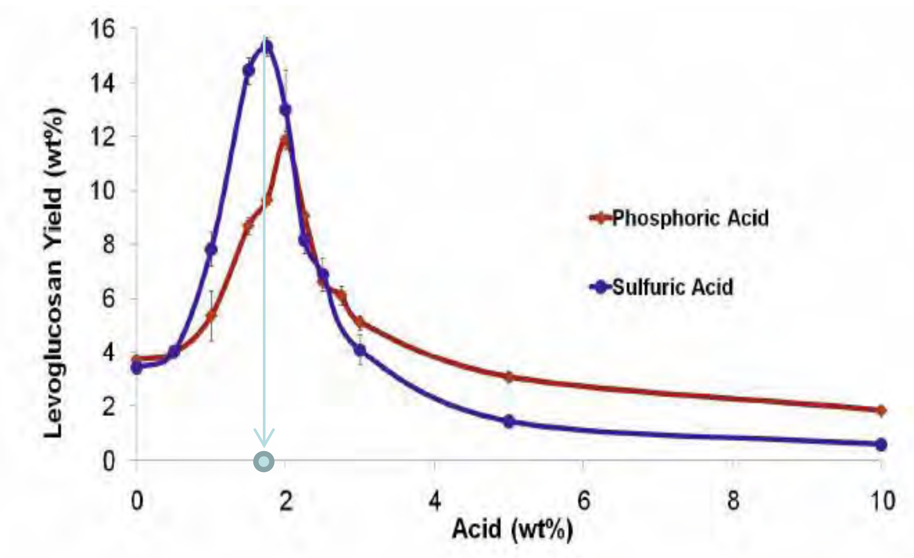
Substrate	Washing	Ash	Char	Tar	Levoglucosan
CF-11	Acid		5	68	36
CF-11 + H_2SO_4	Acid		7	63	35
Holocellulose	Acid	0.05	8	66	26
Holocellulose + H_2SO_4	Acid	0.05	9	57	23
Wood	Acid	<0.02	16	51	9
Wood + H_2SO_4	Acid	<0.02	17	50	19

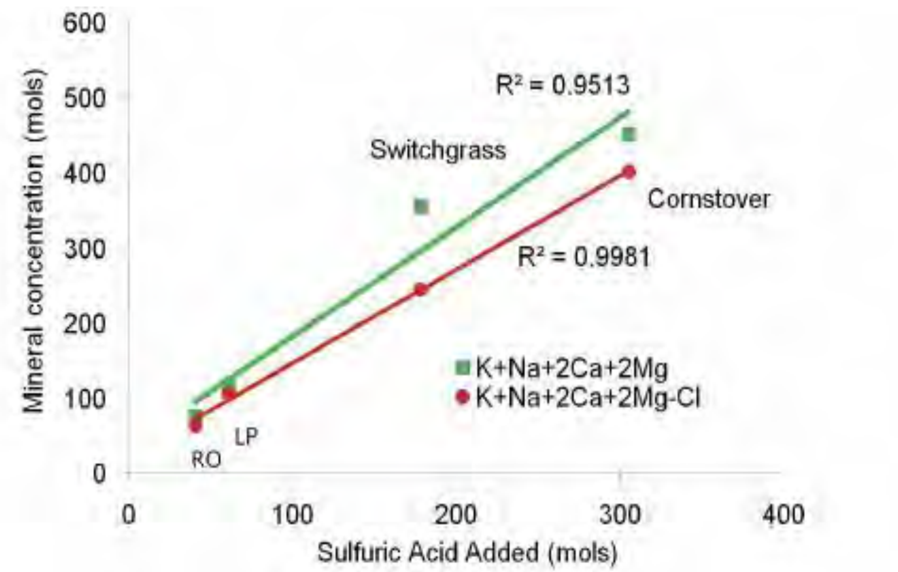
"Under the conditions employed in these experiments, **the addition of small amounts of acid appeared to be most effective when lignin was present**. ***The mechanism of this phenomenon, however, is not clear*** and cannot be simply attributed to cleavage of the lignin-carbohydrate bonds" (Shafizadeh and Stevenson 1982).

Shafizadeh F, Stevenson TT: Saccharification of Douglas-Fir Wood by a Combination of Prehydrolysis and Pyrolysis. Journal of Applied Polymer Science, Vol. 27, 4577-4585 (1982)

PYROLYSIS REACTIONS

Researchers from Iowa State University discovered that *there is a correlation between the amount of minerals in the biomass and the amount of Acid required to achieve optimal levoglucosan yields*.





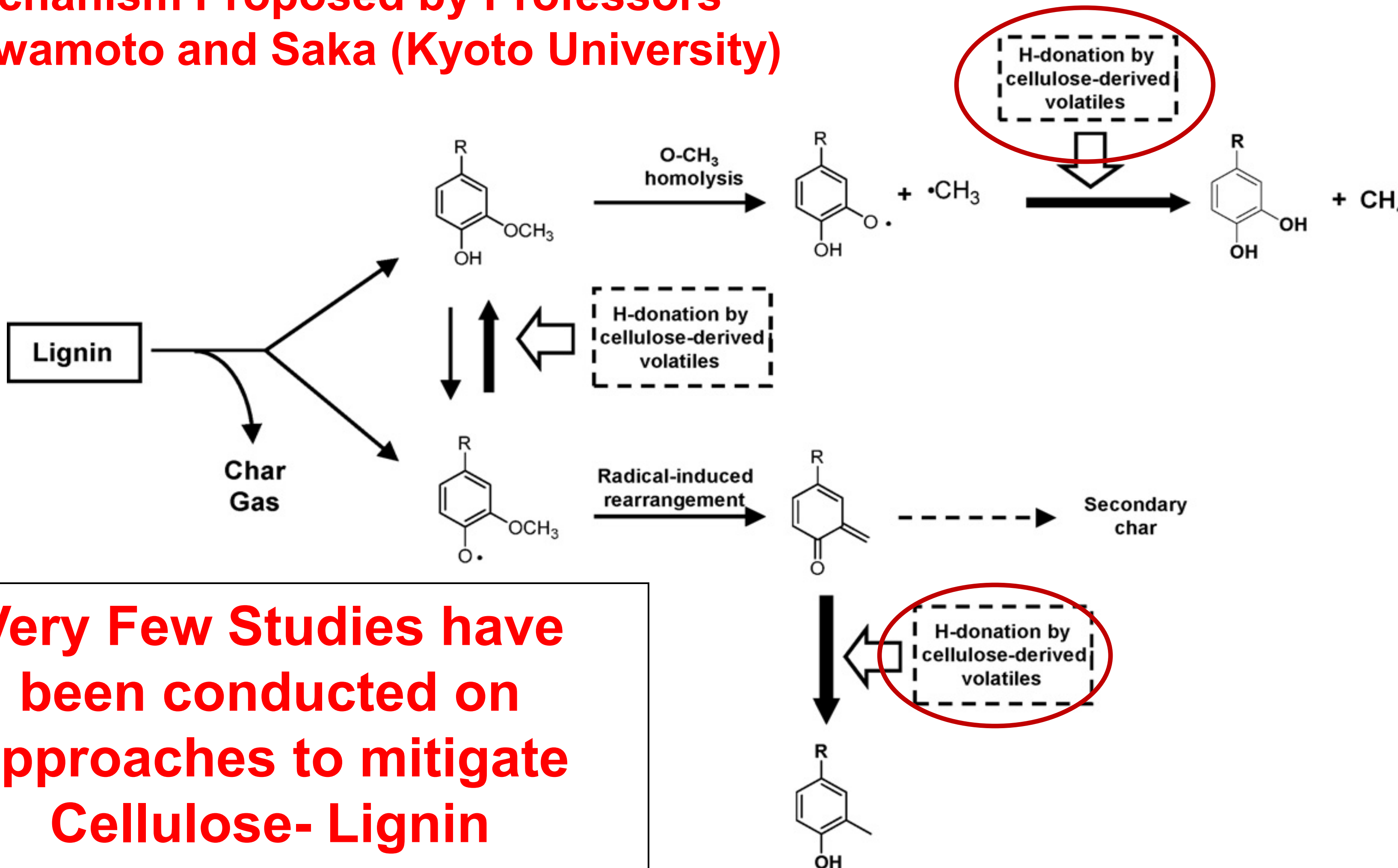
The acids *passivate the catalytic effect of alkalines* and contribute in this way to increase the production of levoglucosan.

Brown RC: Prospects for a Thermolytic Sugar Platform. TC Biomass Conference. Chicago, IL, September 27-30, 2011

PYROLYSIS REACTIONS

CELLULOSE - LIGNIN INTERACTIONS

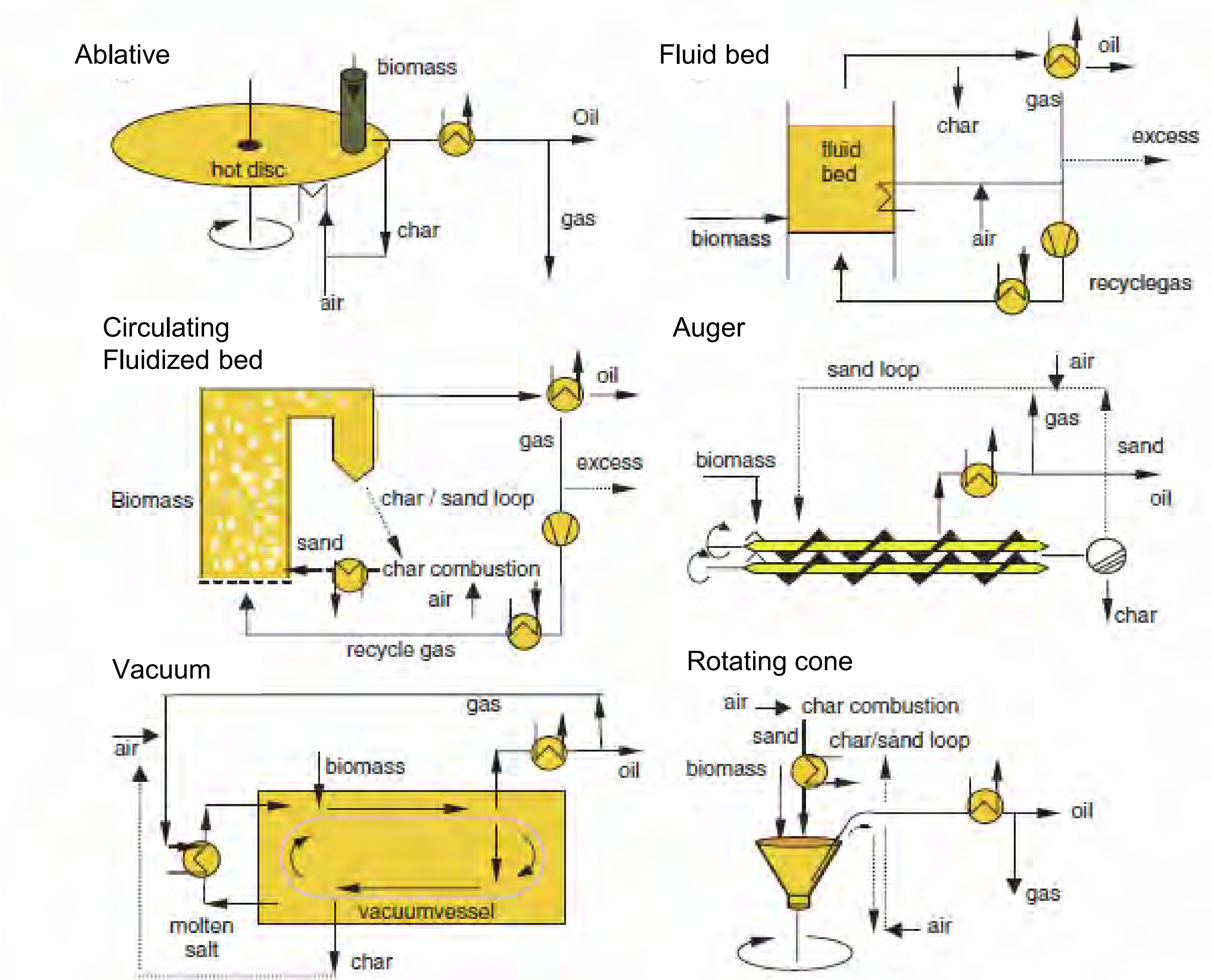
Mechanism Proposed by Professors Kawamoto and Saka (Kyoto University)



Very Few Studies have been conducted on approaches to mitigate Cellulose- Lignin Interactions

PYROLYSIS REACTORS

Fast Pyrolysis Reactors



The sand used to achieve high heating rates contaminates the bio-char and is the source of several technological poblems

Vanderbosch RH, Prins W: Fast pyrolysis technology development . Biofuels, Bioproducts & Biorefining. 2010, p. 178-208

PYROLYSIS REACTORS

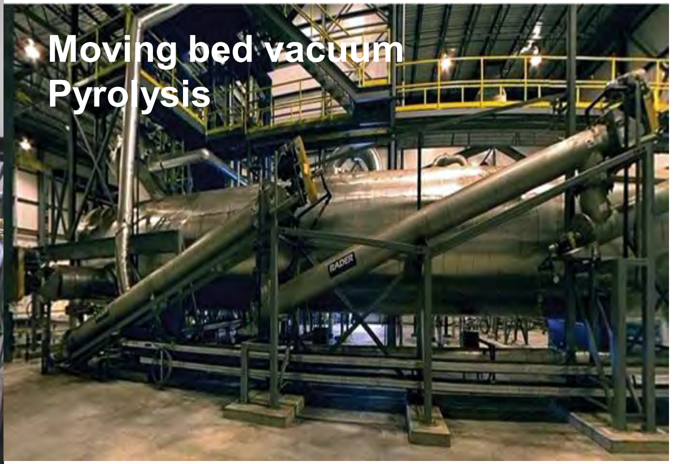
Fast Pyrolysis Reactors

Current technologies **use high volumes of carrier gas** and **sand as heat carriers**. These reactors **have very poor selectivity towards the production of precursors of transportation fuels**.

Are the designs that have been scaled up reliable enough or will they be replaced by new ones when bio-oil refineries are deployed?

PYROLYSIS REACTORS

Intermediate Pyrolysis Reactors

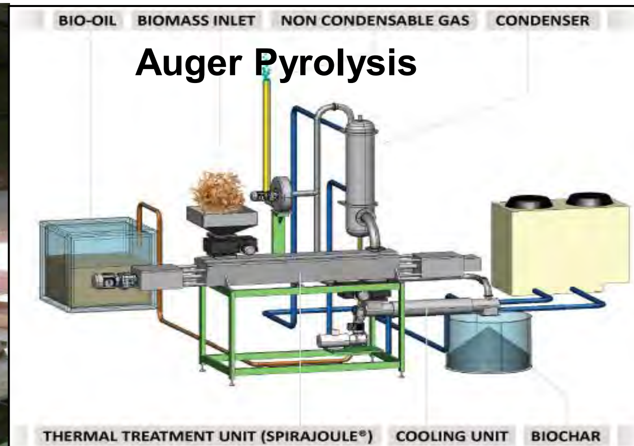


Black is Green Pty Ltd http//www.bio-char.com.au/about.html	Amaron rotary drum reactor (Coates Engineering) http://www.coatesengineering.com	Vacuum Pyrolysis Reactor (Pyrovac)

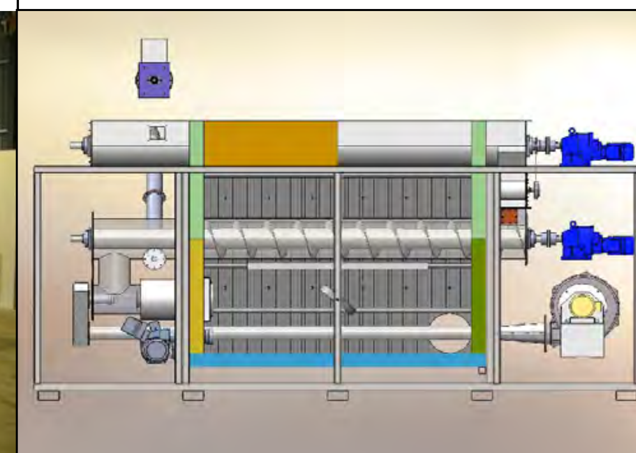
Comprehensive Methodology to Design Pyrolysis Reactors?
Could we increase bio-oil yields?

PYROLYSIS REACTORS

Intermediate Pyrolysis Reactors



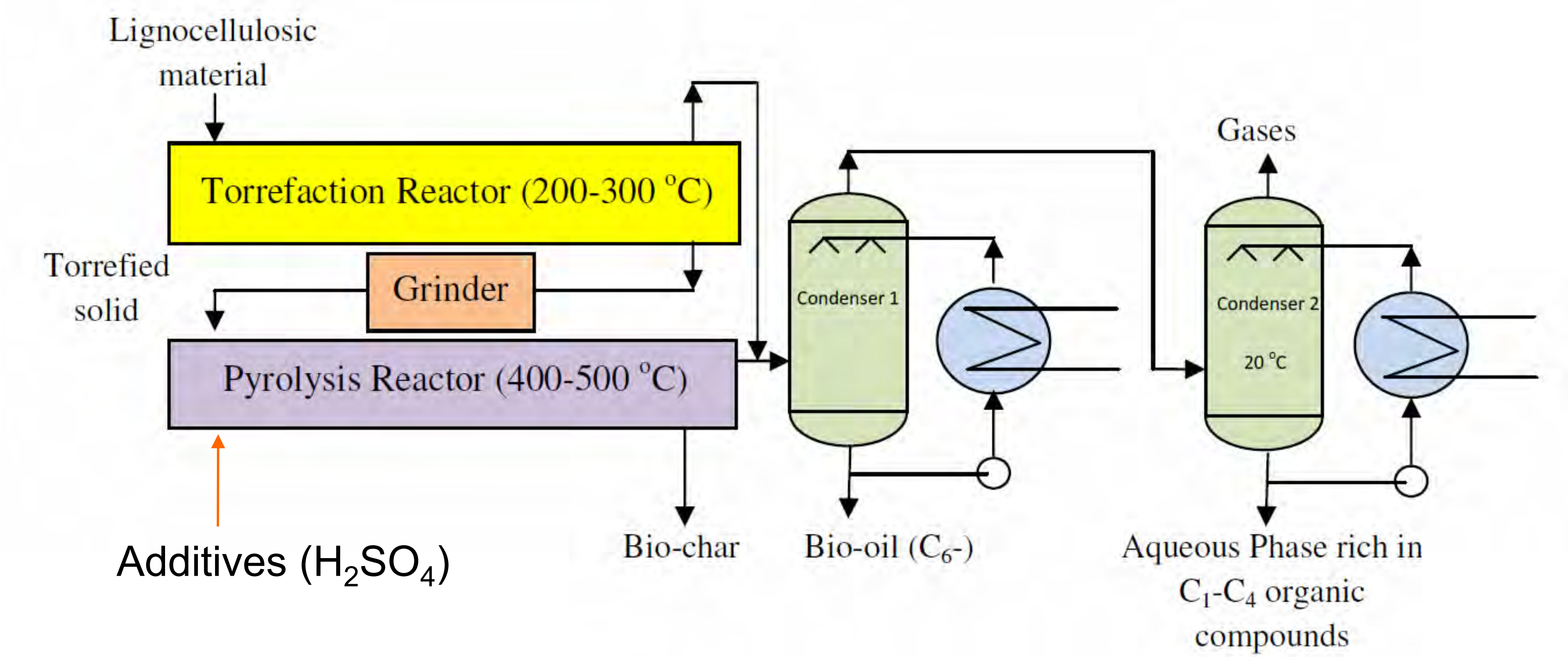
Renewable Oil International Mobile Unit	BiogreenR (http://biogreen-energy.com/bio-green.html)	Agri-Tech Producers (http://www.agritechproducers.com)



International Tech Corporation (http://www.internationaltechcorp.org/IT-info.htm)	eGenesis CR-2 pyrolysis unit (http://www.egenindustries.com)	Whitfield Bio-char LLC

PYROLYSIS REACTORS

Novel Concepts for Pyrolysis Units studied at WSU

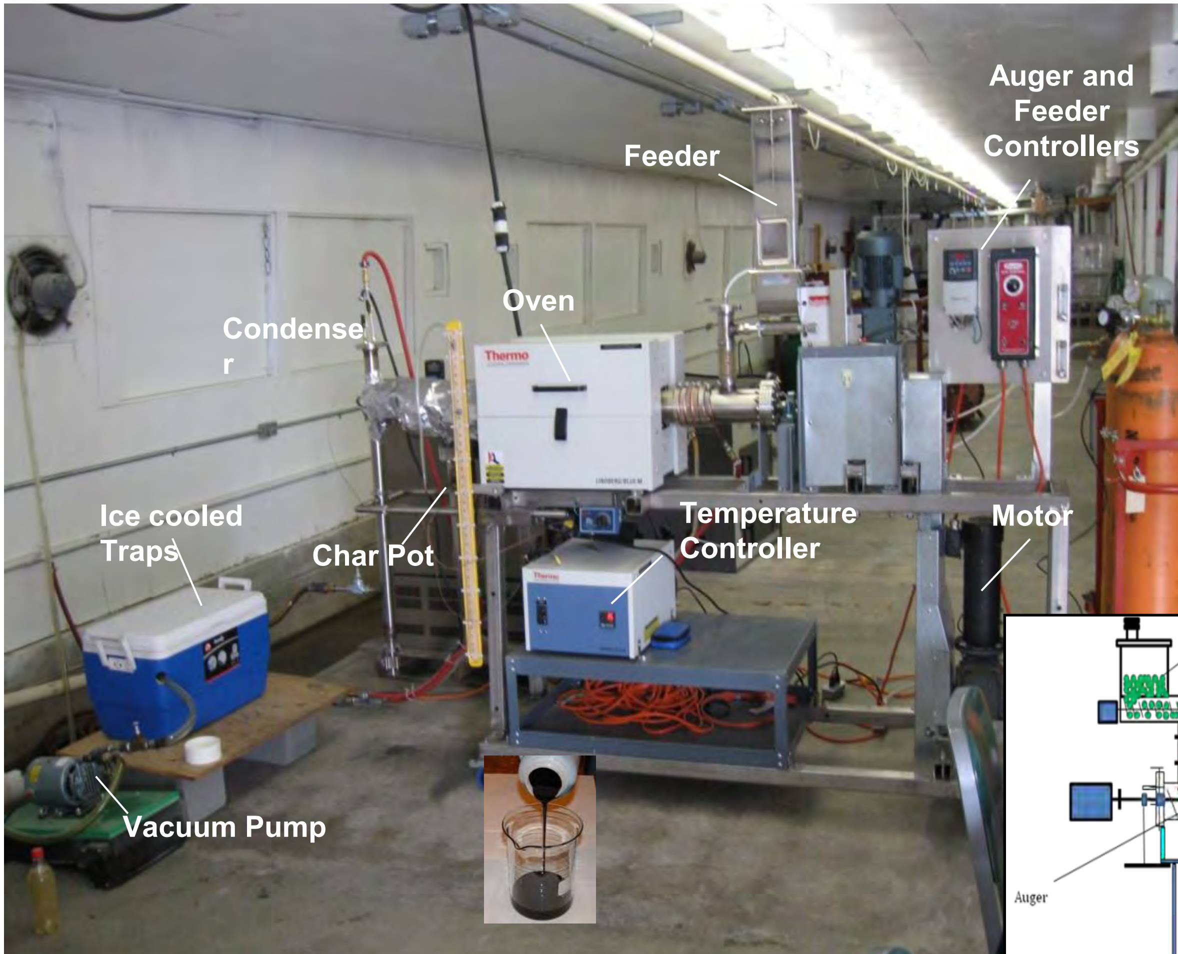


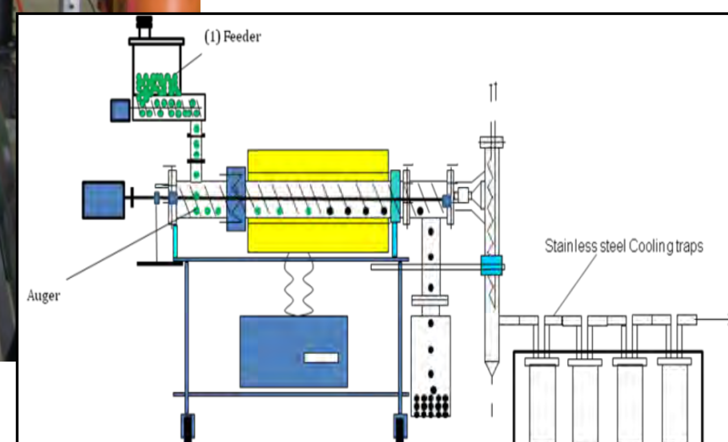
(1) Use of Intermediate Pyrolysis reactors without sand
(2) Two Step Pyrolysis to reduce grinding energy
(3) Two Step Condensation Systems to Separate C1-C4 molecules and water from bio-oil

Collaboration with Twente University (Netherlands) and Curtin University (Australia)

PYROLYSIS REACTORS

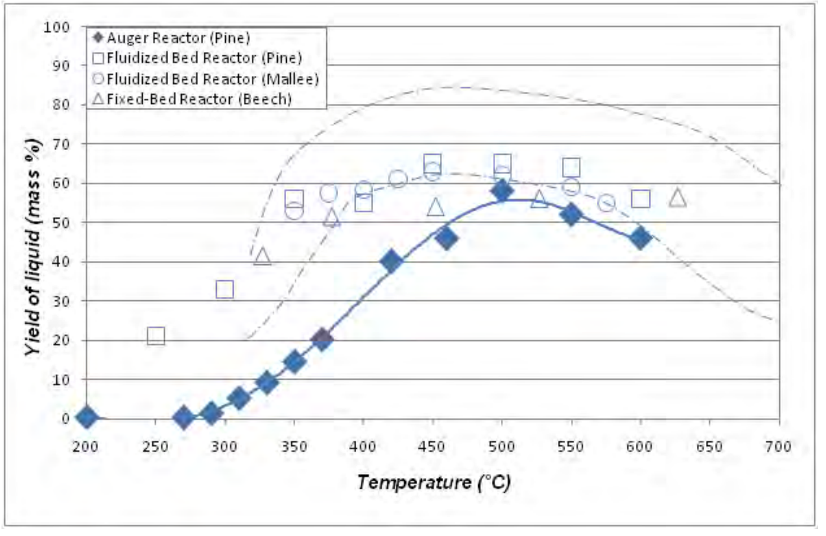
Performance of Auger Pyrolysis Reactor

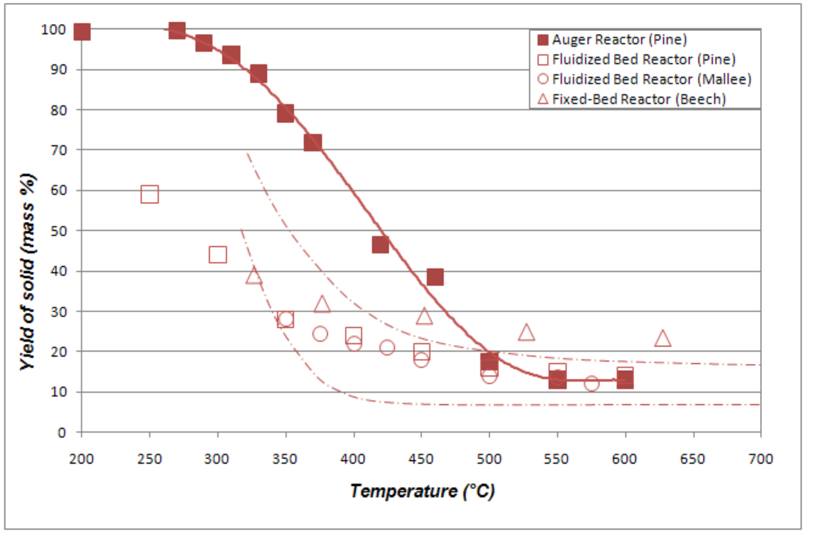


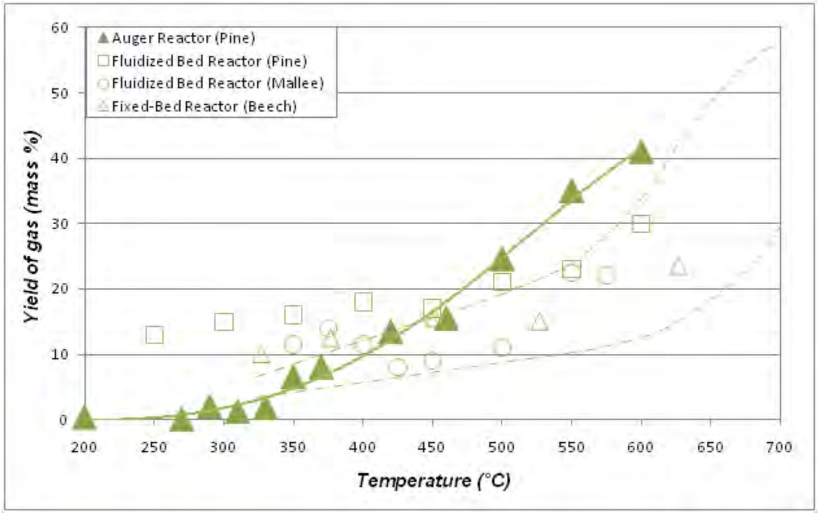


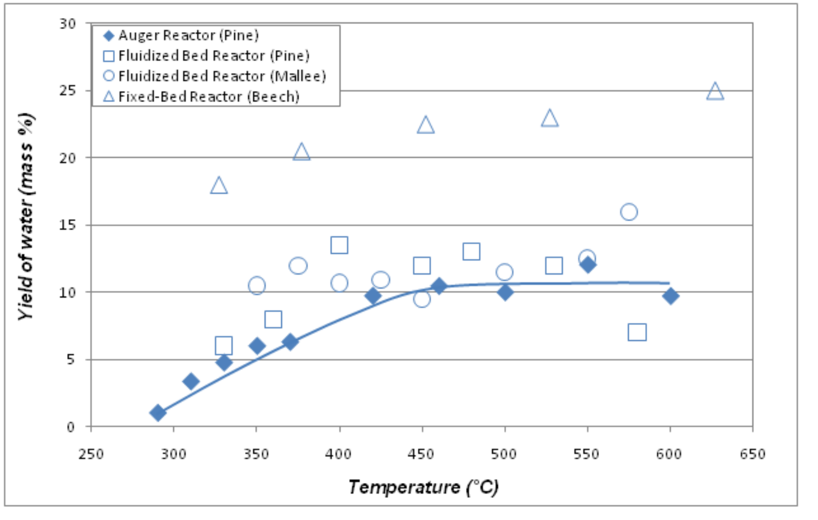
PYROLYSIS REACTORS

Effect of Pyrolysis Temperature









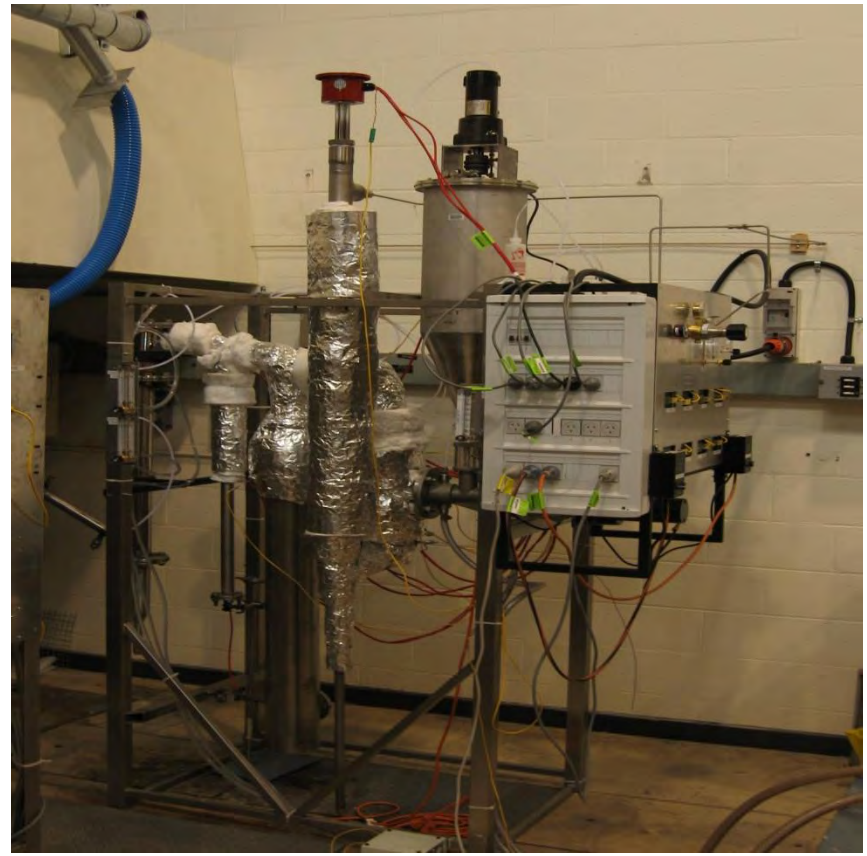
PYROLYSIS REACTORS

Use of sulfuric acid as additive to passivate alkalines

Auger Pyrolysis Reactor

Washington State University

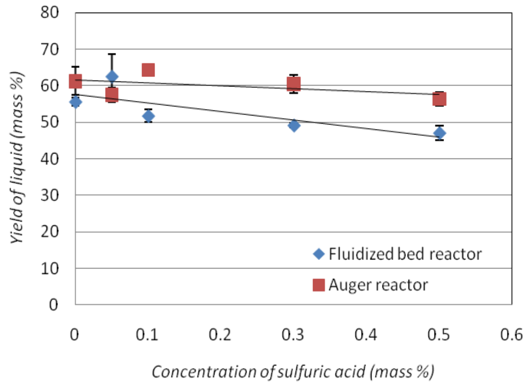
Fluidized Bed Pyrolysis Reactor

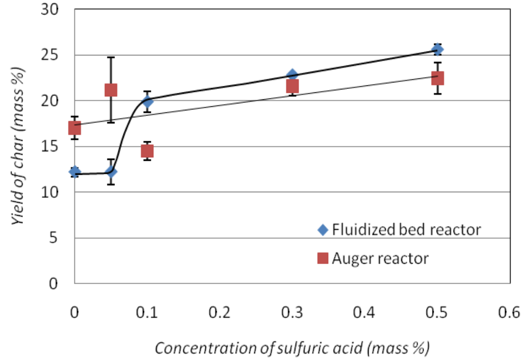


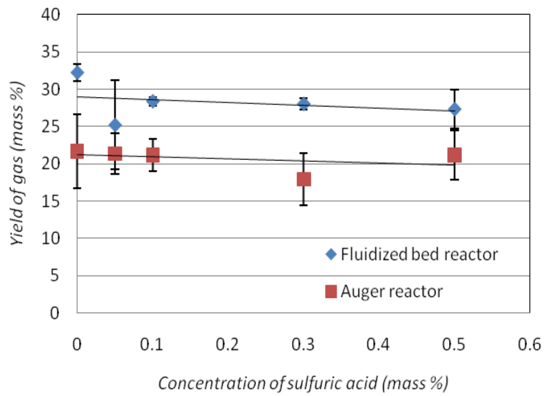
Curtin University (Australia)

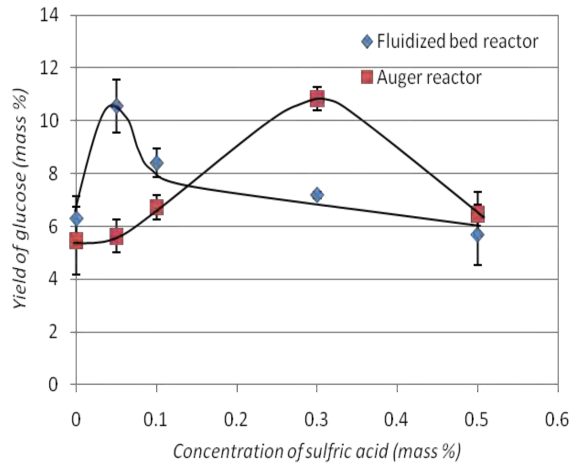
PYROLYSIS REACTORS

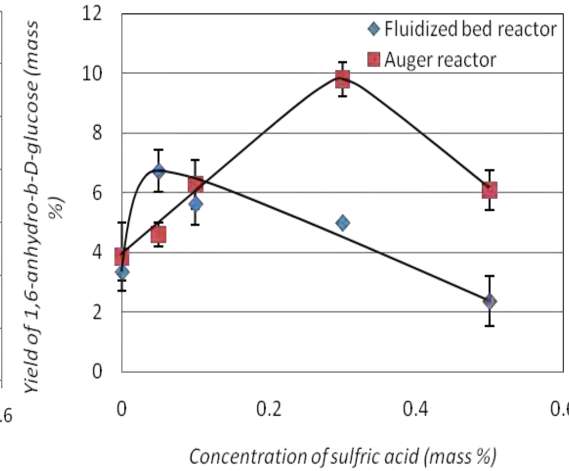
Effect of Sulfuric Acid Concentration









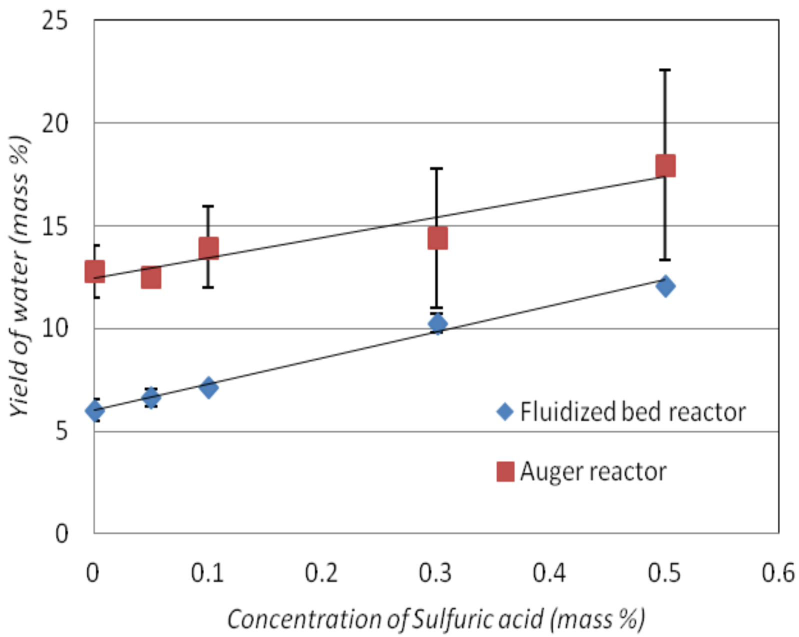


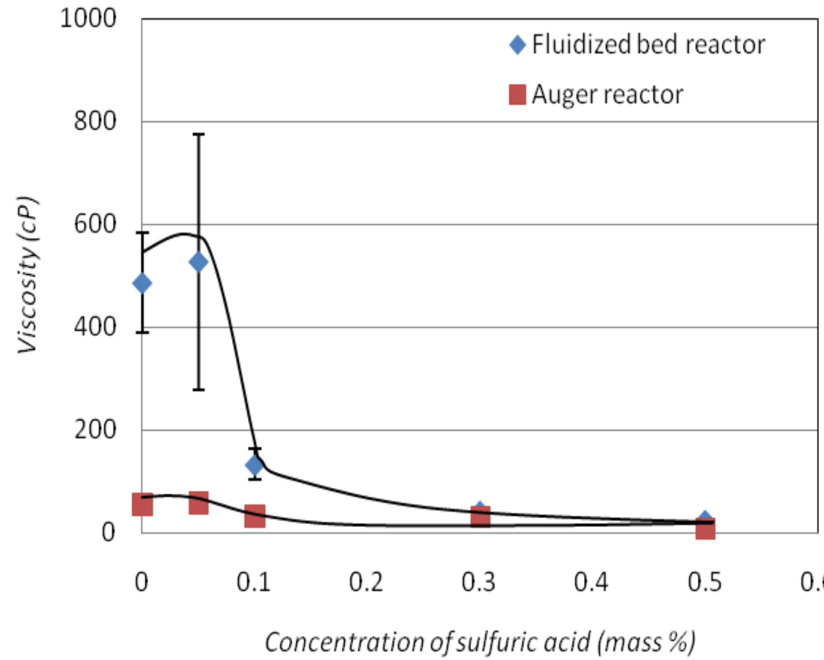
Collaboration with Curtin University (Australia)

PYROLYSIS REACTORS

Effect of Sulfuric Acid Concentration

Yield of Water and Viscosity



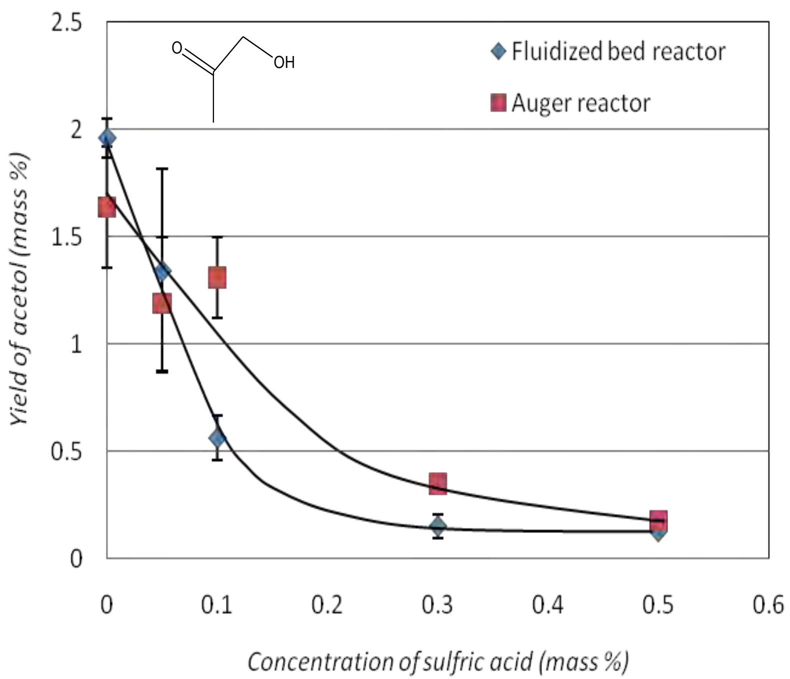


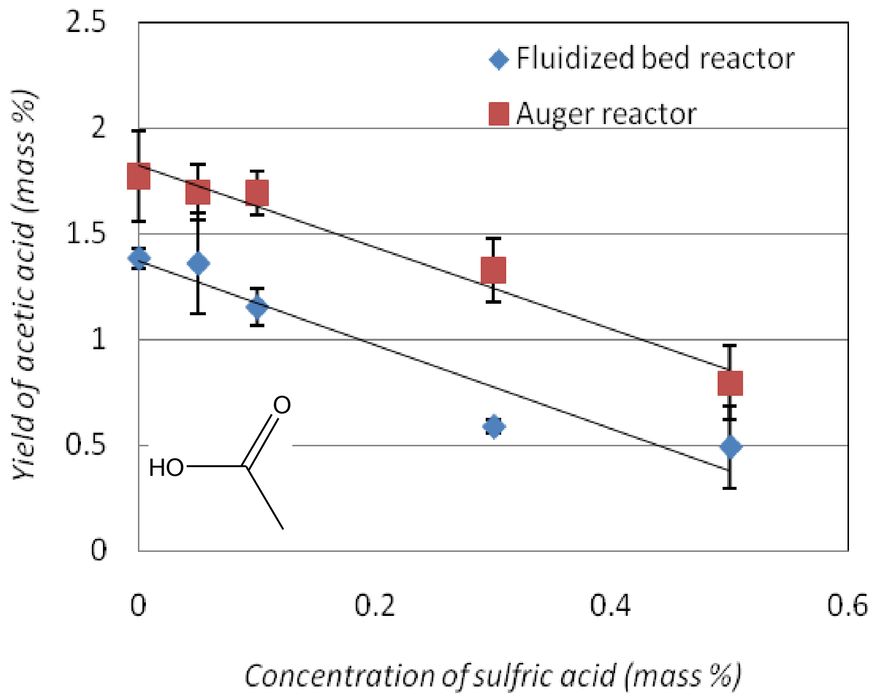
In both reactors the ***water yield increased linearly*** with the concentration of sulfuric acid indicating ***acceleration of dehydratation reactions***. Bio-oil viscosity decreases as sulfuric acid concentration increases.

PYROLYSIS REACTORS

Effect of Sulfuric Acid Concentration

Yields of Light Molecules: GC/MS



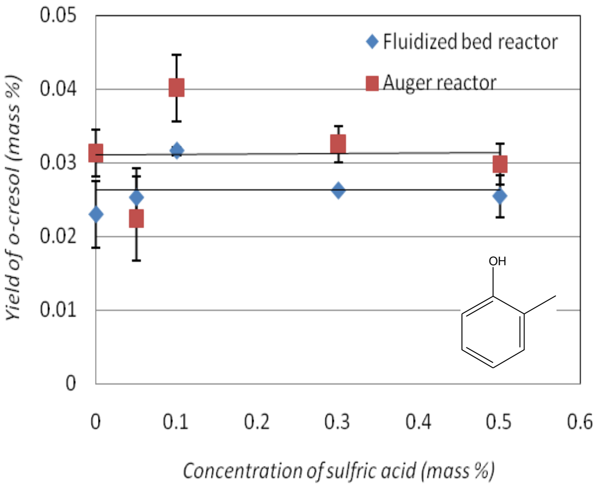


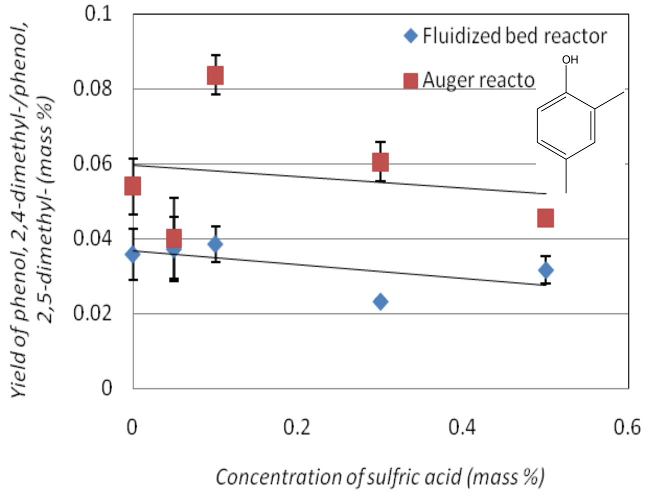
The yield of ***acetol and acetic acid, from the fragmentation of cellulose and hemicelluloses decreased as sulfuric acid concentration increased***. The acetic acid is derived from the acetate group attached to the hemicellulose structure and from the fragmentation of cellulose.

PYROLYSIS REACTORS

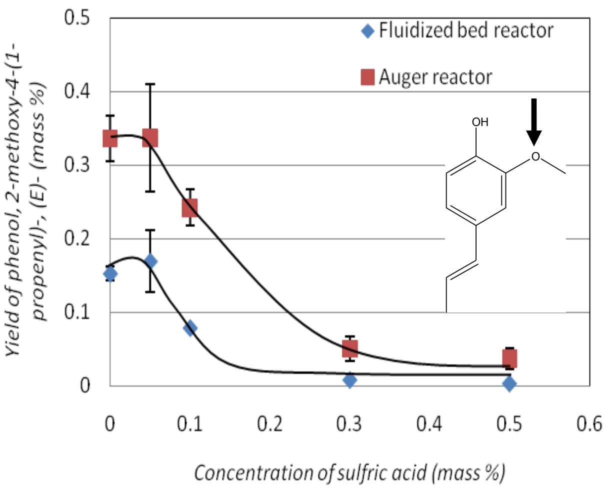
Effect of Sulfuric Acid Concentration

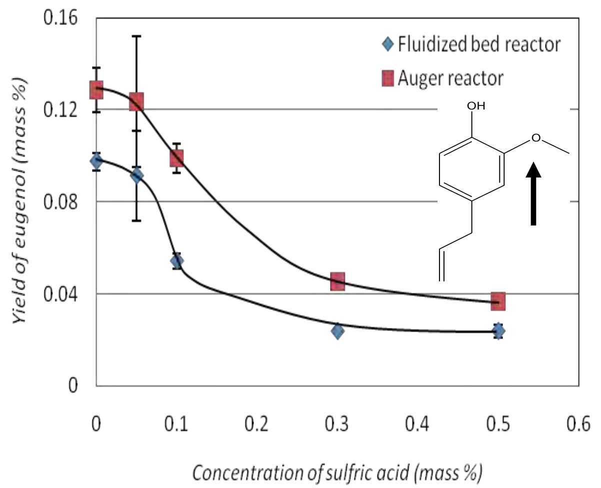
Yields of Mono-Lignols: GC/MS

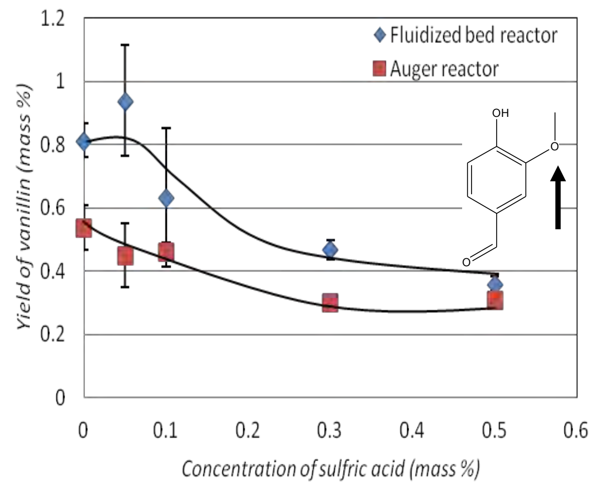




The production of vanillin, phenol - 2 - methoxy - 4 - (1 -propenyl)- and eugeol was drastically reduced as the concentration of sulfuric acid increased. **These compounds have methoxy groups in their structures** which make them very reactive.



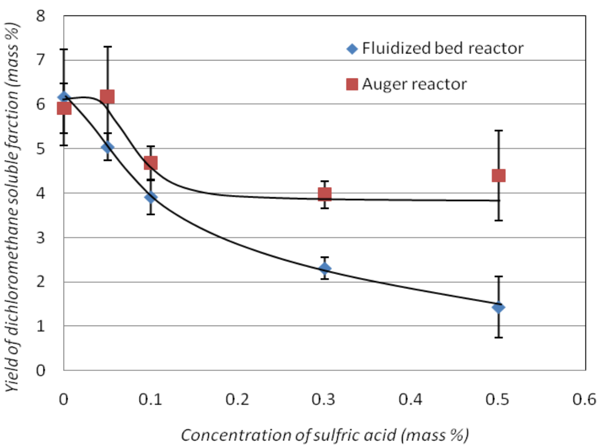


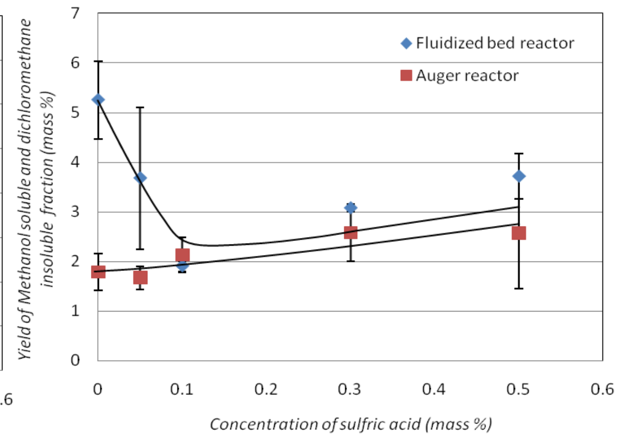


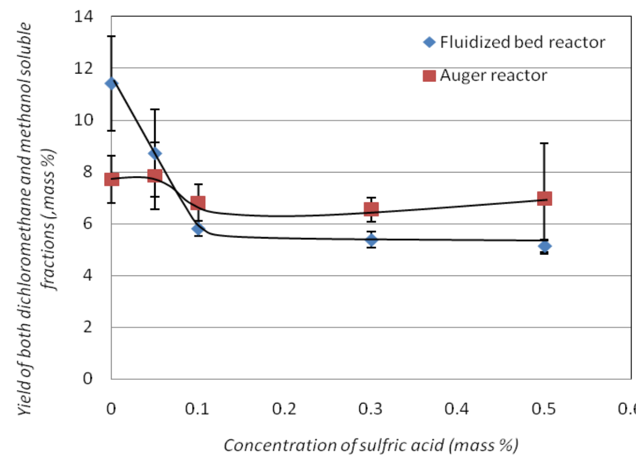
PYROLYSIS REACTORS

Effect of Sulfuric Acid Concentration

Yields of Lignin Oligomers





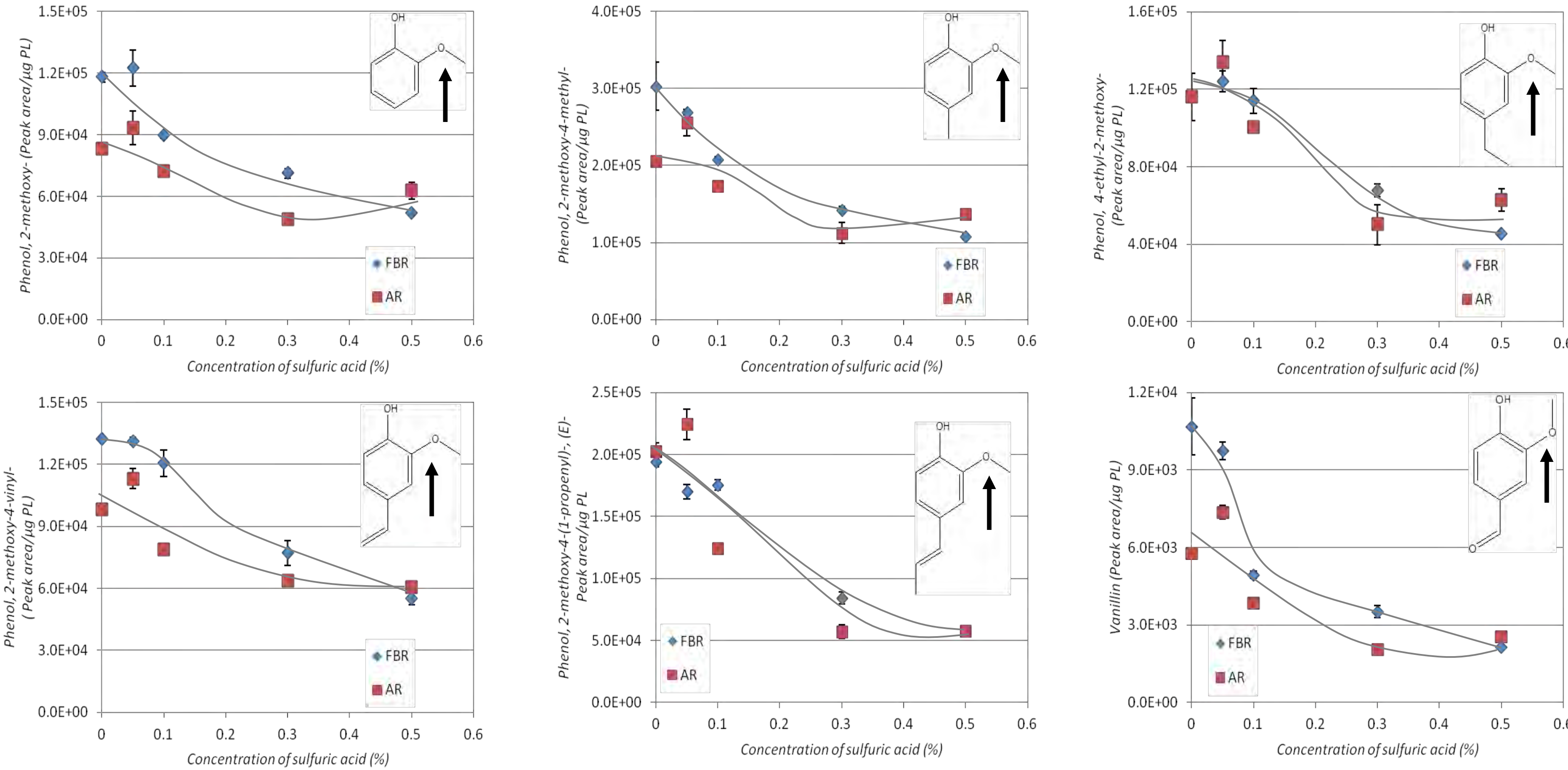


The oils produced in the auger reactor showed higher yields of water insoluble-CH_2Cl_2 soluble fraction (low molecular weight oligomers) but lower yields of the water-CH_2Cl_2 insoluble-methanol soluble fraction (high molecular weight oligomers). ***The addition of sulfuric acid reduces the yield of all lignin oligomeric fractions for both the auger and the fluidized bed pyrolysis reactor***.

PYROLYSIS REACTORS

Effect of Sulfuric Acid Concentration

Analysis of Lignin Oligomers: Py-GC/MS

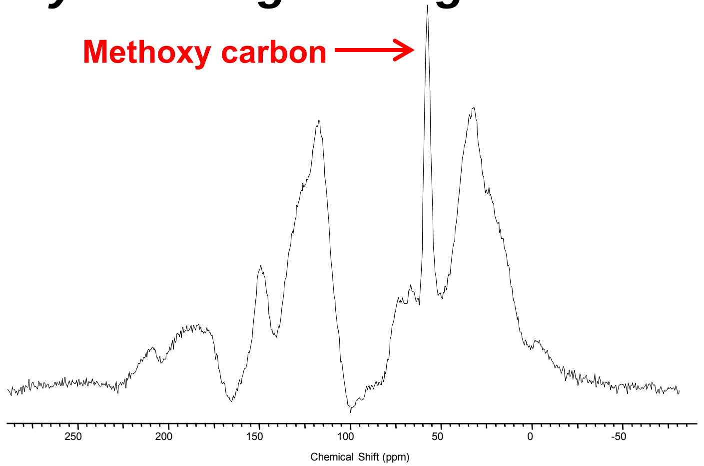


The use of sulfuric acid **significantly reduces the yield of phenolic compounds with methoxy group**. The methoxy groups are known to be electron donors.

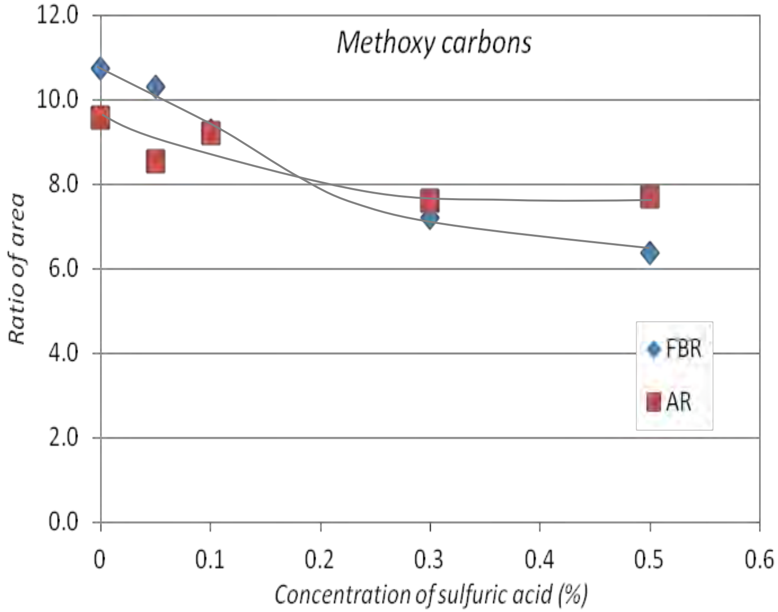
PYROLYSIS REACTORS

Effect of Sulfuric Acid Concentration

Analysis of Lignin Oligomers: *^{13}C Solid State NMR*



Solid state ^{13}C NMR spectra of lignin oligomer



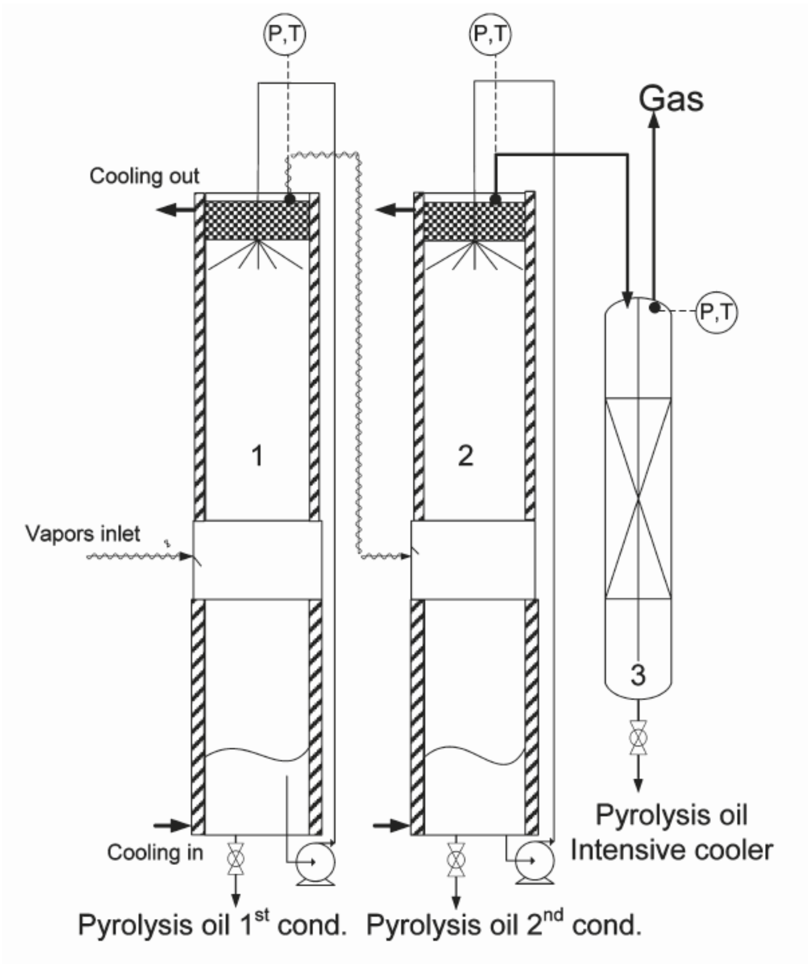
Peak assignment

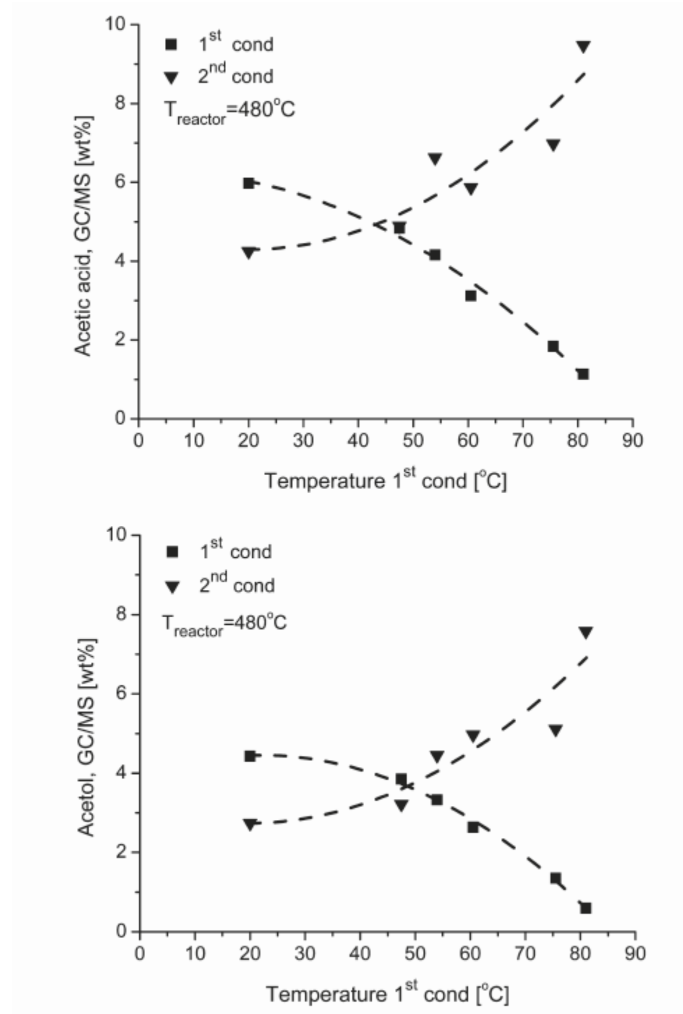
Chemical shift / ppm	Functional groups
0-50	Aliphatic carbons
50-60	Methoxyl carbons
60-80	Aliphatic C-O carbons
100-140	Aromatic carbons
140-165	Oxygenated aromatic carbons
165-230	Carbonyl carbons

A dramatic decrease in the content of methoxy groups confirms the Py-GC/MS findings and clearly suggest that the presence of this functional group activate the ring and accelerate the formation of polyaromatic structures in the bio-char produced.

PYROLYSIS REACTORS

Evaluation of Condensation Systems





Westerhof RM, Brilmant DW, Garcia-Perez M, Wang Z, Oudenhoven SRG, van Swaaij WPM, Kersten SRA: Fractional Consensation of Biomass Pyrolysis Vapors. Energy Fuels, 2011, 25 (4), 1817-1829

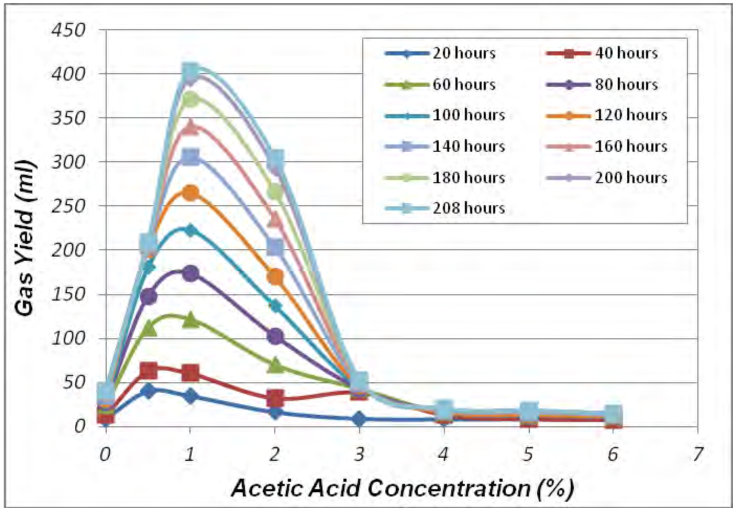
PRODUCT DEVELOPMENT

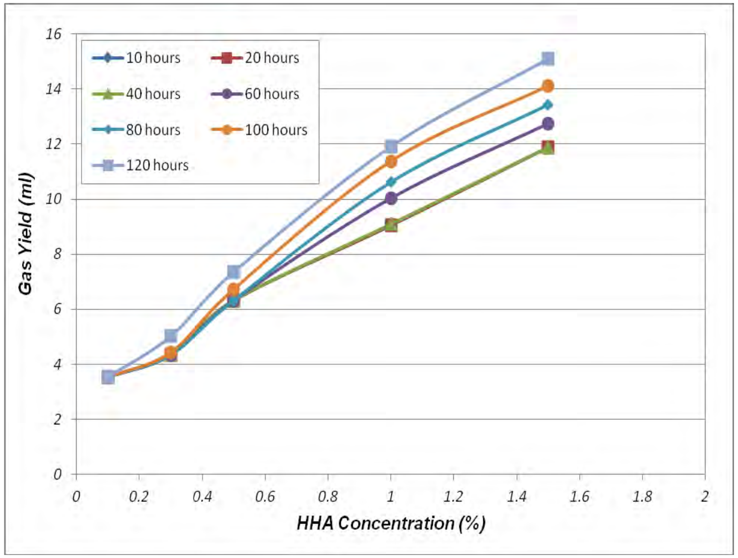
Chemicals that can be obtained from bio-oils

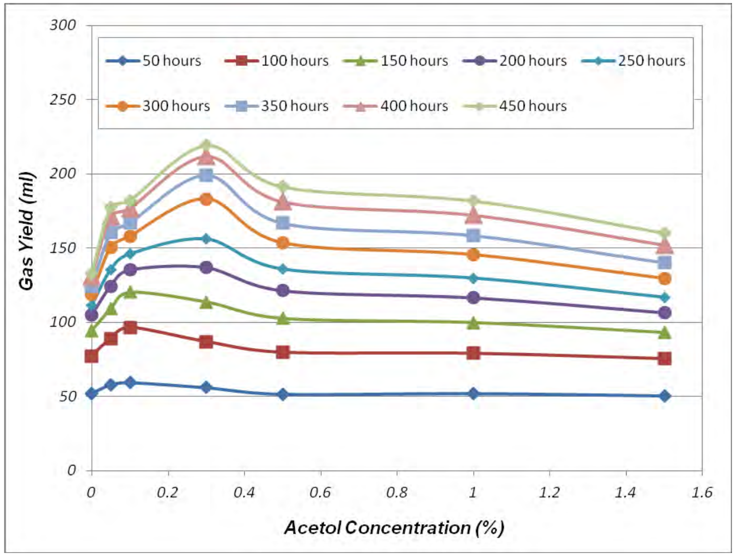
Chemical	Note	Reference
Acetic Acid	World Production: 7 million tons/year, potential price: 0.6 $/kg	Patel et al. 2006, Rasrendra et al. 2010
Adhesives	Phenol substitute for the production of adhesives for the production of Wood panels (plywood, MDF, particle board and OSB).	Czernik and Bridgwater 2004, Effendi et al. 2008, Mohan et al. 2006
Aldehydes and ketones	Separation of aldehydes and ketones have been investigated by bio-coup	Vitasari et al. 2010,
Alkylaromatics	Conversion using zeolites	Resasco et al 2010
Antioxidants	Antioxidant properties of lignin derived compounds	Garcia-Perez et al 2010
Asphalt paving substitution	Production of asphalt emulsions	Mullaney et al. 2002
Bio-carbon electrodes	Production of electrodes, calcinations at 1000 ^{o}C and graphitization at 2700 ^{o}C.	Cautinho et al. 2000
Coal dust suppression	The current product used to coat coal piles is a plasticizer that is bio-degradable and does not contaminate ground water	Mullaney et al 2002
Fertilizer	Amides, imines and mannich reaction products, are produced from the reaction of bio-oil functional groups (carbonyl, carboxyl, hydroxyl, phenolic and methoxyl) with ammonia, urea, and other amino compounds and can function as slow release organic fertilizers	Radlein et al. 2005
Food additives	Commercialized by Red Arrow Products and RTI. A new method for the separation of glycoaldehyde from pyrolysis oil via physical extraction has been reported by researchers from the Eindhoven University of Technology	Mohan et al. 2006, Czernik and Bridgwater 2004, Vitasari et al 2010
Glucose	Can be obtained by hydrolyzing hydrolyzable sugars (levoglucosan, cellobiosan)	Lian et al. 2010, Patel et al. 2006
5-hydroxymethyl furfural (HMF)	Attractive building block for further derivatization	Patel et al. 2006
Levoglucosan	By using demineralized cellulose, high yields of levoglucosan (up to 46 wt. %) and levoglucosenone (up to 24 wt. %) can be generated	Radlein et al (1999), Czernik and Bridgwater 2004
Methanol	Can be produced from the distillation of pyrolighneous water	Emrich 1985
Pesticides	Significant activity against two bacteria and and the Colorado potato beetle were shown using bio-oil derived from dried coffee grounds	Bedmutha et al. 2011, Booker et al. 2010
Impermiabilizer	Black residue of tar distillation commercialized to impermiabilize ships.	Emrich 1985
Road de-icer	Calcium salts of carboxylic acids	Czernik and Bridgwater 2004
Sufactants	More than 10 commercial grades are used for ore flotation	Emrich 1985
Wood preservatives	Bio-oils can act as insecticides and fungicides due to some of the terpenoid and phenolic compounds present	Czernik and Bridgwater 2004, Mohan et al. 2008

PRODUCT DEVELOPMENT

Bio-Methane Production from C1-C4 Pyrolytic Products

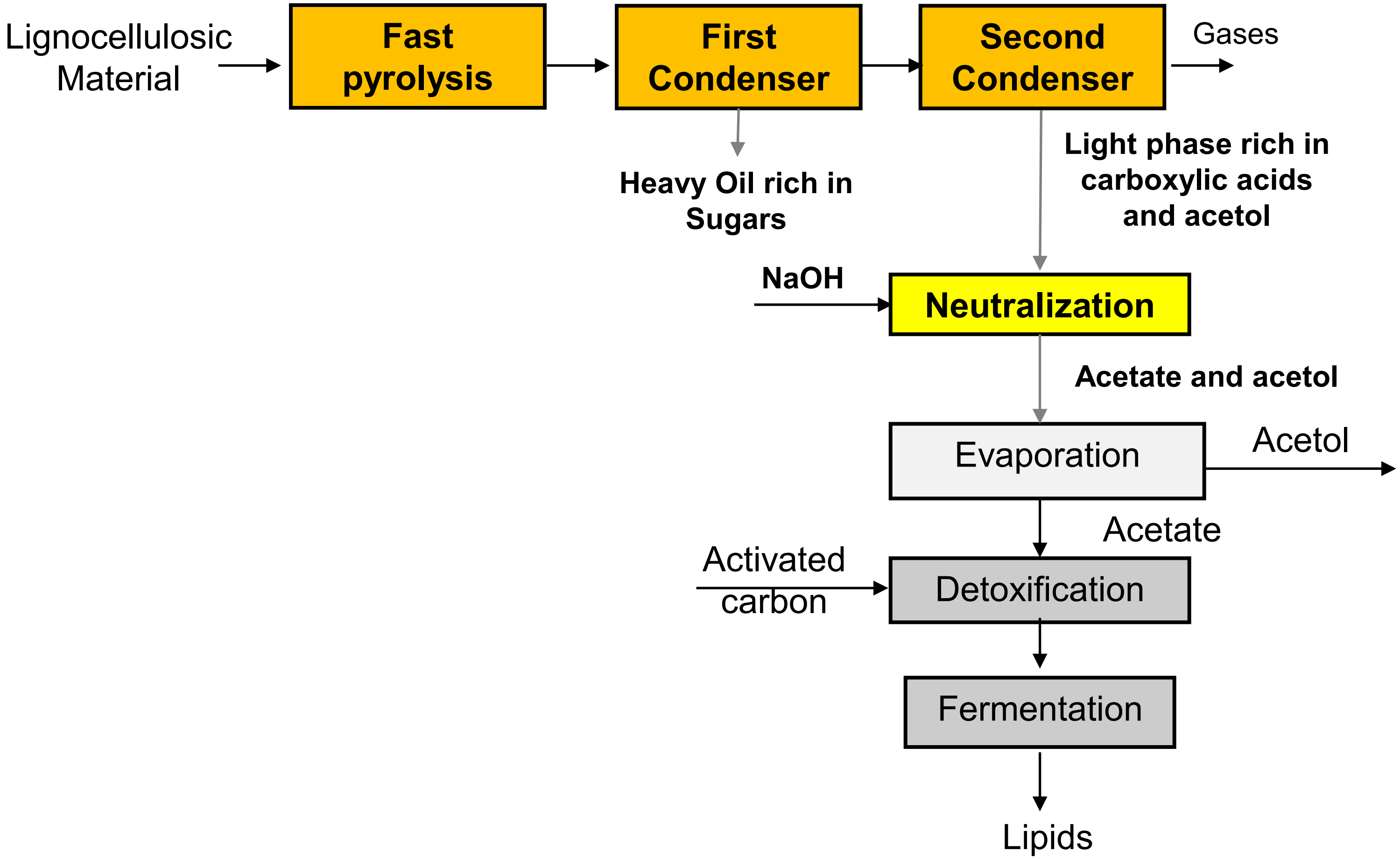






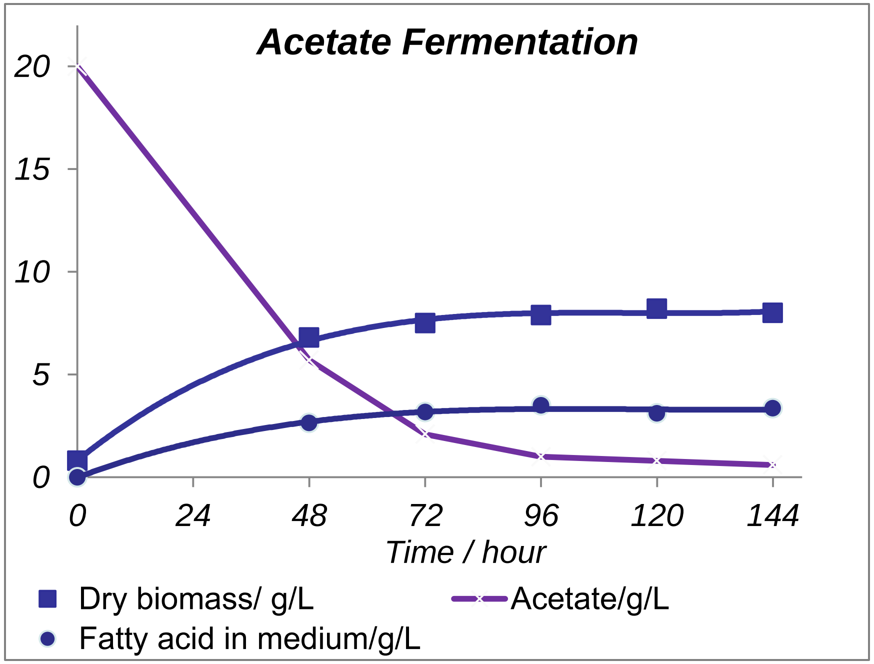
PRODUCT DEVELOPMENT

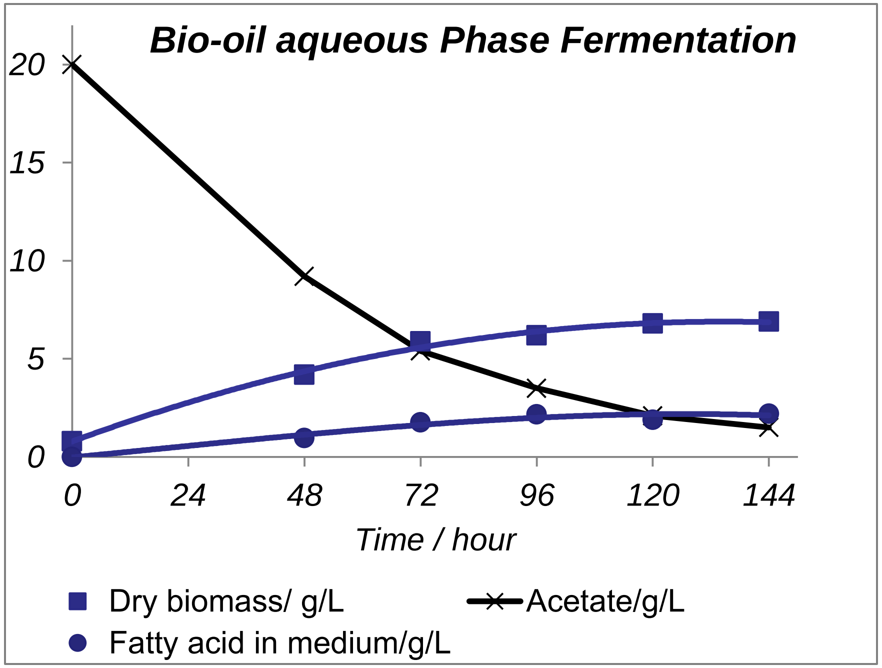
Conversion of acetic acid contained in the aqueous phase collected in the second condenser into lipids



PRODUCT DEVELOPMENT

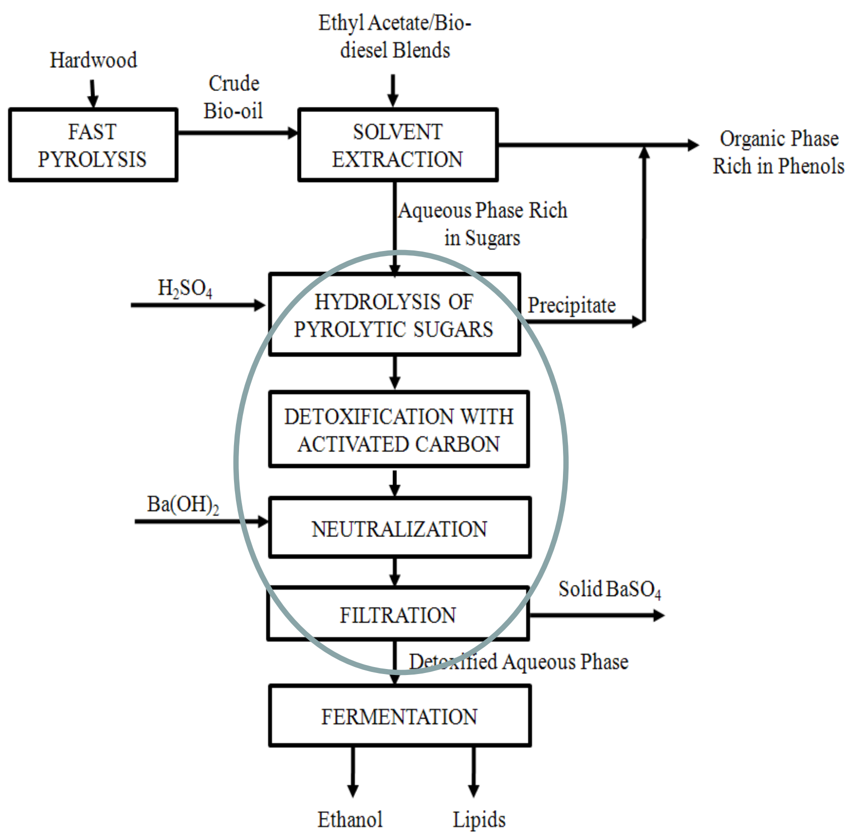
Aqueous phase rich in C1-C4 compounds and acetate fermentation (C. Curvatus)



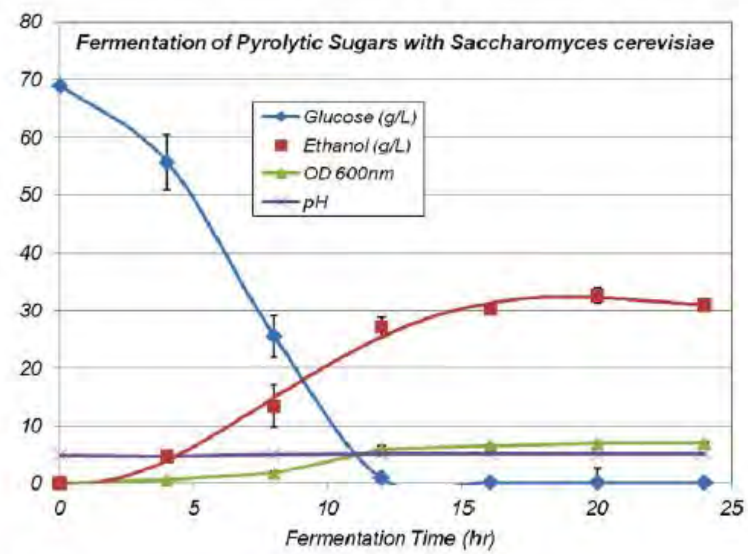


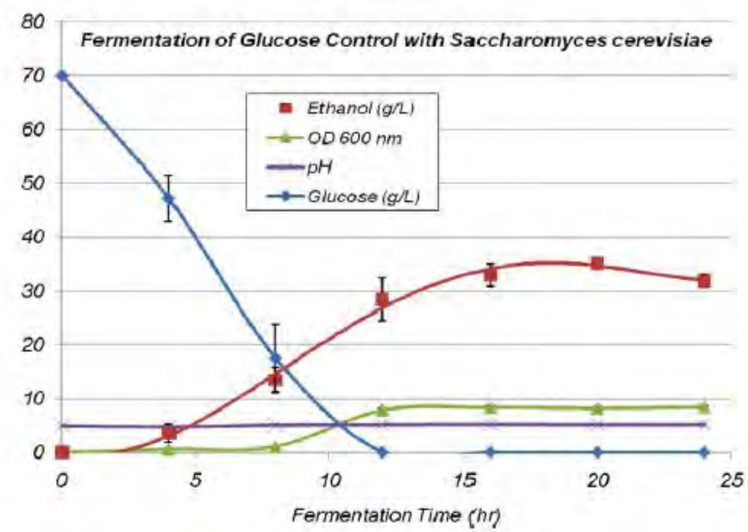
PRODUCT DEVELOPMENT

Conversion of Pyrolytic Sugars into Ethanol or Lipids



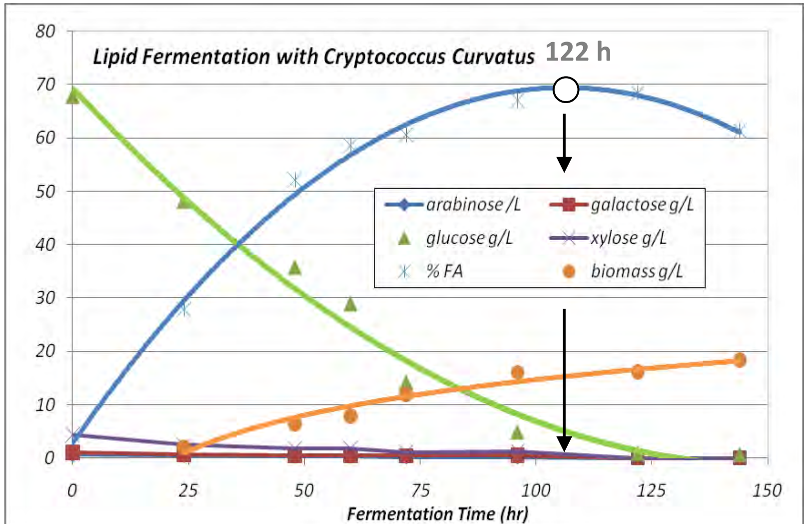
Production of Ethanol

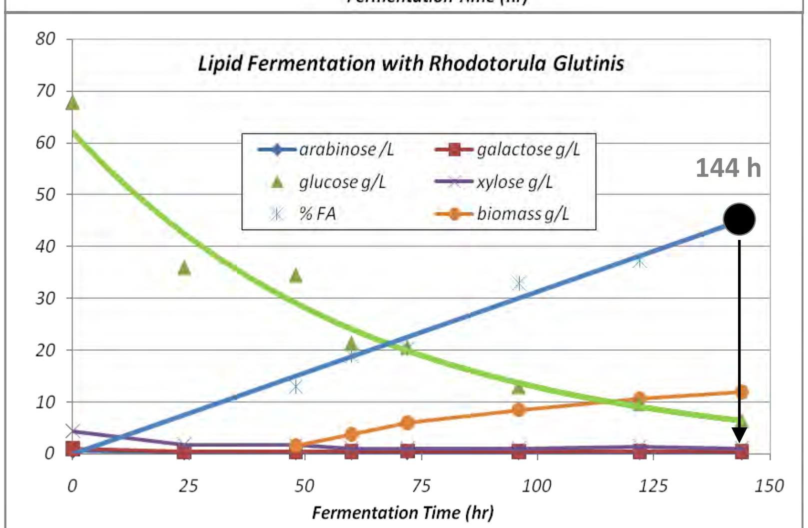




PRODUCT DEVELOPMENT

Cryptococcus curvatus and *Rhodotorula glutinis* for Lipid Fermentation





Cryptococcus curvatus could produce up to 68 % lipid mass/cell mass in 122 hr and 16 g lipid / 100 g glucose conversion in144 hr.

Rhodotorula glutinis could produce up to 46 % lipid mass/cell mass and 8.9 g lipid / 100 g glucose conversion in144 hr.

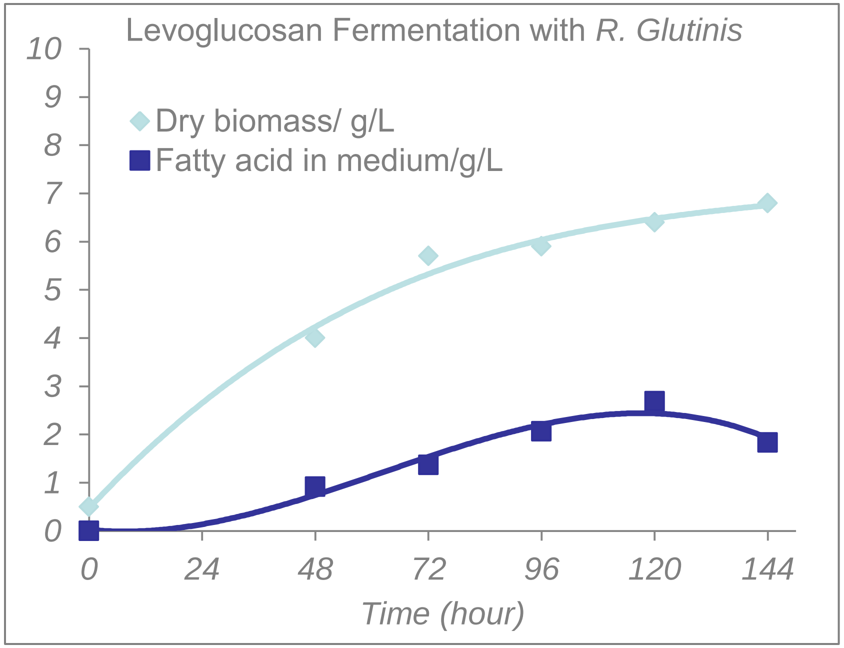
Direct Conversion of Levoglucosan into Lipids

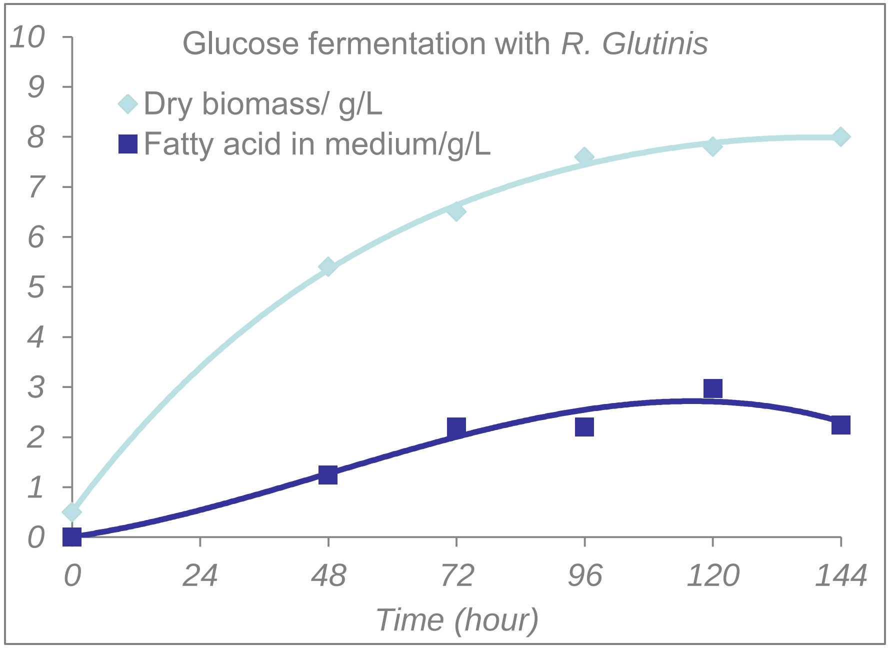
Oleaginous Yeasts Strain Selection for Levoglucosan Fermentation

Strains	Growth
Lipomyces starkeyi ATCC12659	-
Cryptococcus curvatus ATCC20509	+
Yarrowia lipolytica ATCC20460	-
Rhodosporidium toruloides ATCC10788	++
Rhodotorula glutinis ATCC204091	++

PRODUCT DEVELOPMENT

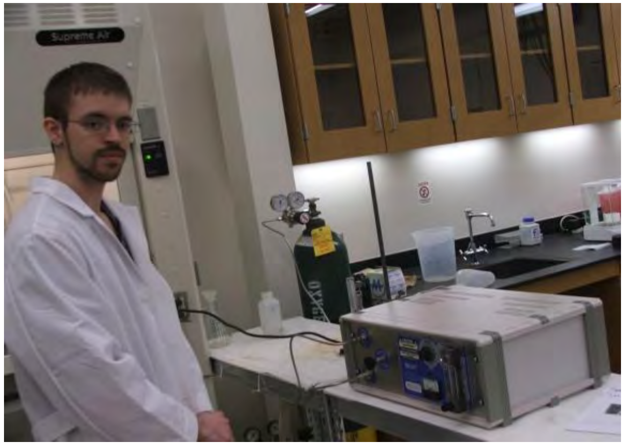
Levoglucosan and glucose fermentation with oleaginous yeast *R. glutinis*





PRODUCT DEVELOPMENT

TO DEVELOP ***NEW PRODUCTS FROM BIO-CHARS***

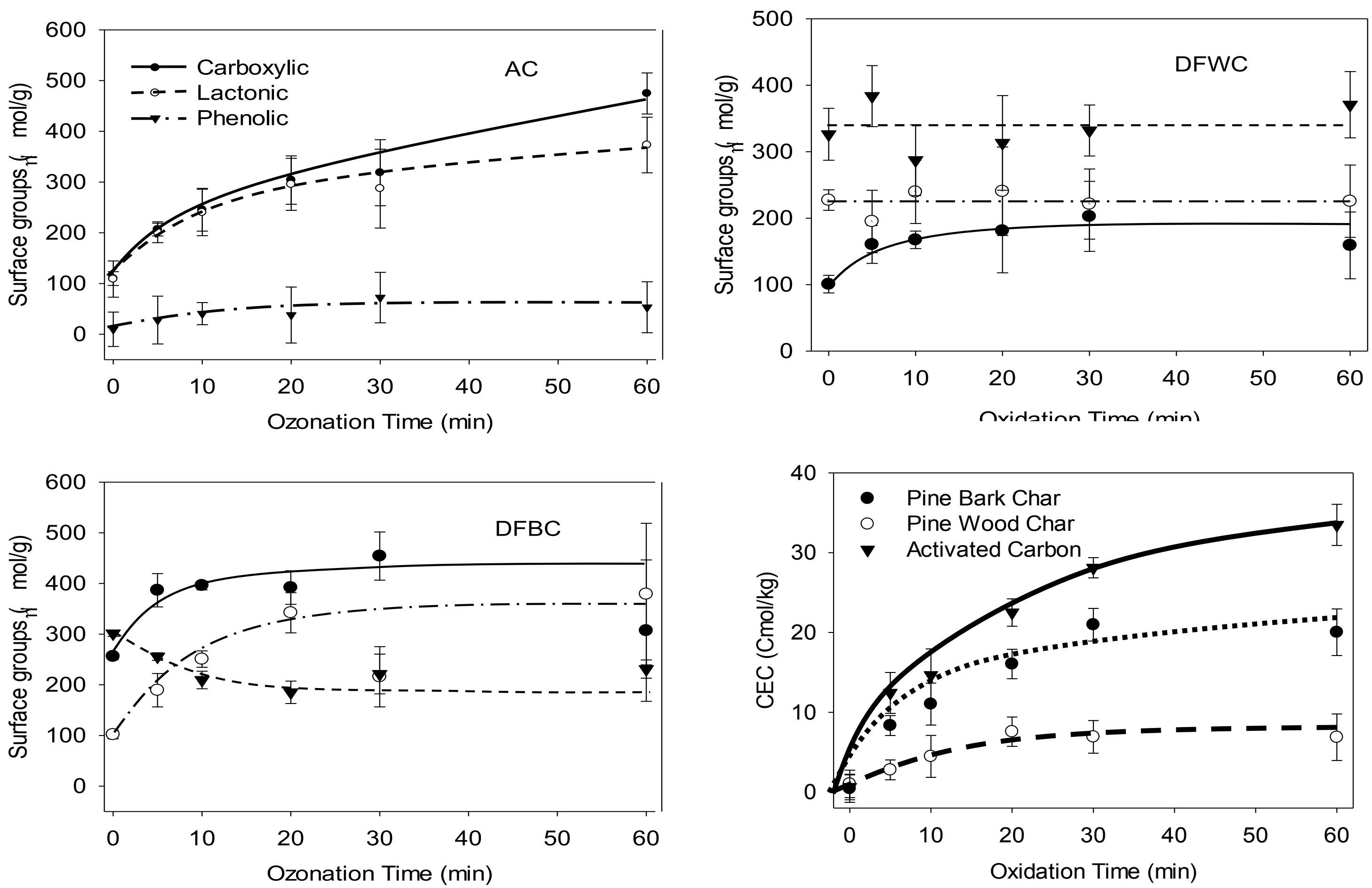


Bio-char — Modifications of bio-char surface chemistry and the development of new Products

- Advanced Soil Amendments for carbon sequestration
- Construction materials
- **Bio-Char for Environmental Applications**

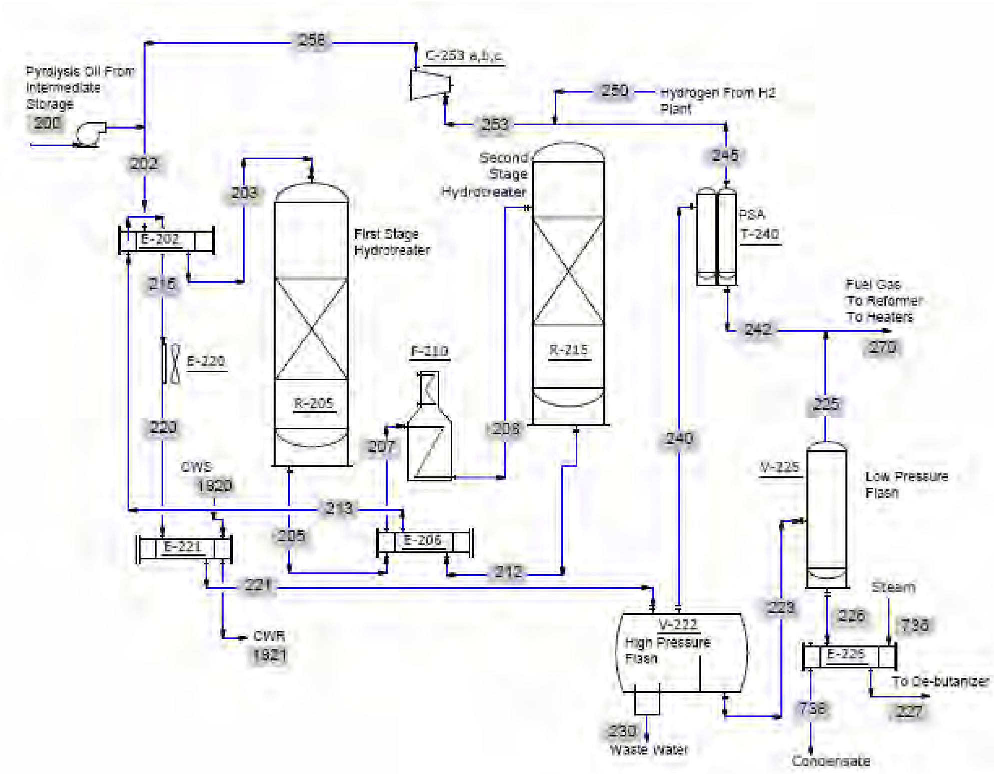
PRODUCT DEVELOPMENT

- Carboxylic groups form rapidly, then Lactone Groups
- Oxidation Slows after first 10-20 minutes
- CEC increases strongly with oxidation



BIO-OIL REFINERIES

Two Step Hydrotreatment (PNNL)



1.- **High hydrogen consumption** making the process cost-prohibitive to get 3 $/gallon of bio-fuel

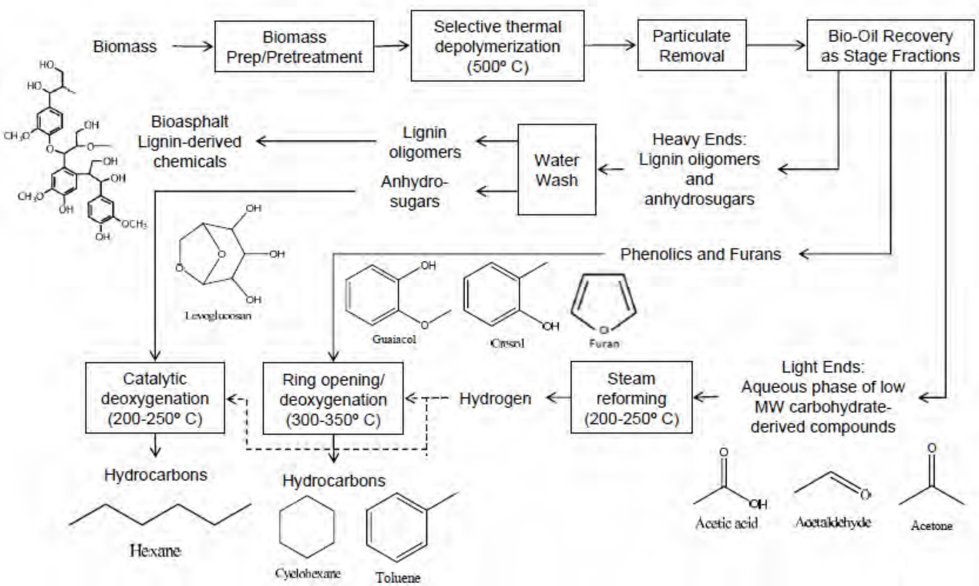
2.- **No high value by-products are produced** to make the plant economics viable

3.- The **fuel produced** from the hydrotreatment of bio-oil **is rich in aromatics and naphthalene** but has low content of paraffins and iso-paraffins. This limits its application as a jet fuel.

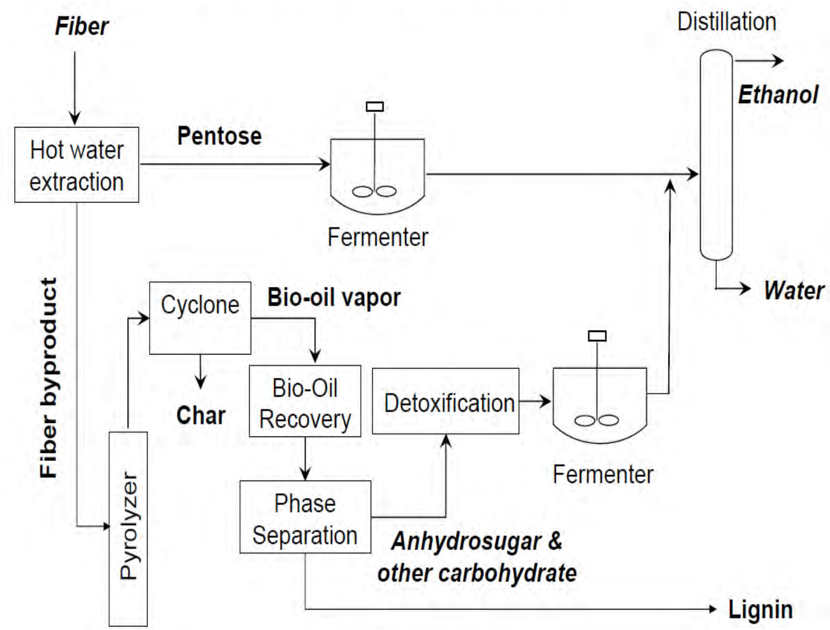
Source of Figure: http://www1.eere.energy.gov/biomass /pdfs/pyrolysis report summary.pdf

BIO-OIL REFINERIES

Strategy for up-grading bio-oil (Brown 2010).

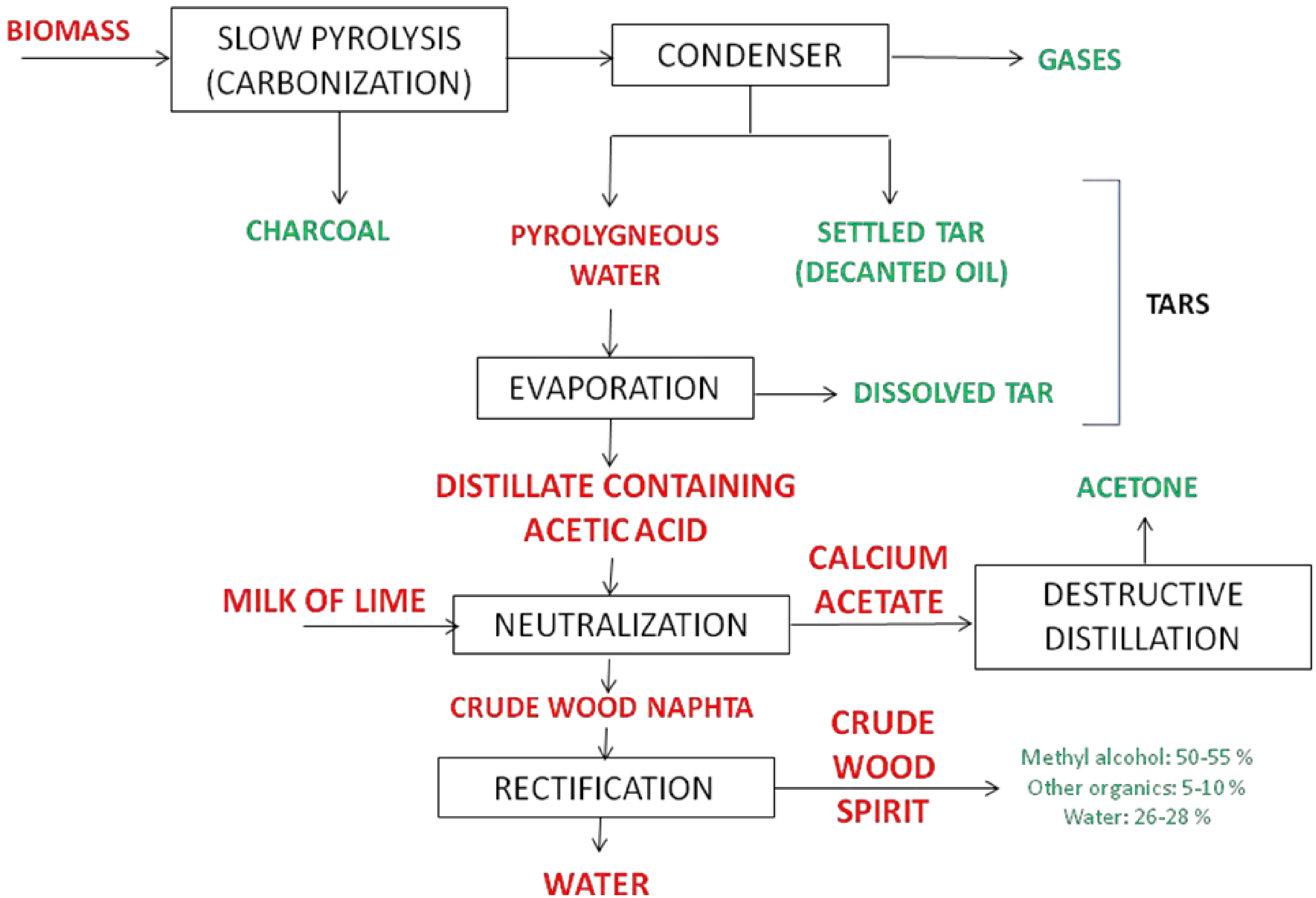


Hybrid Refining Technologies



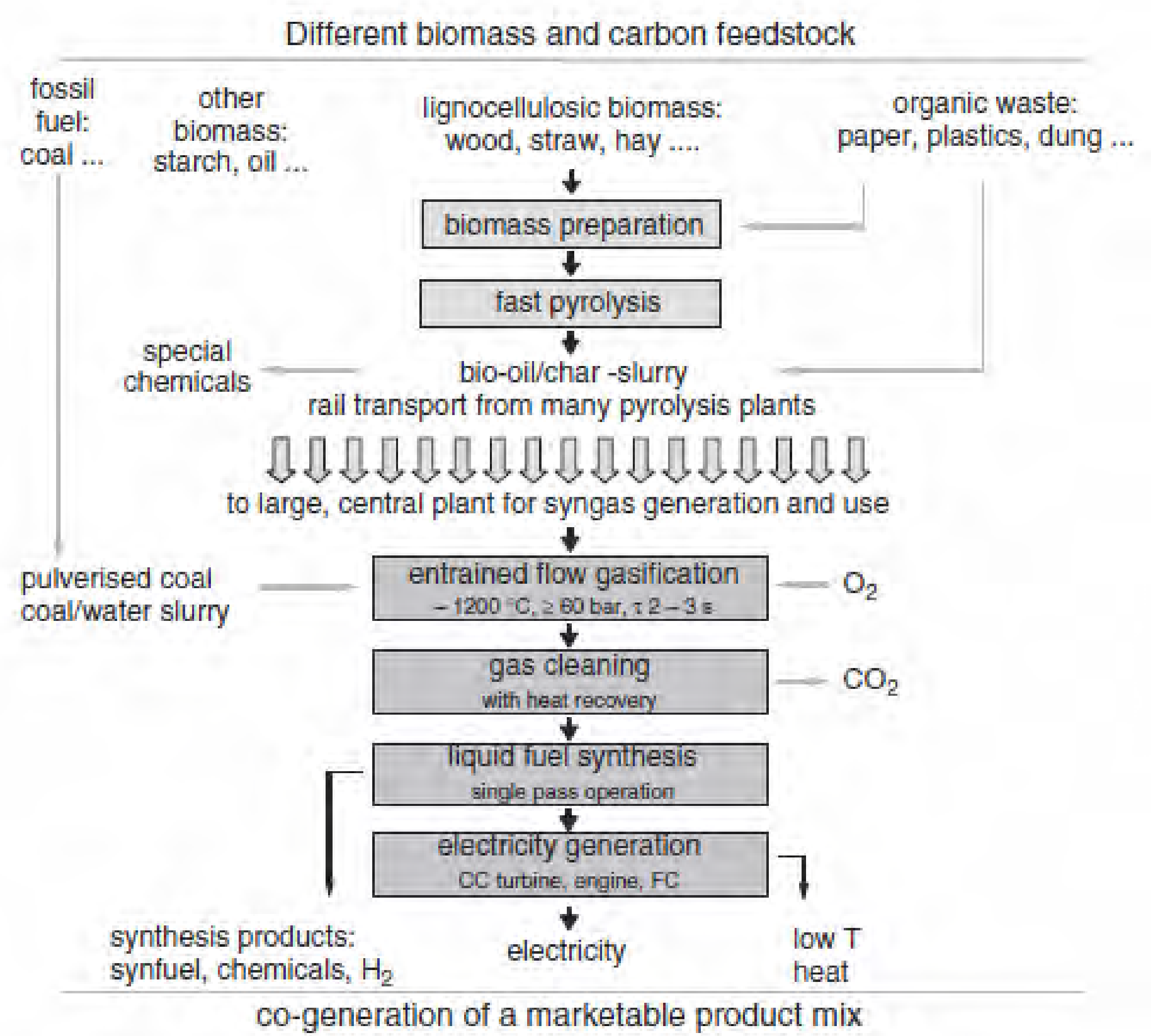
BIO-OIL REFINERIES

Old wood distillation industry's bio-refinery concept (Klar and Rule 1925).



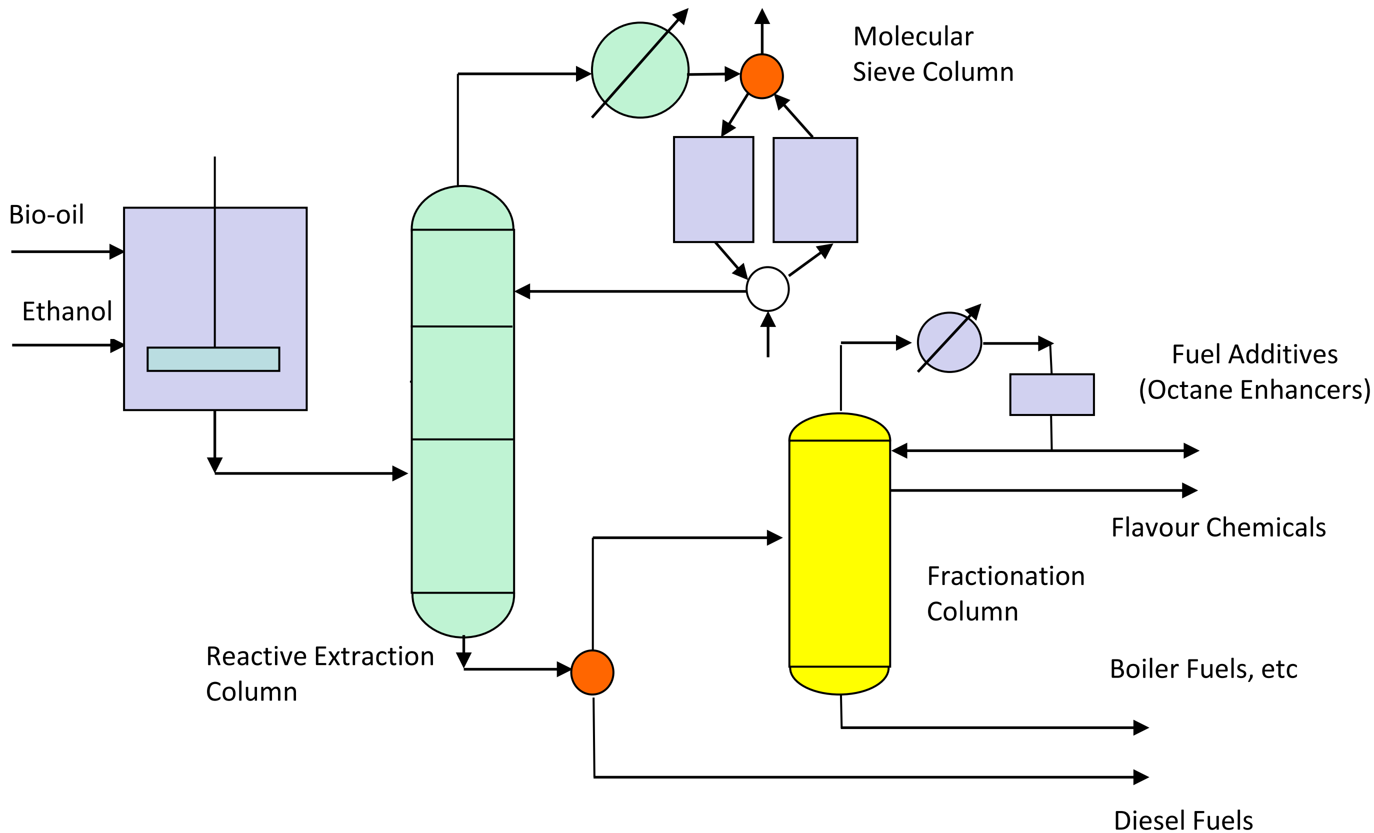
BIO-OIL REFINERIES

Simplified scheme which uses bio-oil/biochar slurries to produce Fischer-Tropsch (FT) syngas (Henrich et al. 2009).



BIO-OIL REFINERIES

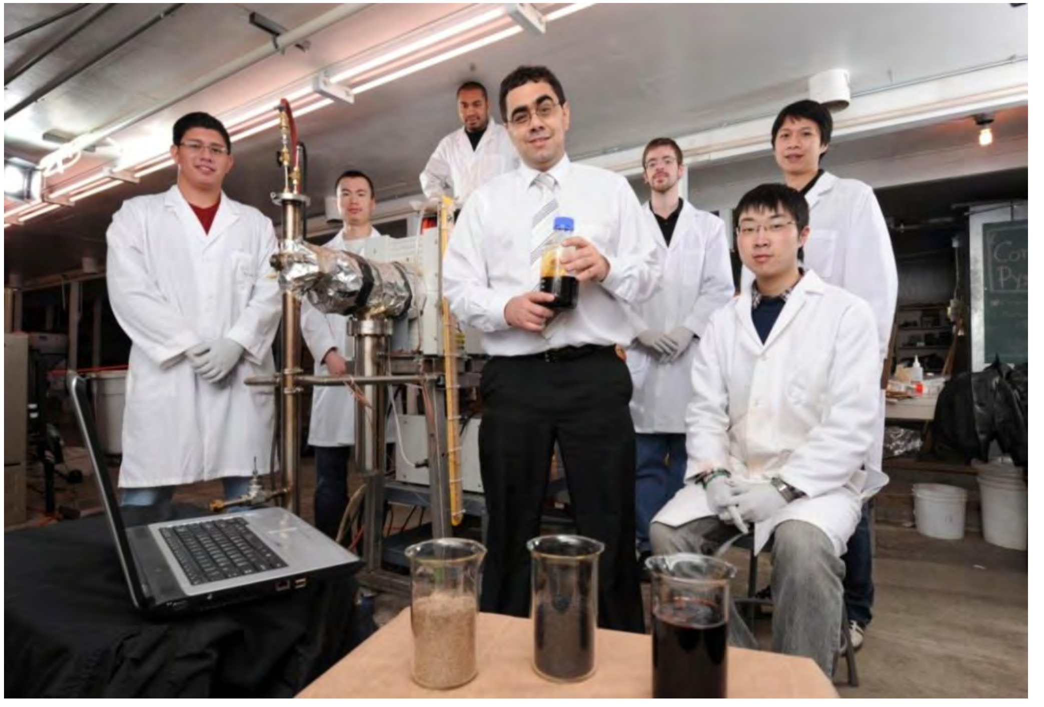
Bio-refinery Concept based on Bio-oil Esterification (Radlein 2005). This concept is being studied by the group of Professor Chun-Zhu Li at Curtin University (Australia).



CONCLUSIONS

- **Two types of Pyrolysis Technologies can be developed *(1)*** Slow Pyrolysis units to produce bio-char and heat (electricity, mostly from Agricultural wastes) ***(2) More selective*** fast pyrolysis to produce bio-char and bio-oil. Bio-oil has to be further processed in a rural refinery to obtain stabilized **bio-oil compatible with existing petroleum refineries** and **high value chemicals**.
- Using **bio-char as a soil amendment is one of the most promising methods for carbon sequestration**. Implementing this method could provide a large market for the bio-char produced. However, **in order for this to be economically viable high value bio-chars with enhanced agronomical functions must be developed**.
- The development of **high value products** from **bio-oil** is critical for the survival, development and economic viability of the fast pyrolysis technologies identified.
- A balanced investment in the creation of new knowledge (**science**) in the design, testing and scale up of **new technologies** for pyrolysis reactors, bio-oil refineries, and **the development of new products** (from bio-oils and bio-char) which address the needs of the **market** are all critical for the deployment of a biomass economy based on pyrolysis technologies.

Acknowledgement



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QUESTIONS ?