Pyrolysis of Lignocellulosic Materials for the Production of Bio-fuels, Bio-chemicals and Bio-char

Manuel Garcia-Perez

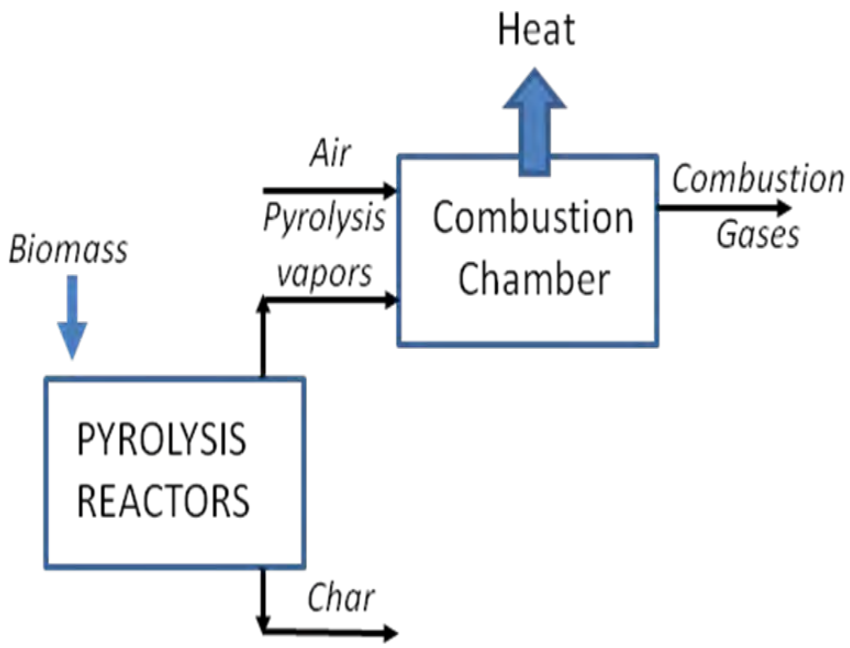
Washington State University

Northwest Wood-Based Biofuels + Co-Products Conference

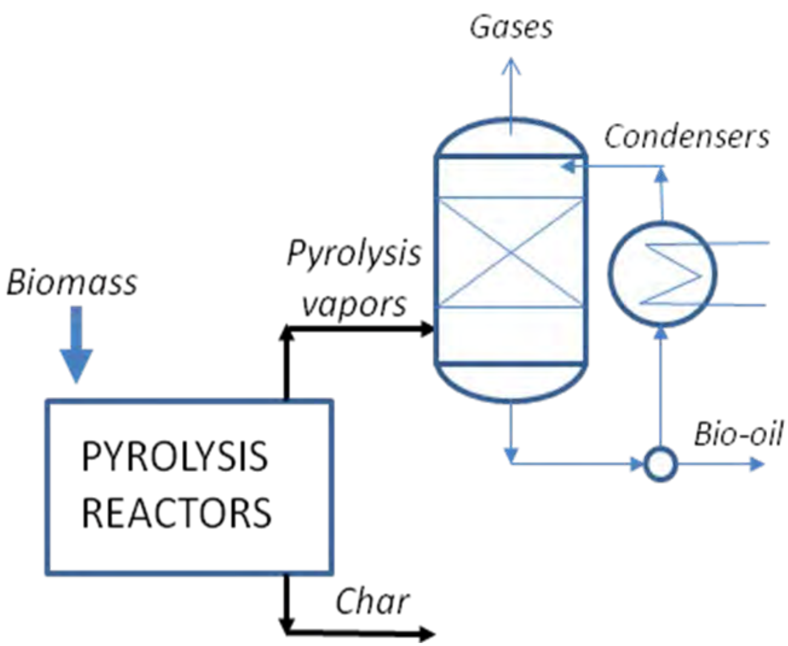
Seattle, April 28-30, 2014

BUSINESS MODELS

Pyrolysis Scheme to Produce Bio-char and Heat

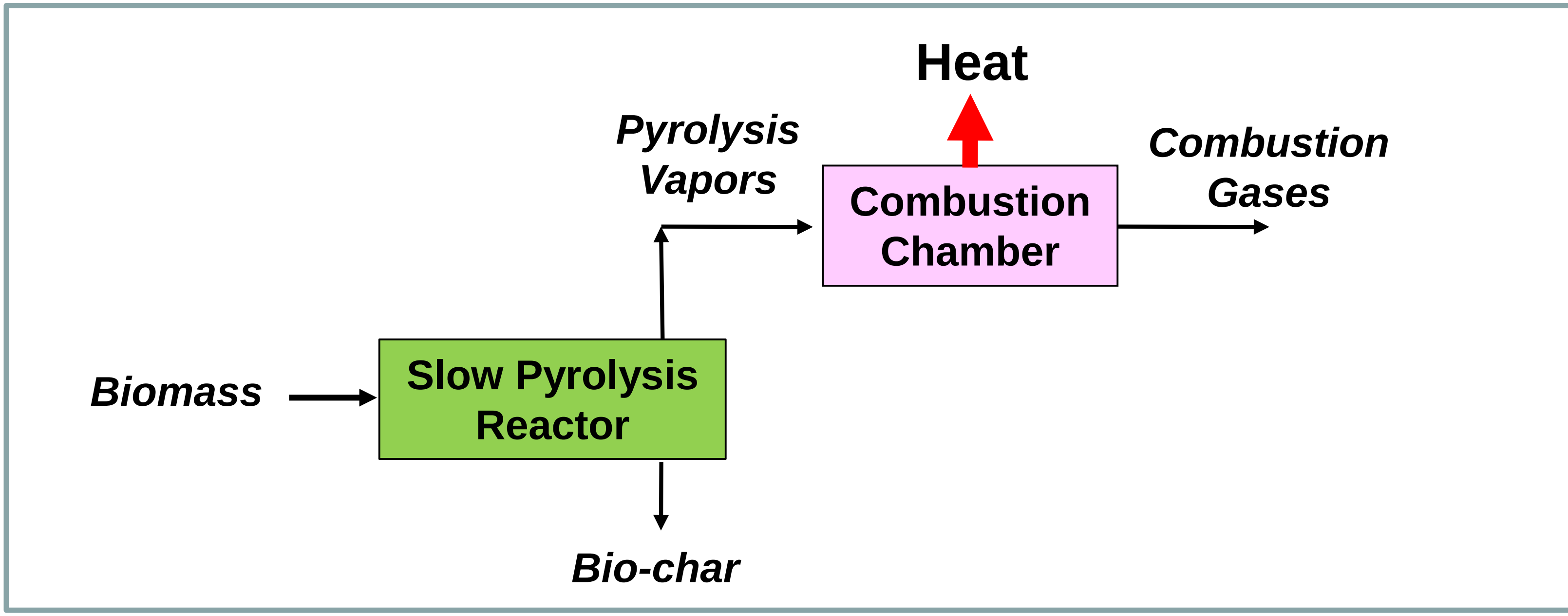


Pyrolysis Scheme to Produce Bio-char and bio-oil



SLOW PYROLYSIS

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 %

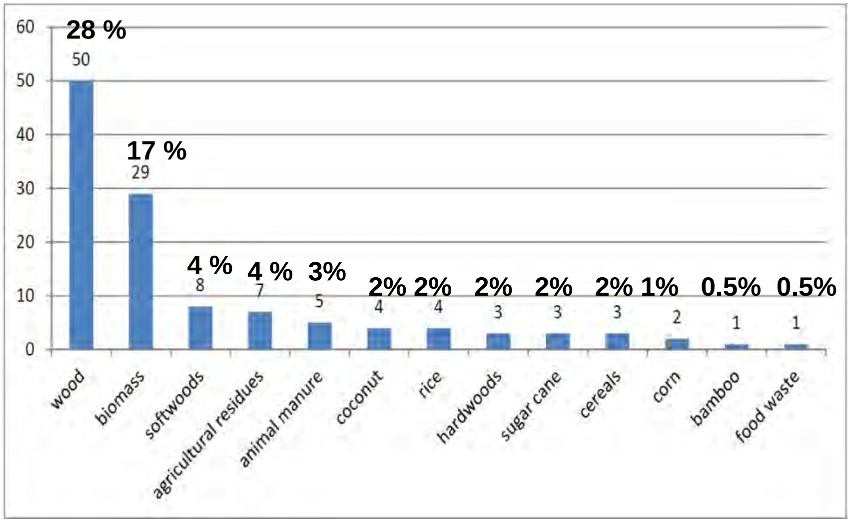
SLOW PYROLYSIS

Current State of the Bio-char industry (IBI Survey[1])

Main Feedstock used: **Woody Biomass**.

Main product: **Gardening** and **tree care**[1]. Biochar has not make a substantial entry into large scale agricultural operations.

Average retail price: **$ 2.48/kg**.

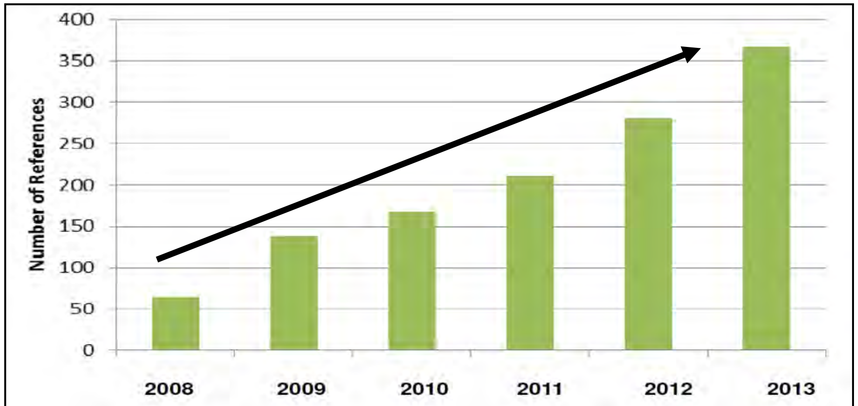


Main equipment used: Varies from **micro-scale cookstoves to large scale industrial facilities**.

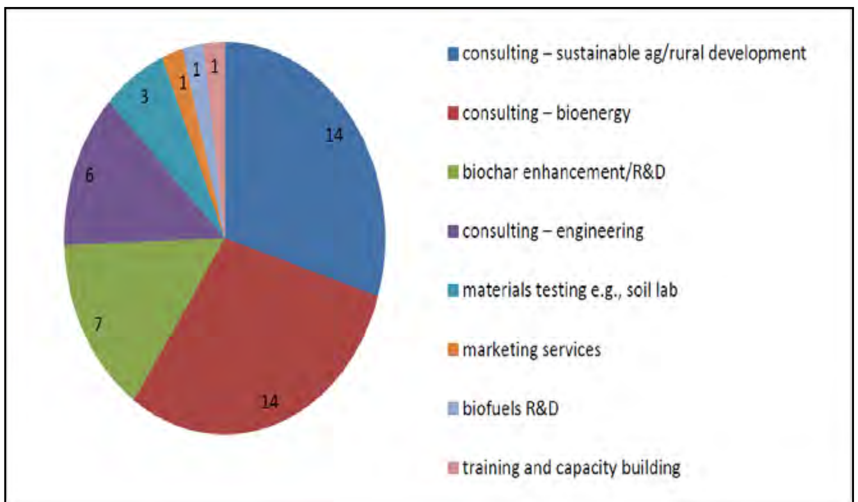
Source: [1]Stefan Jirka, Tomlinson T: 2013 State of the Art of the Bio-char Industry. A survey of Commercial activity in the Bio-char Field. A Report by the International Biochar Initiative (IBI) March 2014

SLOW PYROLYSIS

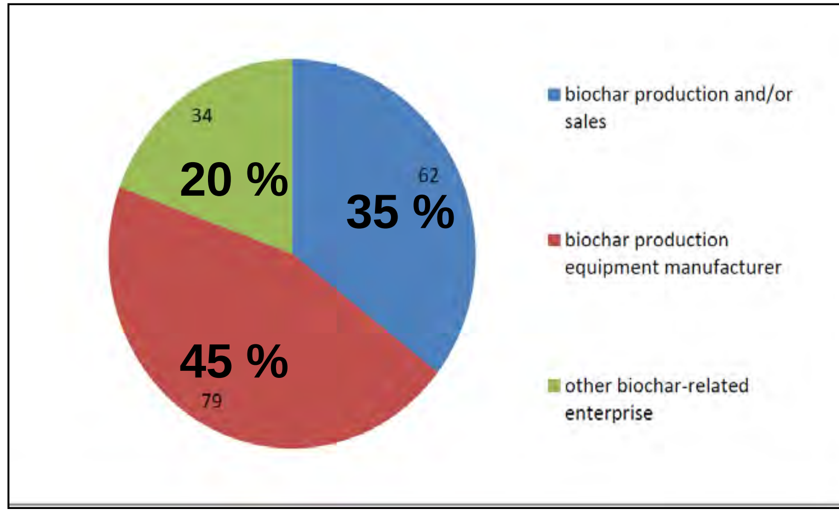
Scientific research: Number of peer-reviewed bio-char related publications increased **nearly five-fold over the last five years[1]**.

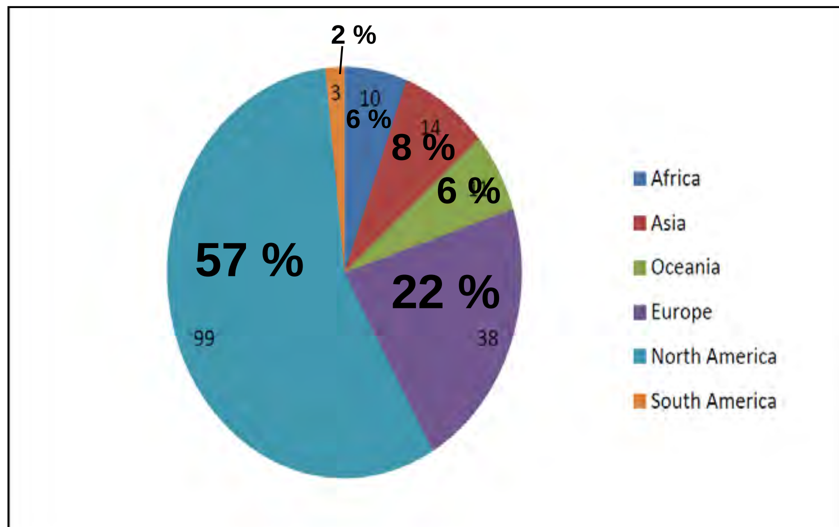


Services Provided to the Bio-char industry



Pyrolysis Companies by Sectors and Countries (IBI Survey)





Source: Jirka S, Tomlinson T: 2013 State of the Art of the Bio-char Industry. A survey of Commercial activity in the Bio-char Field. A Report by the International Biochar Initiative (IBI) March 2014

SLOW PYROLYSIS

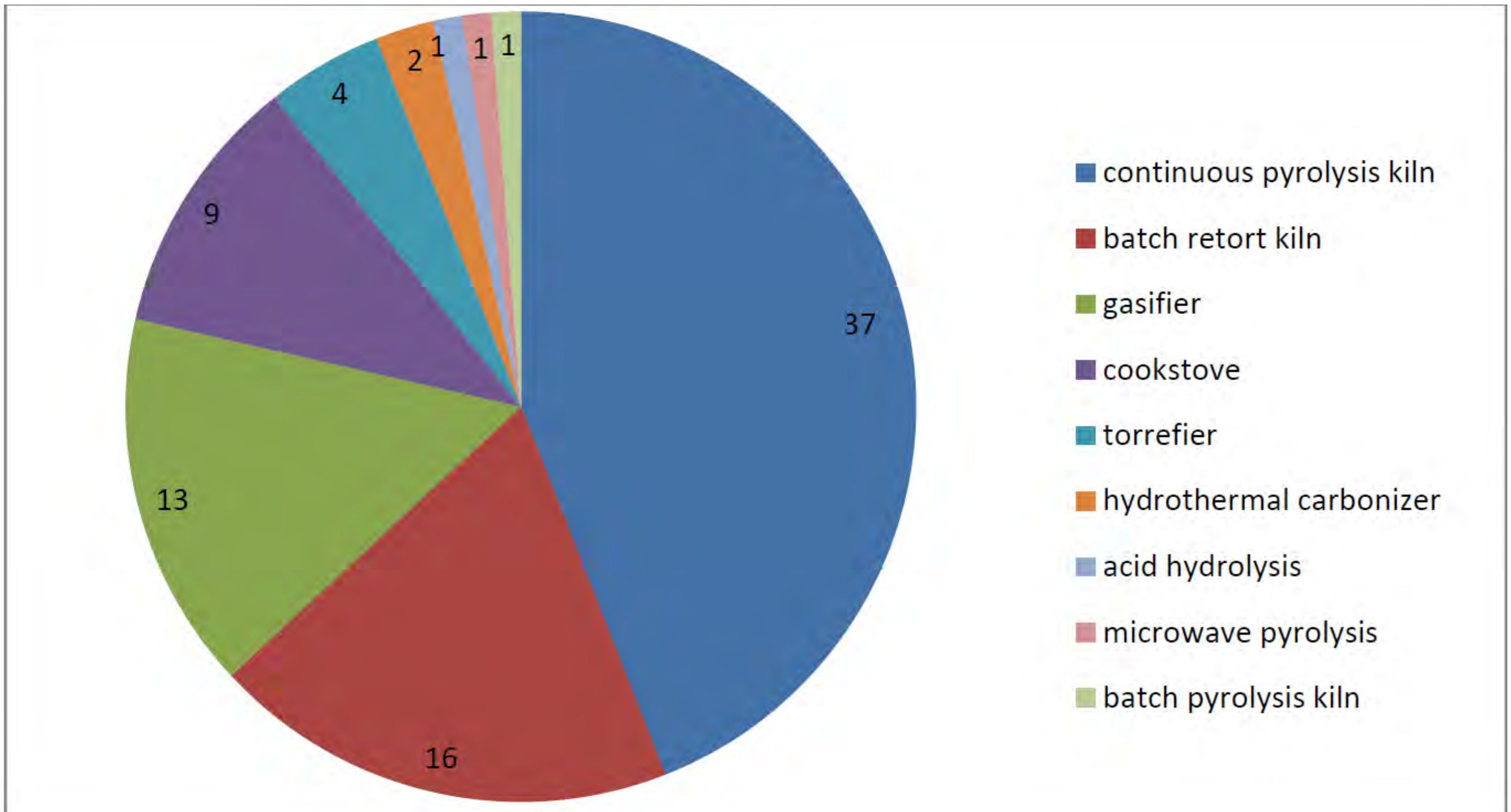
Despite the growing interest in producing bio-char and heat, the lack of available information on clean designs hinders those interested in developing this industry. **The inadequate flow of information for potential users forces the design of pyrolysis units to remain an art.**

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

SLOW PYROLYSIS

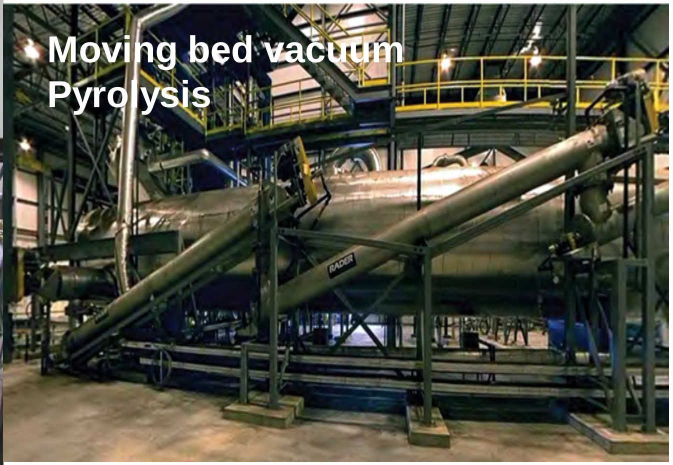
Frequency of Pyrolysis Technology (IBI Survey)



Source: [1]Stefan Jirka, Tomlinson T: 2013 State of the Art of the Bio-char Industry. A survey of Commercial activity in the Bio-char Field. A Report by the International Biochar Initiative (IBI) March 2014

SLOW PYROLYSIS

Intermediate Pyrolysis Reactors

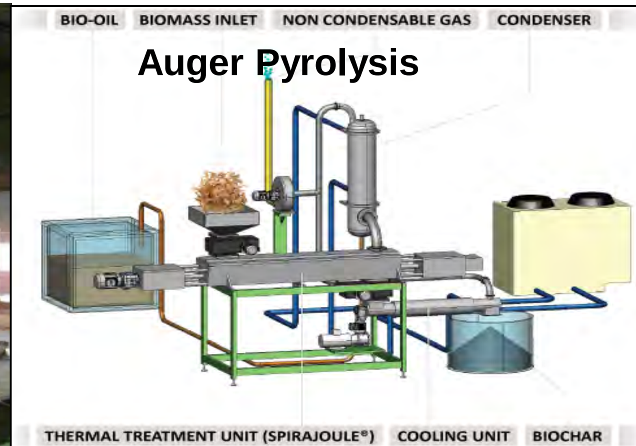


Black is Green Pty Ltd http//www.bio-char.com.au/about.html	Amaron rotary drum reactor (Coates Engineering) http://www.coatesengineering.com	Vacuum Pyrolysis Reactor (Pyrovac)

SLOW PYROLYSIS

Intermediate Pyrolysis Reactors

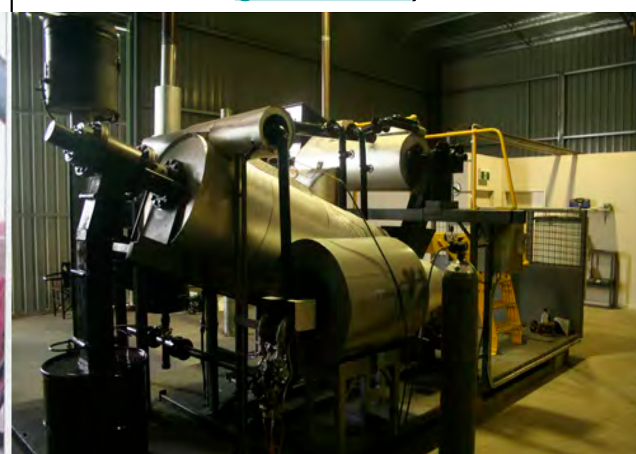
Renewable Oil International Mobile Unit



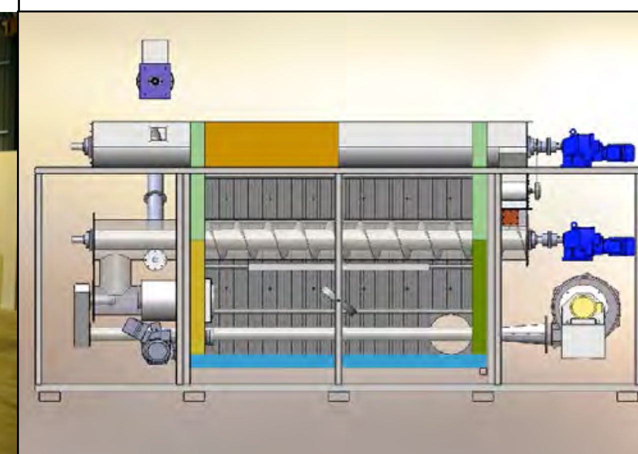
BiogreenR (http://biogreen-energy.com/bio-green.html)

Agri-Tech Producers (http://www.agritechproducers.com)

International Tech Corporation (http://www.internationaltechcorp.org/IT-info.htm)



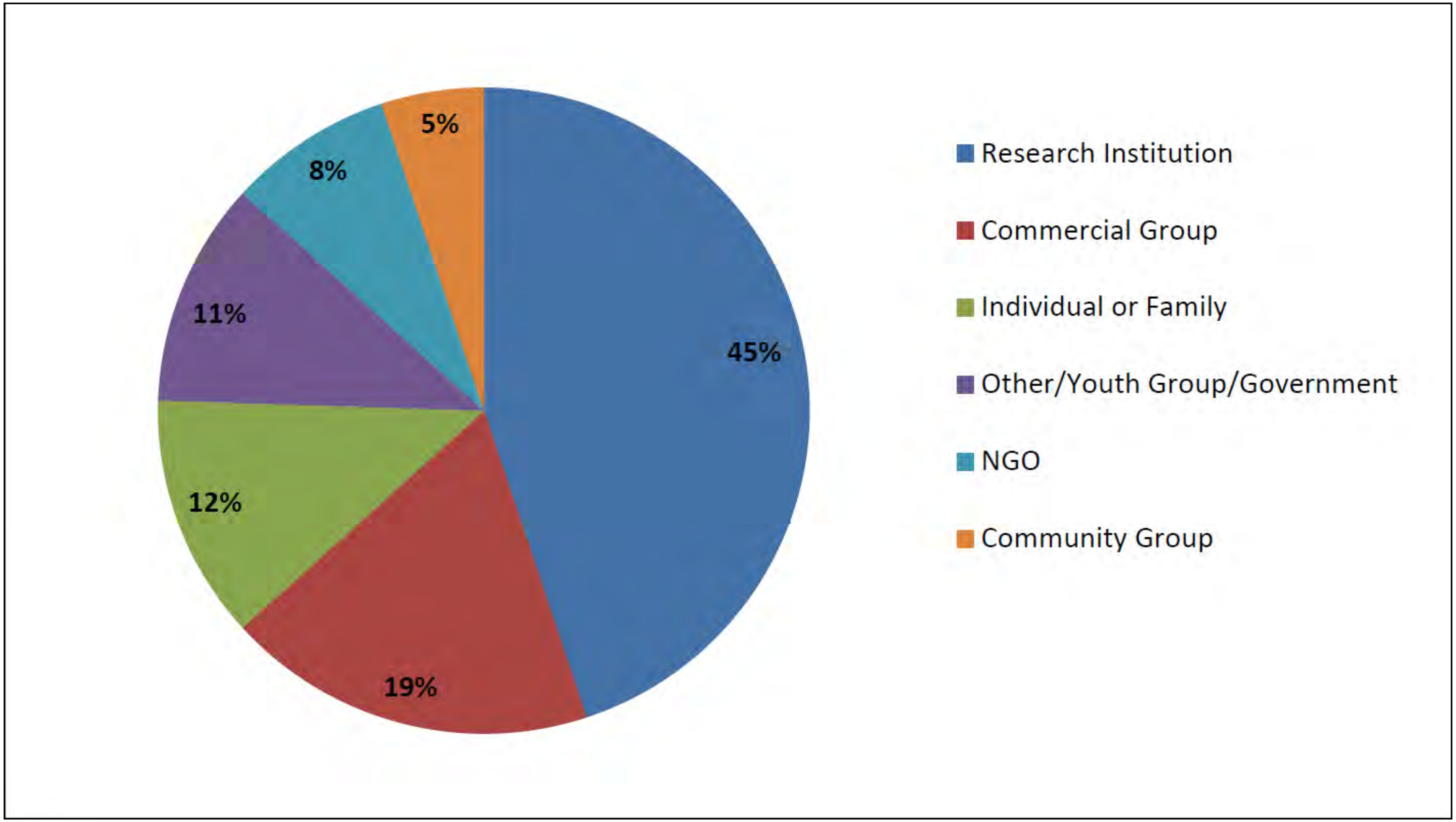
eGenesis CR-2 pyrolysis unit (http://www.egenindustries.com)



Whitfield Bio-char LLC

SLOW PYROLYSIS

Frequency of type of organization leading bio-char projects (IBI survey)



Stefan Jirka, Tomlinson T: 2013 State of the Art of the Bio-char Industry. A survey of Commercial activity in the Bio-char Field. A Report by the International Biochar Initiative (IBI) March 2014

SLOW PYROLYSIS

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 (Technological constrainsts)***

Higher value products from bio-char have to be developed

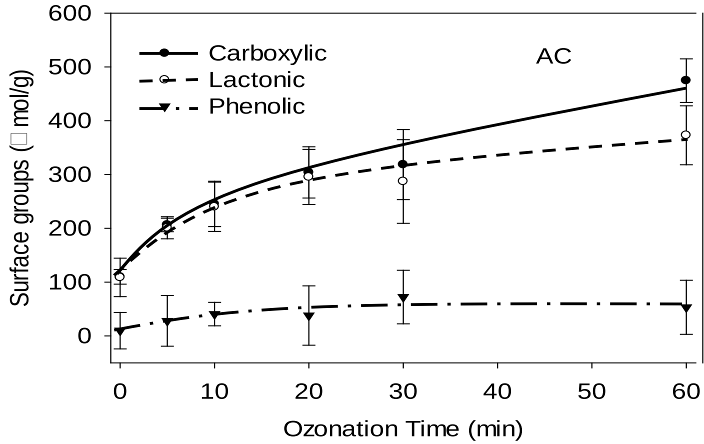
Lack of consumer awareness

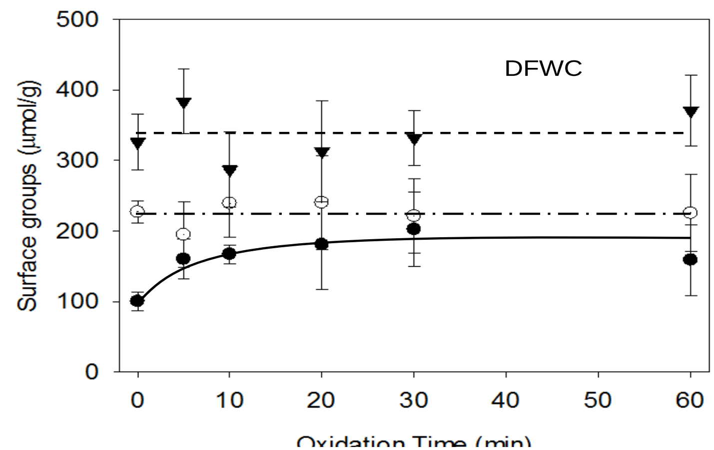
Access to financing

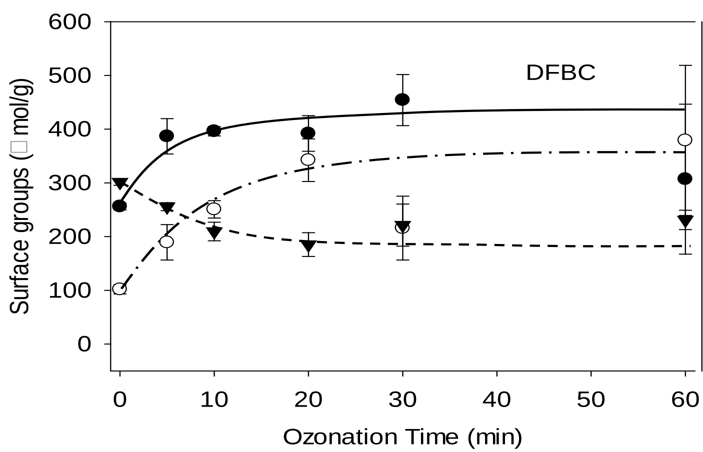
Not possible to predict yield gains (lack of performance certification)

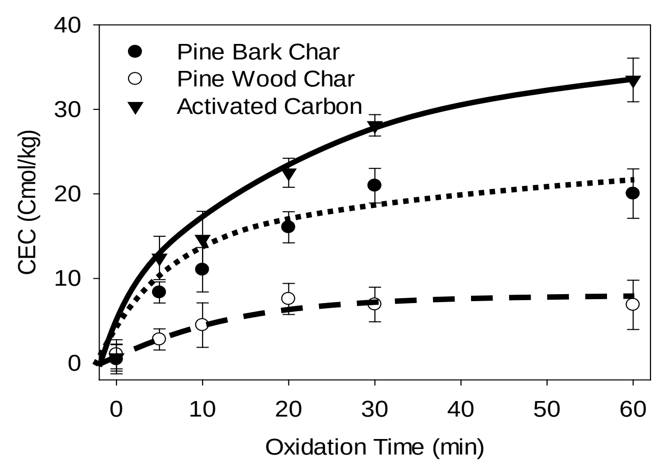
SLOW PYROLYSIS (RESEARCH)

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





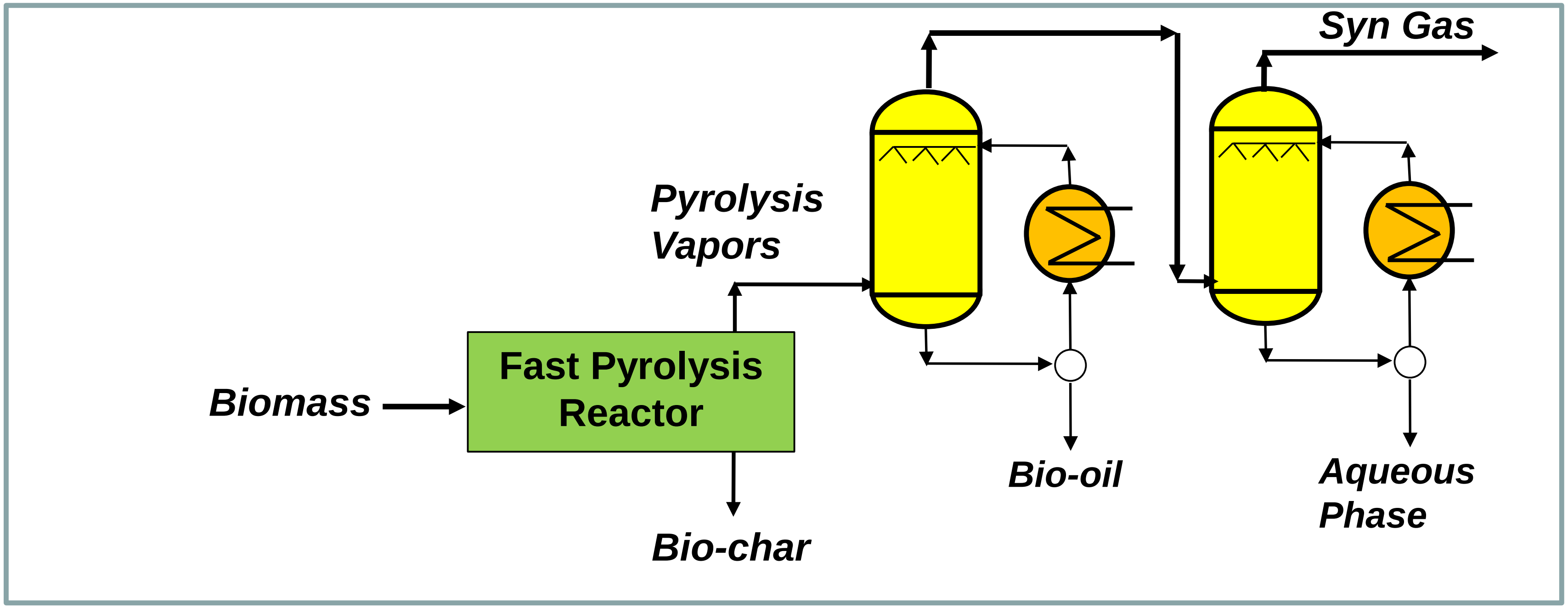




FAST PYROLYSIS

Fast Pyrolysis

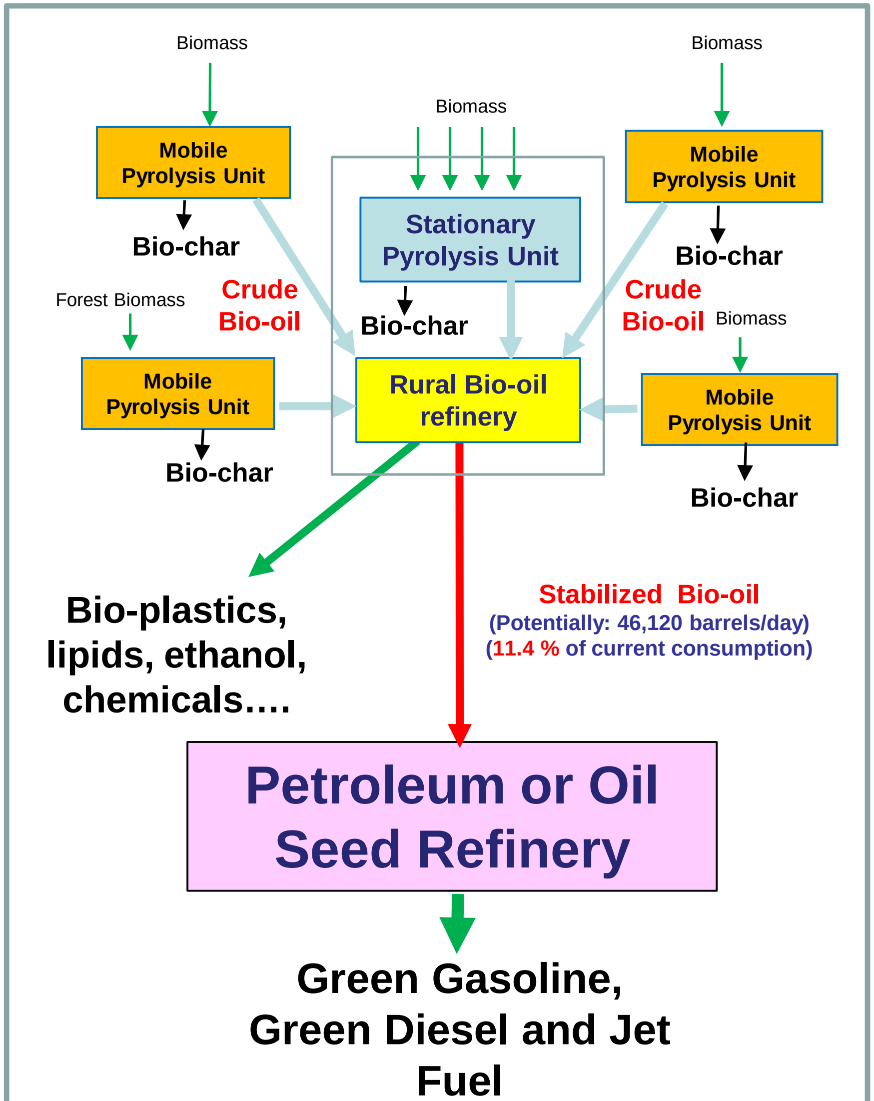
Fast pyrolysis is a process in which very small biomass particles (less than 2 mm diameter) are heated at 450 – 600 °C in the absence of *air/oxygen to* produce high bio-oil yield (60-75 mass%).



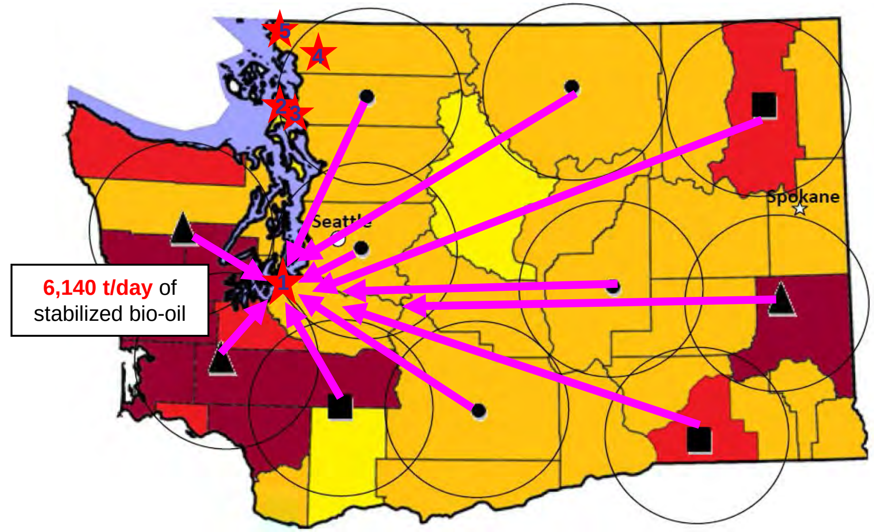
Conditions	Liquid	Char	Gas
High heating rates, small particles, short residence time of vapors	60-75 %	12-20 %	13-20 %

FAST PYROLYSIS

Model of Biomass Economy Based on Pyrolysis and Rural Refineries



Potential Production (11.4 % of Current WA Oil Consumption)



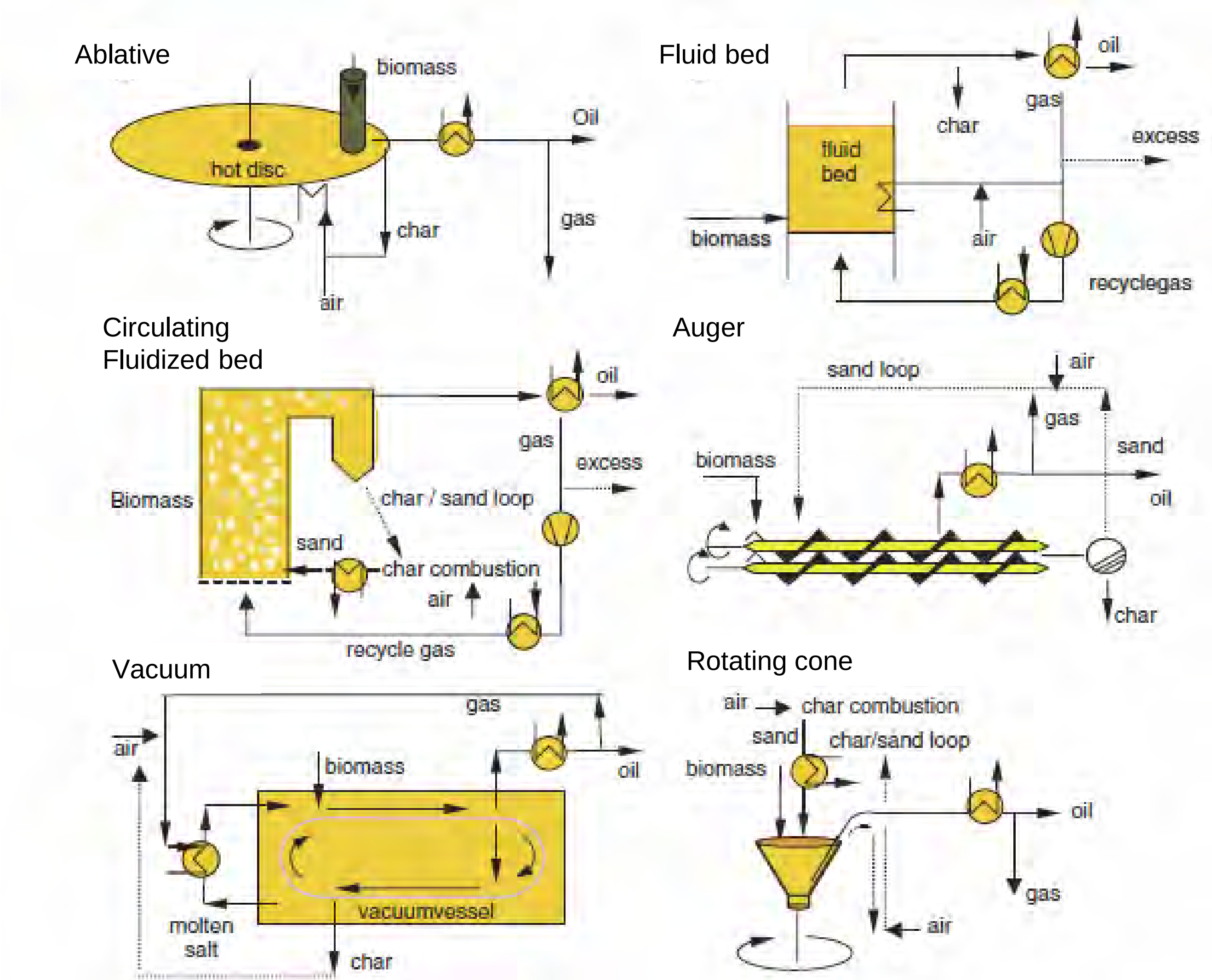
Petroleum Refineries			Rural Bio-oil Refineries
1	Tacoma (Oil US):	4,600 t crude oil/day	● 300 t crude bio-oil/day
2	Anacortes (Tesoro):	14,400 t crude oil/day	■ 1,200 t crude bio-oil/day
3	Anacortes (Shell):	19,000 t crude oil/day	▲ 2,400 t crude bio-oil/day
4	Ferndale (Conoco):	14,000 t crude oil/day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

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

FAST PYROLYSIS

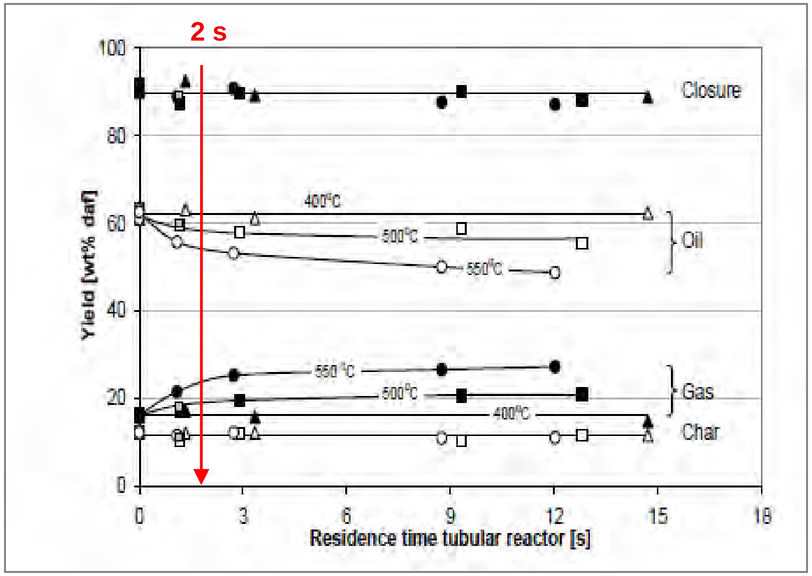
Fast Pyrolysis Reactors

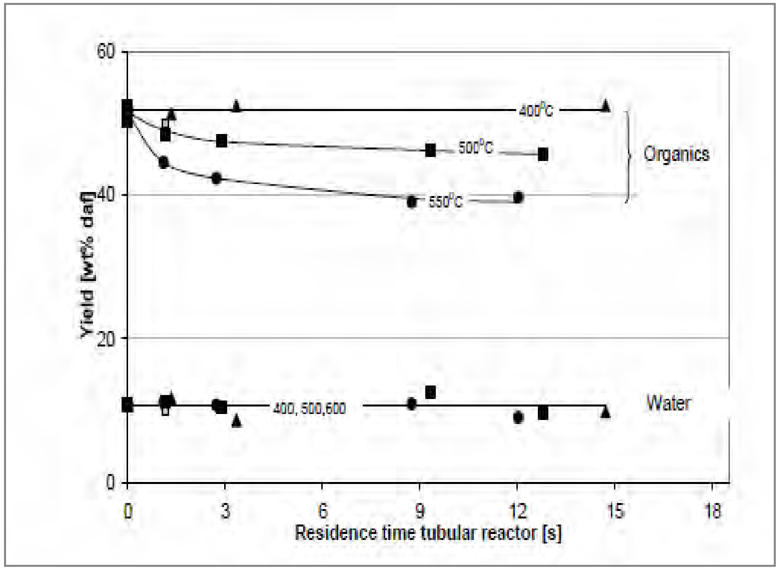
Current technologies **use high volumes of carrier gas** and **sand as heat carriers**. High yields of oil (60-75 wt. %)

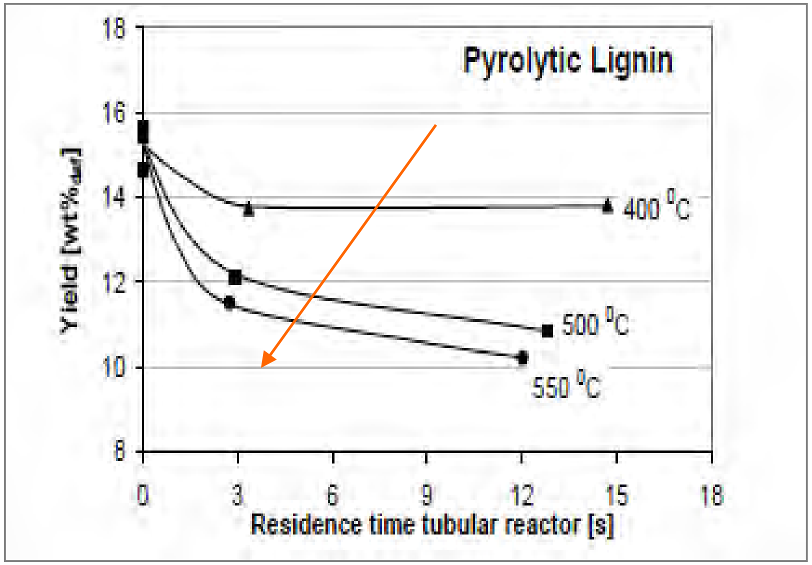
Are the designs that have been scaled up reliable enough or will they be replaced by new ones when bio-oil refineries are deployed?

FAST PYROLYSIS

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



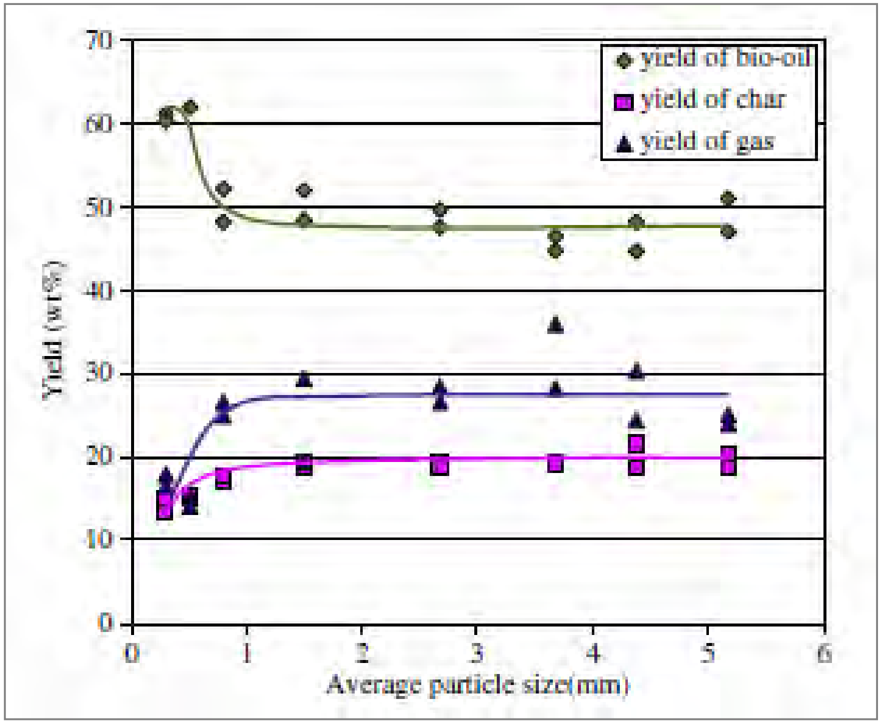


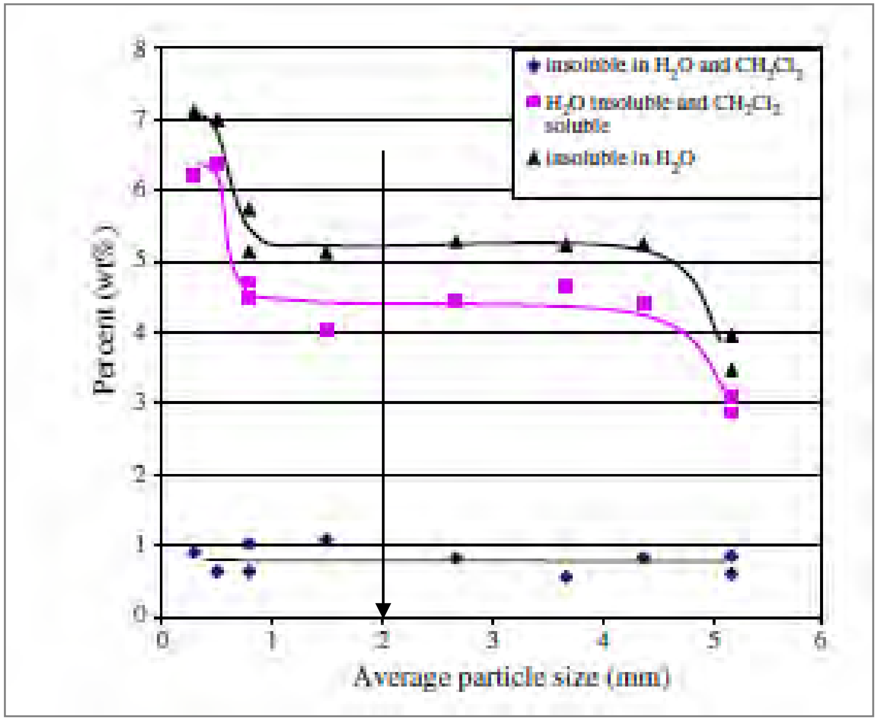


Roel JM Westerhof: Refining Fast Pyrolysis of Biomass. PhD Thesis University of Twente 2011

FAST PYROLYSIS

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

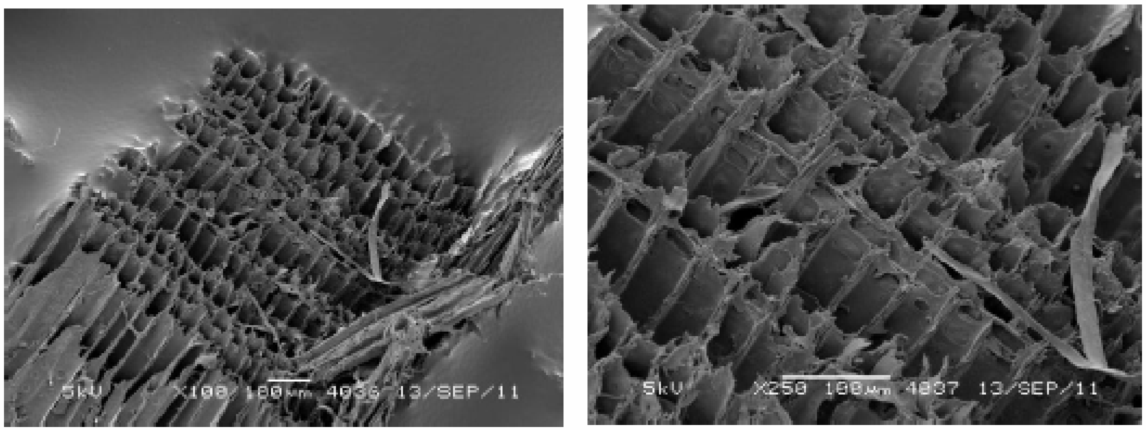




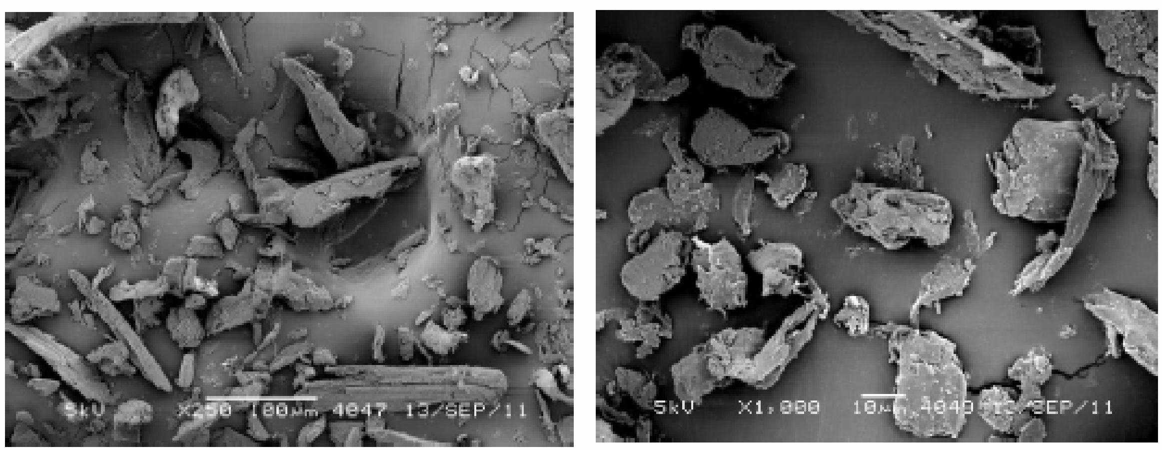
Shen J, Wang X-S, Garcia-Perez M, Mourant D, Rhodes MJ, Li C-Z: Effects of particle size on the fast pyrolysis of oil malee woody biomass. Fuel 88 (2009) 1810-1817

FAST PYROLYSIS

EFFECT OF PARTICLE SIZE (University of Twente)



SEM Pictures of 1 mm beech wood particles

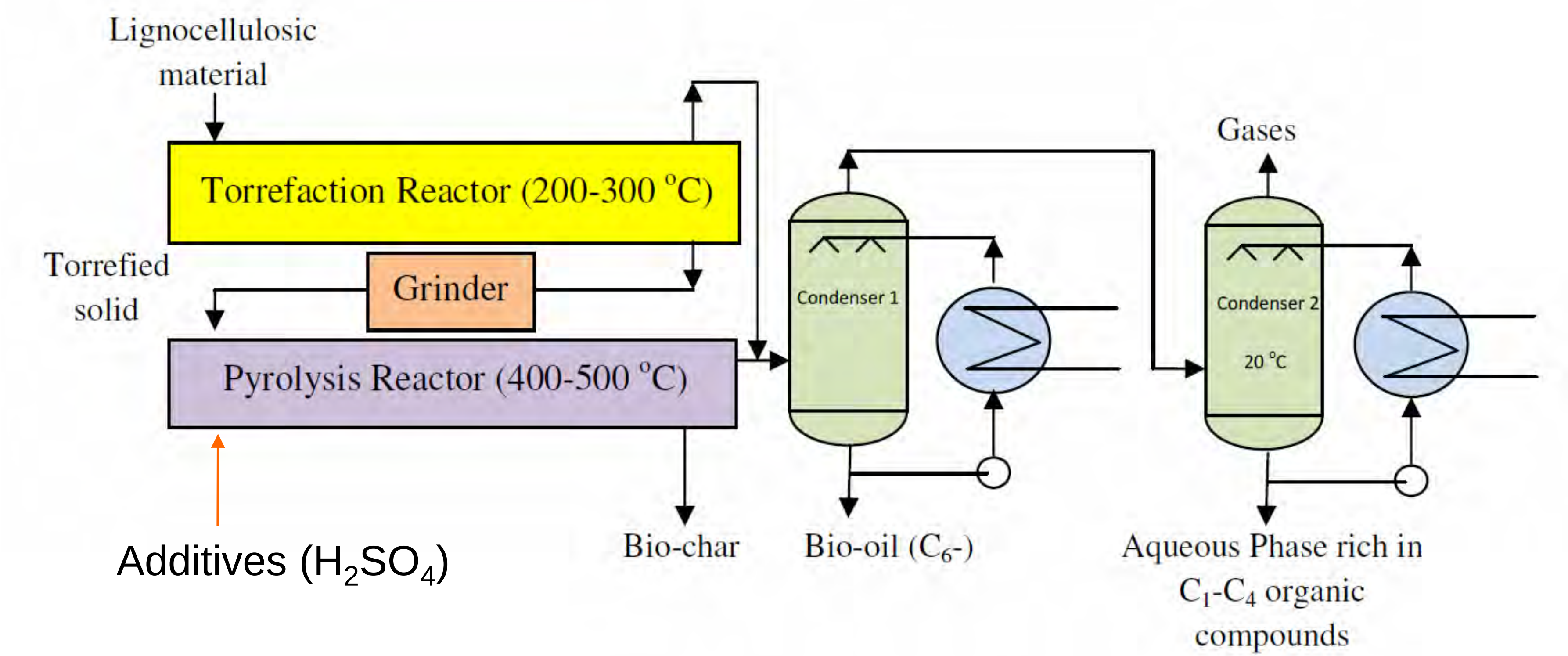


SEM Pictures of beech wood particles smaller than 80 micron

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

FAST PYROLYSIS

Novel Concepts for Pyrolysis Units studied at WSU

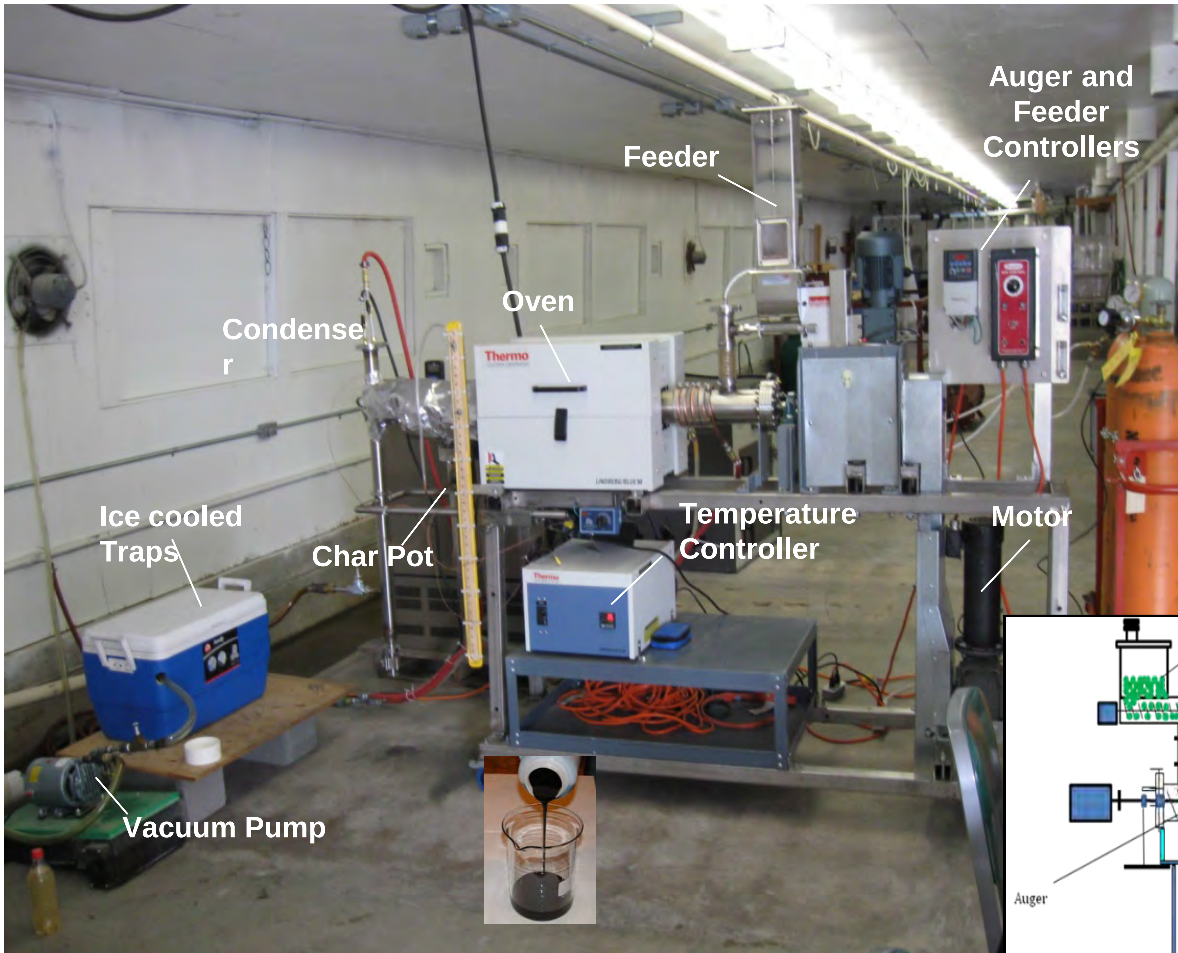


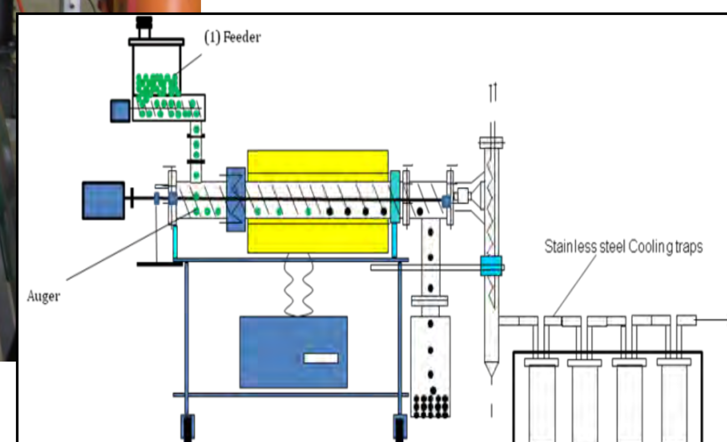
(1) Use of Intermediate Pyrolysis reactors without sand
(2) Two Step Pyrolysis to reduce grinding energy
(3) Two Step Condensation Systems to Separate C1-C4 molecules and water from bio-oil

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

FAST PYROLYSIS

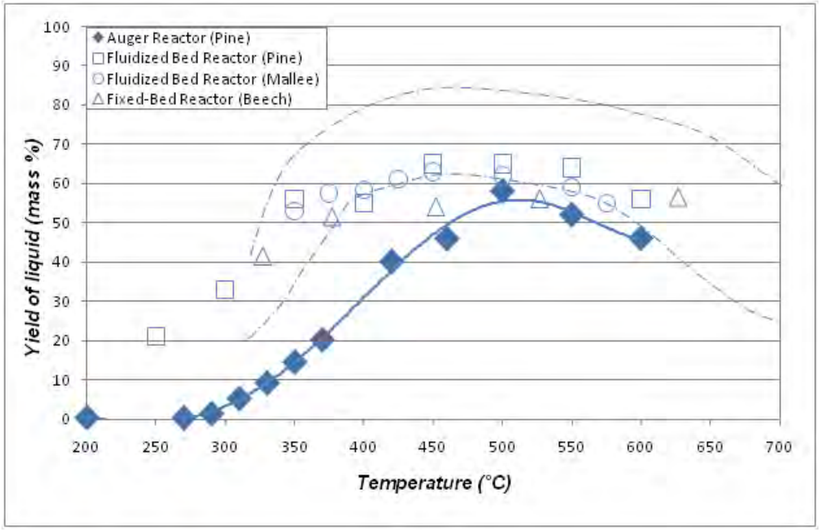
Performance of Auger Pyrolysis Reactor

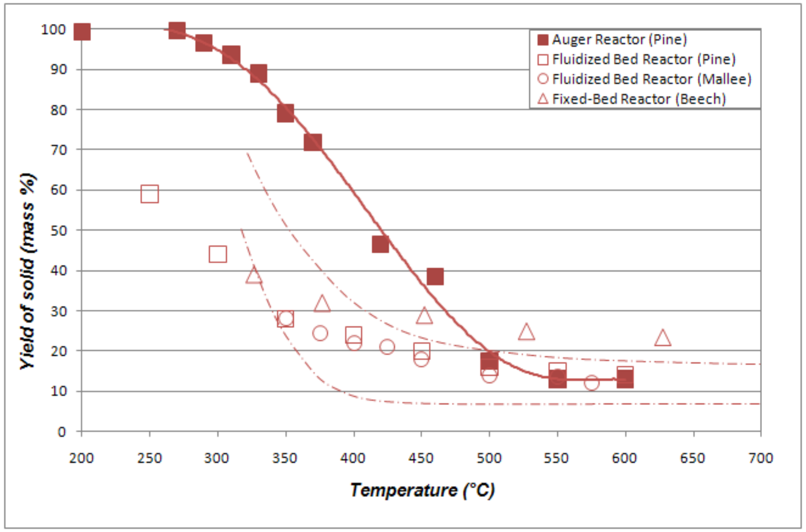


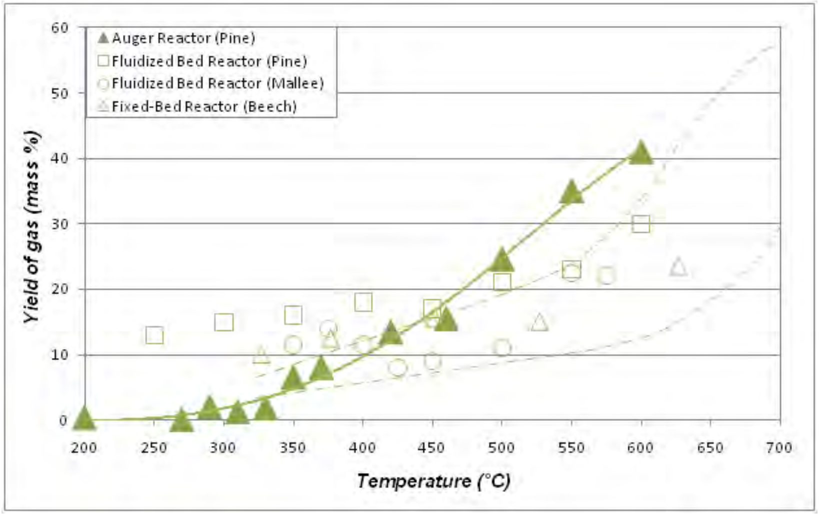


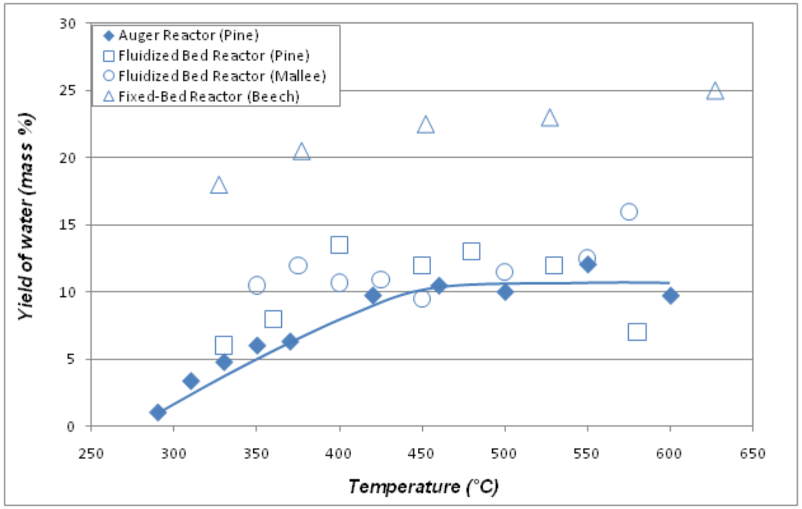
FAST PYROLYSIS

Effect of Pyrolysis Temperature



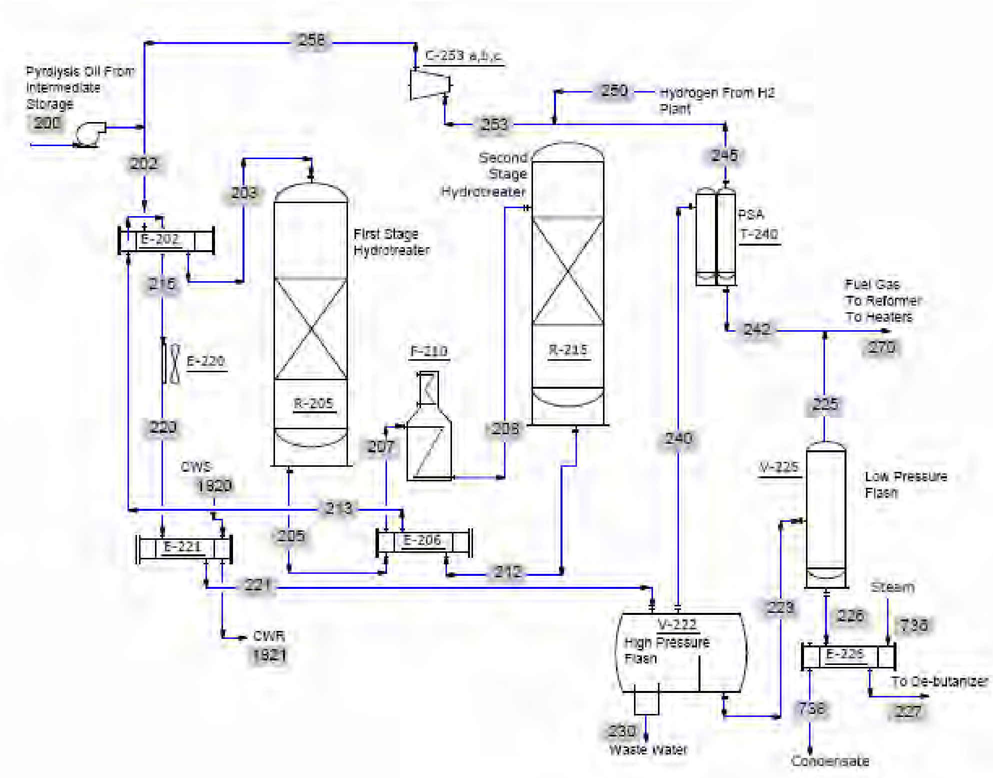






FAST PYROLYSIS

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

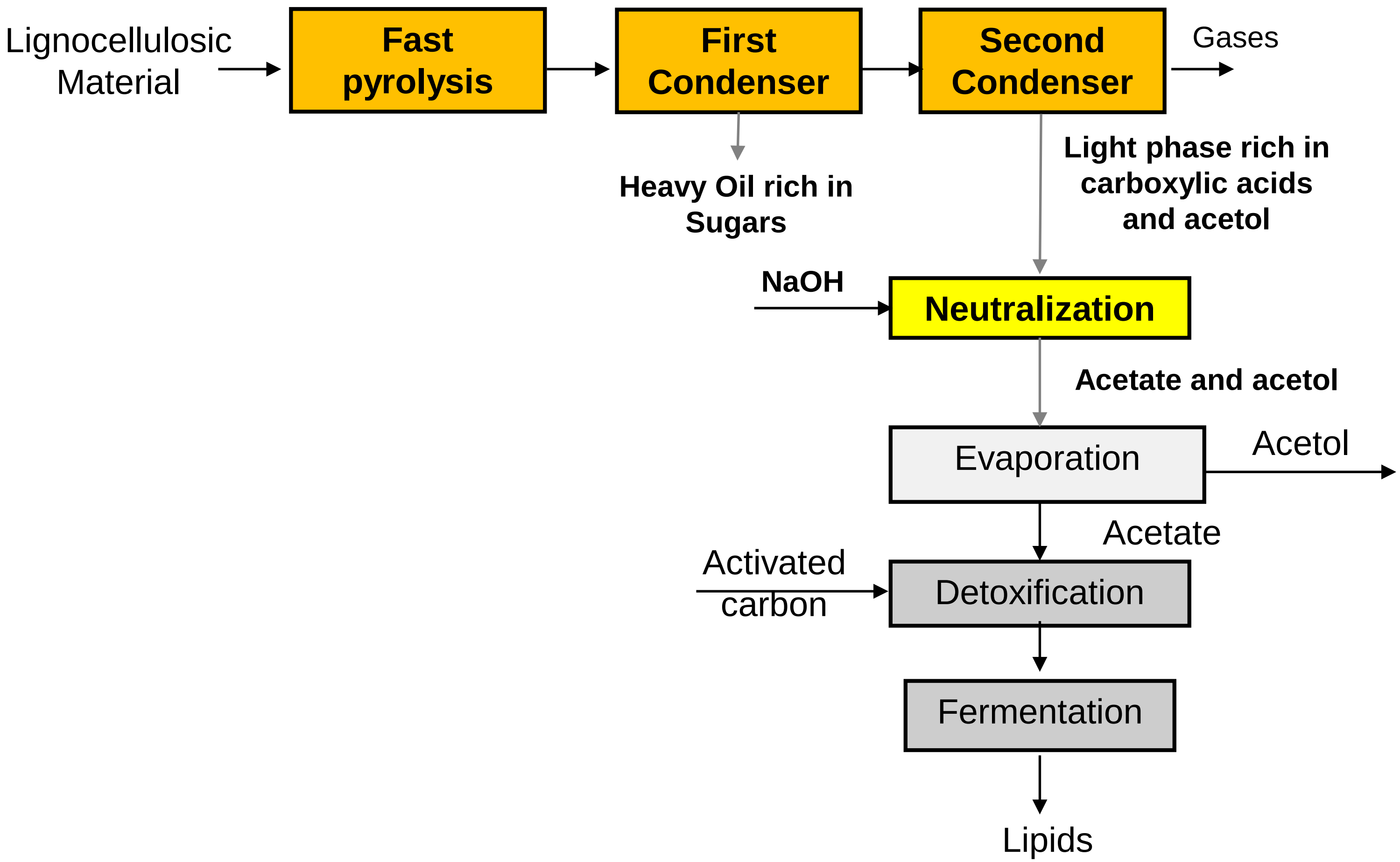
FAST PYROLYSIS

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

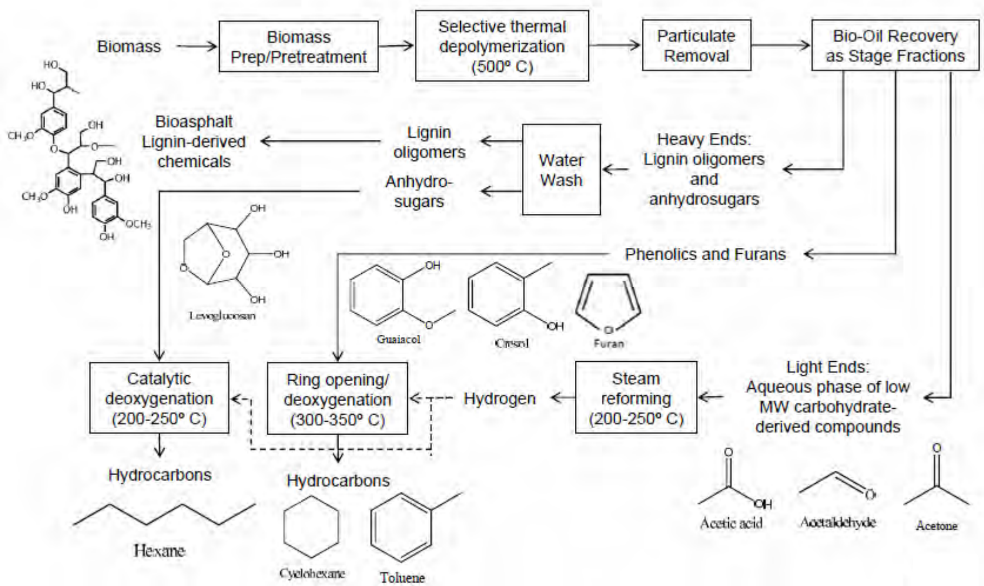
FAST PYROLYSIS

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

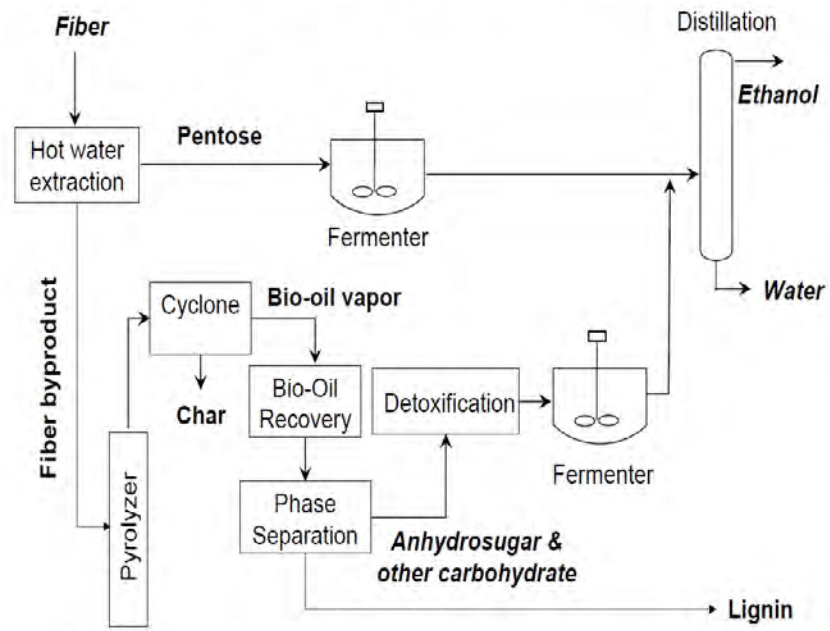


FAST PYROLYSIS

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

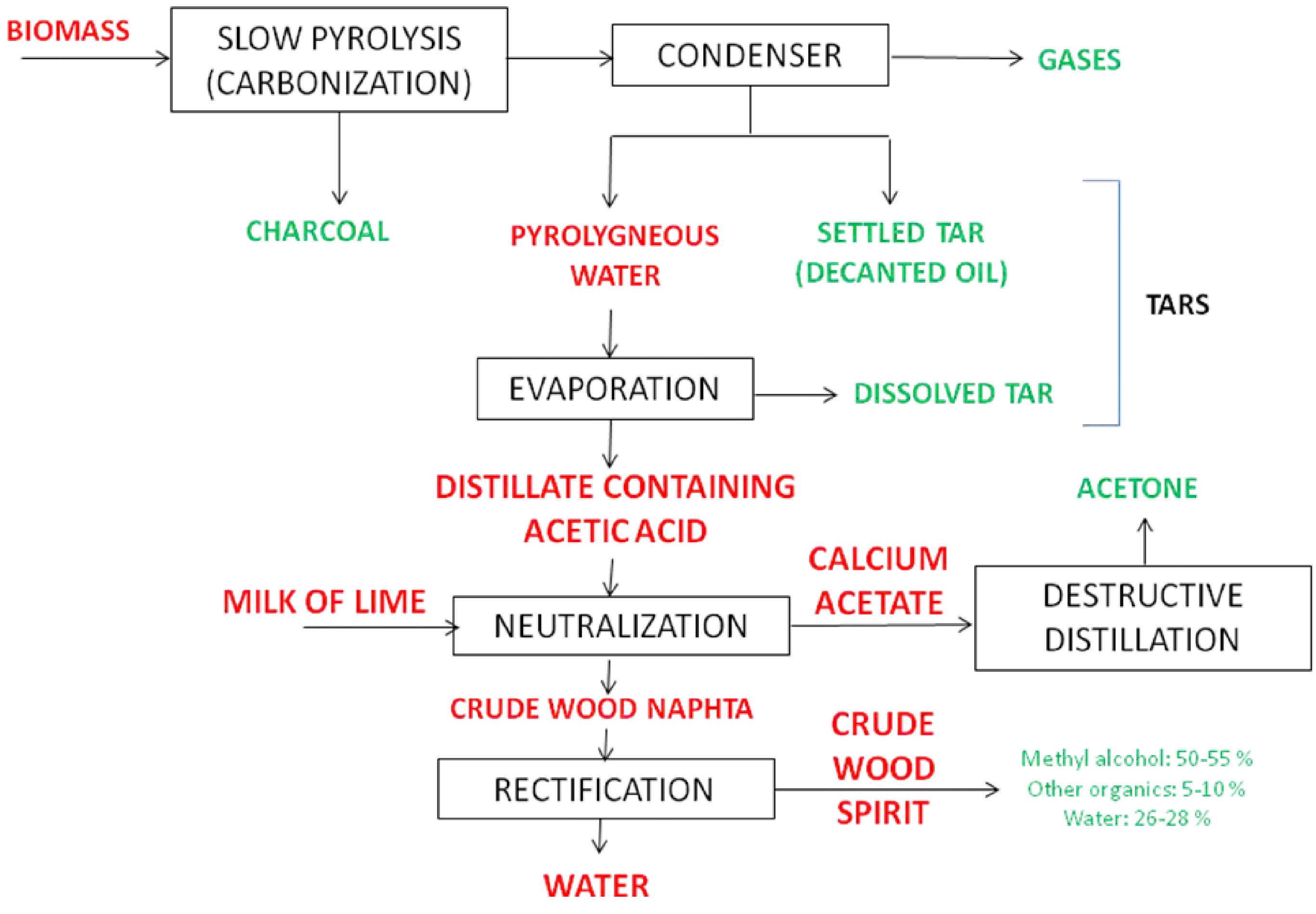


Hybrid Refining Technologies



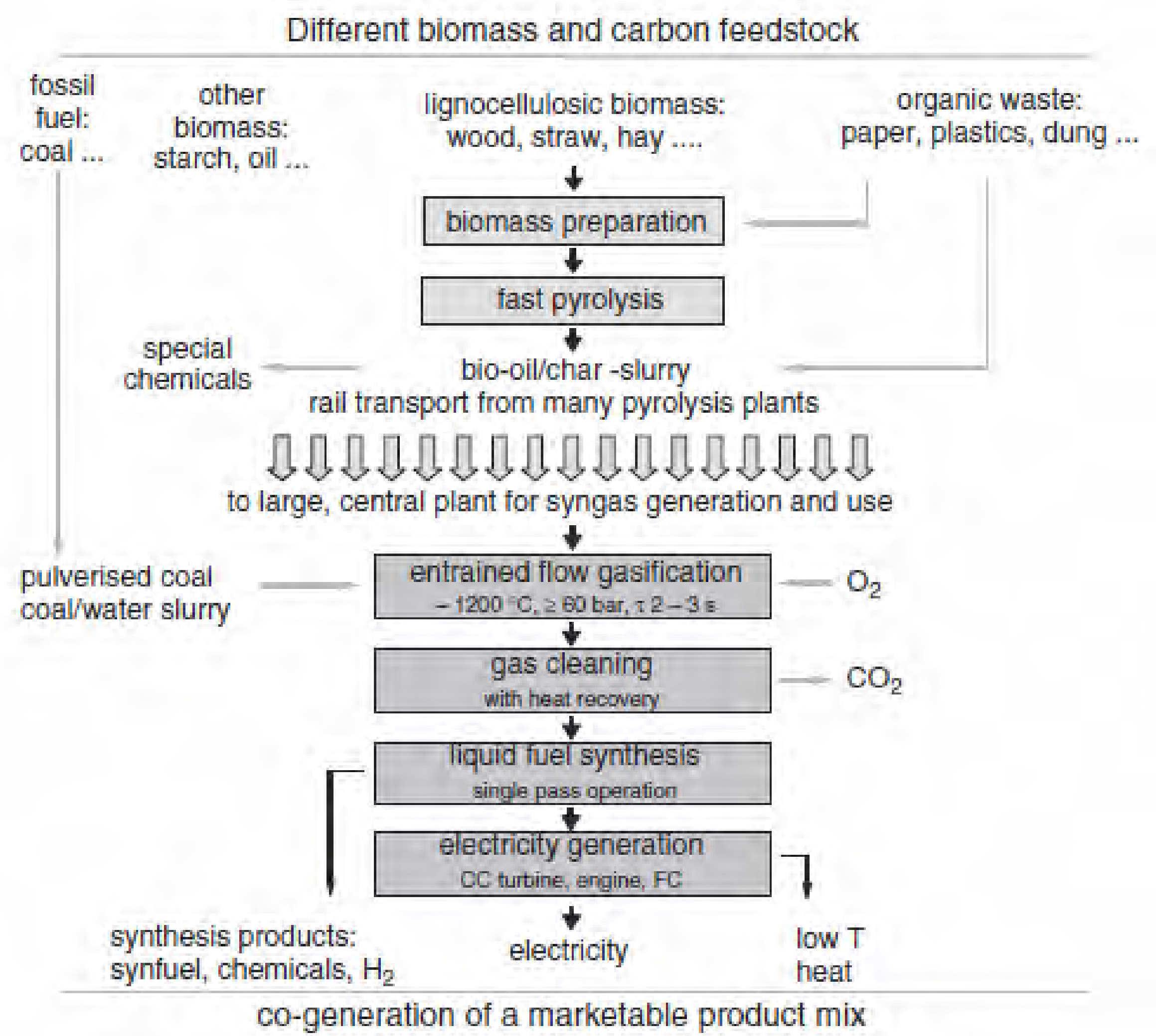
FAST PYROLYSIS

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



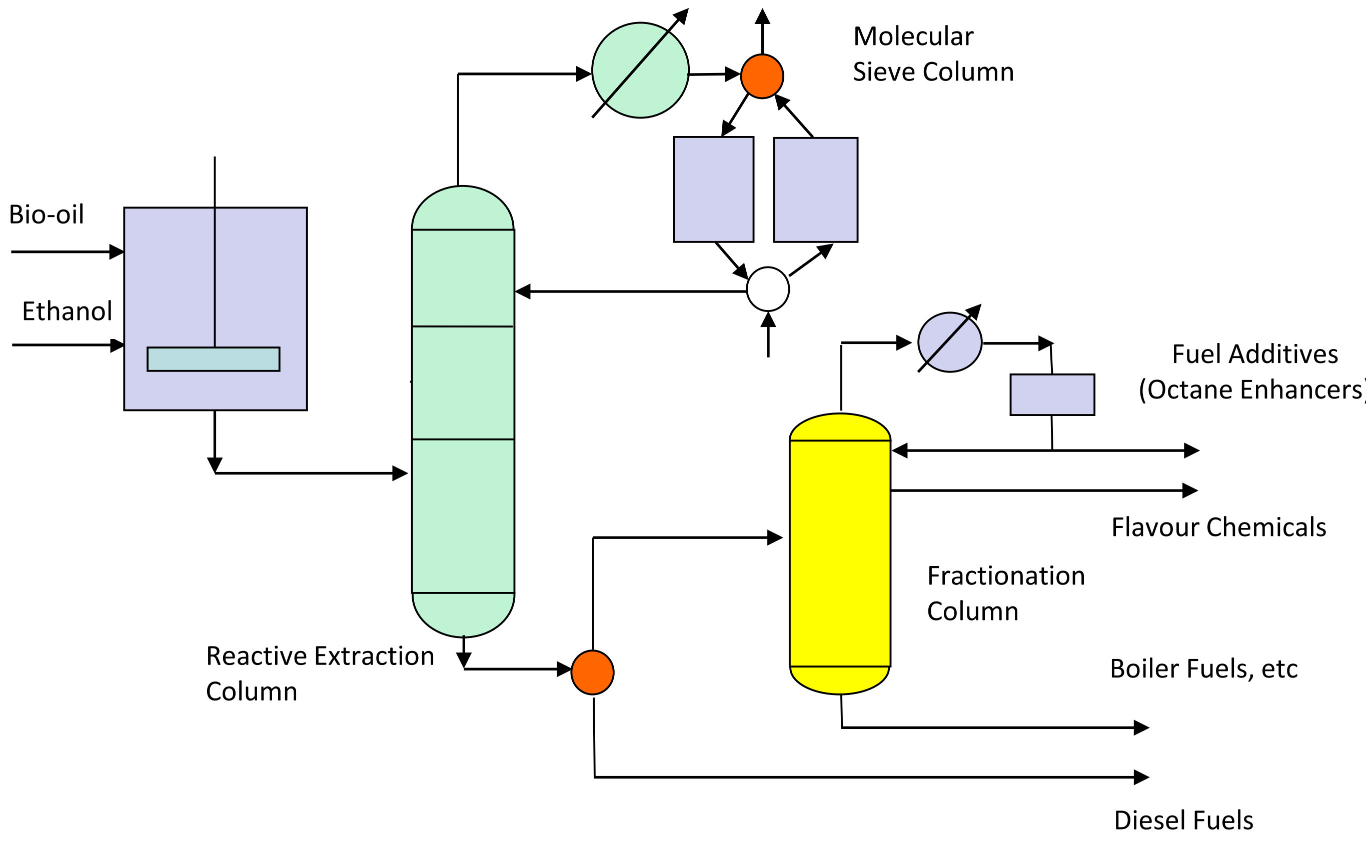
FAST PYROLYSIS

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



FAST PYROLYSIS

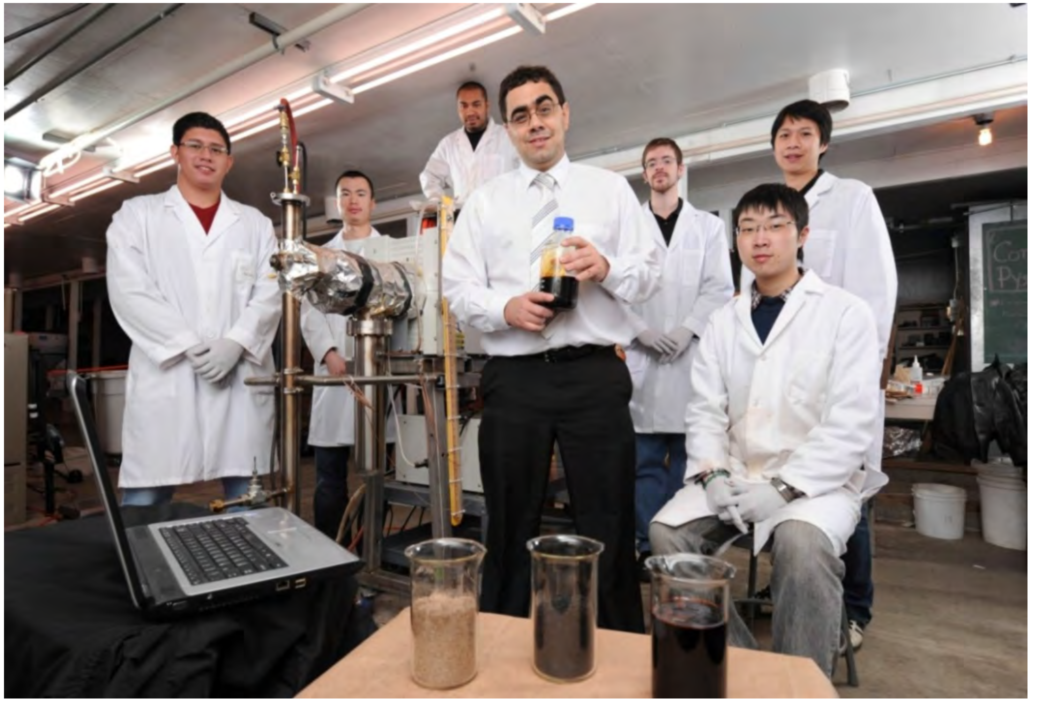
Bio-refinery Concept based on Bio-oil Esterification (Radlein 2005). This concept is being studied by the group of Professor Chun-Zhu Li at Curtin University (Australia).



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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WASHINGTON STATE UNIVERSITY AGRICULTURAL RESEARCH CENTER

WASHINGTON STATE DEPARTMENT OF ECOLOGY

WASHINGTON STATE DEPARTMENT OF AGRICULTURE

SUN GRANT INITIATIVE, U.S. DEPARTMENT OF TRANSPORTATION, USDA

U.S. NATIONAL SCIENCE FOUNDATION

U.S. DEPARTMENT OF ENERGY

QUESTIONS ?