Liquid Fuel Production by Fast Pyrolysis of Biomass

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Publication date:
2013

Citation (APA):
Jensen, P. A. (2013). Liquid Fuel Production by Fast Pyrolysis of Biomass. Sound/Visual production (digital)
http://www.natlab.dtu.dk/Energikonferencer/DTU_International_Energy_Conference_2013

Liquid Fuel Production by Fast Pyrolysis of Biomass

September 2013. DTU International Energy Conference

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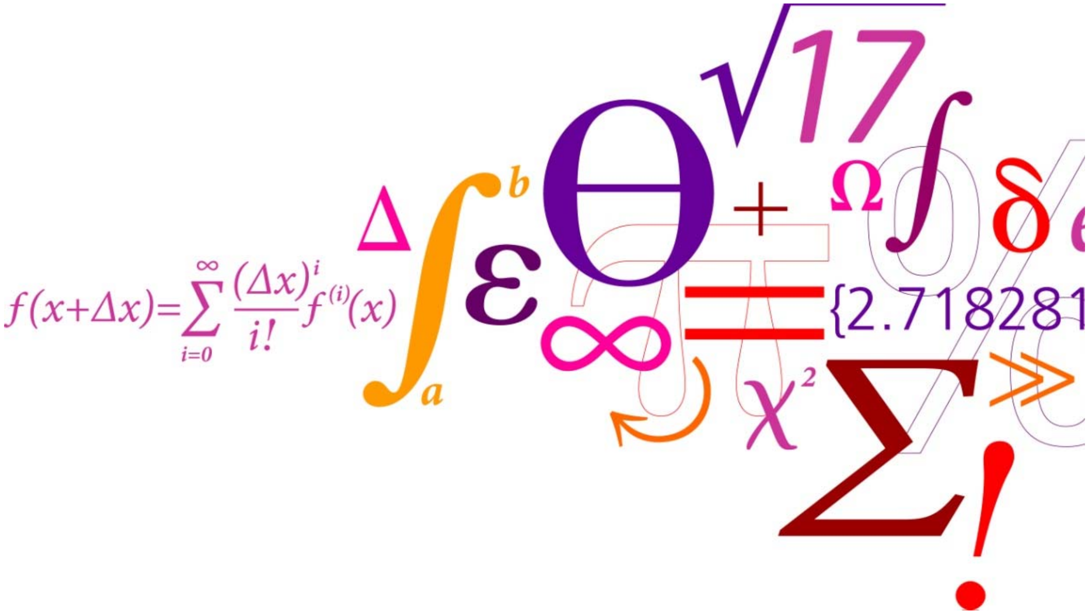
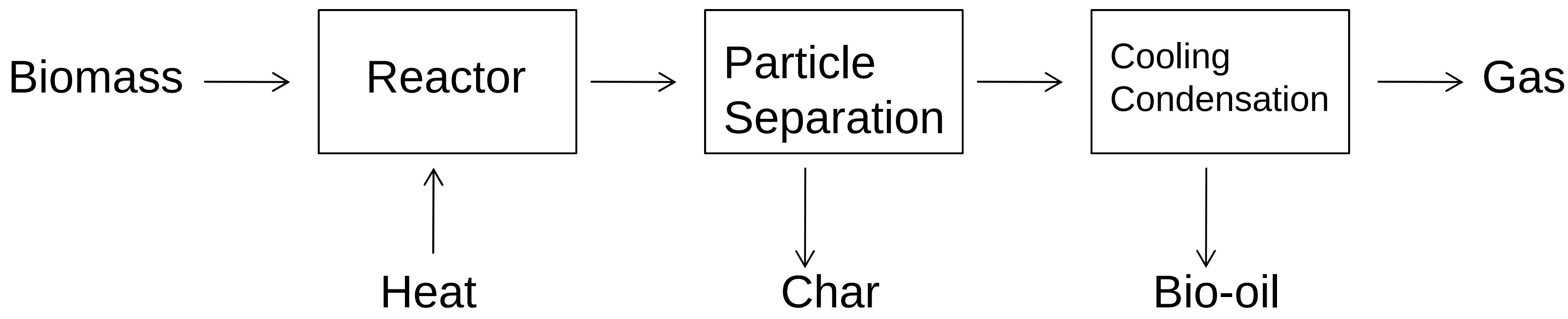
DTU, Chemical Engineering, CHEC



Flash pyrolysis process



Fast inert heating of biomass to produce a liquid product (bio-oil)
Also gas, water, and char is produced

<u>Typically operation values</u>

Heating rates:	> 300 k/s
Gas residence time:	< 2 s
Maximum temperatures:	450 – 600ºC
Feedstock types:	Wood, Straw …

Flash pyrolysis product – Typical bio oil properties

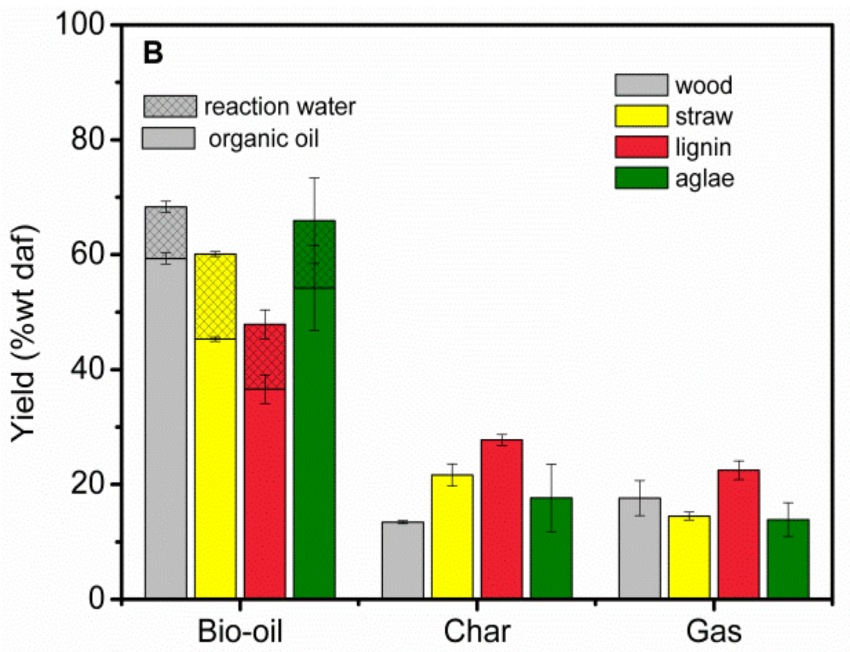
Bio-oil: Liquid organics plus water –(immiscible with fossil oil)

	Bio-oil	Heavy fuel oil
Water content:	15-30 wt%	0.1 wt%
(On dry basis)		
Heating value:	16-19 Mj/kg	42-44 Mj/kg
C content:	55-65 wt%	83-86 wt%
O content:	28-40 wt%	<1 wt%
H content:	5-7 wt%	11-14 wt%
Density:	1.2 kg/l	0.86 kg/l
Viscosity:	25 – 1000 cp	
PH	2 – 4	
Ash:	0,1-1 %wt	
Species:	- Oxygenated compounds 18 to 10,000 g/mol Acids, Alcohols, Sugars, Aldehydes, ketones, lignin residuals - Can be unstable when stored	

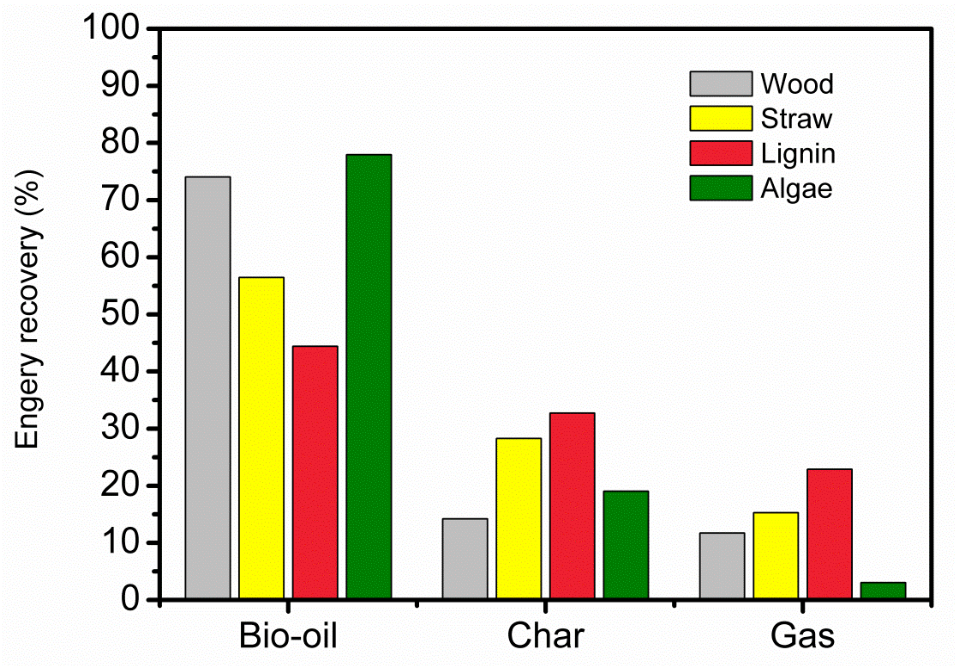
Reference: Venderbosch 2009, Review

Fast Pyrolysis bio-oil yields of different biomasses

Yields based on dry ash free basis



Energy Distribution



From reference: PhD work by Trung Ngoc Trinh, 2012.

Production of biomass based liquid fuels – comparison of different technologies

The production capacity (transportation fuel) per land area of different Bio-based technologies for liquid transportation fuels

	Land utilization [MJ/(m^2 y)]
Fischer-Tropsch	20.9-25.5
Second generation ethanol	18-25.2
HDO (H_2 from biomass)	30.1-35.0
HDO (H_2 from solar energy)	49.8

Reference. System study by: N. R. Singh, W. N. Delgass, F. H. Ribeiro, P. K. Agrawal, Environ. Sci. Technol. 44 (2010) 5298-5305.

<u>Fast pyrolysis bio-oils:</u>

Limitations: Relatively low quality oil

Advantages: high energy yield, simple technology

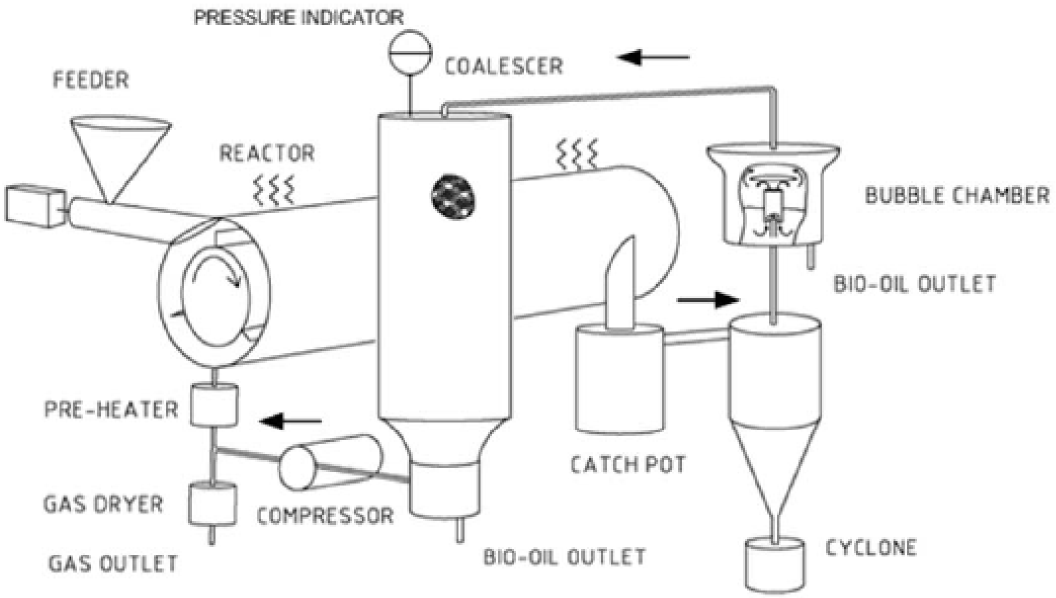
The use of fast pyrolysis bio-oil

Use as fuel in:	Limitations	Oil improvements
• Boilers	Stability, viscosity	Not needed Few boiler plant modifications
• Gas turbines	bio-oil ash	Filtering sufficient?
• Diesel engines (heavy)	Ignition delay, acidity	Emulsifications with biodiesel of fossil oil
• Diesel engines(light)	High viscosity, acidity, inhomogeneous, slow combustion.	Hydrodeoxygination (+ distillation)
• As a feed for oil refinery	Immiscible with fossil oil char formation when heated	Hydrodeoxygination

Fast pyrolysis process equipments – Ablative pyrolysis

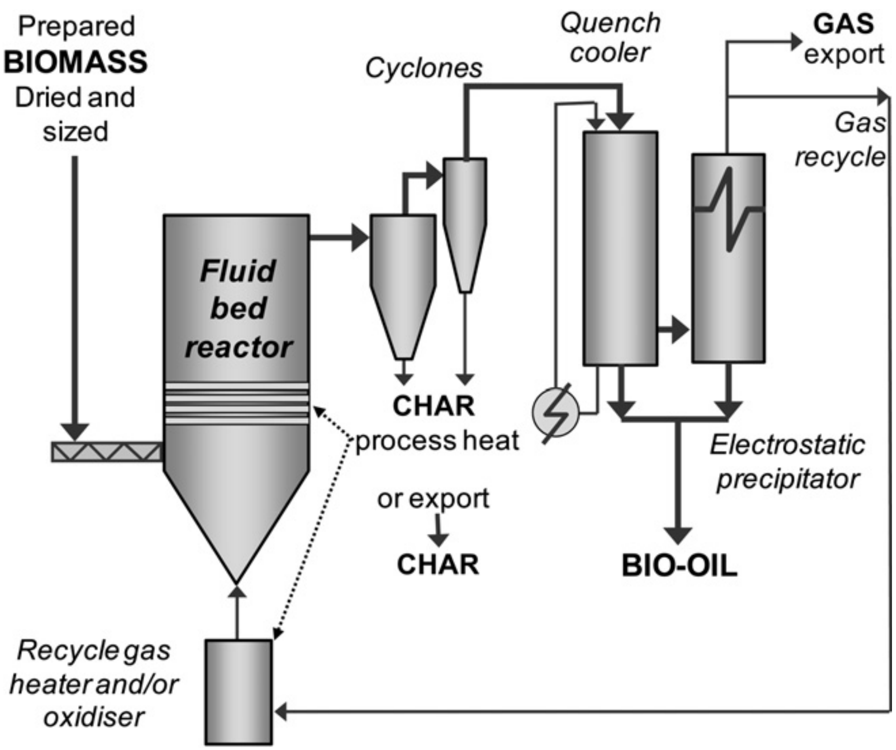
Pyrolysis of pine particle at high heating rate

DTU Pyrolysis Centrifuge Reactor PCR



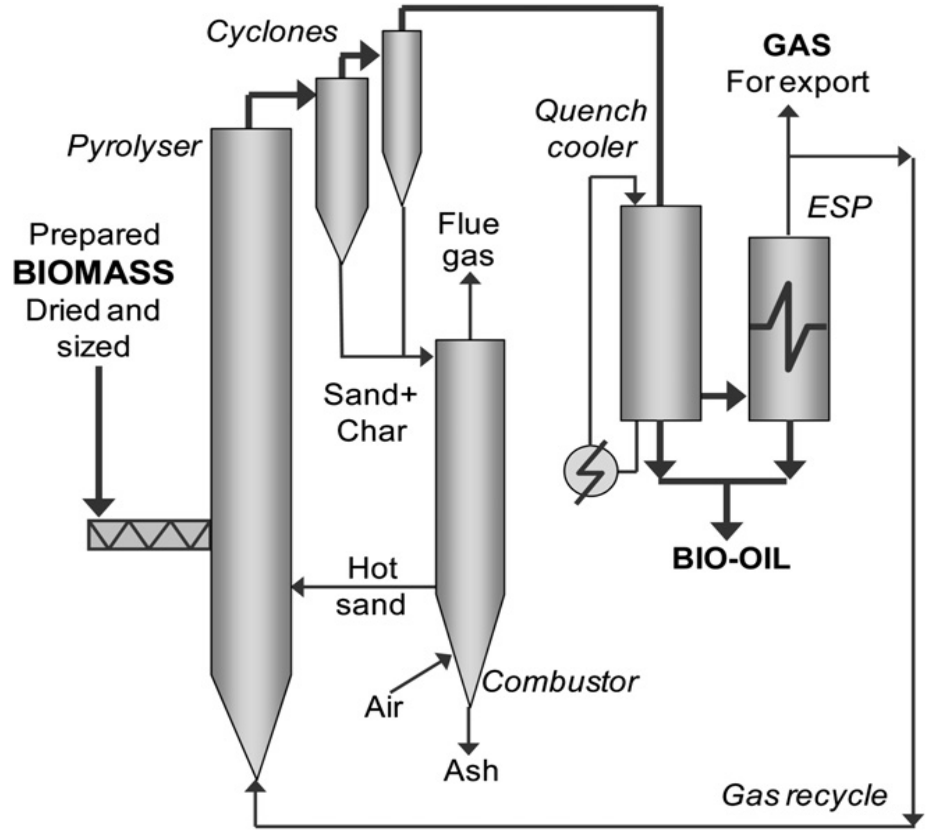
Fast pyrolysis process equipments – Fluid bed systems

Bubbling fluid bed reactor



Dynamotive type

Circulating fluid bed reactor

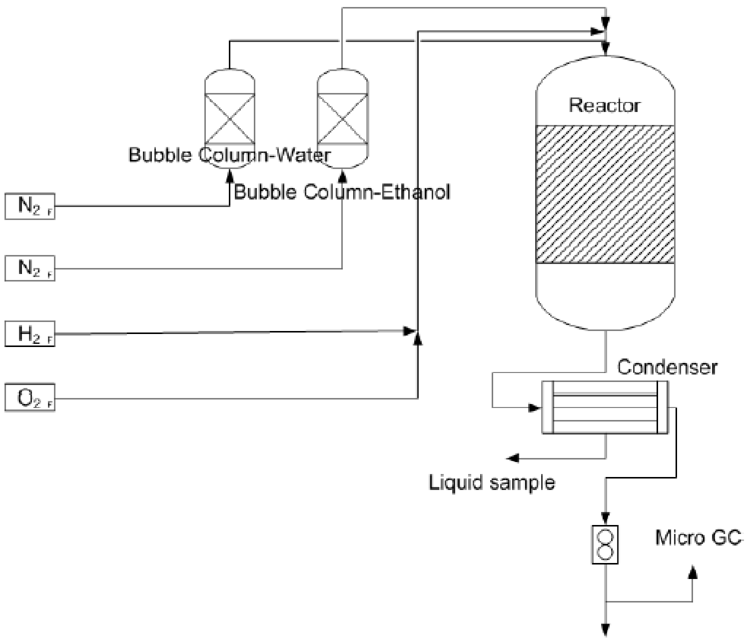


Ensyn type

From reference: Bridgewater A.V. Biomass and Bioenergy. **2012**.

Ongoing fast pyrolysis related research at DTU, Chemical Engineering

- Study on pyrolysis of different feedstock's on PCR and oil properties
- Studies on catalytic pyrolysis
- Up scaling of PCR



Study on catalysts for Steam reforming of pyrolysis oil

Study on catalysts for hydrodeoxygenation of pyrolysis oil – High pressure flow reactor, up to 125 bar and 550ºC

Global status of pilot/commercial biomass pyrolysis plants

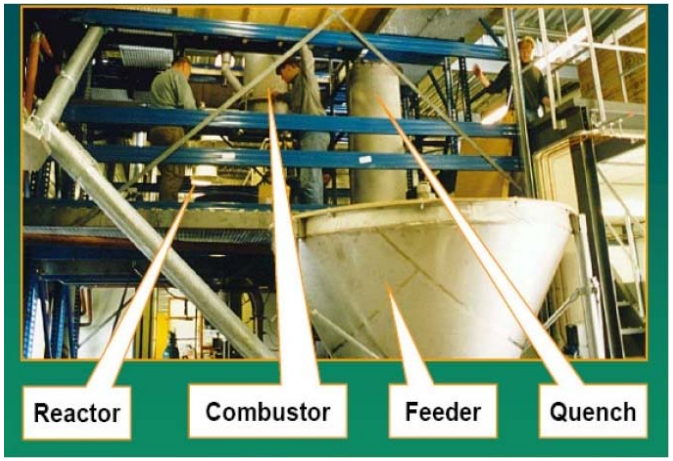
Some operating larger pyrolysis plants

Company	Technol	Developments
Dynamotive	BFB	Several plants, largest is 200tpd at west Lorne (CAN)
Ensyn	CFB	Several plants, largest is 100tpd plant in Renfrew (CAn); Construction of 9 plants in Malaysia by 2015 announced
BTG	RCR	120 tpd plant in Hengolo (NL) production of bio-oil, electricity, organic acids
B-O H N.V.	RCR	Largest plant is 12 tpd. Construction of two 5 tpd plants underway in NL and BEL
Biomass Eng.	BFB	4.8 tpd facility (UK)
KIT/Lurgi	Auger	12 tpd pilot plant in Karlsruhe (GER)

Circulating Fluidized Bed

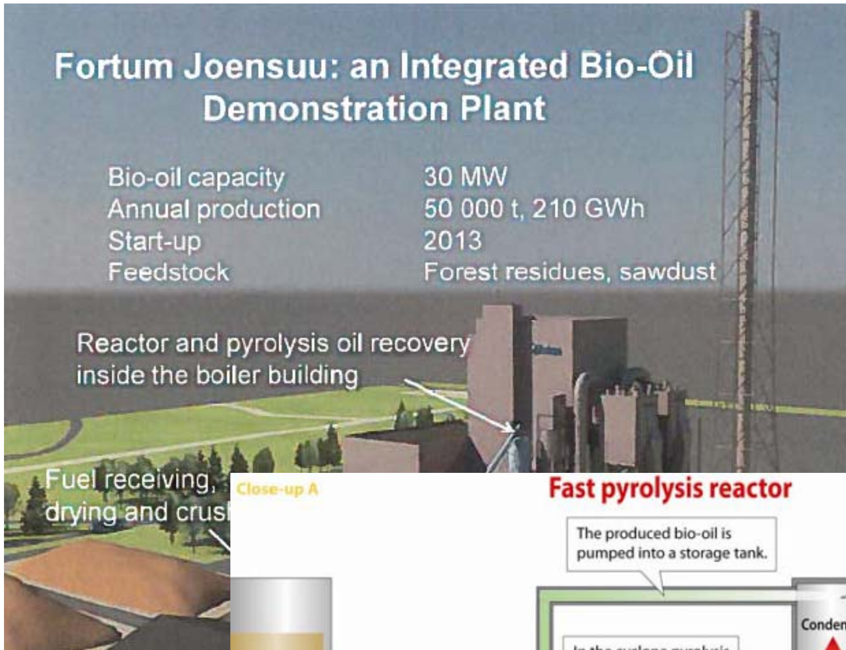
Ensyn(Canada):

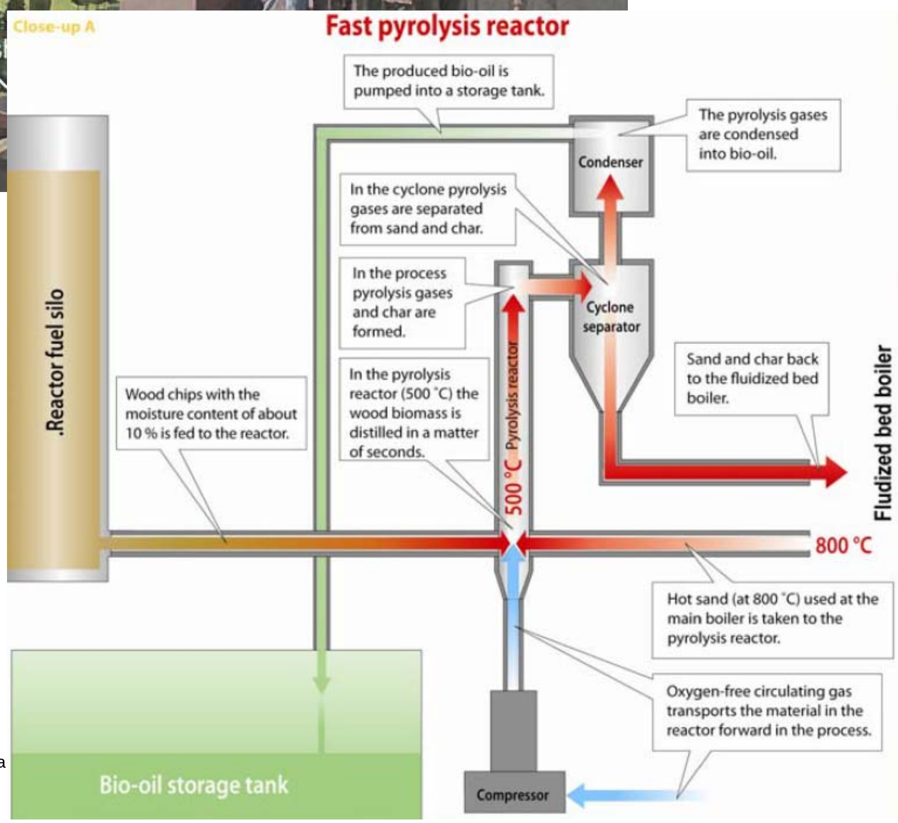
Rotating cone



BTG (NL)

Commercial biomass pyrolysis plants – Joensuu Finland

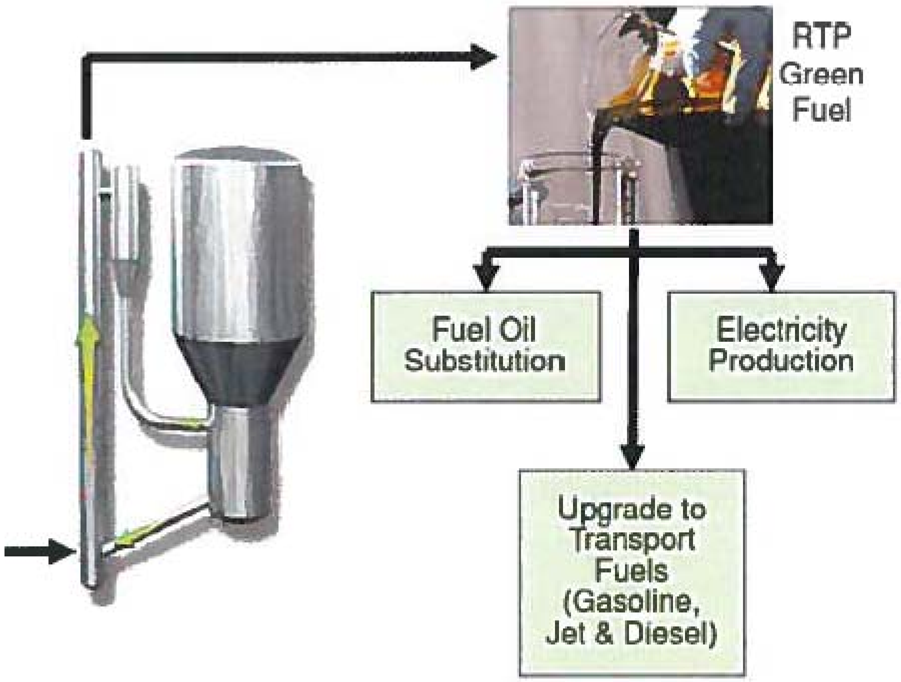




Company: FORTUM(FI)

- 170 t wood pd
- Two integrated fluid beds, combustion and pyrolysis,
- Reduce heavy fuel oil consumption
- First integrated plant with heat and electricity
- Start 2013
- Pyrolyser integrated fluid bed

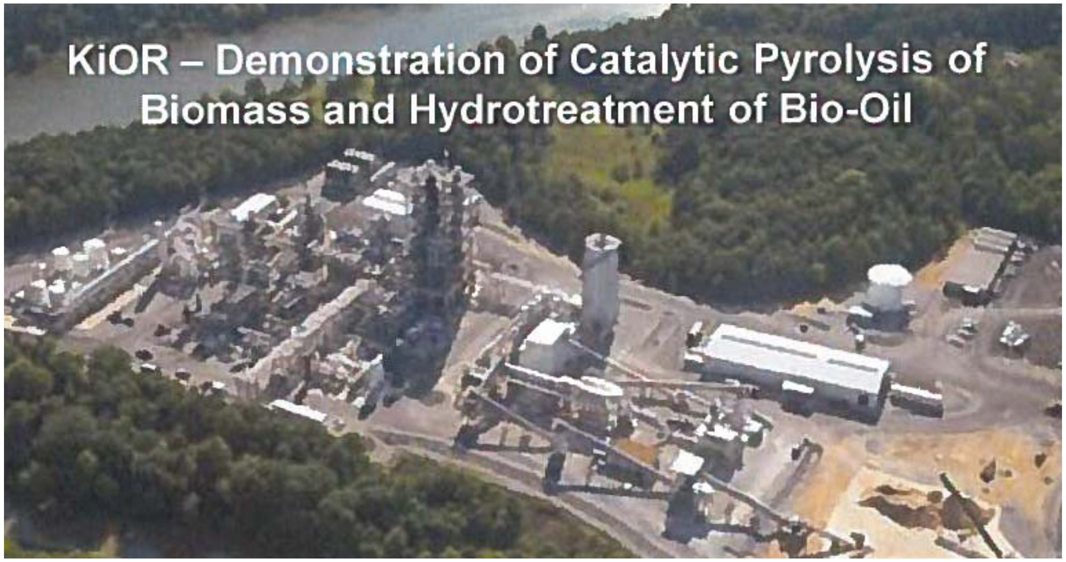
Commercial biomass pyrolysis plants – Evergent – Kapolei - Hawaii



Company: Envergent = Honeywell UOP + Ensyn Corp.

- pilot - 1 t biomass pd
- Integrated Pyrolysis and Catalytic Hydroconversion
- To produce transportation fuels
- Operations starts 2014
- Pyrolyser – Ensyn
- Financed by: US department of energy

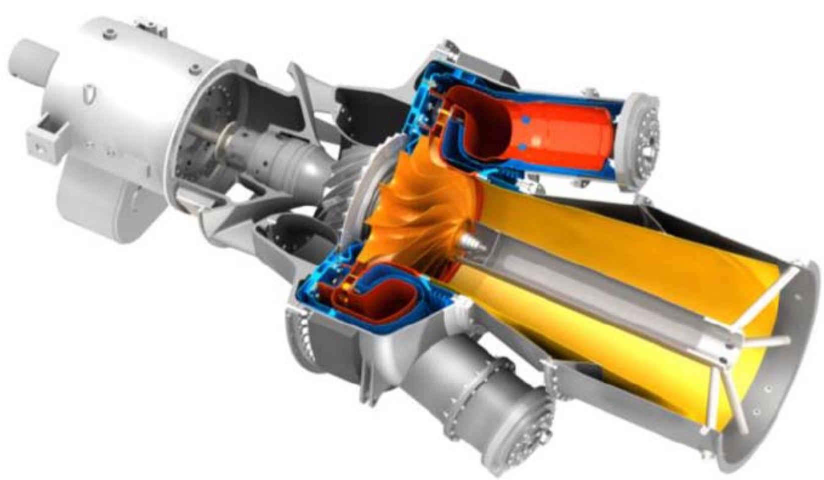
Commercial biomass pyrolysis plants – KiOR – Columbus US



Company: KiOR. (Taxas, US)

- 500 t biomass pd processed
- $213 mill
- Integrated Catalytic Pyrolysis and Catalytic Hydrotreatment
- To produce bio-crude to be processed in conventional refineries
- initial crude for diesel/gasoline produced in the start of 2013
- tech?

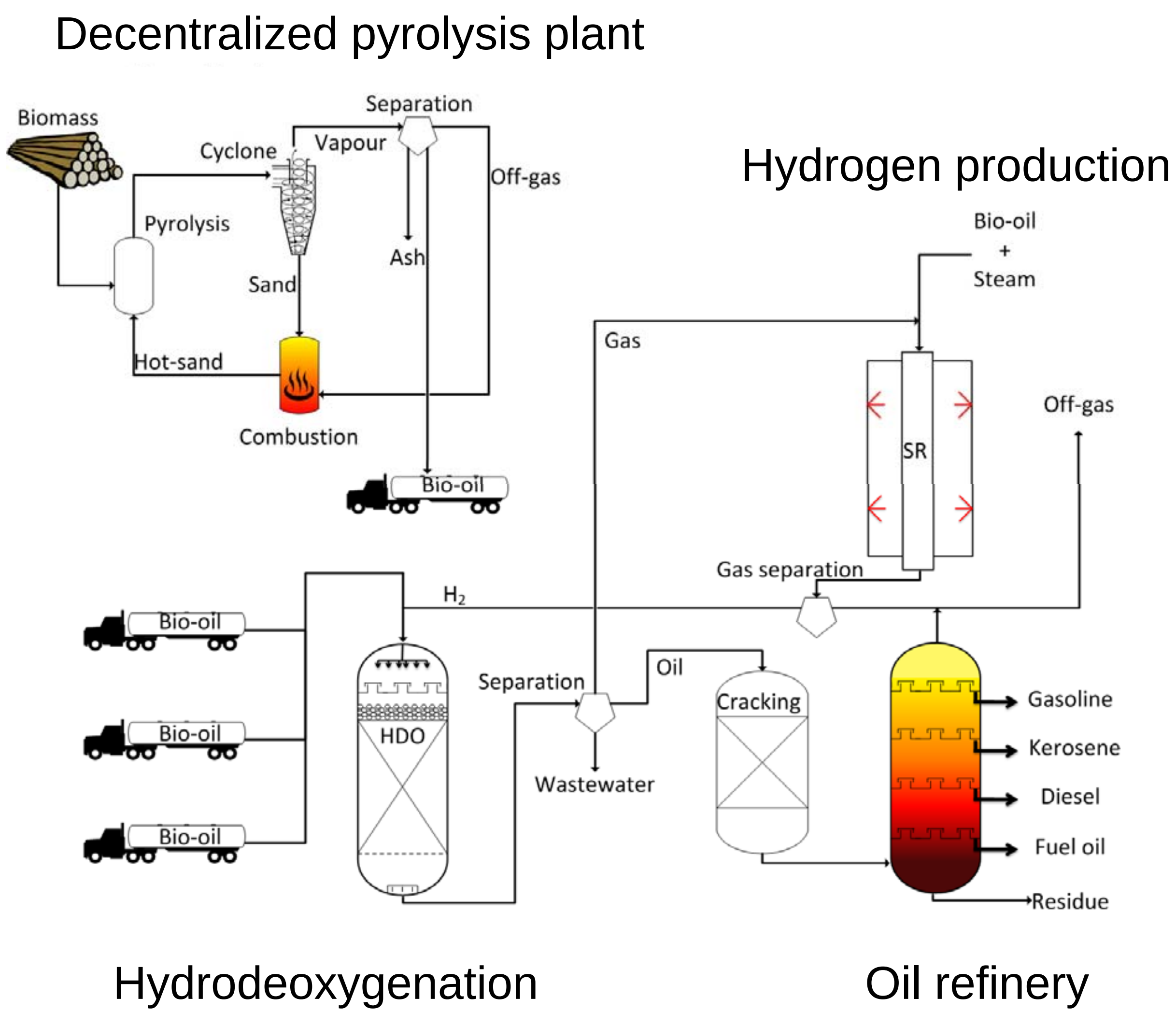
Commercial biomass pyrolysis plants – Tweente Netherlands



Company: BTG(NL).

- 200 t biomass pd
- Modified rotary cone pyrolysis reactor
- To produce electricity by use of gas turbine
- Operations starts 2014

Upgrading of fast Pyrolysis bio-oil



Upgrading of fast Pyrolysis bio-oil

Global ideal reaction HDO (hydrodeoxygenation):

$$CH_{1.43}O_{0.43} + 0.71H_2 \longrightarrow 1\text{"}CH_2\text{"} + 0.43H_2O$$

Exothermic production of gas, oil and water

- Reactor conditions: 80 – 200 bars, 300 – 400ºC
- Type of catalysts: Co-MoS_2/Al_2O_2, Pd/C, Ni/ZrO_2 ,Ni-MoS_2/…
- Limitations: - Coke formation and de activation by Cl, S, K
  - High hydrogen consumption

Zeolite cracking Global ideal reaction:

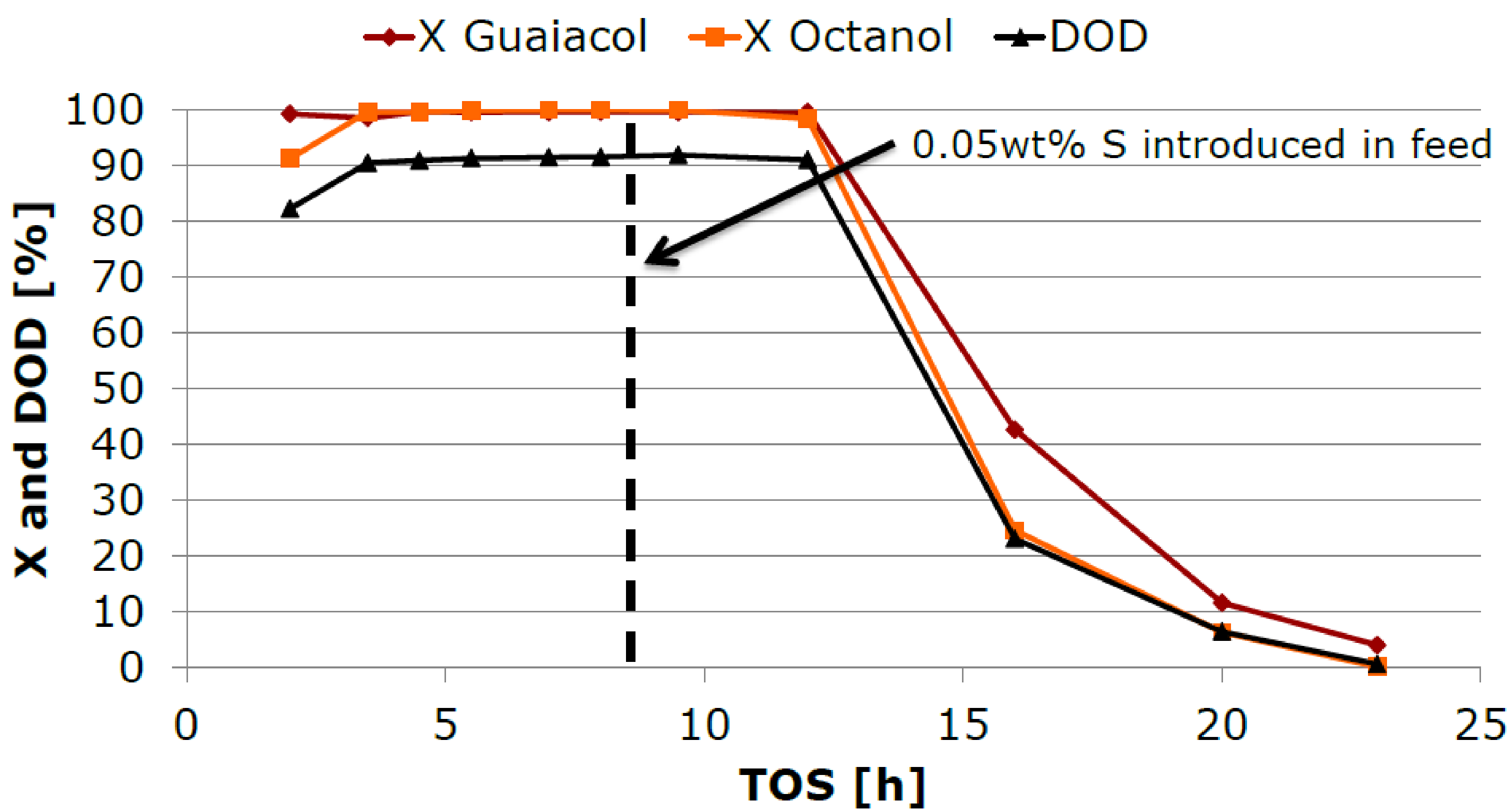
$$CH_{1.43}O_{0.43} \longrightarrow 0.88\text{"}CH_{1.2}\text{"} + 0.12CO_2 + 0.19H_2O$$

- Reactor conditions: 330 – 500ºC, 1 bar
- Limitations: - Low H/C content of product
  - Coke formation on the zeolite

Reference: Mortensen P. M. et Al. Applied Catalysis A. 2011, vol 407, 1-2, pp. 1-19.

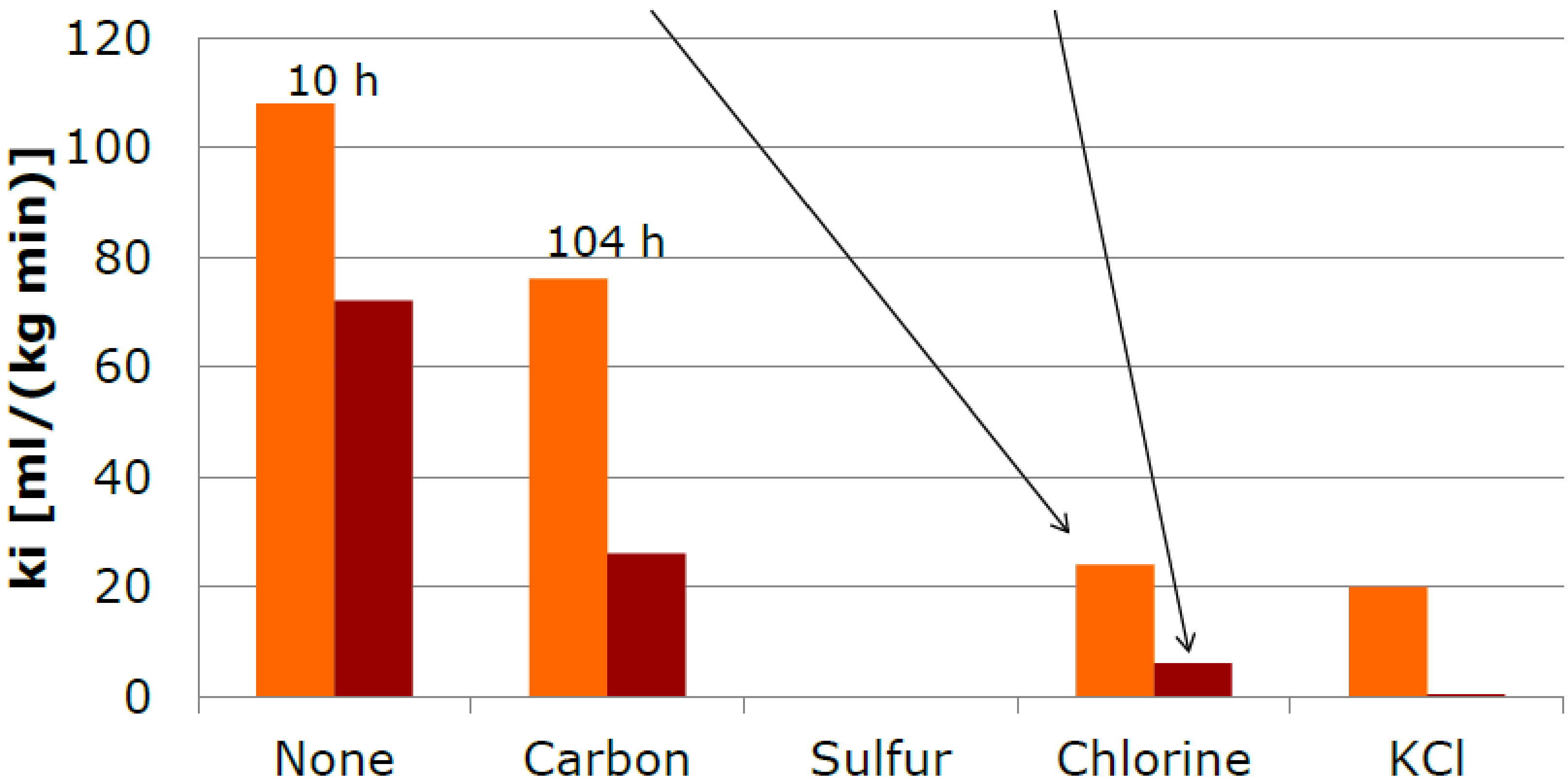
Upgrading of fast Pyrolysis bio-oil – deactivation of catalyst

Guaiacol hydrodeoxygenation at 100 bar and 250ºC
Sulfur deactivation of Ni/ZrO_2 catalyst

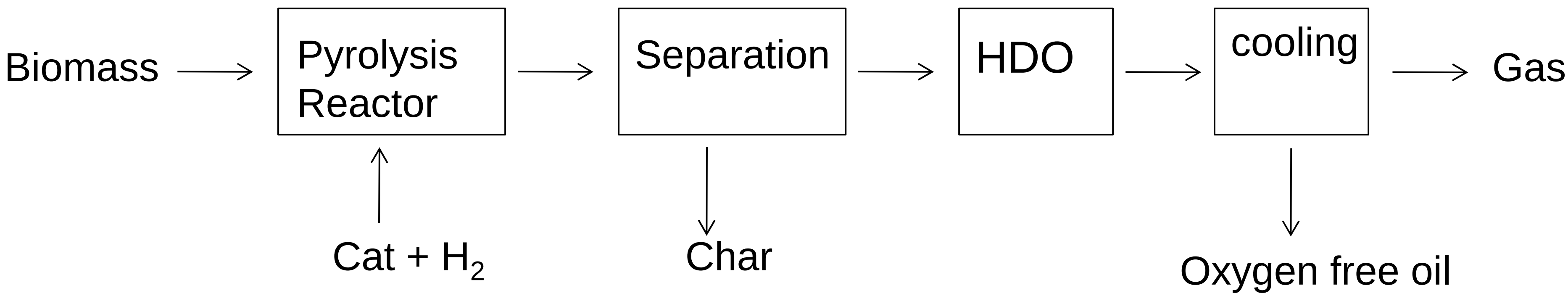


Upgrading of fast Pyrolysis bio-oil – deactivation of catalyst

Guaiacol hydrodeoxygenation on Ni/ZrO_2 catalyst
Deactivation by: Carbon formation/ S / Cl / K



Integrated catalytic hydropyrolysis and hydrodeoxygenation

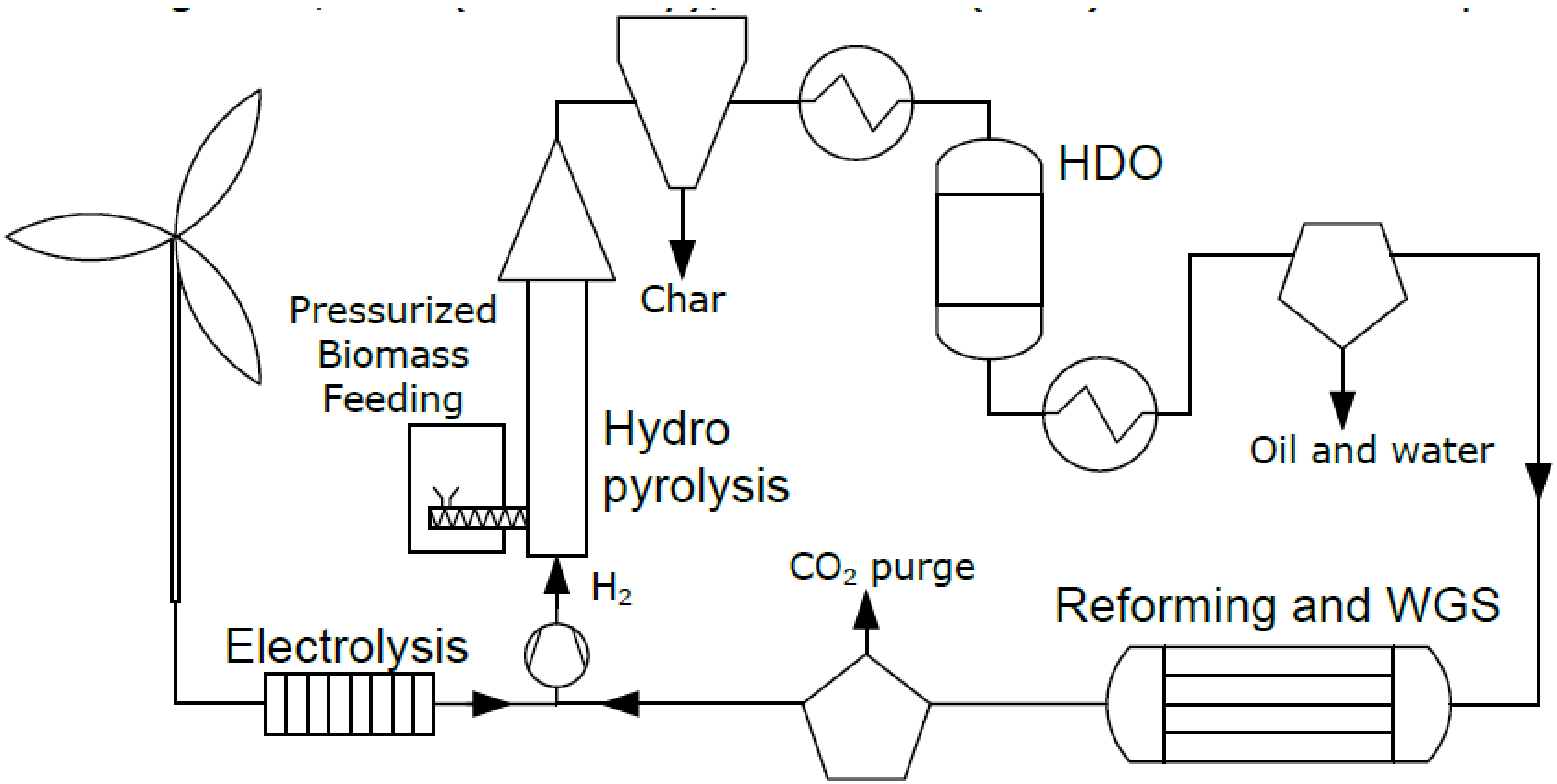


Advantages:
- No re-heating of bio-oil is needed (prevent polymerization)
- Partial deoxygenation during pyrolysis

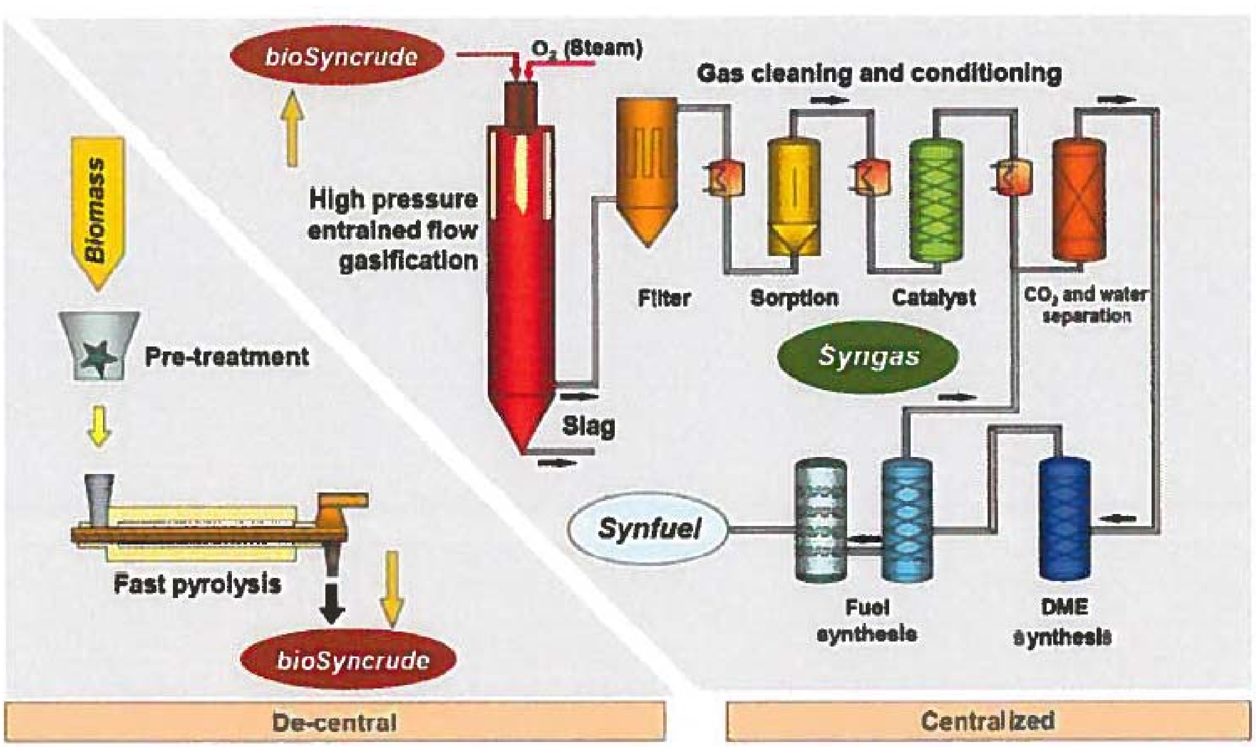
The GTI (IH^2) process:
- Temp: 350-480ºC/340-400ºC pressure 20 – 35 Bar.
- Yields: 20 -30 wt% (energy 55-80% Including a lot from H_2)
- Oxygen in product: < 1wt%
- Cat: ? De-activation and Cat stability ?
- Easy separation of water and oil

Gasoline-Range Hydrocarbons | Diesel/Jet-Range Hydrocarbons | Aqueous Product

Integrated catalytic pyrolysis



Alternative uses of the fast pyrolysis Technology – Oxygen blown pressurized gasification to produce liquid fuels

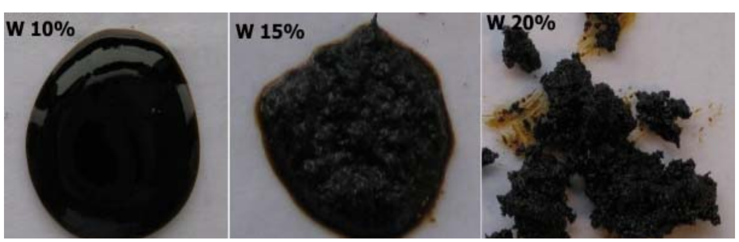


Research center Karlsruhe

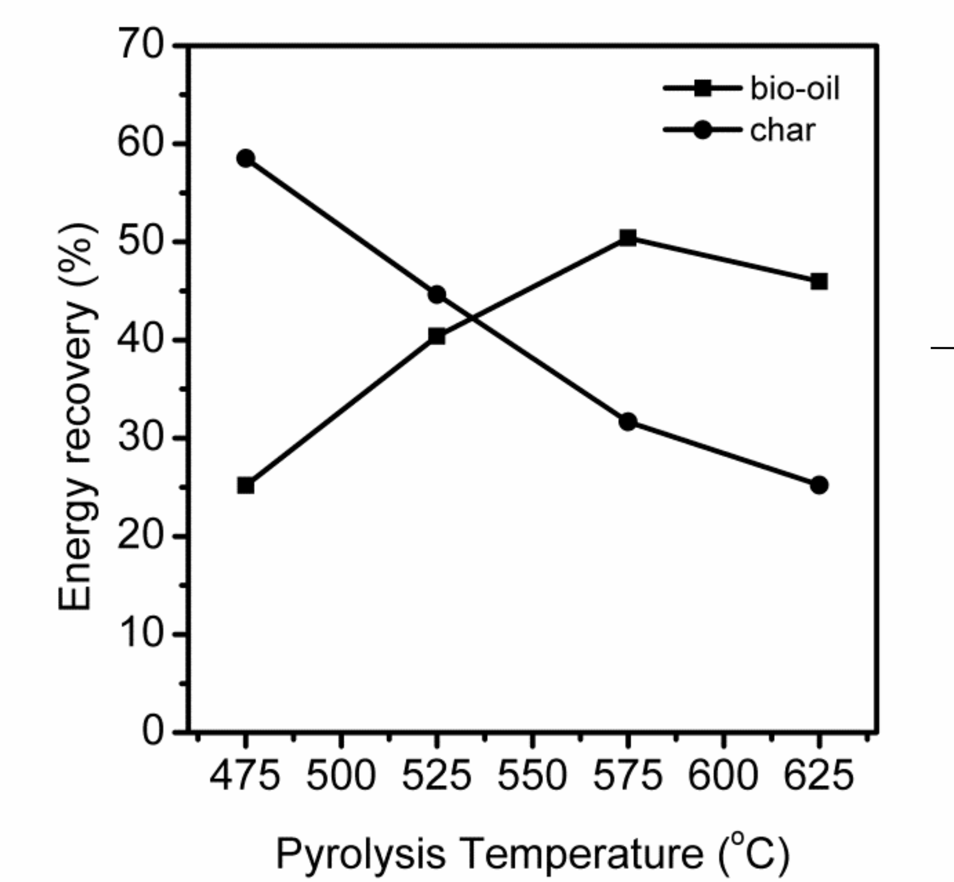
Decentralized pyrolysis followed by centralized gasification

Feeding of char and pyrolysis oil to gasifier

Char/bio oil Slurries



Alternative uses of the fast pyrolysis Technology - Pyrolysis treatment of sewage sludge



Pyrolysis Reactor

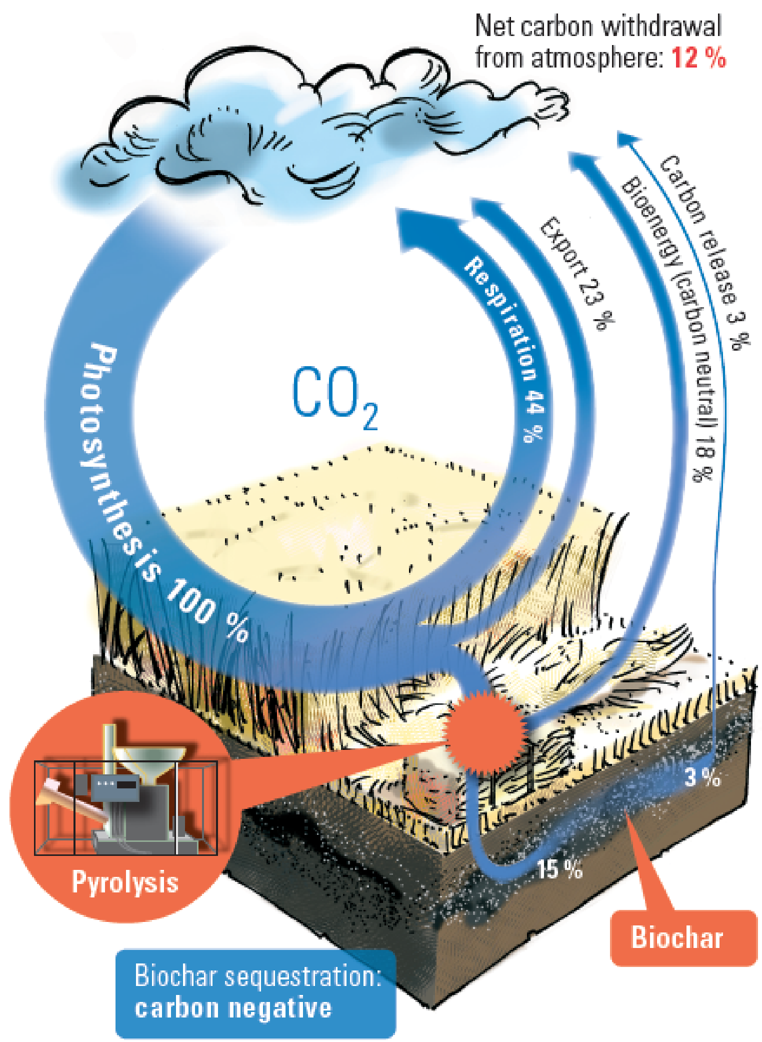
Oil:
- Most of heating value

Char:
- Containing P, K ..
- Reduced volume to disposal

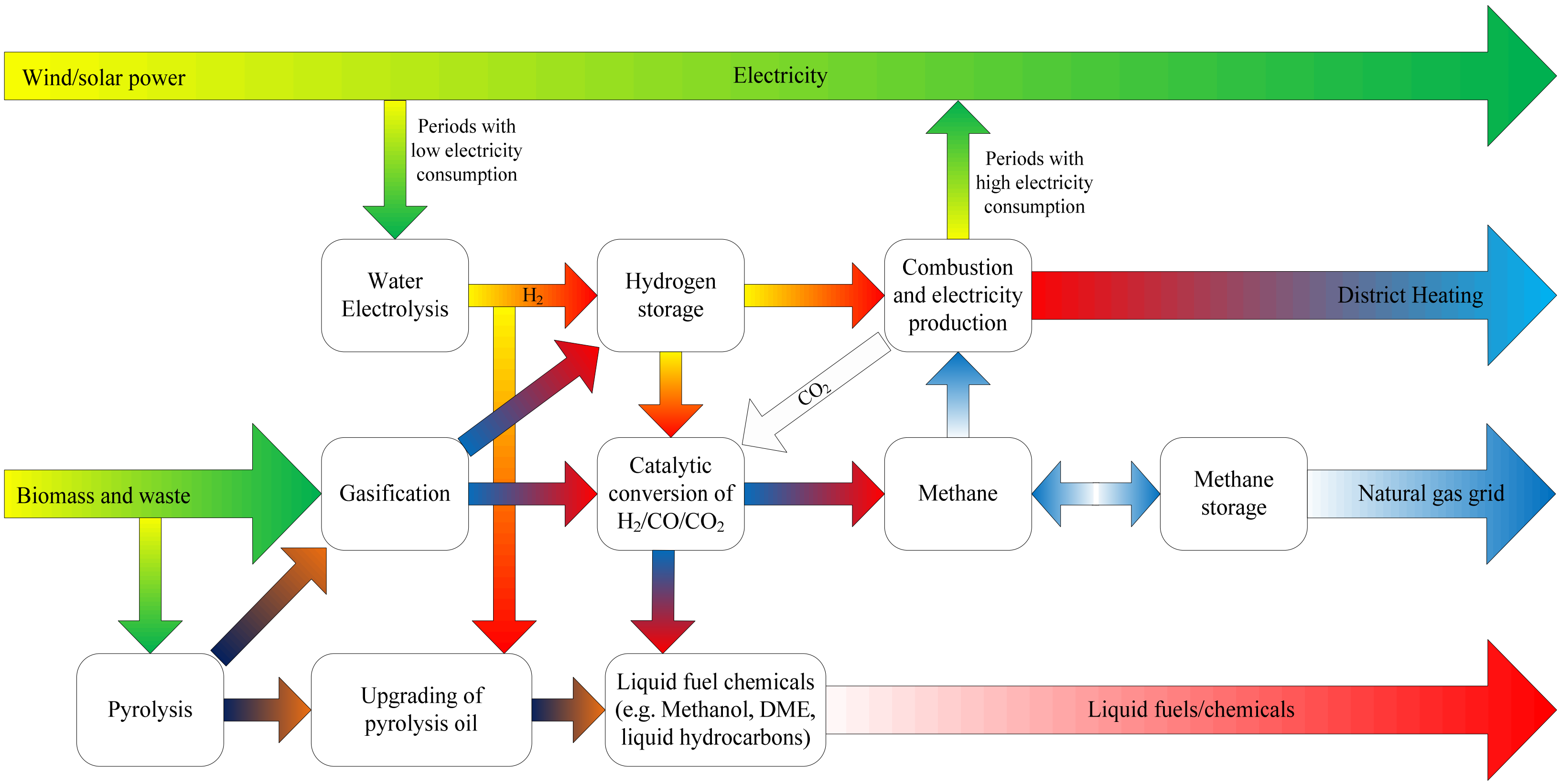
Alternative uses of the fast pyrolysis Technology
Pyrolysis on the field combined with bio-char

Concept of in-situ treatment

Bio-Char carbon sequestration



Integration of renewable electricity production and production of liquid fuels



Perspectives

- A lot of research and commercial activities globally

- Difficult to asses the status of commercial activities

- Is pyrolysis the future biomass transport fuels technology?: - limit plant complexity – cheap catalyst that: – not deactivates – have a high yield – limited H_2 consumption.

- Limited upgrading and use as ship engine fuels

- Pyrolysis as a process step in biomass treatment plants:
  - Pressurized gasification feeding of slurries
  - Sludge treatment
  - Lignin from ethanol plant treatment

- Possibly a on fields in-situ technology