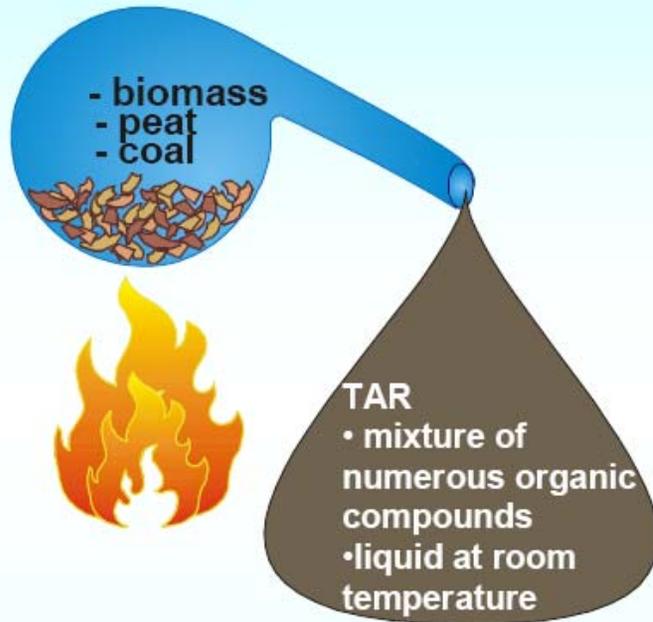


# Catalytic pyrolysis of biomass/upgrading of bio-oil

# Pyrolysis



*"if sauna, vodka and tar won't help, the disease is fatal"*

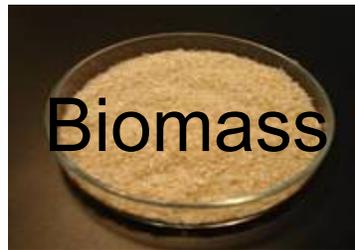


# Pyrolysis

**Gasification**

High temperature  
Long residence time

CO, CO<sub>2</sub>,  
H<sub>2</sub>, HC



Biomass

Pyrolysis

Upgrading  
over  
Zeolites

Condensation

**Carbonization**

Low temperature  
Long residence time



Char

**Fast pyrolysis**

Moderate temperature  
Short residence time



Bio oil

# Fast pyrolysis

- Moderate temperature
  - 400-500°C
- High heating rate
- Short residence time
  - 1-2s
- Rapid cooling
  
- Fluidized bed reactor

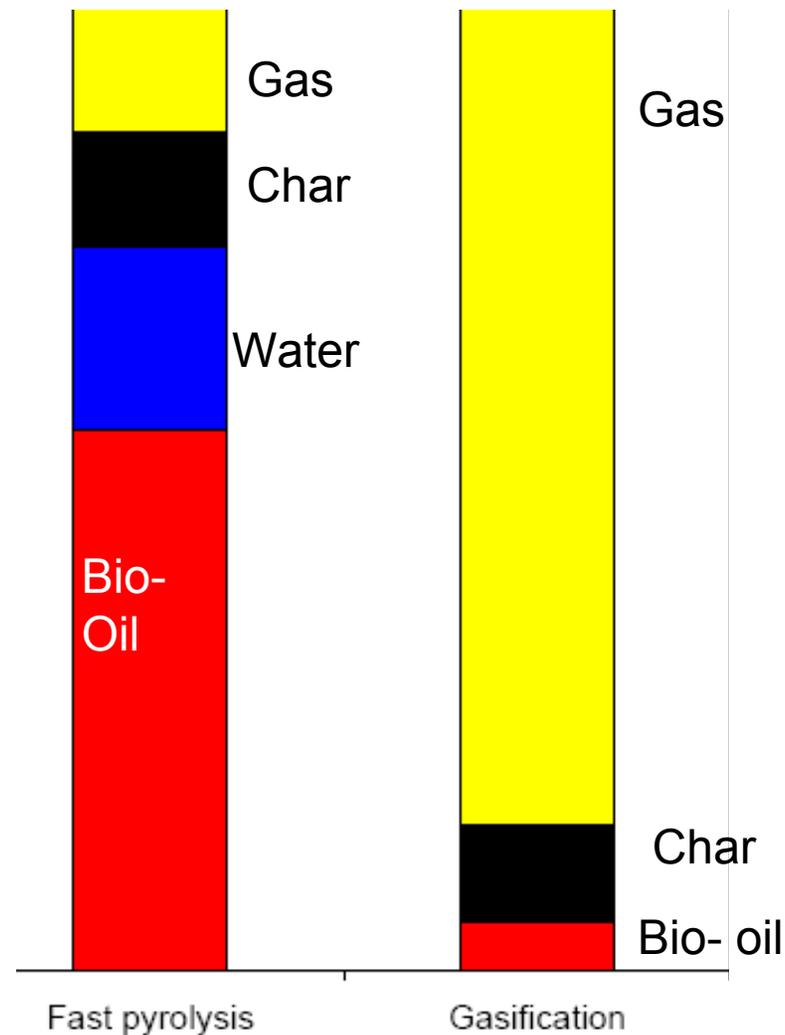


# Fast pyrolysis

	Liquid	Char	Gas
<b>FAST PYROLYSIS</b> moderate temperature (~500C) short hot vapour residence time (<2 s)	75% mostly organics	12%	13%
<b>SLOW PYROLYSIS</b> Low-moderate temperature, long residence times	30% mostly water	35%	35%
<b>GASIFICATION</b> high temperature (>800C), long vapour residence time	5% tars	10%	85%



Pyrolysis of Wood/Biomass for Bio-oil: A critical review.  
D. Mohan, C.U. Pittman, P.H. Steele, Energy Fuels, 20  
(2006) 848.



# Biomass

- Pine
- Cellulose
- Galactoglucomannan
- Sugar beet pulp



[<http://commons.wikimedia.org/wiki/File:SugarBeet.jpg>]

[[http://www.innventia.com/templates/STFIPage\\_\\_\\_\\_6935.aspx](http://www.innventia.com/templates/STFIPage____6935.aspx)]

[<http://www.lifepinlaricio.org/pin-fi.htm>]

# Scaling -up

## **Fluid Bed Reactors**

Good temperature control

Easy scaling

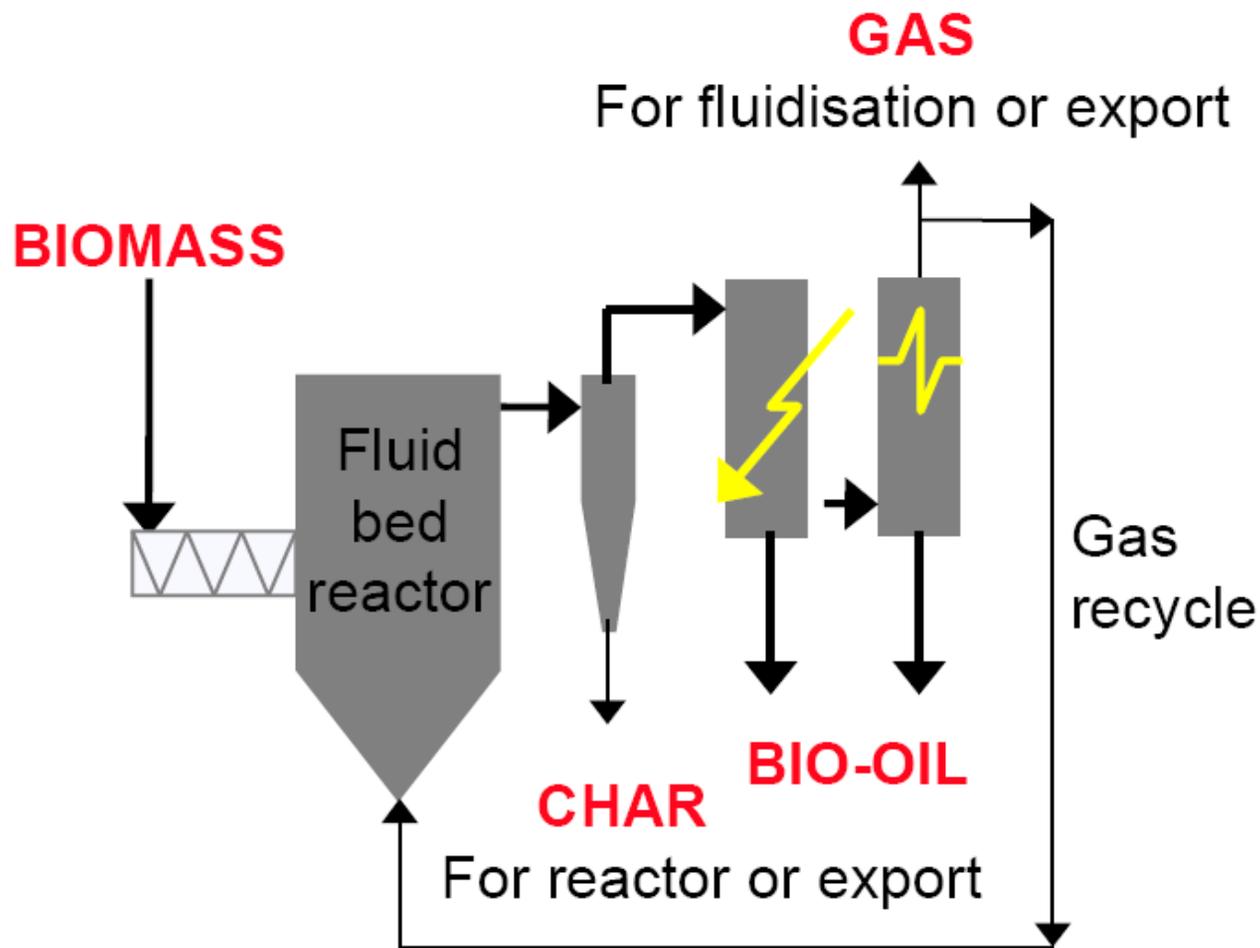
30 years of experience since first experiments at  
University of Waterloo in 1980s

Small particle sizes needed

Heat transfer to bed at large scale has to be proven

# Industrial installations

## Bubbling Fluid Bed Pyrolysis

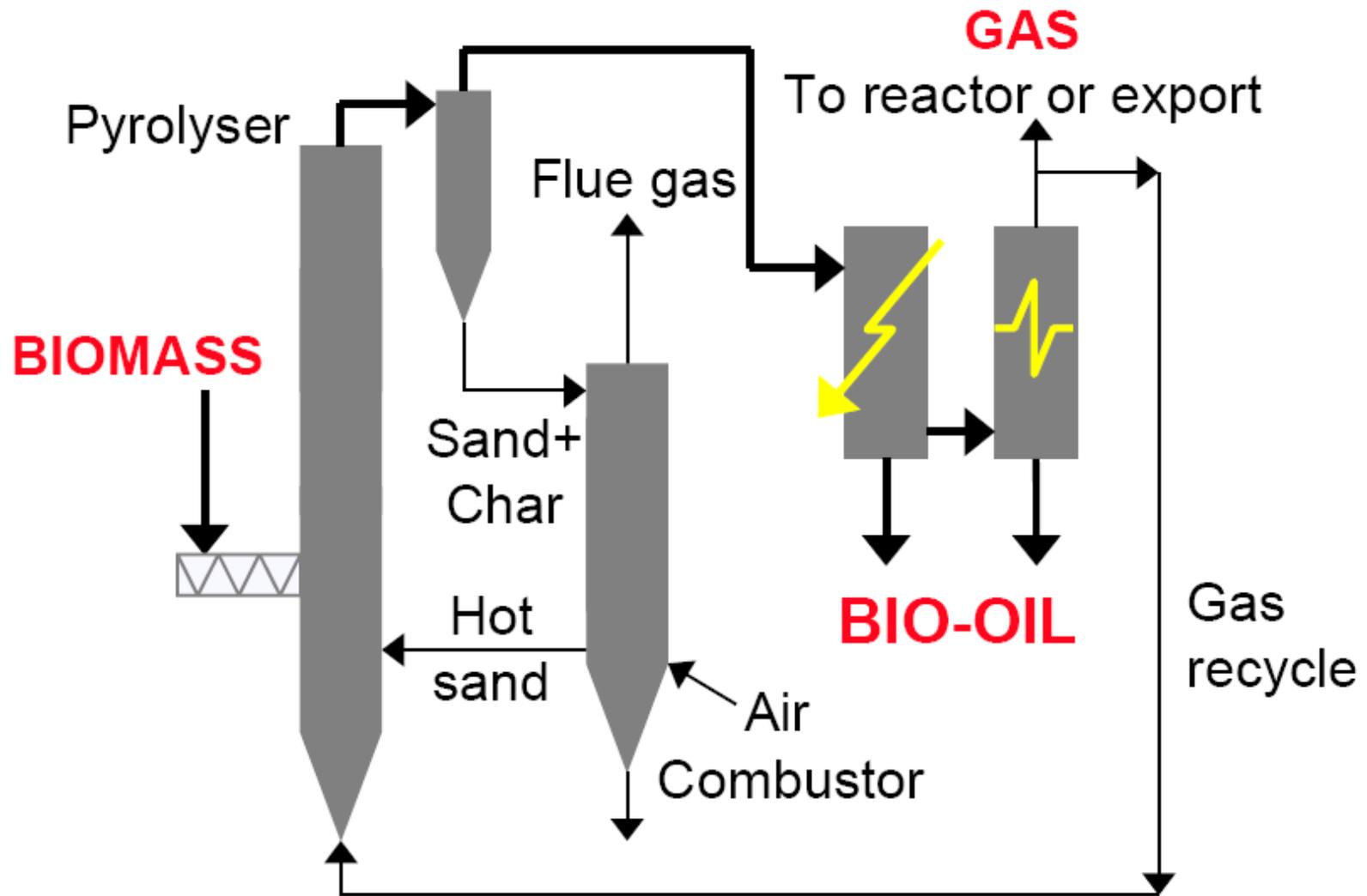


# Bubbling Fluid Bed



**250 kg/h pilot plant at Wellman, UK**

# Circulating Fluid Beds



# CFD

Good temperature control in reactor

- Larger particle sizes possible,
- CFBs suitable for very large vthroughputs,

Well understood technology,

Hydrodynamics more complex,

Char is more attrited due to higher velocities; separation is by cyclone,

Heat transfer to bed at large scale has to be proven.

# Fast Pyrolysis Liquid

Bio-oil is water miscible and is comprised of many oxygenated organic chemicals.

- Dark brown mobile liquid,
- **Combustible**,
- Not miscible with hydrocarbons,
- Heating value ~ 17 MJ/kg,
- Density ~ 1.2 kg/l,
- Acid, pH ~ 2.5,
- Pungent odour,
- “Ages” - viscosity increases with time



# Properties

- The complexity and nature of the liquid results in some unusual properties
- Due to physical-chemical processes such as:
  - ∅ Polymerization/condensation
  - ∅ Esterification and etherification
  - ∅ Agglomeration of oligomeric molecules
- Properties of bio-oil change with time:
  - ∅ Viscosity increases
  - ∅ Volatility decreases
  - ∅ Phase separation, deposits, gums

# Bio-oil

**Cost** : 10% – 100% more than fossil fuel,

**Availability**: limited supplies for testing

**Standards**; lack of standards and inconsistent quality inhibits wider usage,

**Incompatibility** with conventional fuels,

**Unfamiliarity** of users

**Dedicated fuel handling** needed,

**Poor image.**

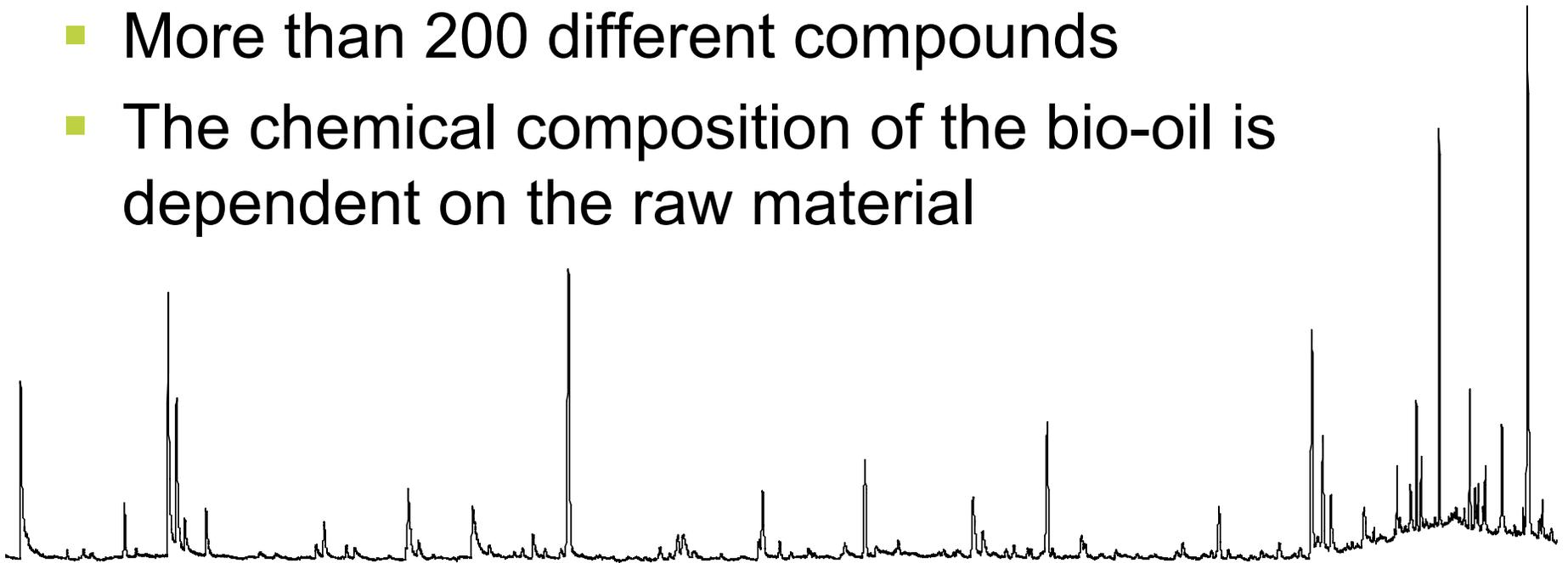
# Problems with bio-oil

- Poor volatility, high viscosity, coking, corrosiveness, and cold flow problems
- In diesel engines: difficult ignition (due to low heating value and high water content), corrosiveness (acids), and coking (thermally unstable components).
- Bio-oil upgrading (catalytic) is needed
  - hydrodeoxygenation
  - zeolite upgrading via cracking



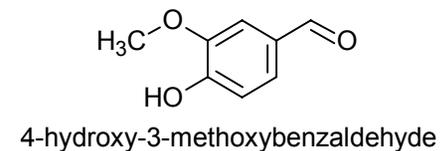
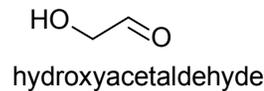
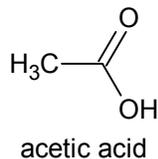
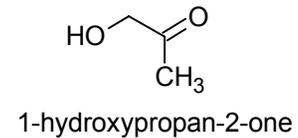
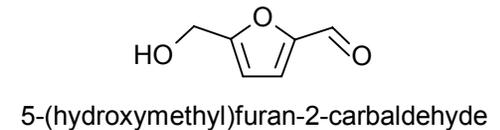
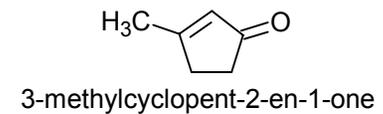
# Bio-oil

- Complex mixture of organic molecules and water
  - Aldehydes, acids, alcohols, ketones, phenols, polyaromatic hydrocarbons etc.
- More than 200 different compounds
- The chemical composition of the bio-oil is dependent on the raw material



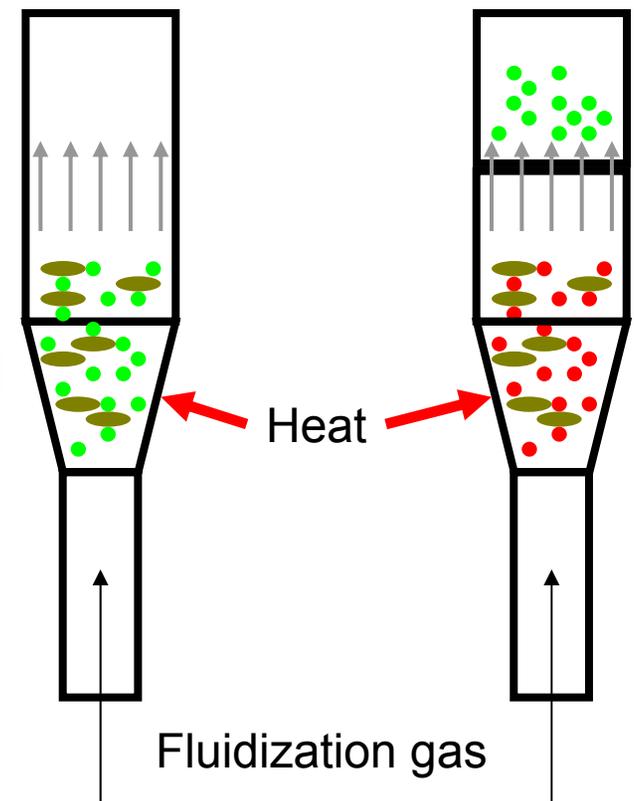
# Bio-oil

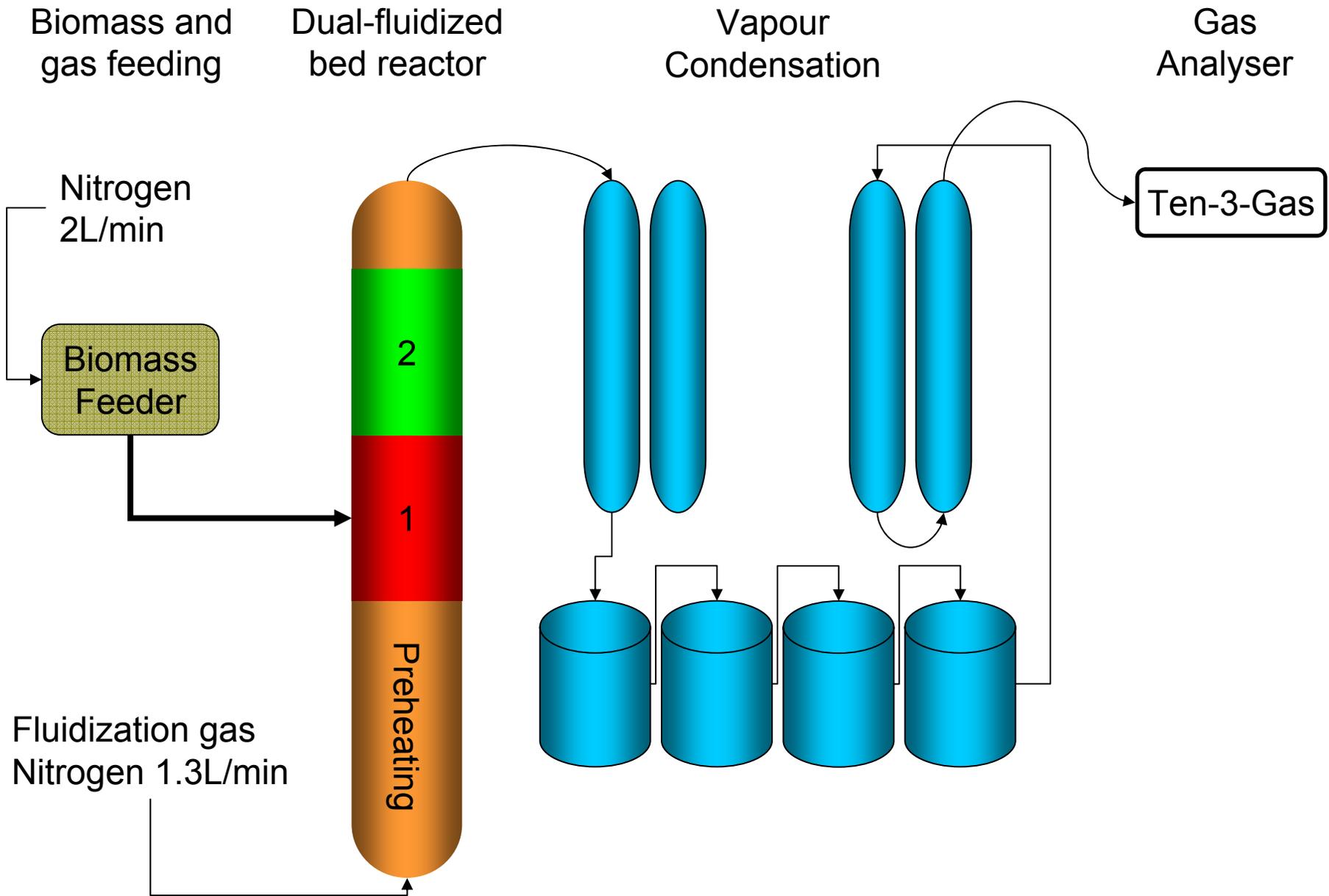
- Carbohydrates, cellulose and hemicellulose
  - Furans, cyclopentanones
  - Open chain acids, aldehydes, ketones and alcohols
- Lignin
  - Alkyl, methoxy, carbonyl and hydroxy substituted phenols



# Catalytic pyrolysis experiments

- Thermogravimetric analysis (TGA)
- Two fluidized bed reactors
  - Zeolites as bed material providing heat and upgrading products
  - Separation of pyrolysis and catalytic upgrading



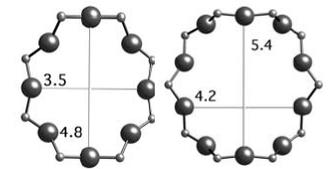
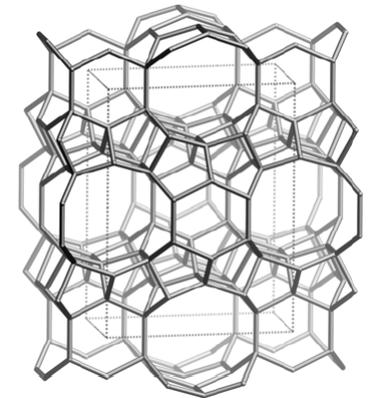
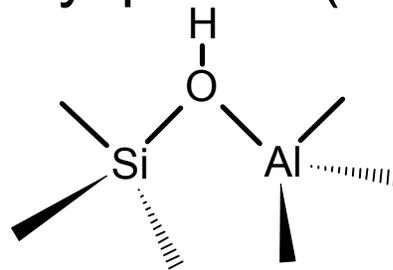


# Reactor set-up



# Acidic zeolite catalysts

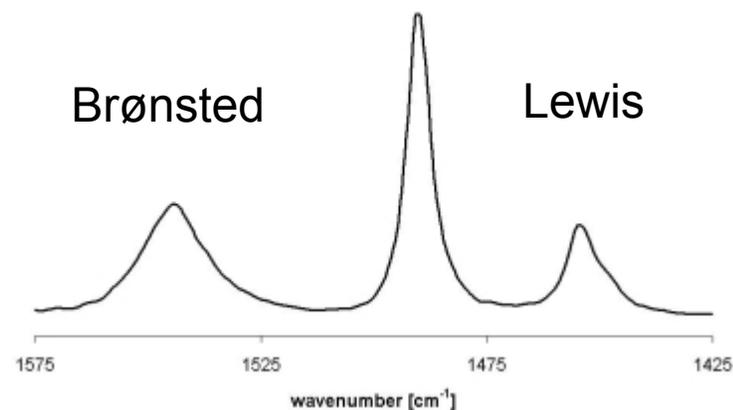
- Crystalline aluminosilicate minerals
- 3-D microporous framework structure
- Tetrahedrons of silicon ( $\text{Si}^{4+}$ ) and/or aluminium ( $\text{Al}^{3+}$ ) surrounded by four oxygen ( $\text{O}^{2-}$ ) anions
- Neutral framework (silicon and oxygen)
- Negatively charged framework (aluminium, silicon and oxygen)
- Framework balanced by a metal cation (Lewis acid) or a hydroxyl proton (Brønsted acid)



Ferrierite

# Determination of acidity

- Pyridine is adsorbed to the zeolite sample
- FTIR is used to determine the acid sites
  - Brønsted  $1545\text{ cm}^{-1}$   
(hydron  $\text{H}^+$  donor)
  - Lewis  $1450\text{ cm}^{-1}$   
(electron acceptor)
- Quantitative amount of acid sites calculated with the constants of Emeis



# TGA

- Polymers (LDPE)
  - C-C bonds breaks at high temperatures
  - Brønsted acidity decreases the temperature needed for cracking
  - Energy saved
- Biomass
  - Different zeolites tested
  - No difference in non-catalytic and catalytic thermograms

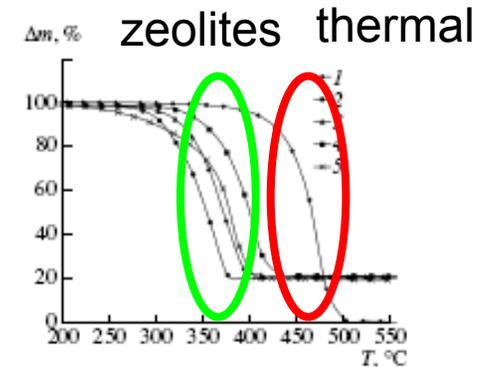


Fig. 2. TG curves of different "polymer+ zeolite" mixtures. Structurally different zeolites exhibit different catalytic behaviors in LDPE degradation. (1) LDPE; (2) LDPE + H-β-25; (3) LDPE + MORD-20; (4) LDPE + H-FER-20; (5) LDPE + H-Y-12.

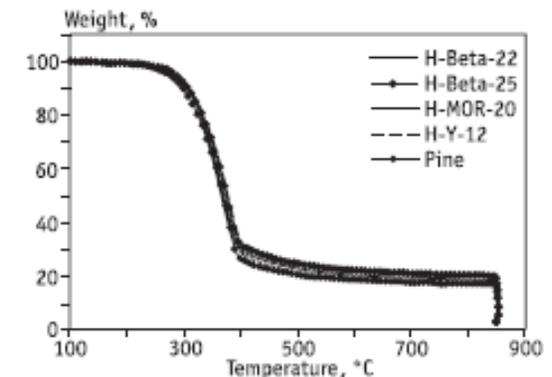
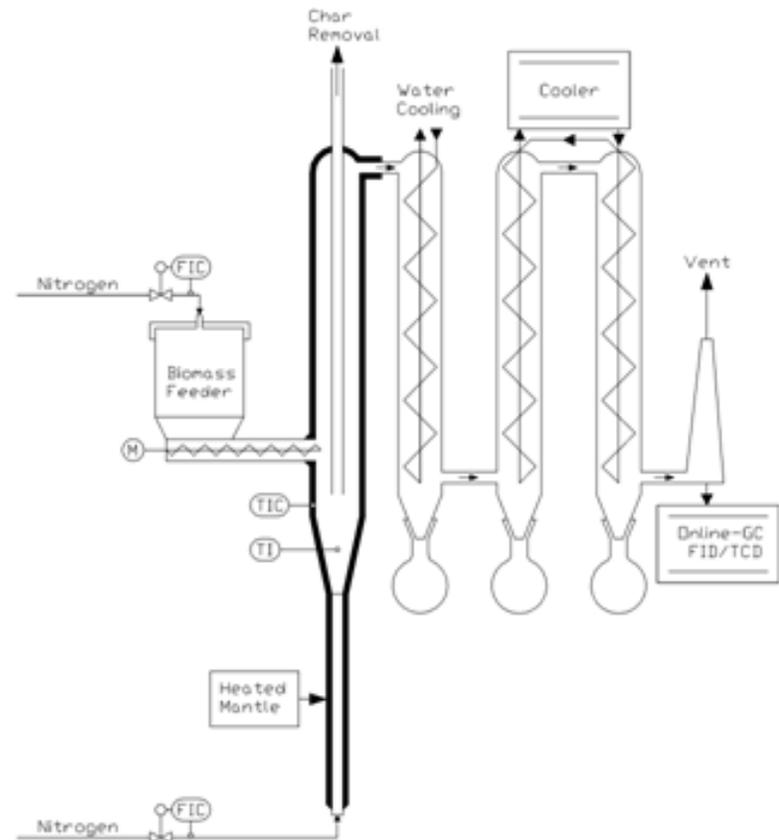


Fig. 3. TGA-curves from the run with a ground sample

# Fluidized bed reactor

- Zeolites as heat carrier and catalysts in same reactor
- Study the influence of acidity and structure of the zeolites
- Pine wood
- 450°C

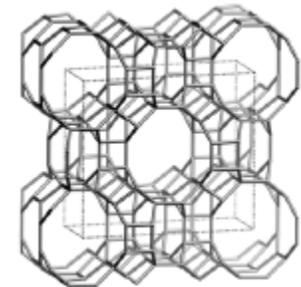


# Influence of structure and acidity

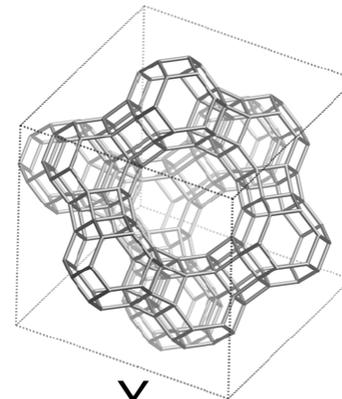
- Zeolite structures
  - ZSM-5, 3-D **10 ring** **5.2 x 5.7Å** and 5.3 x 5.6Å Intersection cavity: 9Å
  - Beta, 3-D **12 ring** **6.6 x 6.7Å** and 5.6 x 5.6Å
  - Mordenite, 2-D **12 ring** **7.0 x 6.5Å** and short 8-ring channels 3Å
  - Y, 3-D **12 ring** **7.4 x 7.4Å** and 11.8Å supercages
- Beta zeolites with different silica-alumina ratios (acidity)



ZSM-5



Mordenite

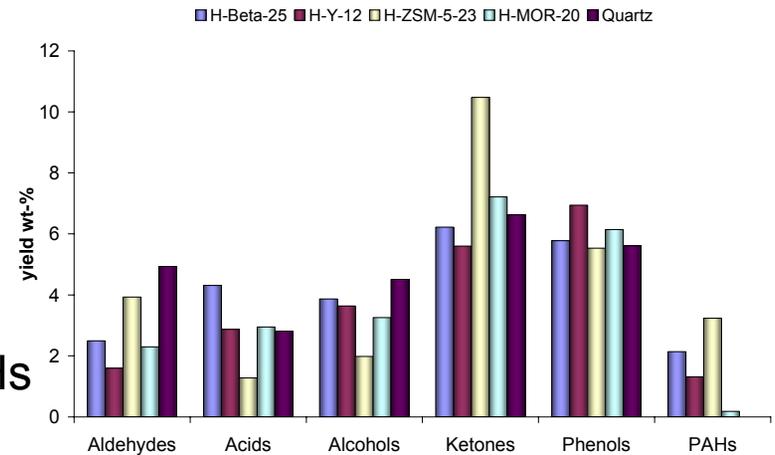


Y

# Results

## ■ Pyrolysis over zeolites compared to non-catalytic pyrolysis

- Decreased the bio-oil yield
- Increased the water yield
- Changed the chemical composition of the bio-oil
- Acidity influenced the formation of PAHs
- Coke was formed on the zeolites



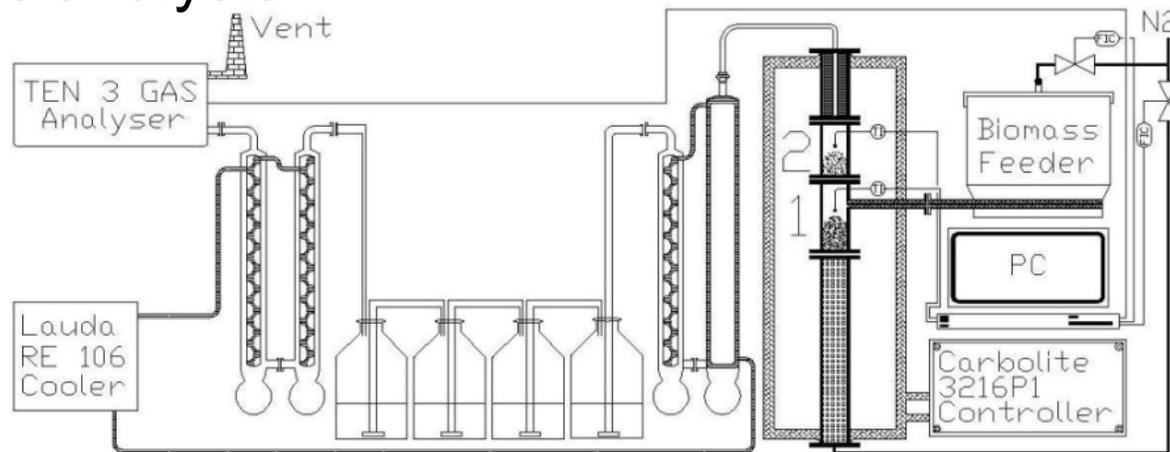
## ■ Possible to partly de-oxygenate the bio-oil over zeolite catalysts



fresh spent

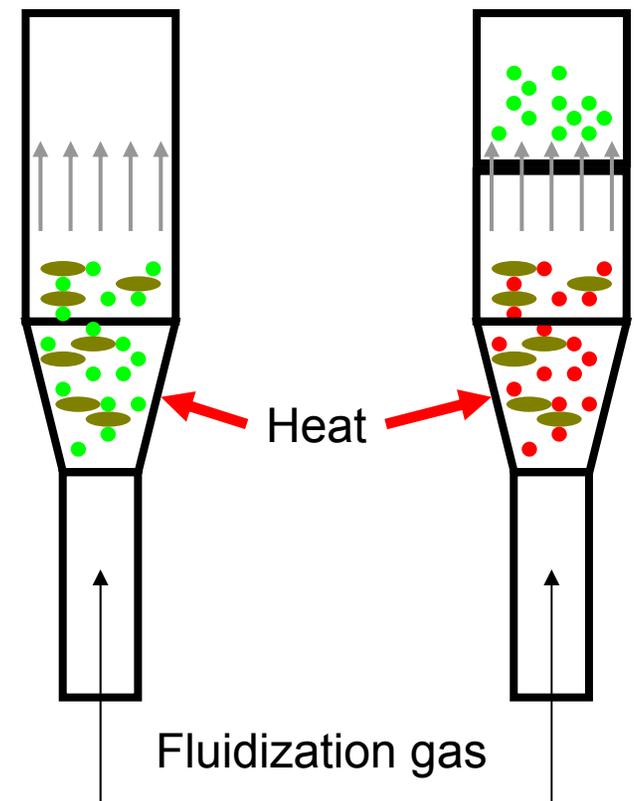
# Dual-fluidized bed reactor

- Smaller amount of zeolites needed
- Easier to separate char and spent zeolites
- Separation of pyrolysis and catalysis reactors
- Improved condensation
  - Gas analysis

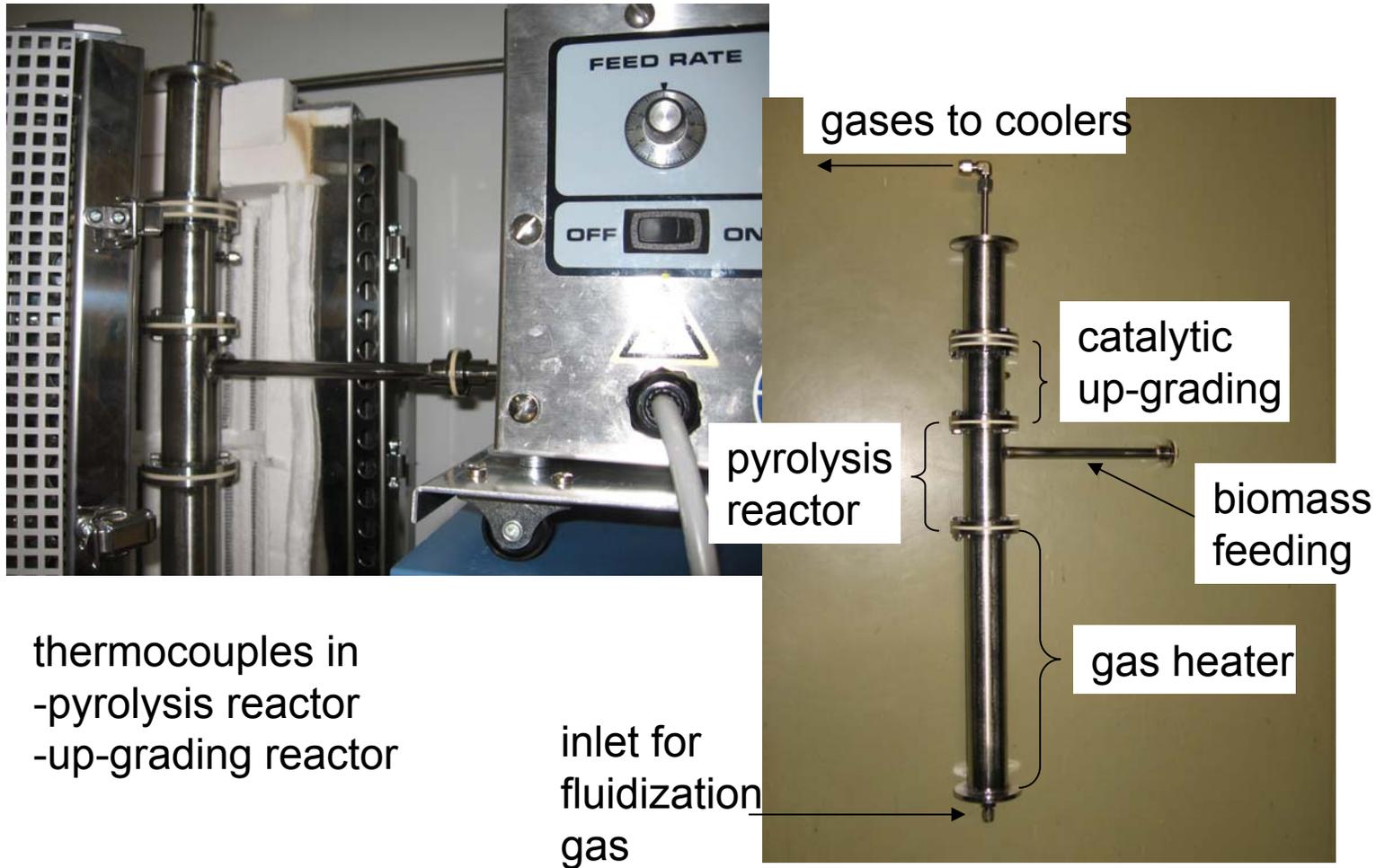


# Catalytic pyrolysis

- Zeolites as bed material providing heat and upgrading products
- Separation of pyrolysis and catalytic upgrading



# Thermal pyrolysis and catalytic upgrading



# Dual-fluidized bed reactor

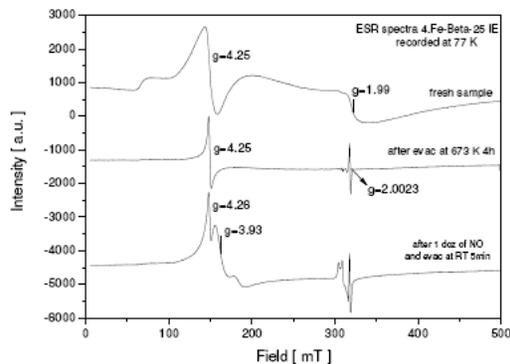
- Effect of binder (bentonite)
  - Beta and ZSM-5
- Iron modification (ion-exchange)
  - Beta, ferrierite and Y
- Reaction conditions
  - Pyrolysis reactor 400°C
  - Catalytic upgrading reactor 450°C
  - Pine

# Zeolite characterization

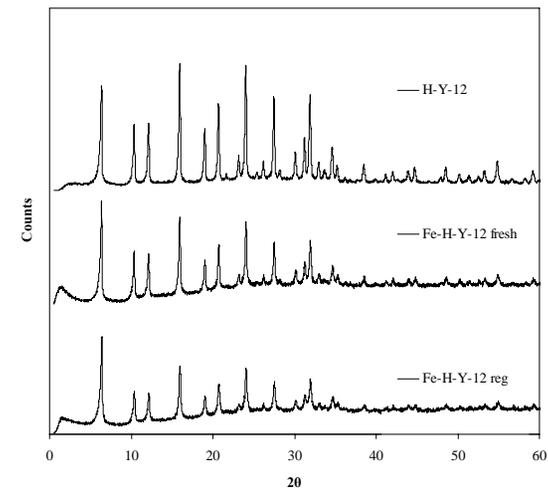
Iron content analysed by ICP-OES  
*inductively coupled plasma - optical emission spectrometry*

<b>Fe-H-FER-20</b>	<b>0.1 wt-%</b>
<b>Fe-H-Beta-25</b>	<b>3.4 wt-%</b>
<b>Fe-H-Y-12</b>	<b>5.4 wt-%</b>

The oxidation state and coordination of iron were investigated by ESR  
*Electron spin resonance spectroscopy*



Structure and phase purity analysed by XRD

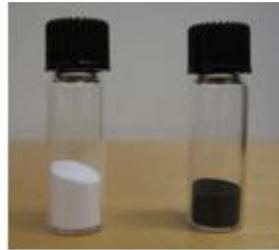


**Based on ESR the iron on Beta was mostly tetrahedral Fe<sup>3+</sup>**

**Iron modification and regeneration of the iron modified Y does not change the structure nor the phase purity**

# Zeolite regeneration

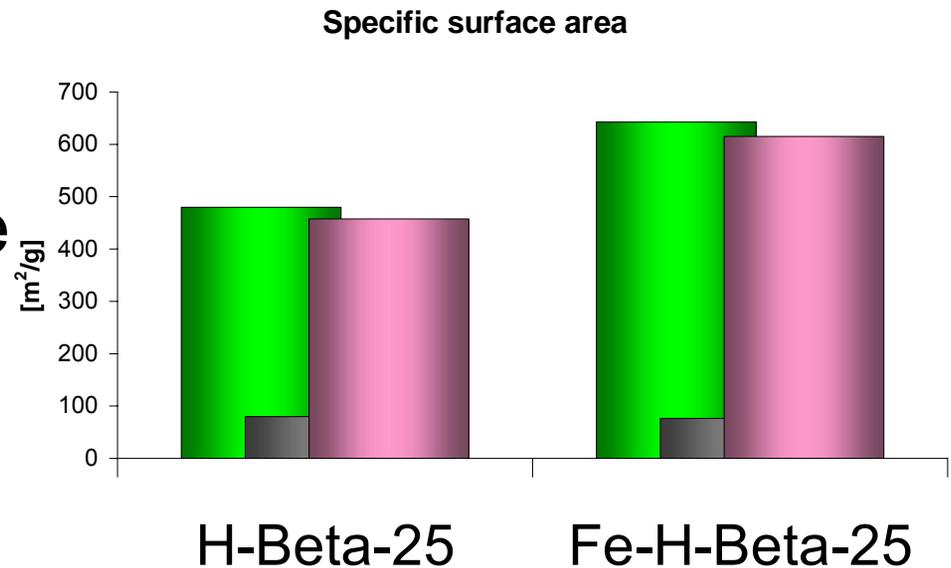
- Coke was formed on the zeolites



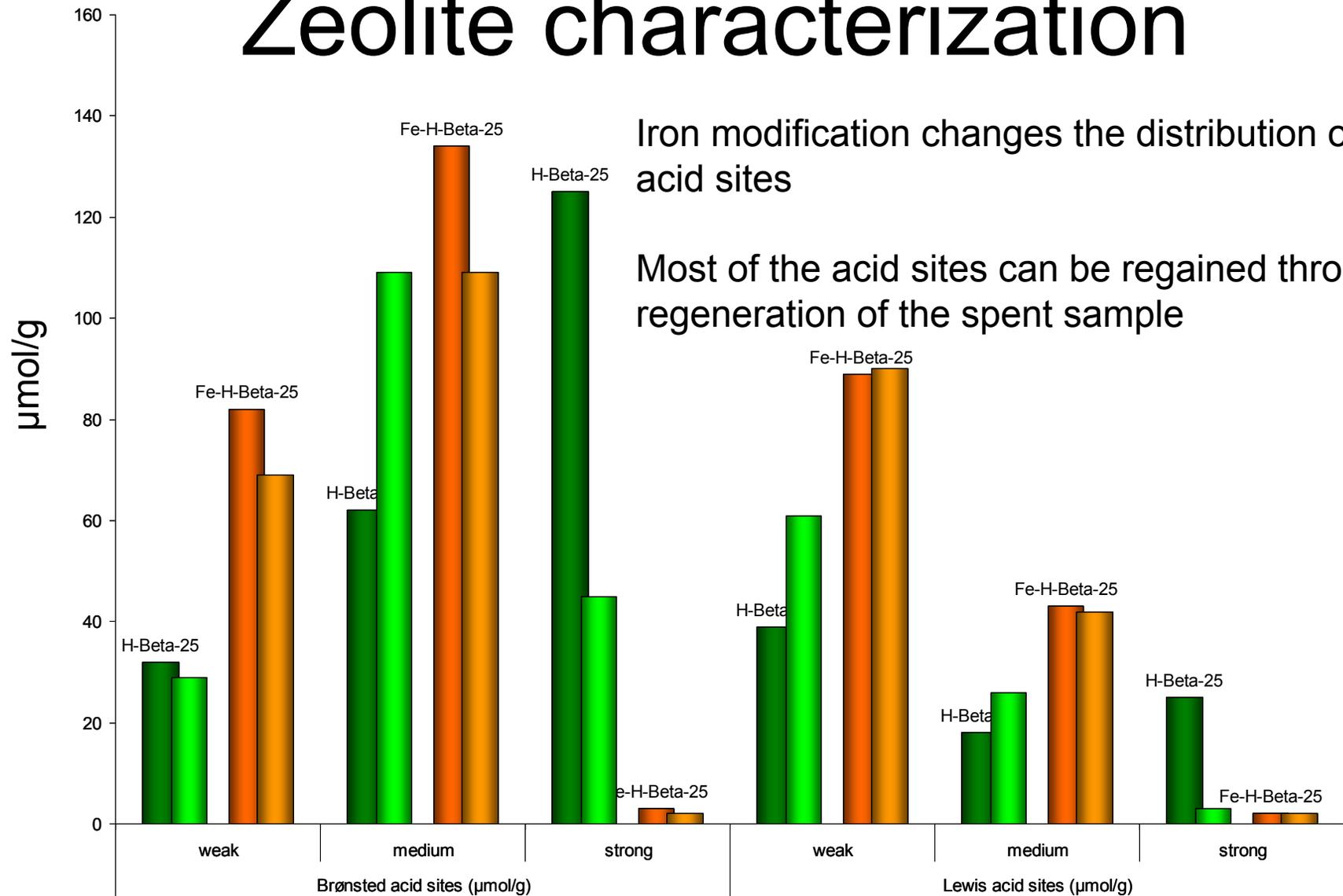
fresh spent

- Regeneration by burning away the coke
- 2h, 450°C in air atmosphere

Iron modification increases the specific surface area  
The spent zeolites has a fairly low area  
Possible to regain the surface area through regeneration

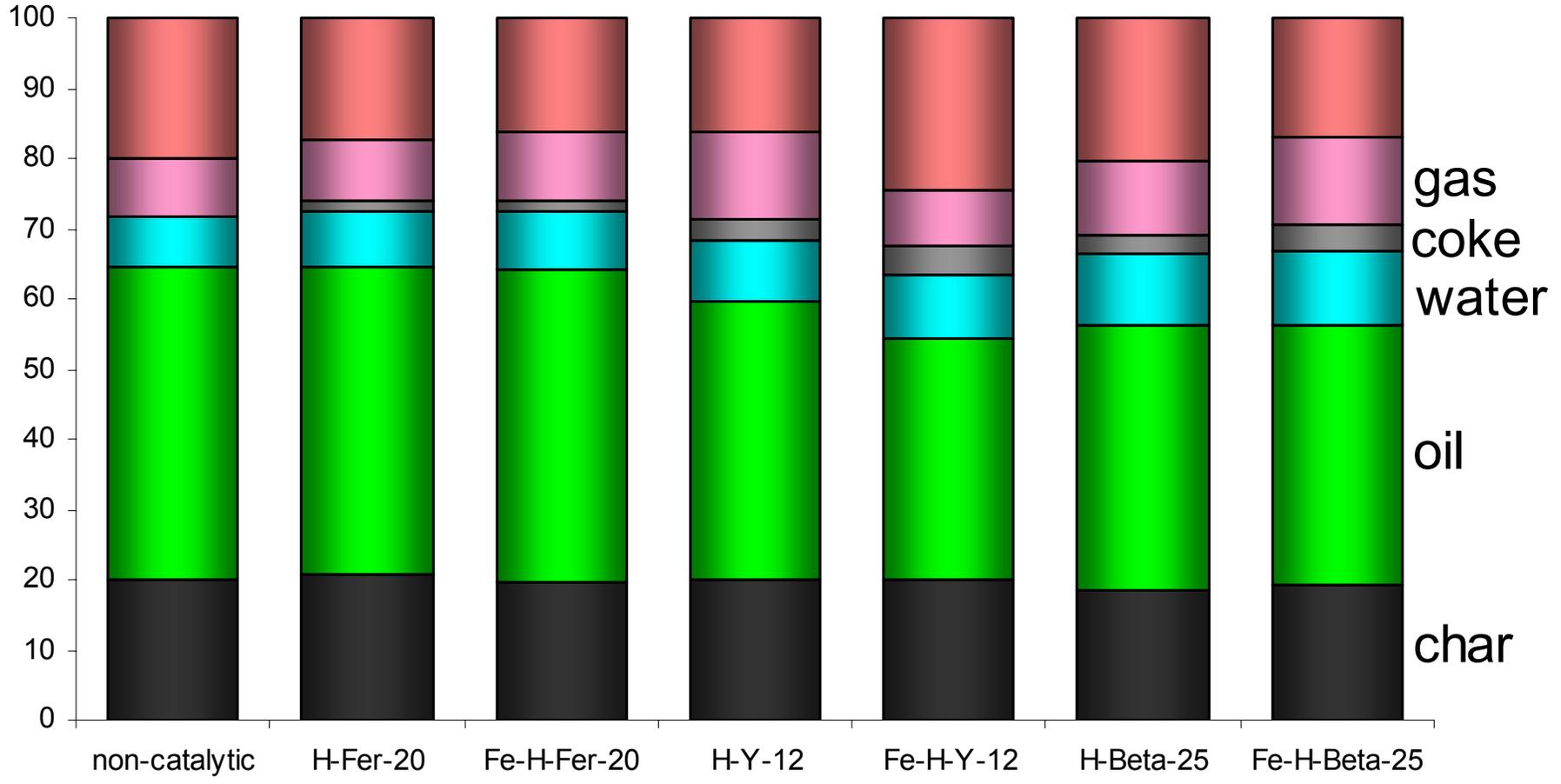


# Zeolite characterization

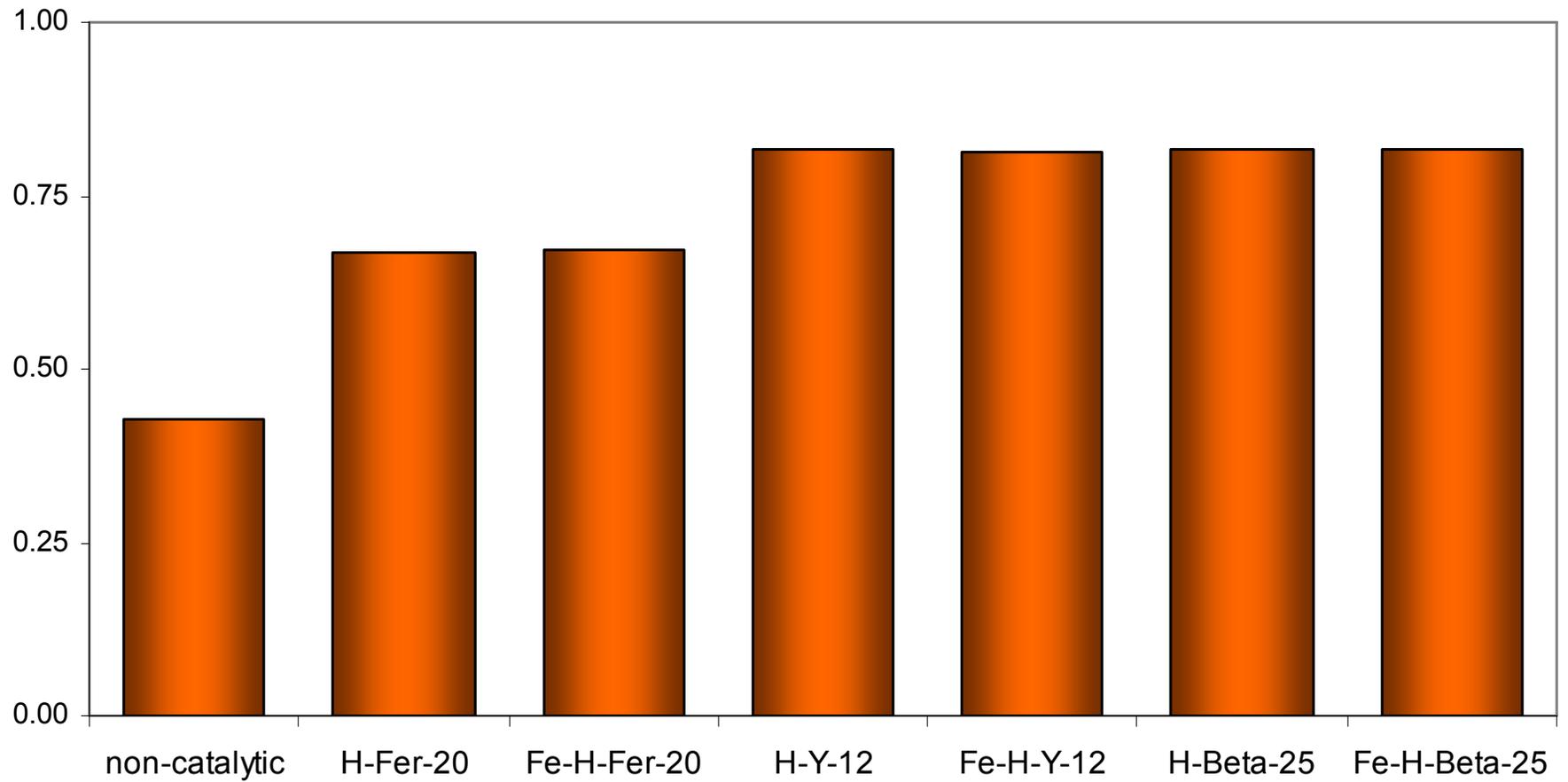


# Mass balance

yield [%]

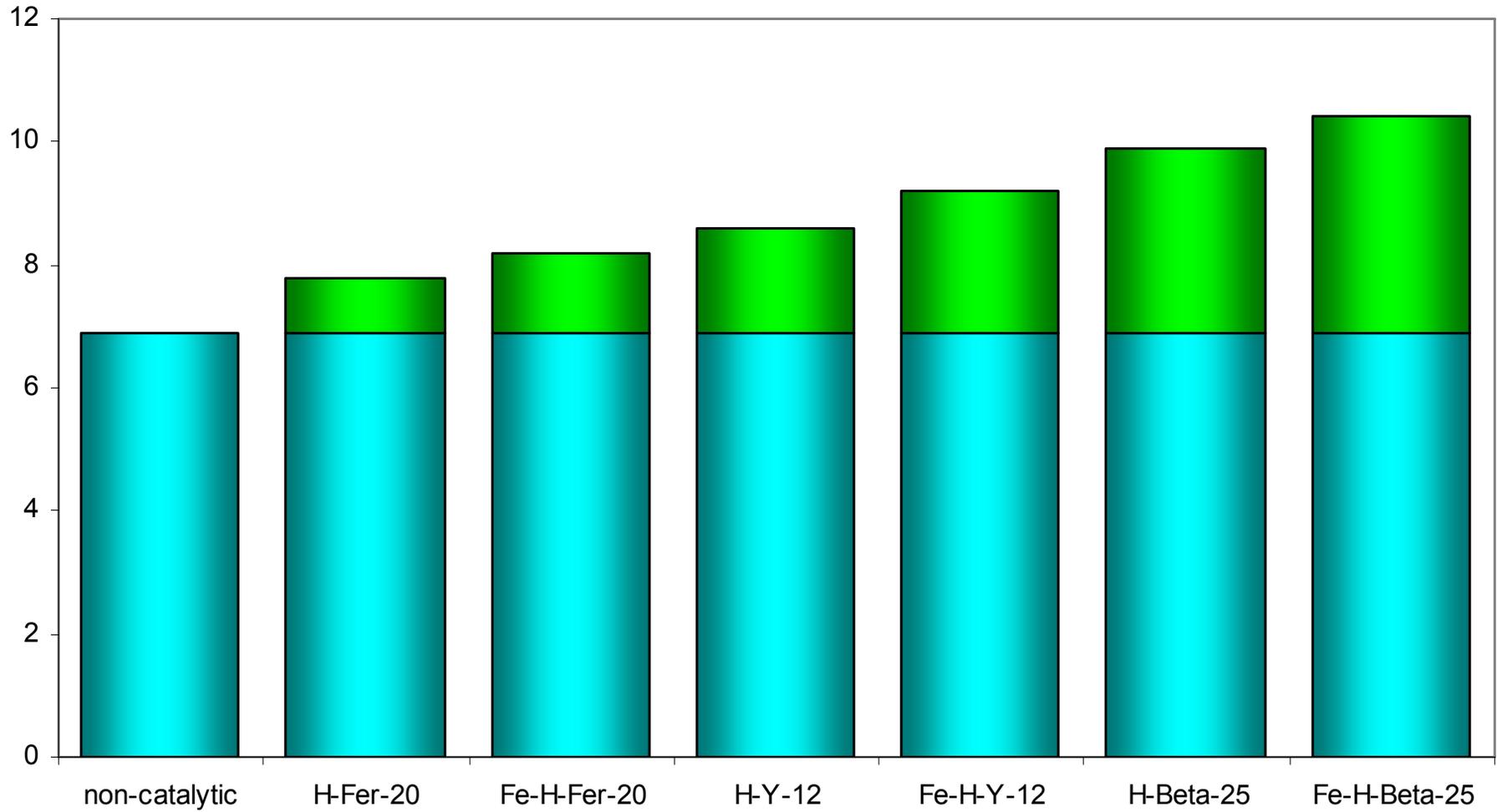


# CO/CO<sub>2</sub>



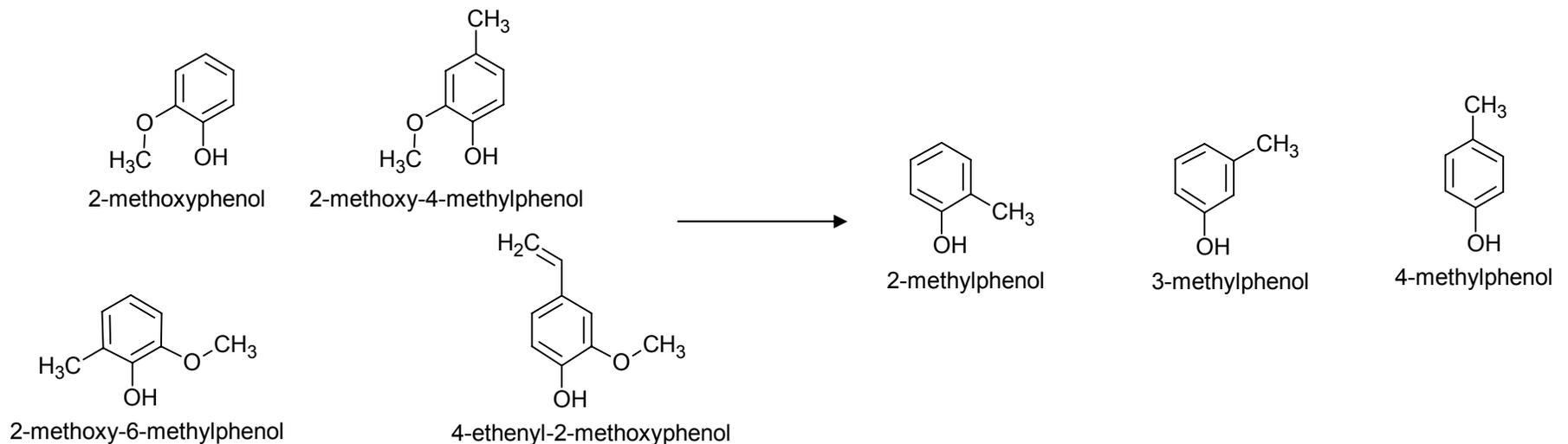
# Water yield

yield [%]



# Chemical composition

- Levoglucosan transformed into
  - Glycolaldehyde, formaldehyde, acetaldehyde, acetic acid and furfural
- Concentration of methoxy substituted phenols decreased
- Concentration of methyl substituted phenols increased



# Conclusions: Bio-oil

- Many challenges including:
  - Scale-up
  - Cost reduction
  - Better oil quality
  - Norms and standards for bio-oil

# Conclusions: catalytic

- TGA not suitable for investigating catalytic pyrolysis of woody biomass
- Possible to use zeolites as heat carriers and catalysts simultaneously
- Easier screening of catalysts by separating the pyrolysis and catalytic upgrading reactors

# Conclusions

- Catalytic upgrading resulted in a less oxygenated bio-oil
- More CO and water formed
- Methoxy phenols transformed into methyl phenols
- Possible to regain acidity and surface area through regeneration of the spent zeolite