



# **Second generation biofuels; Fast pyrolysis liquids**

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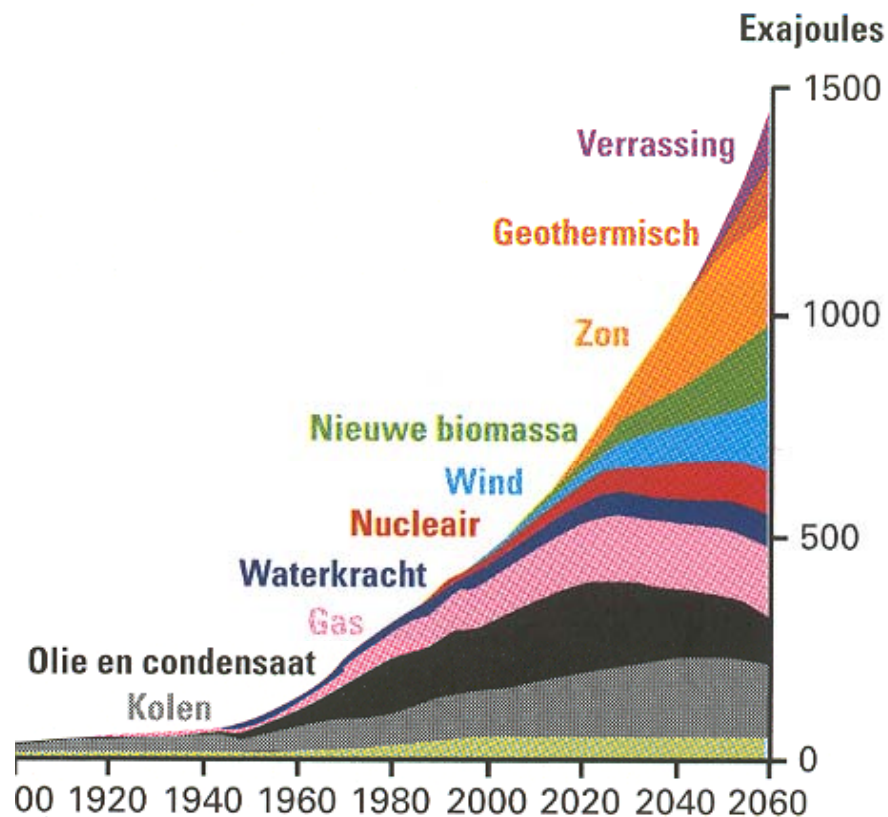
# Outline

- › Introduction
  - Role of biomass
  - Biomass conversion technology
  - Second generation biofuels
- › Fast pyrolysis oil
  - Properties
  - Processes
  - Potential
- › Research example
- › Conclusions





# Role of biomass in energy transitions



Source:  
Shell Sustained Growth  
scenario



# Biomass conversion technology

- › Combustion
- › Gasification
- › Liquefaction
  - Pyrolysis
  - HTU
- › Fermentation
- › Extraction



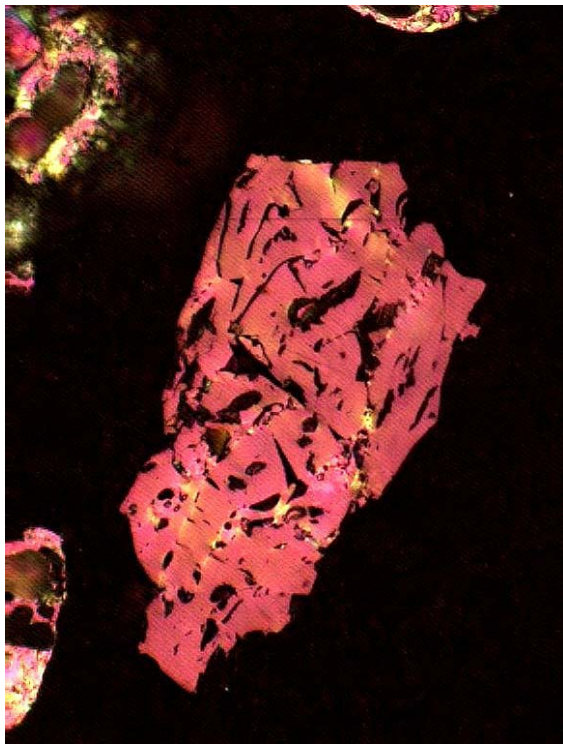


## Second generation biofuels

- › Bioethanol from lignocellulosic biomass
  - › **Pyrolysis oil**
  - › HTU (hydrothermal upgrading)
  - › Syn-gas conversions to FT-diesel, DME, Hydrogen
  - › Hydrocarbons/plant oils from Algae
- 
- › Application of cheap, non-food lignocellulosic biomass



# Fast Pyrolysis



Combustion in the absence of oxygen

Short contacttime in gasphase ( $< 1$  s)

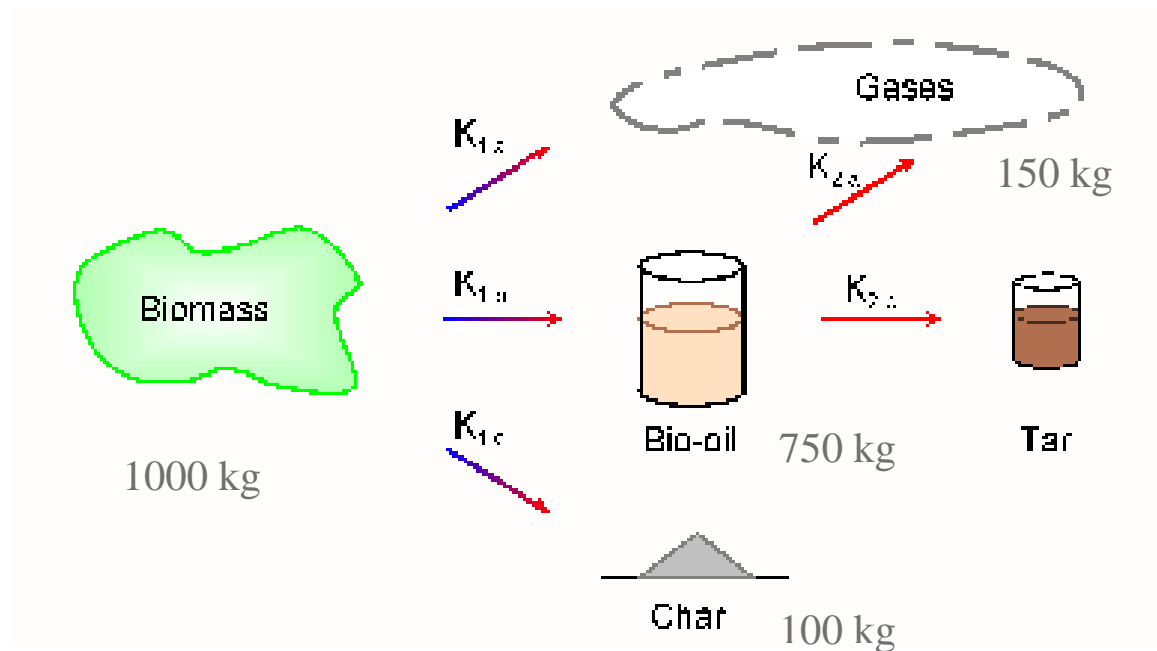
High liquid yields (70+%)

Atmospheric pressure

400 – 600° C



# Fast pyrolysis products



From: <http://www.btgworld.com/>





# Feeds

- › Flexible
  - Woody biomass
  - Waste products
    - Straw
    - Cacao shells
  - Algae
  - Gras
- › Water content < 10 wt%
- › Diameter < 1 cm





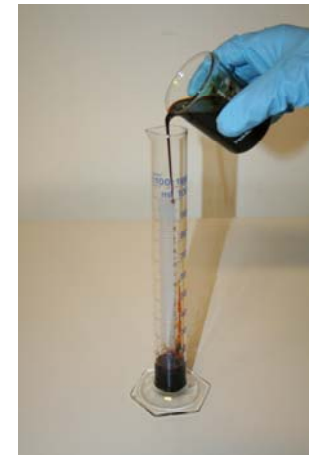
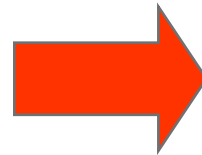


# Typical product properties

- › Oxygen content: 45-50 %
- › pH 2-4
- › Water Content 15-20 wt%
- › Density 1.15 kg/l
- › Caloric value 16-18 MJ/kg
- › Limited storage stability



## Pyrolysis oil versus virgin biomass



### Liquid form of biomass

- Higher energy density (20 versus 4 GJ/m<sup>3</sup>)
- Easier to transport and handle
- Less contaminants (e.g. ash)



# Pyrolysis oil applications

Stand alone  
Boilers

Co-feeding  
Oil refineries

Co-firing  
power  
stations

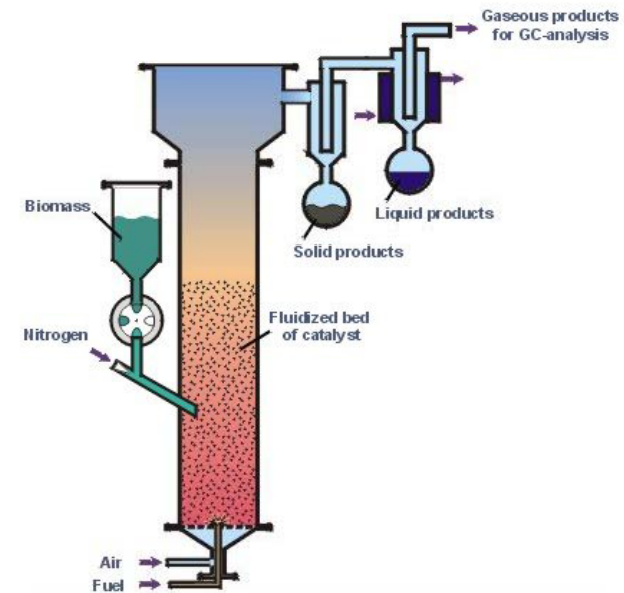
Chemicals

Combustion engines  
Turbines



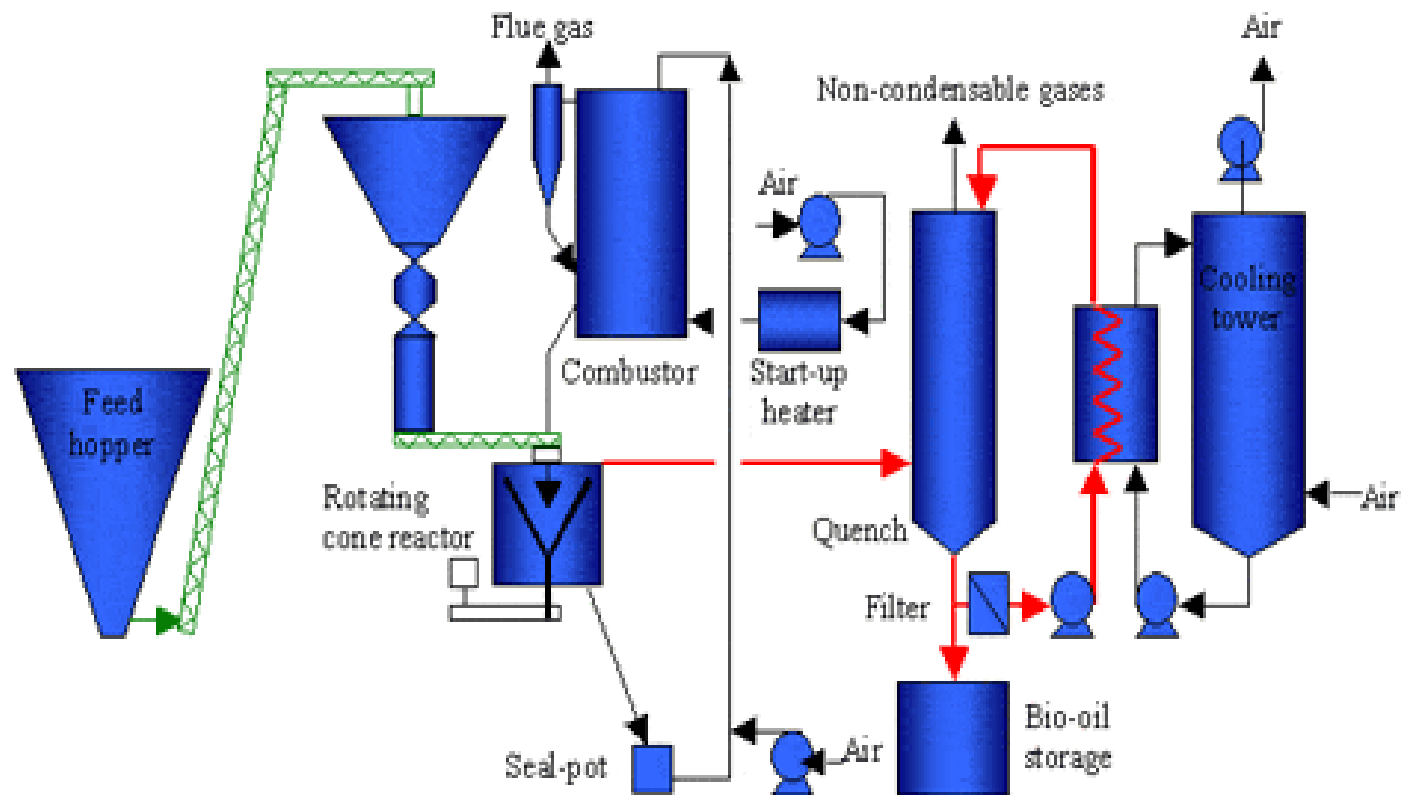
## Available technology

- › Fluidised bed reactors
- › Circulation fluidised bed reactors
- › Vacuum pyrolysis reactors
- › Screw reactors
- › Ablative reactors
- › Rotating cone reactors





## Rotating cone technology





# Rotating cone technology





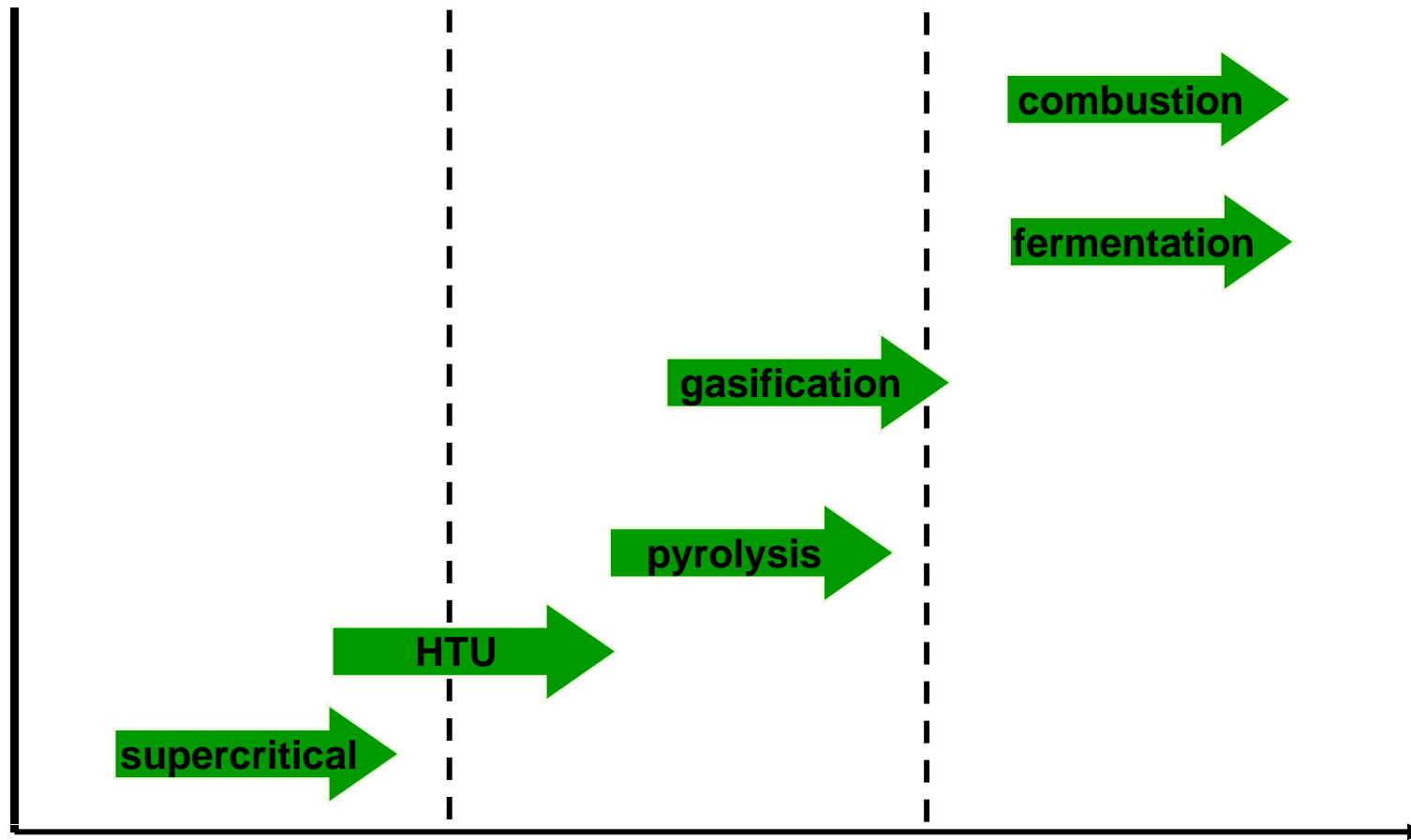


# Technology status

- › Dynamotive
  - 5 t/h Ontario (2004), fluidised bed technology
  
- › BTG
  - 2 t/h Malaysia (2005), rotating cone technology
  
- › Ensys (food flavouring)



# Technology status



R&D

demonstration

Full commercial



# Pyrolysis oil upgrading

- › Extend application range
- › Strategies
  - Physical upgrading
  - Reactive upgrading



## **UOP to Develop Second-Generation Biofeedstock Technology Under U.S. Department of Energy Award**

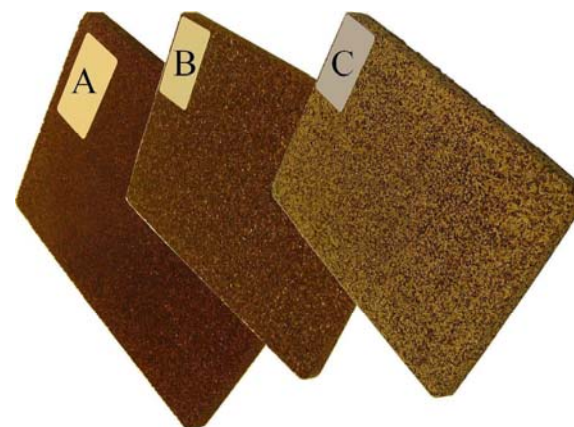
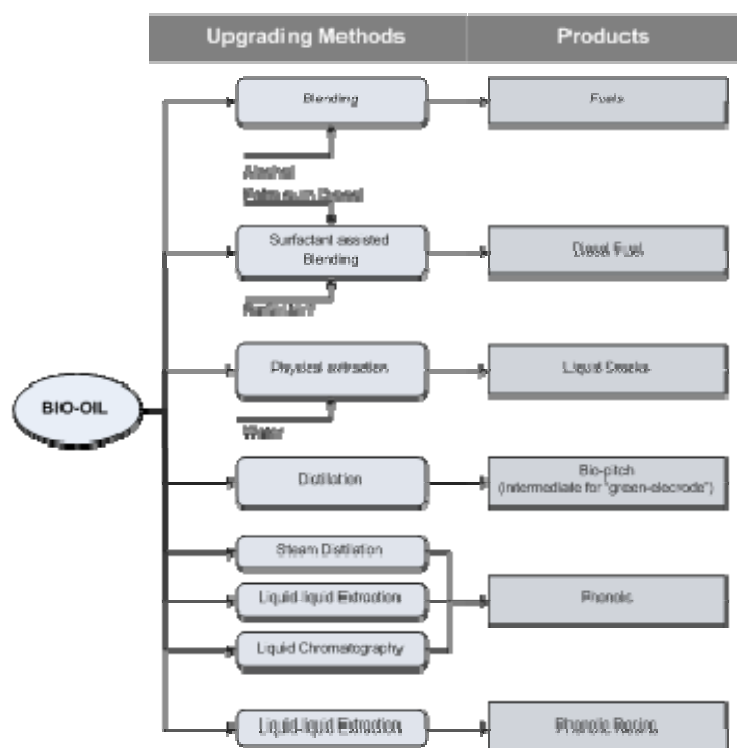
October 28, 2008 10:00 AM ET

**UOP and partners will develop technology to improve the stability of pyrolysis oil to ensure its viability as a source for power and transportation fuels**

DES PLAINES, Ill., Oct. 28 /PRNewswire/ -- UOP LLC, a Honeywell [HON](#) company, announced today that it was awarded a \$1.5 million grant from the U.S. Department of Energy (DOE) to develop economically viable technology to stabilize pyrolysis oil from second generation biomass feedstocks for use as a renewable fuel source.



# Physical upgrading

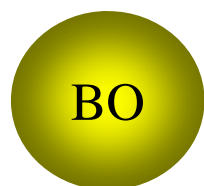


Available in 4oz., 16oz., & 4 Gallon





# Chemical upgrading



Hydrodeoxygenation

Fuel/Chemicals

Steam Reforming

Fuel/Chemicals

Acid recovery using  
calcium salts

Chemicals

Catalytic upgrading  
using zeolites

Fuel/Chemicals

Reactive blending  
with alcohols

Fuel





## Research example: hydrodeoxygenation



- › Reduction of acid content
- › Stabilization
- › Increases energy content (lowering oxygen content)
- › Formation of a two phase system after reaction, easy separation of water



## Objective RUG upgrading activity

- › Determine the technical feasibility of upgrading pyrolysis oil to a liquid biofuel by catalytic HDO

### Approach

- **Exploratory catalyst screening studies using pyrolysis oil**
- Model component studies with selected catalyst
- Catalyst design
- **Process research and development.**
- **Engine tests with HDO oil**



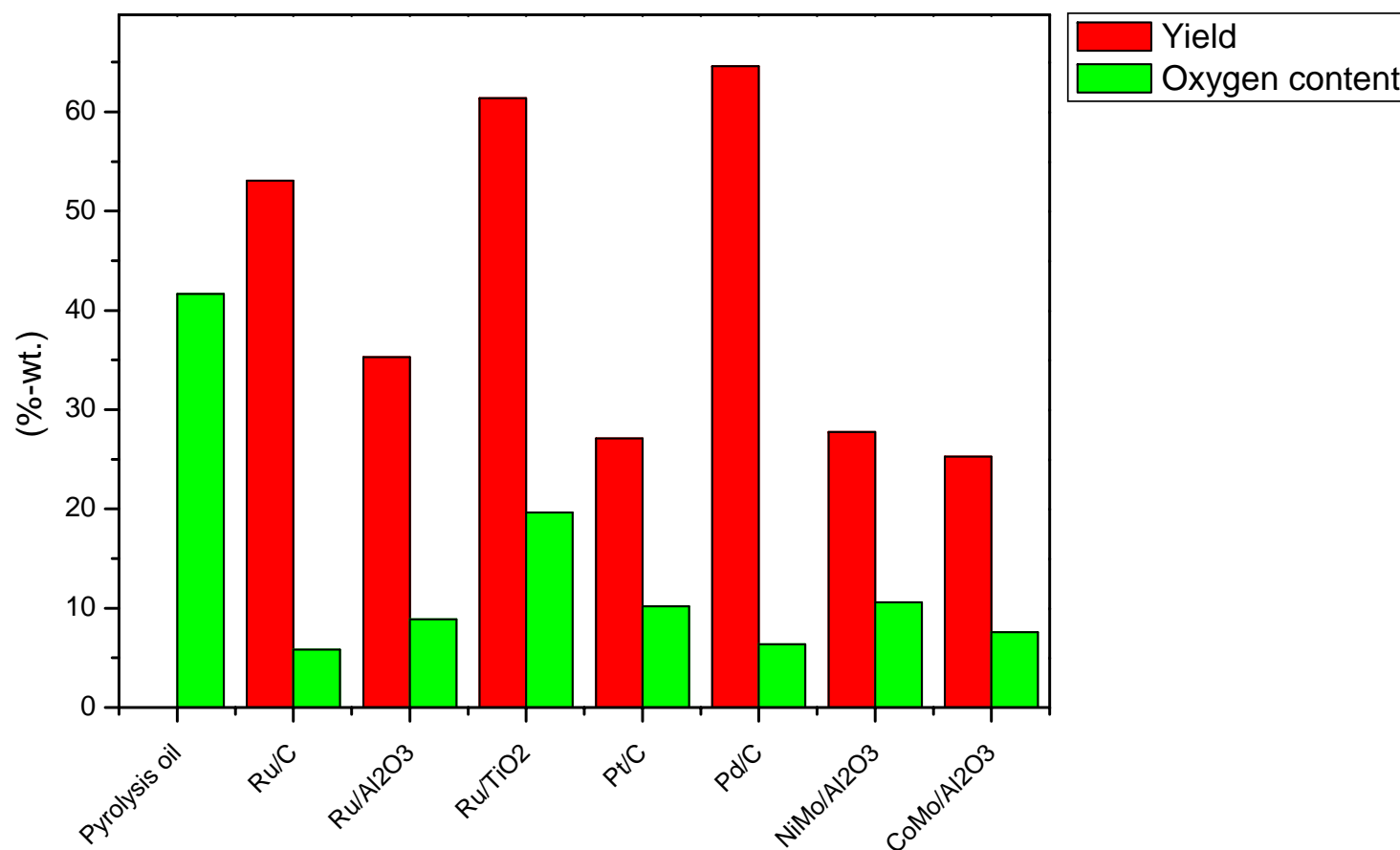
## Visual appearance



Ru/C 5%, 350 °C  
200 bar H<sub>2</sub>,  
Reaction time of 4h.



## Catalyst studies using Pyrolysis oil



Catalyst screening in semi-Batch system at 350 °C and 200 bar of H<sub>2</sub> for 4h.

Wildschut, J., Heeres, H.J., Catalyst Screening for the Hydrodeoxygenation of Pyrolysis Oil., in preparation.



# HDO oil properties

Property	value
Density (kg/l)	0.8 - 0.9
Water content (%-wt)	1-2
Acidity (pH)	5-6
Flash point (°C)	35- 39
Elemental composition (%-wt)	
C	~85
H	~10
O	~5
Heating value (MJ/kg) LHV	40

350 ° C and 200 bar for 4h with a Ru/C catalyst.



# Engine tests

- Hatz engine
- 5 Watt
- Minimal modifications







## Engine tests

Gas	Diesel	HDO oil
O <sub>2</sub> (%)	12.8	12.4
CO (ppm)	<b>643</b>	<b>1146</b>
NO (ppm)	<b>723</b>	<b>371</b>
NO <sub>2</sub> (ppm)	<b>21</b>	<b>7</b>
NO <sub>x</sub> (ppm)	<b>744</b>	<b>378</b>
SO <sub>2</sub> (ppm)	0	0
CO <sub>2</sub> (%)	6	6.3



Red numbers indicate significant differences



## Results engine tests

- Higher CO in exhaust compared to diesel
- Lower NO<sub>x</sub> in exhaust compared to diesel
- Carbon deposition of the atomizer



## Conclusions

- › Fast pyrolysis technology is entering the commercialisation stage
- › Substantial R&D activities ongoing on upgrading to extend application range
- › Catalytic hydrotreatment promising option to obtain hydrocarbon like components to be used for
  - Transportation fuels
  - Co-feeding to existing refineries



# Acknowledgement

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