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Bio-Char II: Production, Characterization and Applications

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9-17-2019

### **Biochar - just a black matter is not enough!**

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Fabian Stenzel

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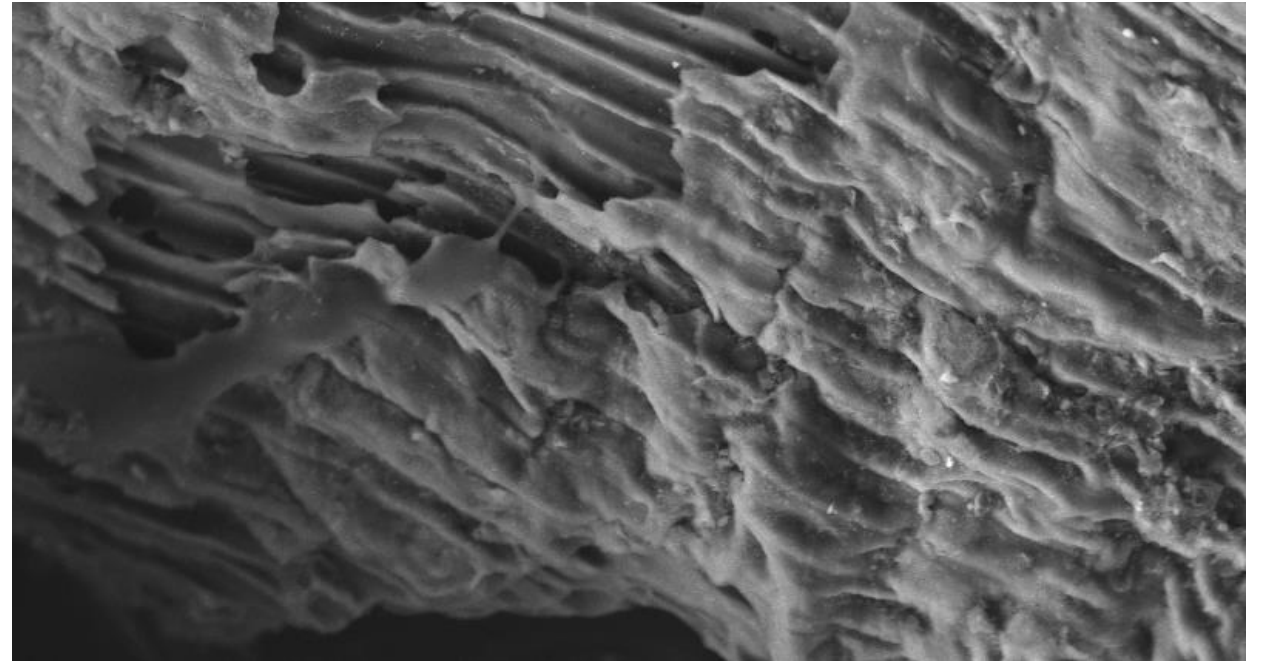
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# BIOCHAR – JUST A BLACK MATTER IS NOT ENOUGH!

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Prof. Dr. Andreas Hornung  
Director of institute branch Fraunhofer UMSICHT  
Sulzbach-Rosenberg, Germany



# General thoughts!

530 billion tonnes, 82 percent of all C in biomass (650 billion tonnes) on earth is stored in wood, the rain forest is storing as much as people burn in 10 years from various sources.

1/3 of world antropogenic CO<sub>2</sub> emissions are taken up every year by world wide forests.

But, CO<sub>2</sub> is also again released by natural processes

Carbon dioxide, naturally captured in wood can be captured as carbon in char.

Feedstocks should show a wider range than wood only, residues from agriculture or sewage sludge and digestates as well as resdiues from modern processes producing ethanol from straw as well as macro algae

Capturing the carbon as a stabile bio-coal or charcoal as single product is just too expensive.

Side products are required to close the bill.

Those products can be liquids, in best case fuels and green hydrogen.

# What is biochar?

## Definition

- Carbonaceous material
- Consists almost of carbon and ash (depends on feedstock)
- oxygen and hydrogen were depleted
- Porous surface structure was formed
- Produced by thermochemical conversion with the absence of oxygen
- Derived from biomass
- Intent to be applied in soil
- Further application options are investigated too



# Feedstock

Any kind of biogenic material



Biowaste



Garden- and greenwaste



Digestate



Manure



Straw



Hay



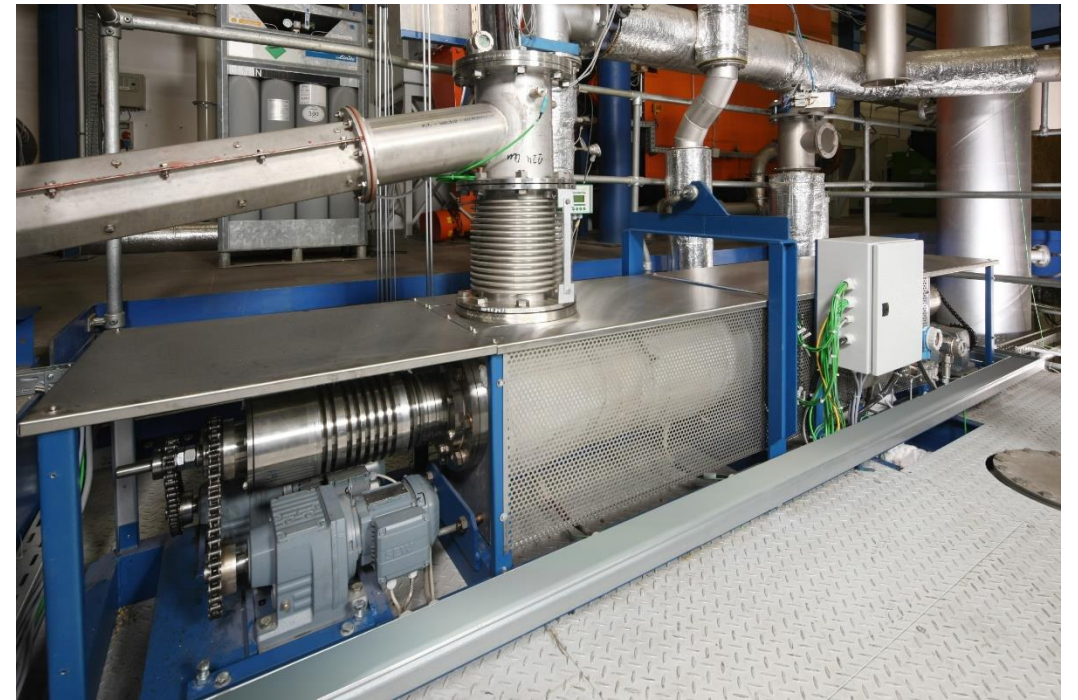
(Residual) wood



Skins of citrus fruits

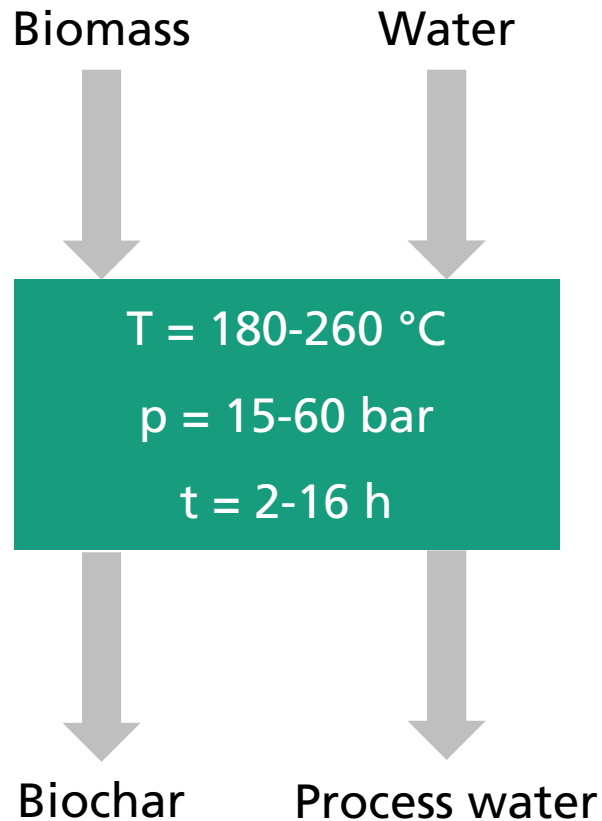
# From charcoal to biochar

## From history to modernity



# Processes

## Hydrothermal Carbonisation (HTC)



- Feedstock biomass with high water content possible (no drying required)
- Biochar with high content of oxygen and hydrogen, but less PAH content
- Biochar has to be dried
- Large quantities of process water containing COD

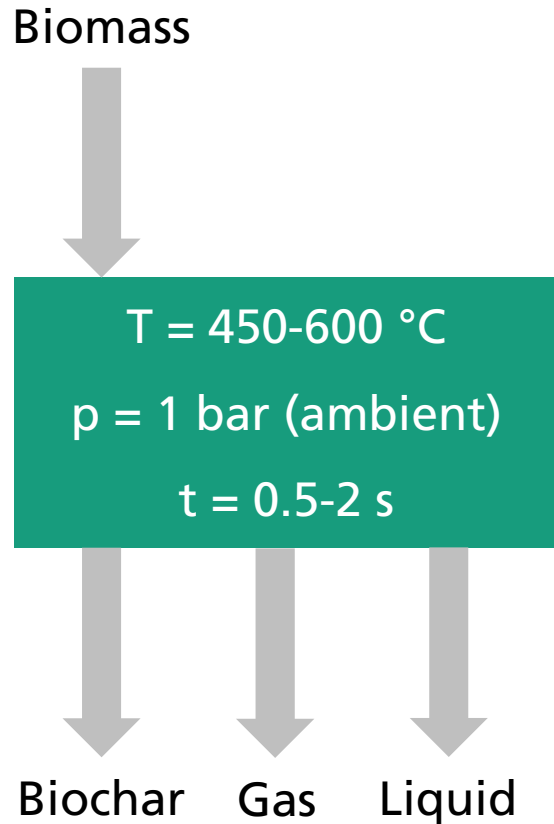






# Processes

## Fast pyrolysis



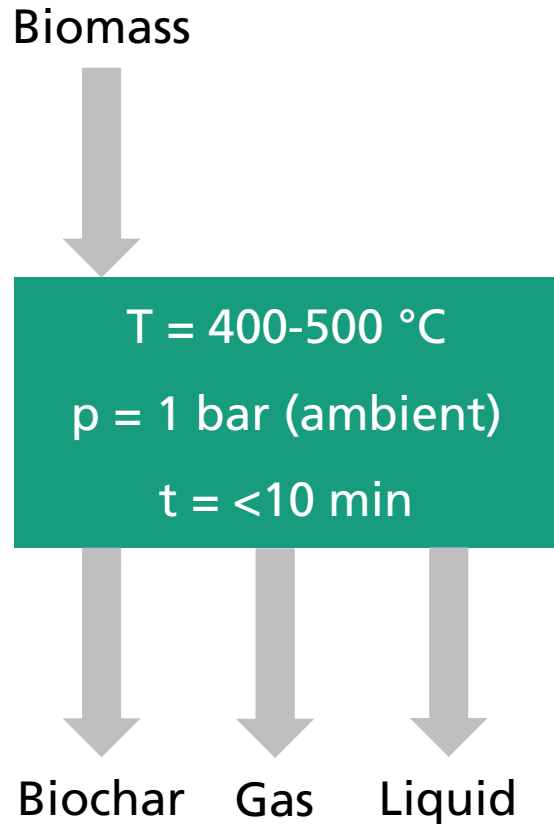
- Absolute dry and finely grounded feedstock is required
- Biochar with high content of oxygen and hydrogen
- High acidity of the oil as well as high water and oxygen content
- Lowest biochar yield compared to slow and intermediate pyrolysis





# Processes

## Intermediate pyrolysis



- Feedstock with a certain percentage of moisture is possible (up to 40%)
- Coarse, shredded, chopped or briquetted material
- Biochar with low content of oxygen and hydrogen
- Biochar yield is between slow and fast pyrolysis

**PYREG**  
CARBON TECHNOLOGY  
SOLUTIONS

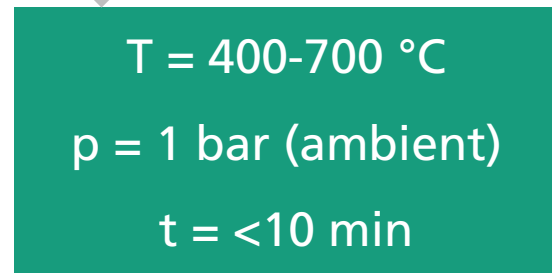
1968 • 2018  
**SEA MARCONI**  
cinquant'anni di energia, innovazione, ambiente

**WSE**  
BIOENERGY

# Processes

## Intermediate pyrolysis combined with post reforming (Thermo-Catalytic Reforming TCR<sup>®</sup>)

Biomass



Biochar



Gas



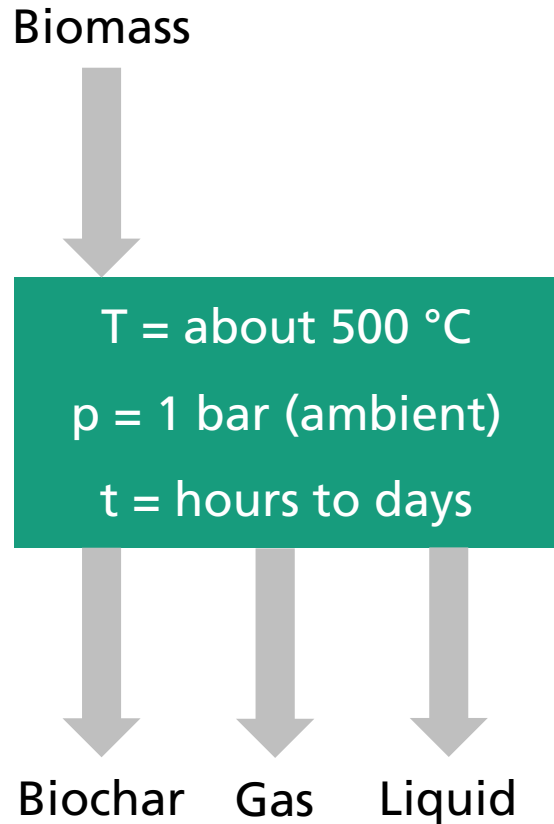
Liquid

- Feedstock with a certain percentage of moisture is possible (up to 40%)
- Coarse, shredded, chopped or briquetted material
- Biochar with very low content of oxygen and hydrogen
- Almost free of PAHs
- Oil has very low acidity as well as in water and oxygen content
- Biochar yield is between slow and fast pyrolysis



# Processes

## Slow pyrolysis



- Feedstock is shaped from briquette size to whole logs
- Usual process for charcoal production
- Pyrolysis vapors are almost used to heat the process
- Liquid products are acetic acid and alcohols
- Highest biochar yield compared to slow and intermediate pyrolysis



Degussa process

# Processes

## Gasification

Biomass



T = about 500 °C  
p = 1 bar (ambient)  
t = hours to days



Gasification  
residue



Gas

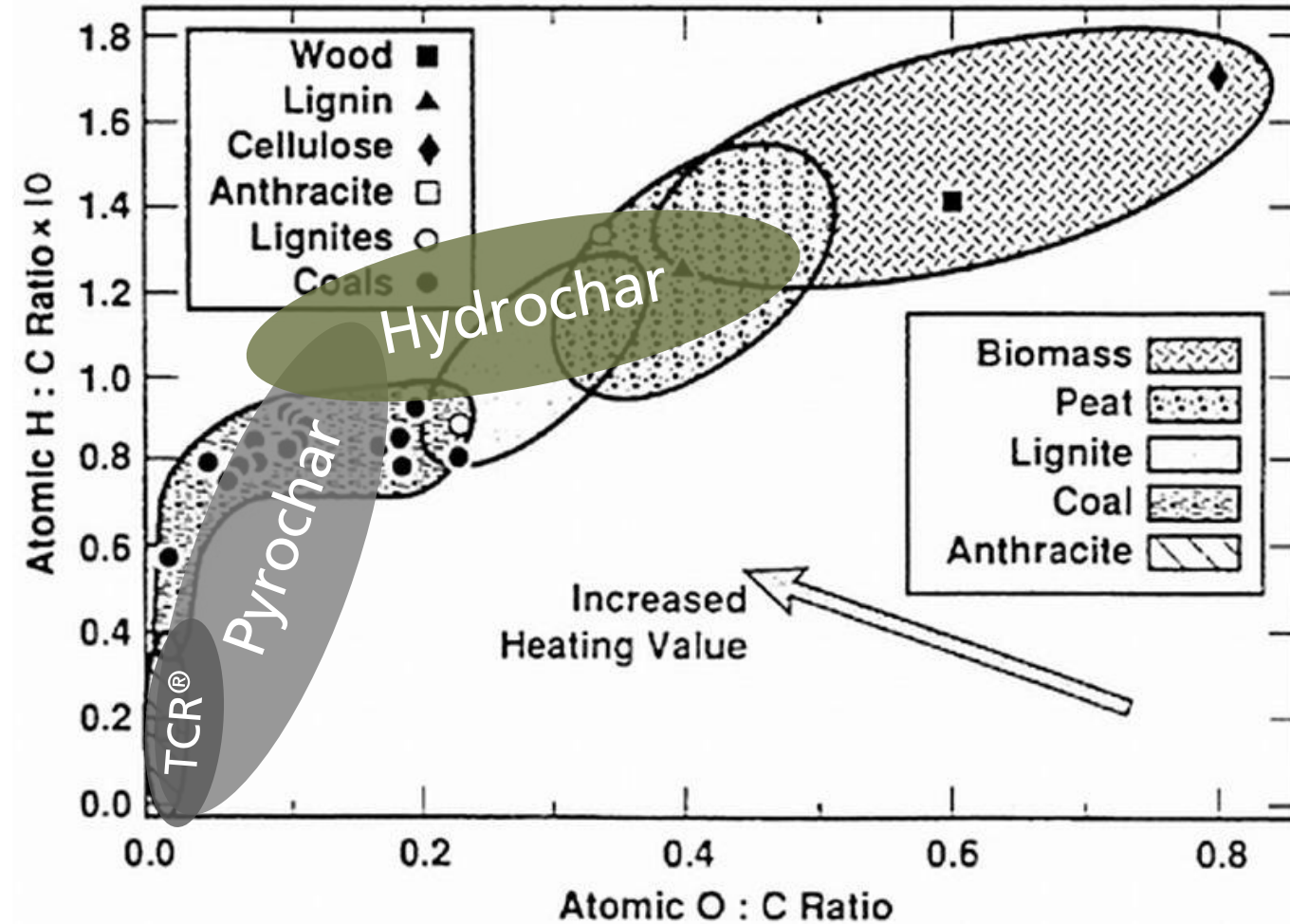
- Main product is the hydrogen and carbon monoxide rich gas
- Depending on gasification agent tar content can increase up to  $100 \text{ g/m}_N^3$
- Process is optimized to reduce the carbon content in the solid gasification residue
- Gasification residue contains often higher concentration of PAHs (no biochar)



\*insolvent

# Properties

## Degree of Carbonisation



# Properties

## Contaminants – polyaromatic hydrocarbons (PAH)

- PAH formation during pyrolysis by two fundamental mechanisms
  1. Pyrosynthesis:  
gaseous hydrocarbon radicals generated  $>500\text{ }^{\circ}\text{C}$  undergo reactions to form polyaromatic ring structures
  2. Low temperature formation:  
through condensation, carbonization and aromatization at  $<600\text{ }^{\circ}\text{C}$
- separation of gases from solids at high temperatures
- Controlled processes are needed

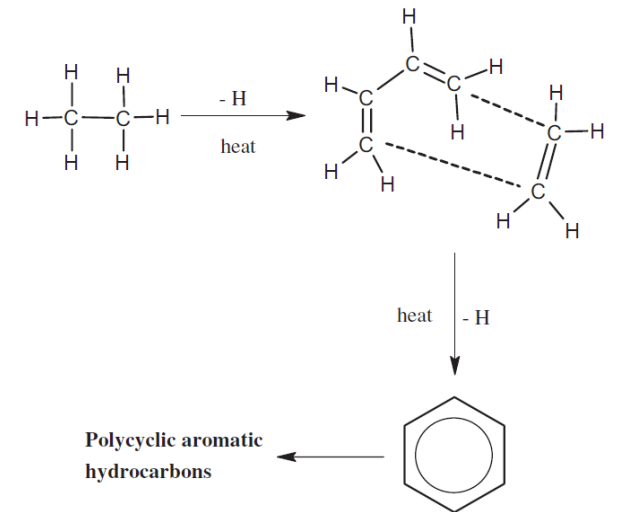
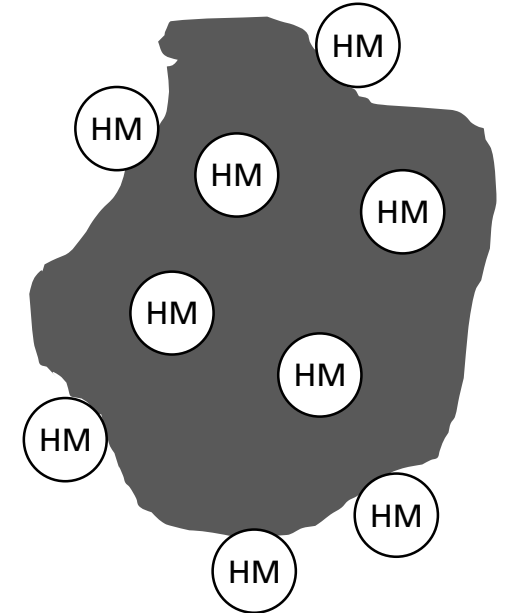


Fig. 2. Pyrosynthesis of PAHs starting with ethane.

# Properties

## Contaminants – heavy metals

- More than 20 different kinds of heavy metals found in nature
- A few of them are toxic to human health (e.g. lead, cadmium, arsenic and mercury)
- Heavy metals are a part of the feedstock
- depending on the material different quantities are possible
  - Low quantities in biochar derived from wood
  - High quantities in biochar derived from sewage sludge
- Most of the heavy metals are concentrated during the conversion process
- Depending of process temperature some heavy metals are transferred into the gasphase, e.g. mercury
- Heavy metals are also found on the surface of biochar by adsorption effects



# Properties

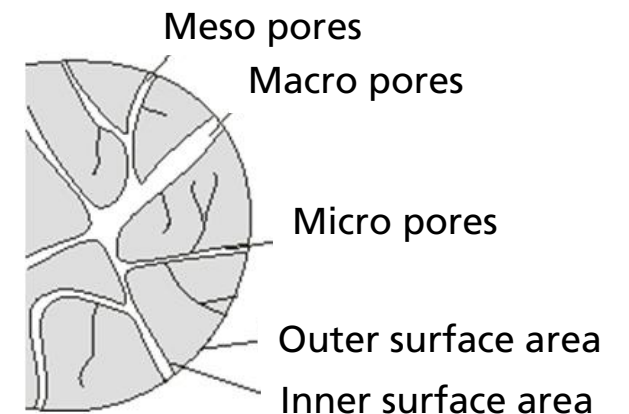
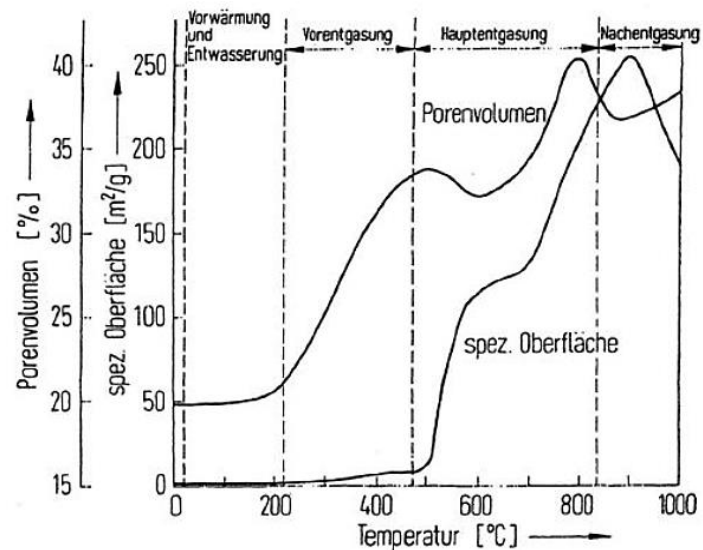
## Surface structure

Influencing parameters for the quality of active carbon:

- Ash content (as low as possible)
- Volatile components (favorable between 8-15 %)
- Pyrolysis conditions (temperature)

Pore classification according to International Union of Pure and Applied Chemistry (IUPAC):

- Macro pores ( $dP > 50 \text{ nm}$ )
- Meso pores ( $dP = 2-50 \text{ nm}$ )
- Micro pores ( $dP < 2 \text{ nm}$ )

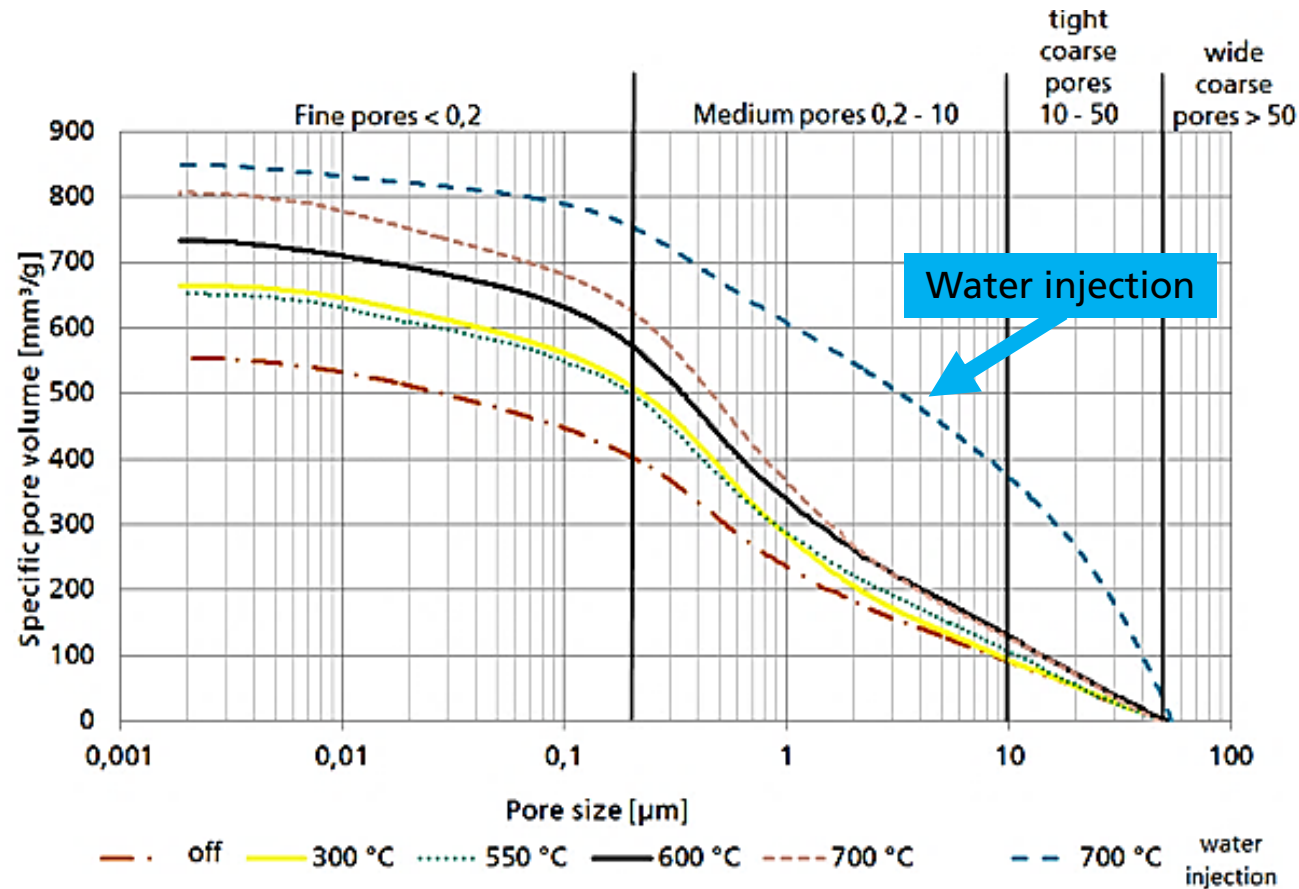


Sources: Benthous, F. - *Rohstoff Kohle. Eigenschaft, Gewinnung, Veredelung 1978*, Elke Heitling et.al. – Adsorbentien/Poren, [www.chemgapedia.de](http://www.chemgapedia.de) (modified)



# Modification examples

## Pore size distribution



Pore size distribution of digestate TCR<sup>®</sup>-biochar by various reforming temperatures

# Application

## Soil conditioner – legal regulation

- Regulations on European and country level
  - Biochar is not listed as a fertilizer product in the European fertilizer ordinance (amended in 2019)
  - Recycling products like biochar, ashes and struvite will be added by the end of 2019
- Restrictions in feedstock, e.g.
  - Germany: only untreated clean wood
  - Italy: agricultural residues (plant material)
- Requirements to nutrients content
- Limits for organic and inorganic pollutants

# Application

## Soil conditioner – International Biochar Initiative (IBI)

- IBI was formed in 2006, Philadelphia, PA.
- The vision: One billion t of biochar produced within 50 years.
- Standardized Product Definition and Product testing Guidelines for Biochar that is used in Soil are developed in 2015
- Requirements to biochar are defined to ensure the quality for use in soil
  - Test category A – basic utility properties
  - Test category B – toxicant assessment
  - Test category C – advanced analysis and soil enhancement properties
- Product classification:  
Class 1: >60%, Class 2: <60% and 30%, Class 3: <30 % ( $C_{org}$ )
- After certification process is successfully passed, the IBI Certified™ biochar seal is valid for one year
- Implemented in United States and Canada only



# Application

## Soil conditioner – European Biochar Certificate (EBC)

- Certification is optional in Europe and mandatory in Switzerland
- Guidelines for the European Biochar Certificate from 2019
- Requirements to biochar are defined to ensure the quality for use in soil
  - Test category A – basic utility properties
  - Test category B – toxicant assessment
  - Test category C – advanced analysis and soil enhancement properties
- Guidelines also for production of biochar as feed additive
- Product classification: Basic, Premium and Fodder (different thresholds for pollutants)
- Only biomass from Europe can be used



# Application

## Soil conditioner – Australien New Zealand Biochar Initiative (ANZBI)

- ANZBI was formed in 2017, Murwillumbah, N.S.W.
- Australian Biochar for Soils Standard was developed in 2019 (draft version)
- Testing criteria quite similar to IBI standards
- Standard based on:
  - Australian Compost Standard AS4454-2012
  - European Biochar Certificate Guidelines 2019
  - IBI Standardized Product Definition and Product Testing Guidelines for Biochar that is used in Soil
- Product classification:
  - High Carbon Biochar (HCB)  $>70\% C_{org}$
  - Medium Carbon Biochar (MCB)  $50-70\% C_{org}$
  - Low Carbon Biochar (LCB)  $30-55\% C_{org}$
  - Partially Combusted Organic Material (not biochar)  $<30\% C_{org}$
- Developed for Australia and New Zealand



**AUSTRALIA NEW ZEALAND**  
**BIOCHAR INITIATIVE** inc. **ANZBI**

# Application

## Feed additive – Good Manufacturing Practice (GMP+)

- GMP+ is a Feed Safety Assurance (FSA) certification process
- The whole production chain needs to be GMP+ certified:  
feedstock → conversion → storage → transport
- There is an optional “Feed Responsibility Assurance” (GMP+ FRA) as additional sustainability certification
- Standards from existing initiatives are applied, e.g. Association Food without Genetic Engineering (VLOG e.V.)
- No feedstock restrictions by certification body
- all commercial chars certified by GMP+ and used as feed additive derived from untreated wood



# Application

## Activated carbon

- Requirements are listed in European standards, e.g.
  - EN 12903 – Powdered Activated Carbon
  - EN 12915 – Granular Activated Carbon
- Any carbon containing feedstock is possible, including coconut shells, wood, peat and coal
- Thresholds for water and ash content are applied
- For the application in water treatment, the content of water extractible substances (heavy metals and PAHs) is limited too



# Application

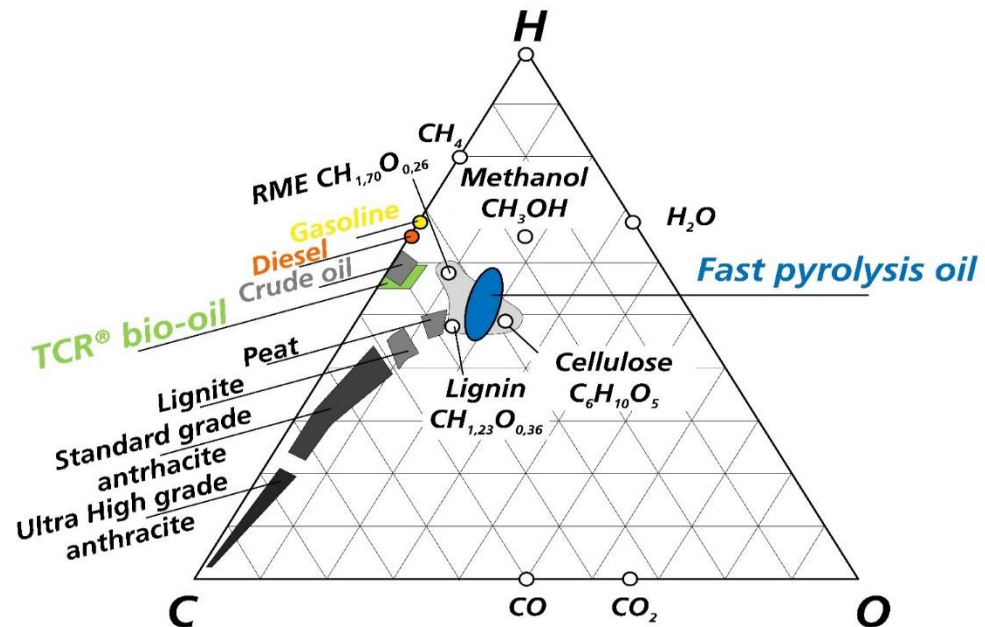
## Market survey

- Price for biochar as soil amendment ranges from 200-2,000 €/t depending on quality and market situation
- European market size in 2018 was 0.31 billion US\$, forecast for 2023 is 0.59 billion US\$
- Global market size in 2018 was 1.48 billion US\$, forecast for 2025 is 3.82 billion US\$
  
- Typical price for biochar as feed additive: 1,000 €/t, depending on quality and market situation the price ranges from 500-1,300 €/t
  
- Activated carbon is available on the market in a range from 700-1,800 €/t
- The total market value worldwide for activated carbon was estimated on 2.35 billion US\$ in 2017



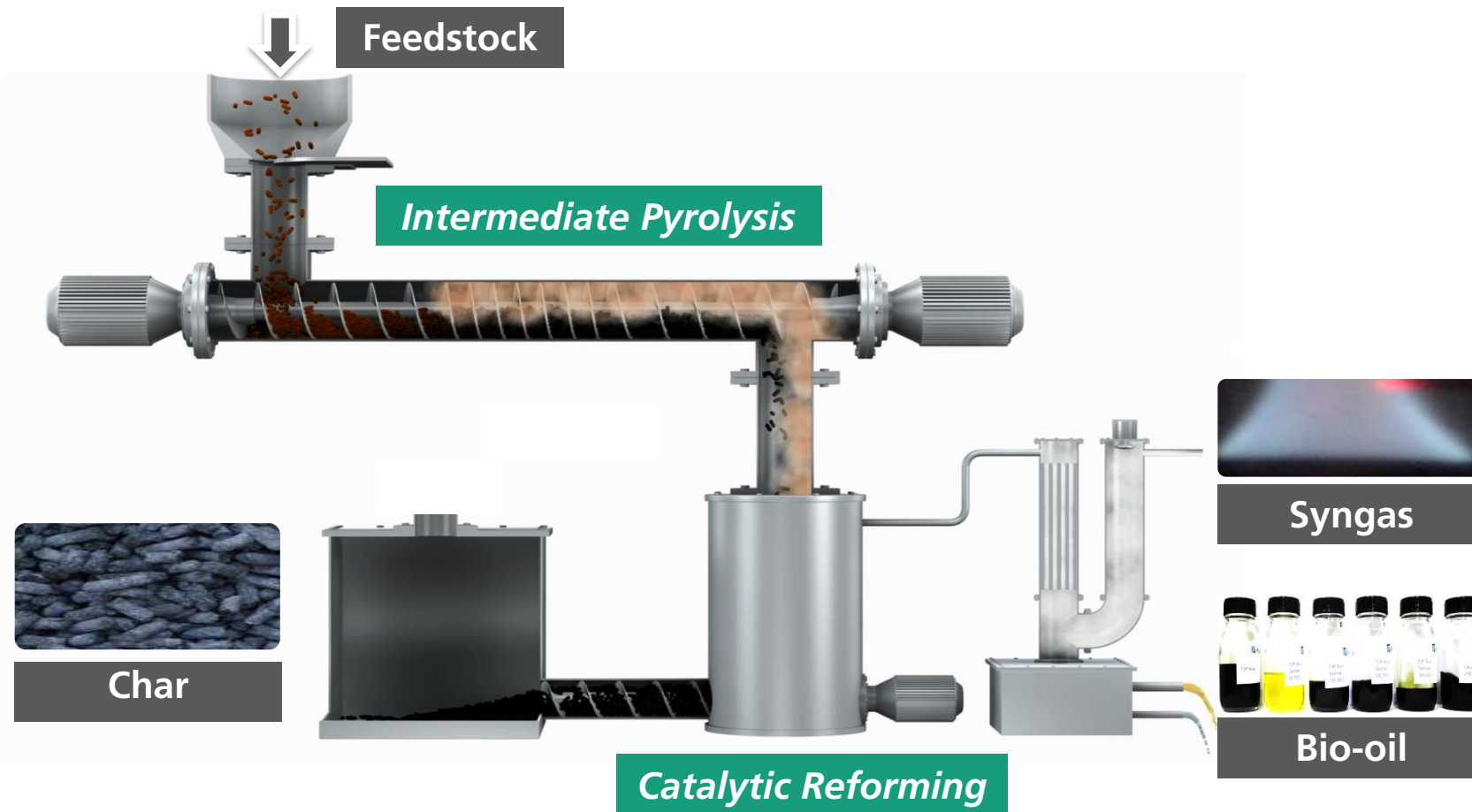
# Sustainable transportation fuels by co-processing of TCR<sup>®</sup>-bio-oil in conventional petroleum refineries, production of hydrogen and biochar

- Comparable to crude oil
- High carbon content
- Low water content
- Low total acid number
- Miscible with fossile fuels and biofuels
- High heating value
- Anthracite char



Source: [1] [2]

# The Thermo-Catalytic Reforming (TCR<sup>®</sup>) technology



# High quality of all product fractions

## BIO-OIL



### High quality, engine-ready

- Miscible with common fuels
- Engine application also as blended fuel
- No tar issues
- High calorific value
- Low acid number

## SYNGAS



### Engine-ready gas

- Tar and dust free syngas
- Direct engine-ready
- adjustable hydrogen content
- practically free of aromatic-compounds

## BIOCHAR



### Transportable and storable biochar

- meets nutrient requirements and specifications of PK fertilisers
- High soil stability
- Very low H and O content
- High calorific value
- Significant ash content

# Conversion of Sewage Sludge

## Analytics of educts and products

### SEWAGE SLUDGE



|                  |            |
|------------------|------------|
| C                | 26,2 m%    |
| H                | 4,3 m%     |
| N                | 3,7 m%     |
| S                | 0,6 m%     |
| O (Diff.)        | 27,3 m%    |
| Ash              | 37,9 m%    |
| H <sub>2</sub> O | 10,7 m%    |
| LHV              | 12,2 MJ/kg |

### EDUCT

### BIO-OIL



|           |               |
|-----------|---------------|
| C         | 77,0 m%       |
| H         | 7,08 m%       |
| N         | 8,53 m%       |
| S         | 1,02 m%       |
| O (Diff.) | 6,3 m%        |
| TAN       | 4,45 mg KOH/g |
| LHV       | 33,8 MJ/kg    |

### PRODUCTS

### SYNGAS



|                               |                        |
|-------------------------------|------------------------|
| H <sub>2</sub>                | 39 v/v%                |
| CO                            | 10 v/v%                |
| CO <sub>2</sub>               | 22 v/v%                |
| CH <sub>4</sub>               | 8,7 ± 1 v/v%           |
| C <sub>x</sub> H <sub>y</sub> | 1,5 ± 1 v/v%           |
| LHV                           | 17,7 MJ/m <sup>3</sup> |

### CHAR

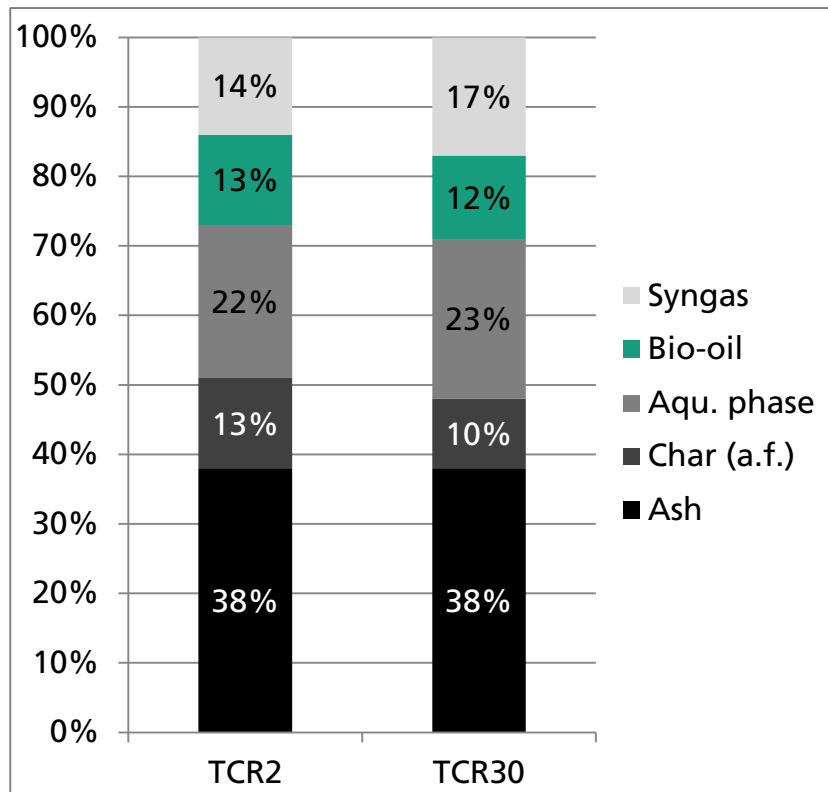


|           |           |
|-----------|-----------|
| C         | 23,8 m%   |
| H         | 0,7 m%    |
| N         | 1,9 m%    |
| S         | 0,7 m%    |
| O (Diff.) | 1,2 m%    |
| Ash       | 74,1 m%   |
| LHV       | 9,0 MJ/kg |

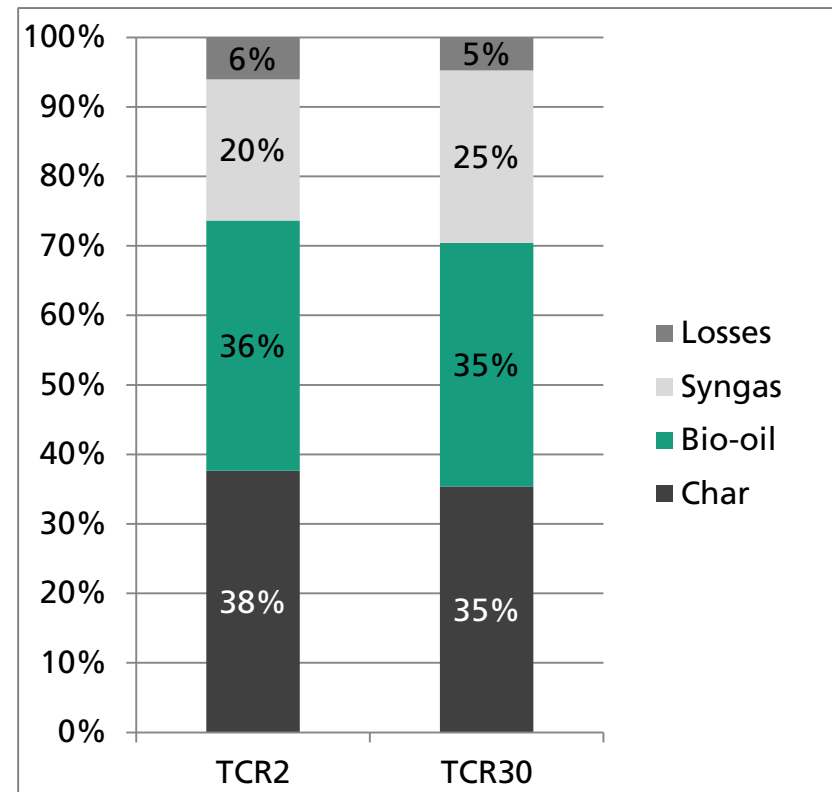
# Thermo-Catalytic Reforming TCR<sup>®</sup>

## Energy and Mass Balance (for sewage sludge)

### MASS BALANCE



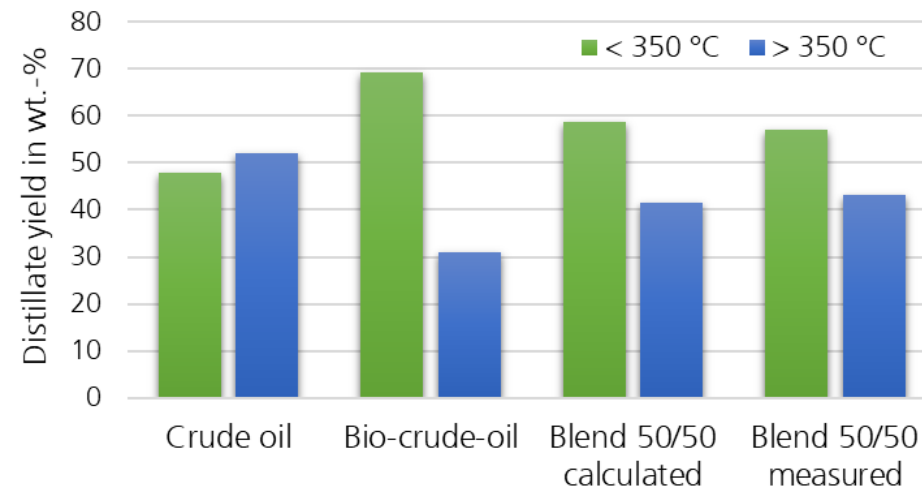
### ENERGY BALANCE



# Sustainable transportation of fuels by co-processing of TCR<sup>®</sup>-bio-oil in conventional petroleum refineries

## Distillation summary for crude oil and TCR<sup>®</sup>-bio-crude-oil

- More atmospheric distillable compounds in bio-oil than in the used crude oil
- Distillation results are comparable to calculated distributions (blend 50:50)
- Hydrotreatment removes 99.99 % of sulfur content
- No polymerization or coking during the upgrade



# Thermo-Catalytic Reforming TCR<sup>®</sup>

Level of development: 2017



Scale Up x10

## TCR300

### Demonstration

Operational capacity: 300 kg/h

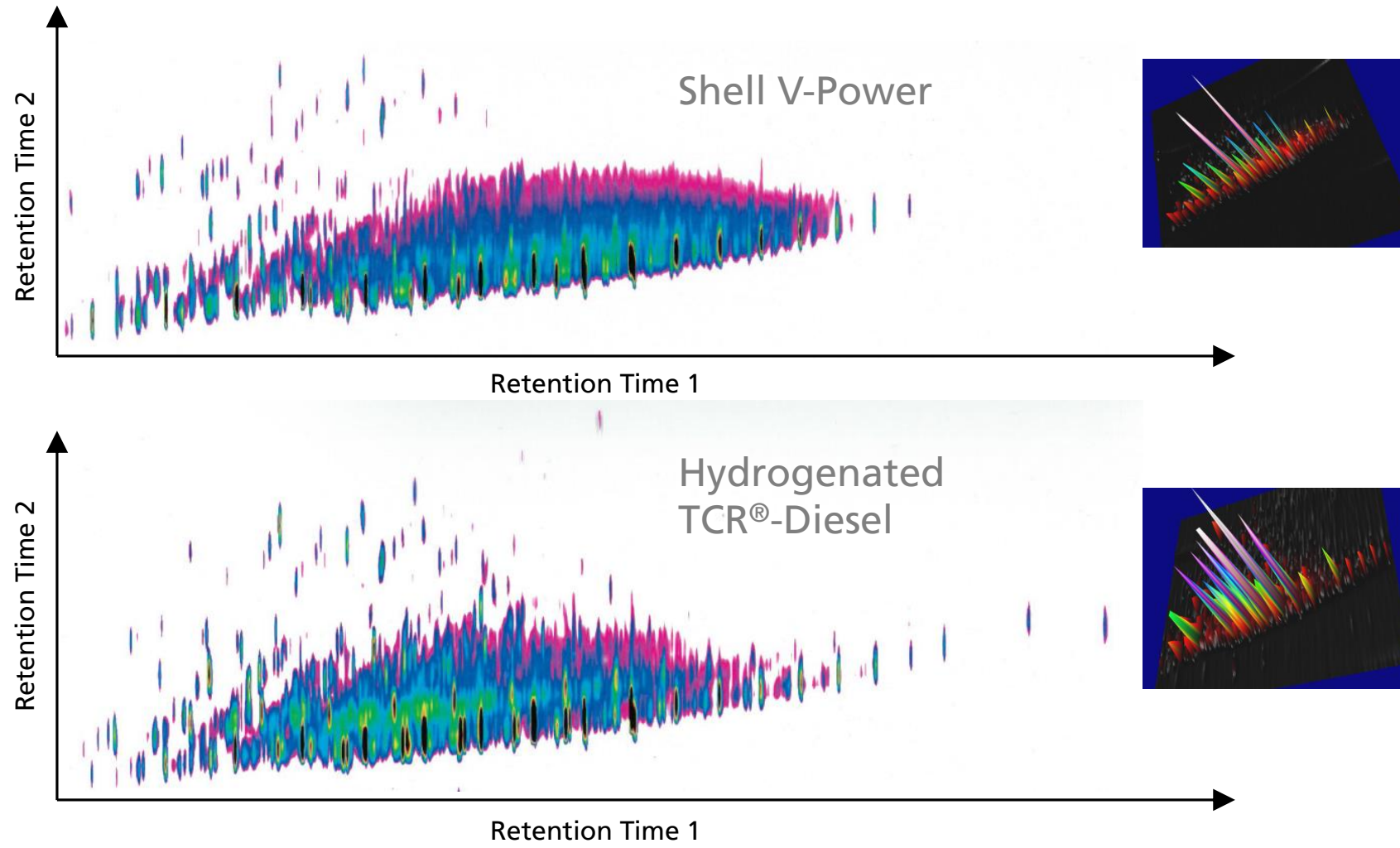
Heat Source: flue gas

Purpose: scale-up, sludge treatment



# TCR<sup>®</sup>-Fuel

## Spectra of Diesel: Shell V-Power vs. TCR<sup>®</sup>-Diesel





# Product application

## Pre-commercial demonstrator within ToSynFuel-project



# Conversion – To-Syn-Fuel

## Demonstration of Waste Biomass to Synthetic Fuels

**2synfoel**

Turning sewage sludge into fuels and hydrogen



Budget: 14,5 Mio. €

Partner:



**FlexJet:**  
Sustainable Jet Fuel from Flexible Waste Biomass



©Ingenieur.de

Start: May 2018 (Horizon 2020)

13 partners

13,4 Mio. € (10 Mio. € funding)

Content: TCR@500 for the production of 1.200 tons green jet fuel

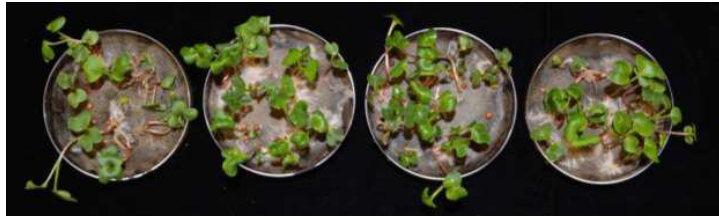
# Thermochemical Gasification



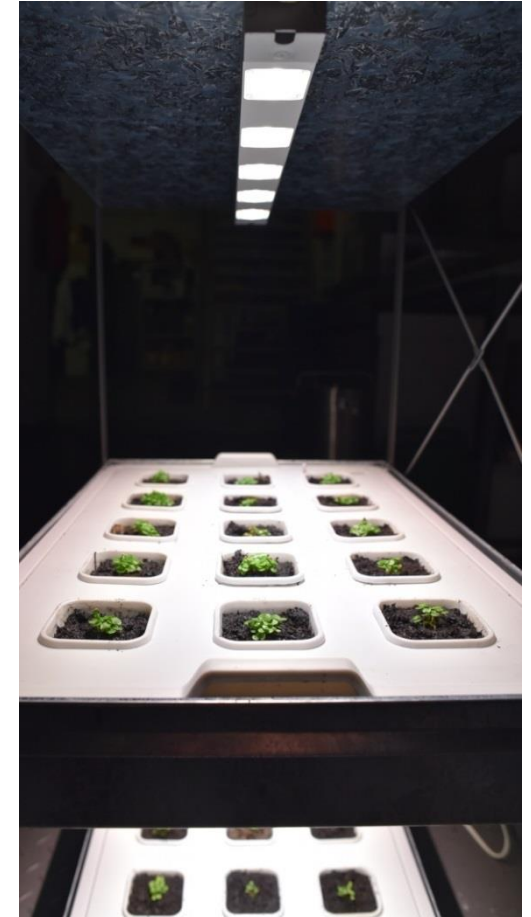
## Thermochemical Gasification

- Char from Sewage Sludge treated by TCR has been applied.
- No tar formation in up-draft gasification
- The phosphate rich ash stays as a powder.
- Plants can take up 80% of this phosphate without further treatment of the ash.

# Application – Biochar/Ash



Germination test on biochar-based planting substrate



Pot trials with lamb's lettuce and rocket

| Sewage Sludge |                   | Digestate      |                   | Brewer Spent Grain |                   | Wood           |                   |
|---------------|-------------------|----------------|-------------------|--------------------|-------------------|----------------|-------------------|
| <b>C</b>      | <b>22.2 wt.-%</b> | <b>C</b>       | <b>64.0 wt.-%</b> | <b>C</b>           | <b>72.6 wt.-%</b> | <b>C</b>       | <b>89.8 wt.-%</b> |
| H             | 0.9 wt.-%         | H              | 1.0 wt.-%         | H                  | 0.1 wt.-%         | H              | 2,2 wt.-%         |
| N             | 2.0 wt.-%         | N              | 1.4 wt.-%         | N                  | 4.6 wt.-%         | N              | 0.3 wt.-%         |
| S             | 1.0 wt.-%         | S              | 0.5 wt.-%         | S                  | 0.4 wt.-%         | S              | 0.1 wt.-%         |
| O             | 0.0 wt.-%         | O              | 0.7 wt.-%         | O                  | 4.9 wt.-%         | O              | 4.5 wt.-%         |
| <b>Ash</b>    | <b>74.4 wt.-%</b> | <b>Ash</b>     | <b>32.0 wt.-%</b> | <b>Ash</b>         | <b>17.5 wt.-%</b> | <b>Ash</b>     | <b>3.1 wt.-%</b>  |
| LHV 8.2 MJ/kg |                   | LHV 23.0 MJ/kg |                   | LHV 26.0 MJ/kg     |                   | LHV 34.4 MJ/kg |                   |

# Team in Sulzbach-Rosenberg



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# BIOCHAR – JUST A BLACK MATTER IS NOT ENOUGH!

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## Thank You!

### Contact:

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