BRNO UNIVERSITY OF TECHNOLOGY
FACULTY OF CIVIL ENGINEERING

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# Use of biochar from microware pyrolysis for removal of pharmaceuticals by filtration

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# Introduction of AdMaS - RG EGAR

***Applied research in the field of environmental technologies, geotechnics and geodesy***

***„Environmental and Geo (Geotechnics and Geodesy) Applied Technological Research“***

***RG EGAR focus:***

✓*geodetic, photogrammetric and metrological support in construction and research;*

✓*development and validation of methodologies for measuring thermal and microclimatic properties of buildings and parts of structures;*

✓*energy, ecological and sustainable conception of municipal and regional development;*

✓*development and verification of the methodology for validating practical applications of field and laboratory measurements, evaluation (including mathematical modelling) and development of methodologies in the field of geotechnical methods of surveys and diagnostics of foundation conditions;*

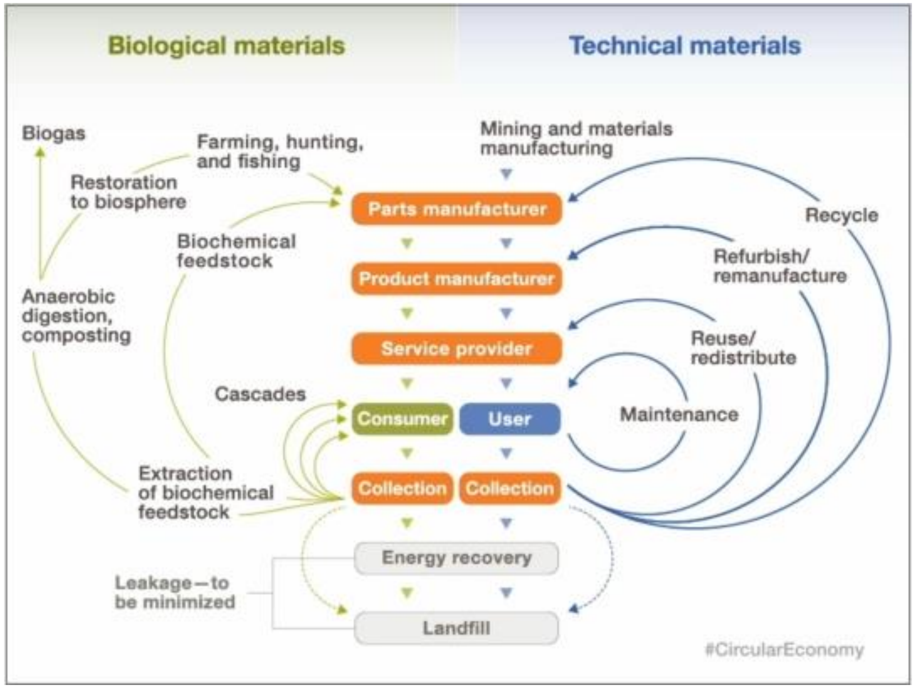
✓*verification and development of new wastewater and water treatment technologies emphasising energy demands and efficiency*

✓*research into the methods of economic analysis of macroeconomic projects.*

# CONTENT

# Circular Economy



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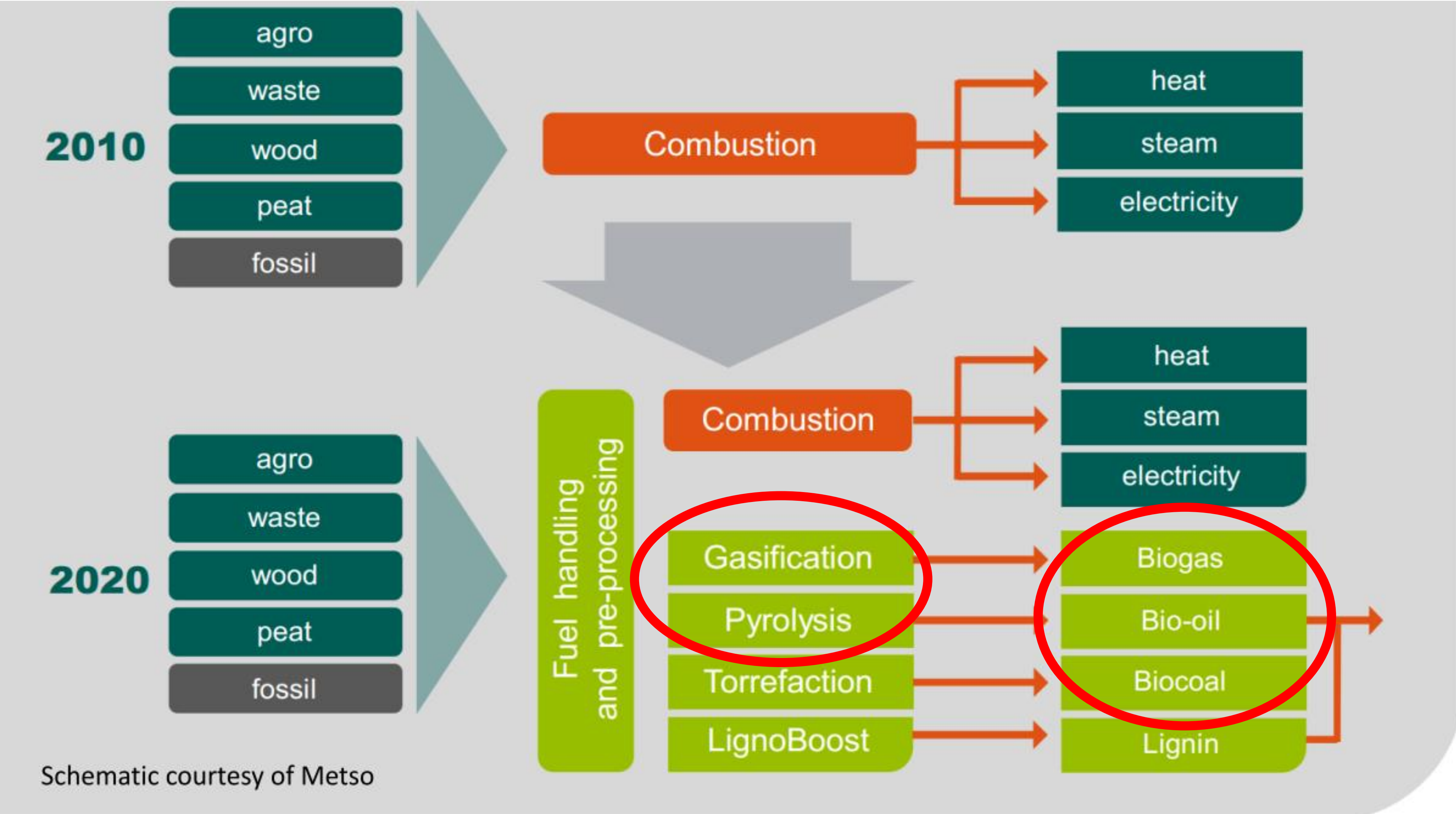
# Termic treatment of waste




Schematic courtesy of Metso

# PYROLYSIS

- Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any halogen).
- It involves the simultaneous change of chemical composition and physical phase, and is irreversible.
- The word is coined from the Greek-derived elements pyro "fire" and lysis "separating".
- Pyrolysis is a type of thermolysis, and is most commonly observed in organic materials exposed to high temperatures.

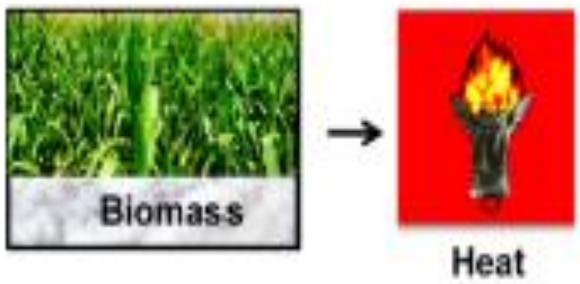
# PYROLYSIS

- Pyrolysis is a step further away from carbonisation and it also takes place with the lack of oxygen.
- Pyrolysis is understood as thermal decomposition of organic materials in the absence of oxygen containing media.
- Pyrolysis is based upon heating the material above the limit of thermal stability of the present organic compounds, leading to their splitting down to stable low molecular weight products and solid residues.

# PYROLYSIS

- From a technological point of view, the pyrolysis process can be subdivided according to the achieved temperatures to:
  1. low temperature (< 500°C),
  2. medium temperature (500 - 800°C),
  3. high temperature (> 800°C).
- The residual energy from gas combustion, not consumed to heat the charge, is utilised in waste heat boilers to produce steam or hot service water.

# PYROLYSIS




**Product Distribution (wt%)**

| | Solid Fraction | Liquid (bio-oil) | Gas |
|---|---|---|---|
| Slow Pyrolysis (carbonization) | 35* | 30 | 35 |
| Fast Pyrolysis | 10 | 70* | 20 |
| Gasification | 10 | 5 | 85* |

* Desired product

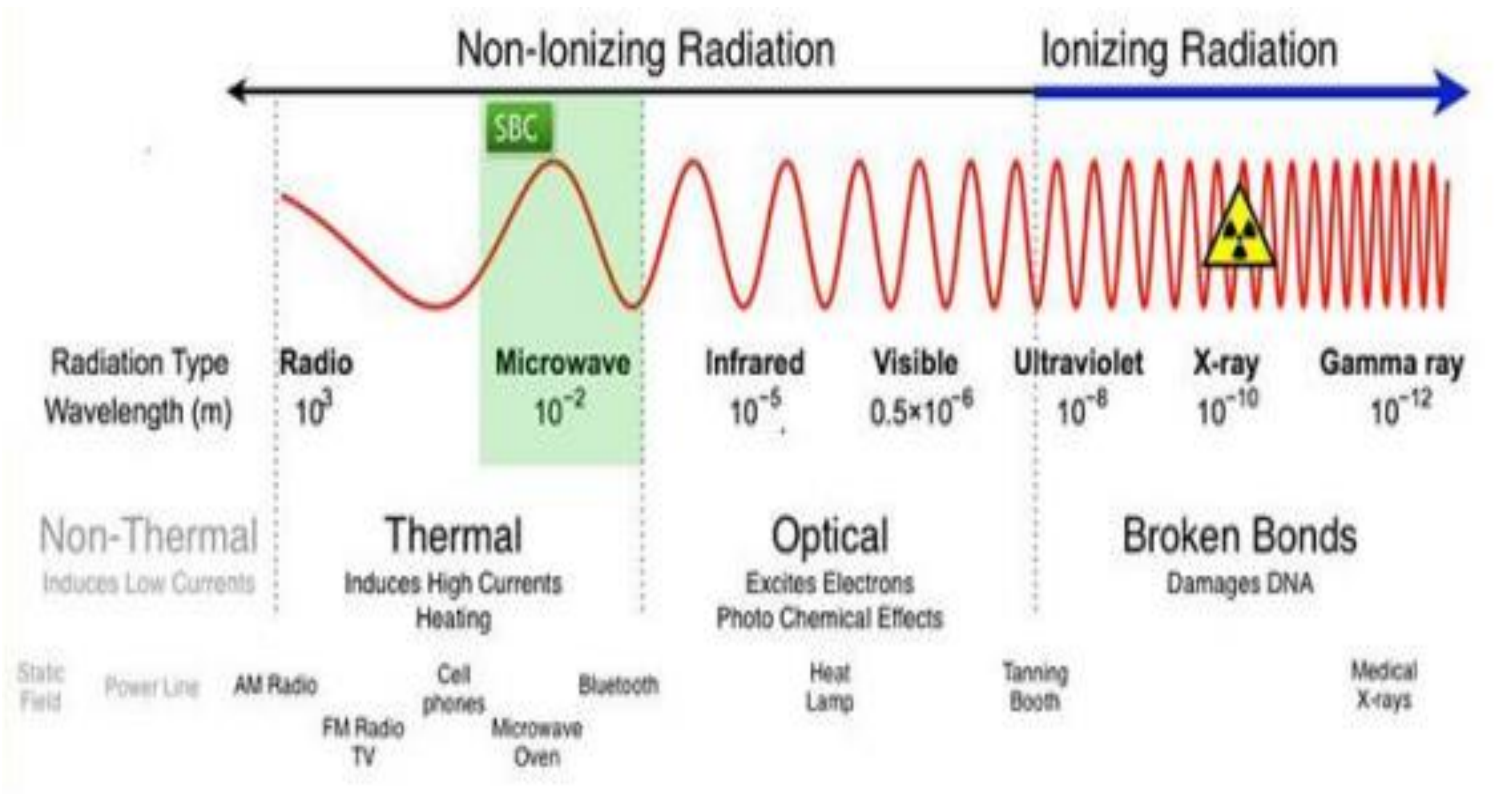
# PYROLYSIS

- The so-called "fast pyrolysis" is one of the modern and highly promising processes in a group of technologies that transform biomass in the form of wood and other waste materials to higher energy level products such as gases, liquids and solids.
- The fast pyrolysis process is determined by fast supply of heat to the feedstock, upkeeping of the desired temperature in the pyrolysis reactor (about 450 ° C to 600 ° C) and a short retention time in the reaction zone (up to 2 seconds).
- The products are mainly steam and aerosols and, to a lesser extent, gas and solid particles.

# MICROWAVE PYROLYSIS

- While the heating effect of microwaves was discovered accidentally in 1946, science has not demonstrated too much interest in the application of microwaves in chemical reactions until recently.
- However, over the last 10-15 years, a large number of scientific studies have begun to explore the use of microwave heating, including in the field of biomass.
- Most of these advantages are highly energy efficient, fast inside out heating and the selectivity of microwave agitation based on molecular electrical properties that have a greater effect than simple heating.

# MICROWAVE PYROLYSIS

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# MICROWAVE PYROLYSIS

- The conversion process is preceded by pre-treatment depending on the type of feedstock.
- Most materials must be dried to a relative humidity of 10% and crushed or ground before it can be mixed with process additives and then pressed into pellets.
- The pellets are fed into the reactor for processing. After preheating, they reach the critical zone of the microwave radiation.
- Precise temperature control under high pressure results in steam generation inside the granules which facilitate the first stage of chemical reactions.

# MICROWAVE PYROLYSIS

- At surface temperatures around 300-350 °C, the combined effects of pulsed microwave radiation, activated carbon particles and catalyst result in the cracking of hydro-carbon molecules in the feedstock into smaller, more volatile molecules and evaporation.
- These broken molecules leave the reactor in the form of oil mist.
- The solid residues remain in the reactor, all the contained oils evaporate. A highly calorific product is produced as the second valuable product of the process of microwave pyrolysis.

# Description of pilot unit

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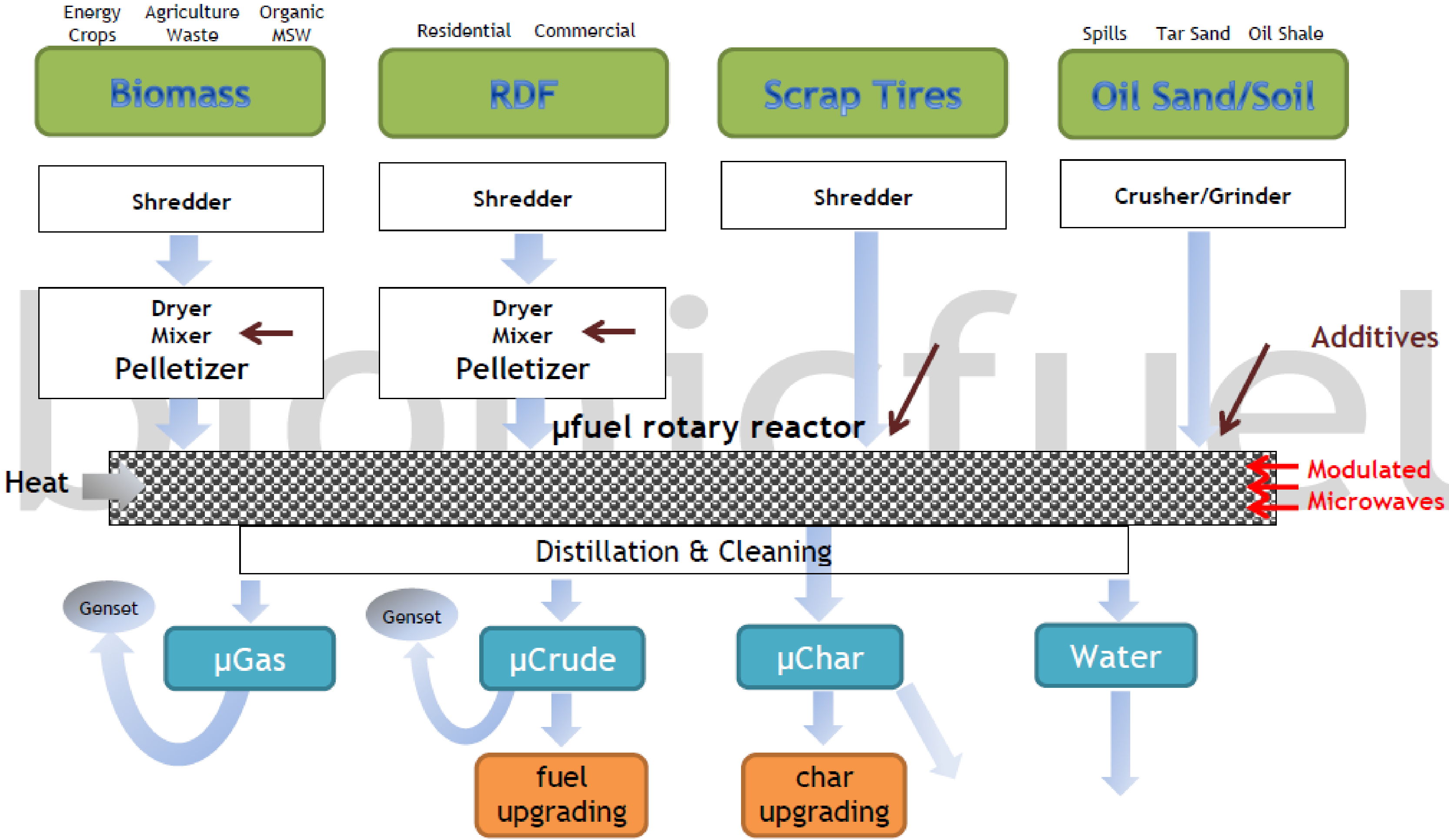
# Description of pilot unit

Feedstock Classes and their Process Flows



# PRODUCTS OF PYROLYSIS

- The pyrolysis product is a liquid fuel, biocoal (BIOCHAR), gas, water, sulphur and inorganic waste.
- The liquid fuel can be used directly in the production of electricity or, following treatment, for standard heating and as a fuel.
- In the EU countries, biofuels from renewable energies can help refineries meet their legal obligations.
- Biocoal (BIOCHAR) is of high carbon purity for most types of feedstock with a calorific value comparable to a high quality coal.
- Besides the use for heating purposes, it can also be applied in other fields (see below).

# PRODUCTS OF PYROLYSIS

# PRODUCTS OF PYROLYSIS

- Gases are a mixture of methane, propane or pentane and other highly volatile organic compounds in the reaction mixture in the initial stage of heating.
- The produced water is the residual moisture of the feedstock in combination with process water.
- Highly clean end product is available for many applications.
- The sulphur content depends on the type of feedstock and the use of liquid sulphur, the product is split during fuel refinement in the desulfurisation unit.

# PRODUCTS OF PYROLYSIS

- Inorganic waste is, depending on the inorganic salts, present in the fraction of sodium soil, calcium and potassium in the form of environmentally neutral silicates.
- The range of biocoal use covers a wide range of sectors which give this biomass material a to make the most of its properties.
- Biocoal, even if used in industrial applications, ensures the removal of anthropogenic $CO_2$ from the atmosphere and carbon storage or at least replaces  fossil carbon sources.

# BIOCHAR USE

***Range of biocoal use in livestock breeding*** Silage, feed additives, breeding additives, semi-liquid manure treatment, manure composting, water treatment for fish breeding

***Biocoal as a soil conditioner***

Carbon fertiliser, compost, peat substitution, plant protection, substitute fertiliser – carrier for trace elements

***Use in building industry***

Insulation, air decontamination, earth foundation decontaminating, air moisture content control, electromagnetic radiation control.

***Decontamination***

Soil improvers for soil remediation (used mainly in former mines, military bases and landfill sites).

Soil substrates  (high adsorption, soil substrates used in wastewater treatment, especially wastewater from urban areas polluted by heavy metals).

A barrier preventing from the leaching of pesticides into surface water ( edges of fields and ponds can be fitted with 30-50 cm deep barriers made of biocoal to filter pesticides).

Pond and lake water treatment ponds (good adsorption of pesticides and fertilisers, improved water oxygenation).

# BIOCHAR USE

***Biogas production***

Biomass additive in fermentation, supernatant  liquid treatment

***Wastewater treatment***

Activated carbon filters, pre-flushing additive, soil substrate for organic soil bed, composting toilets

***Drinking water treatment***

Micro filters, macro filters in developing countries

***Other applications***

Exhaust filters (emission control, interior air filters)
Industrial materials (carbon fibres, plastics)
Electronics (semiconductors, batteries)
Metallurgy (metal reduction)
Cosmetics (soaps, skin creams, admixtures for therapeutic baths)
Paints and dyes (food dyes, industrial paints)
Energy production (pellets, substitutes for brown coal)
Health (detoxification, carrier for active pharmaceutical ingredients)
Protection against electromagnetic radiation

***Textile***

Admixture for functional underwear, thermal insulation for functional clothes, deodorant for shoe inserts

***Wellness***

Mattress filling, pillow filling

# BIOCHAR ROLE FOR REMOVAL

- Increasing contamination of water.
- The toxicity has adverse health effects.
- Many organic compounds are persistent or can be biodegraded or transformed into products that survive conventional treatment processes.
- Development of alternative, cost-effective and environmental-friendly technologies for treating organic contaminants.

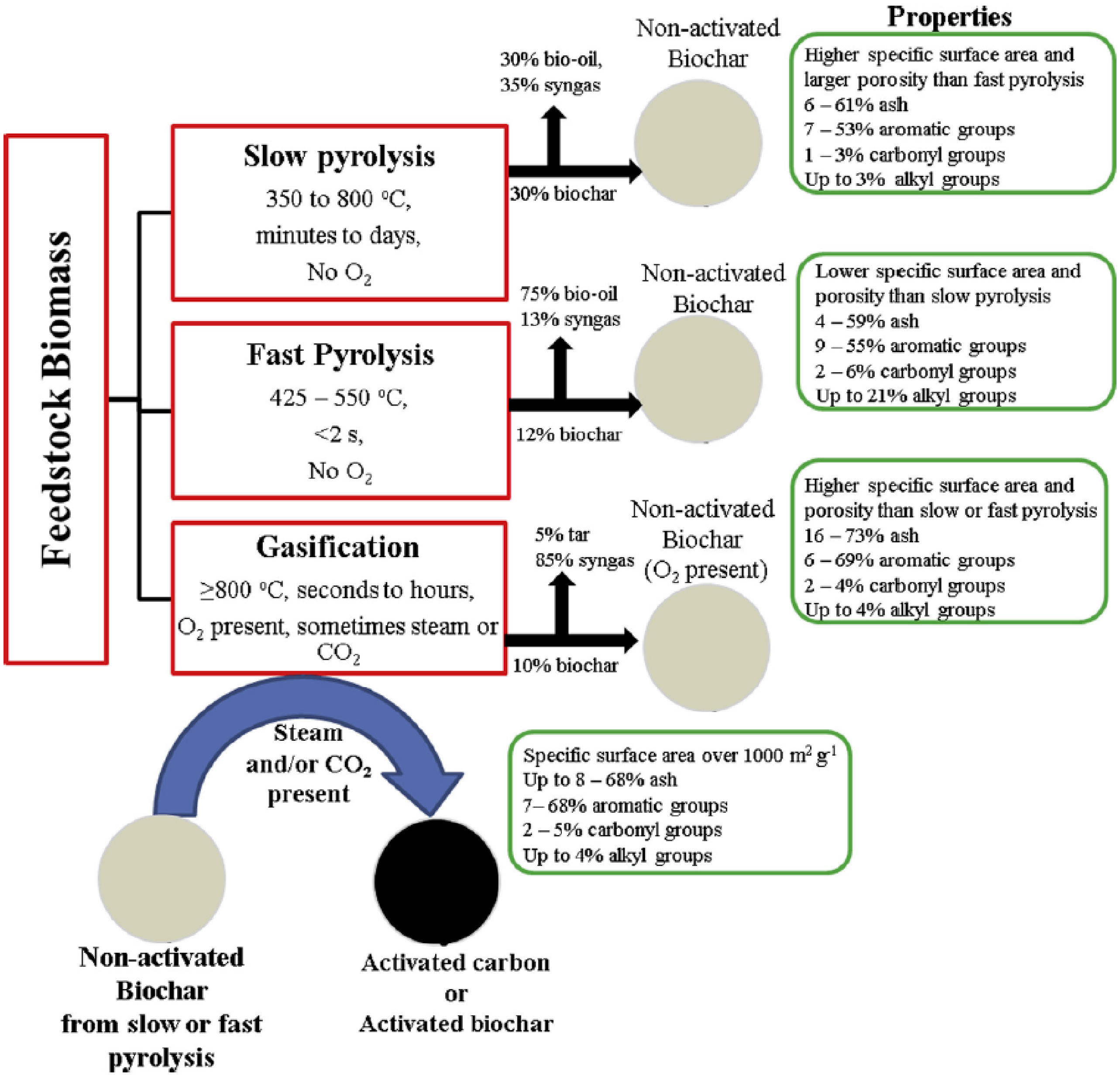
# BIOCHAR ROLE FOR REMOVAL

- To date, there has been a growing body of literature on the application of biochar in water and wastewater treatment.
- In particular, the use of biochar for the removal of persistent organic pollutants from aqueous systems has been documented.
- In some instances, stronger sorption and binding affinities of organic contaminants to biochar than commercial activated carbons were reported.

# BIOCHAR ROLE FOR REMOVAL

- Thermochemical processes used in producing non-activated biochar and activated biochar or carbon are: gasification, slow pyrolysis, and fast pyrolysis.
- The physiochemical properties of biochars produced from each of these processes can vary and are mostly influenced by proces conditions (reaction residence time and temperature), parent feedstock materials, and activation techniques.

# ROLE OF BIOCHAR



# Pharmaceuticals

- Sulfathiazol
- Sulfamethazin
- Sulfamethoxazol
- Erythromycin
- Azithromycin
- Clarithromycin
- Roxithromycin
- Ketoprofen
- Naproxen
- Diclofenac
- Ibuprofen

# Preparation of BIOCHAR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# Preparation of BIOCHAR

FRACTION 1-2

FRACTION 2-4

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# Preparation of BIOCHAR

## Sieving and washing of biochar


# Filtration unit

# Results

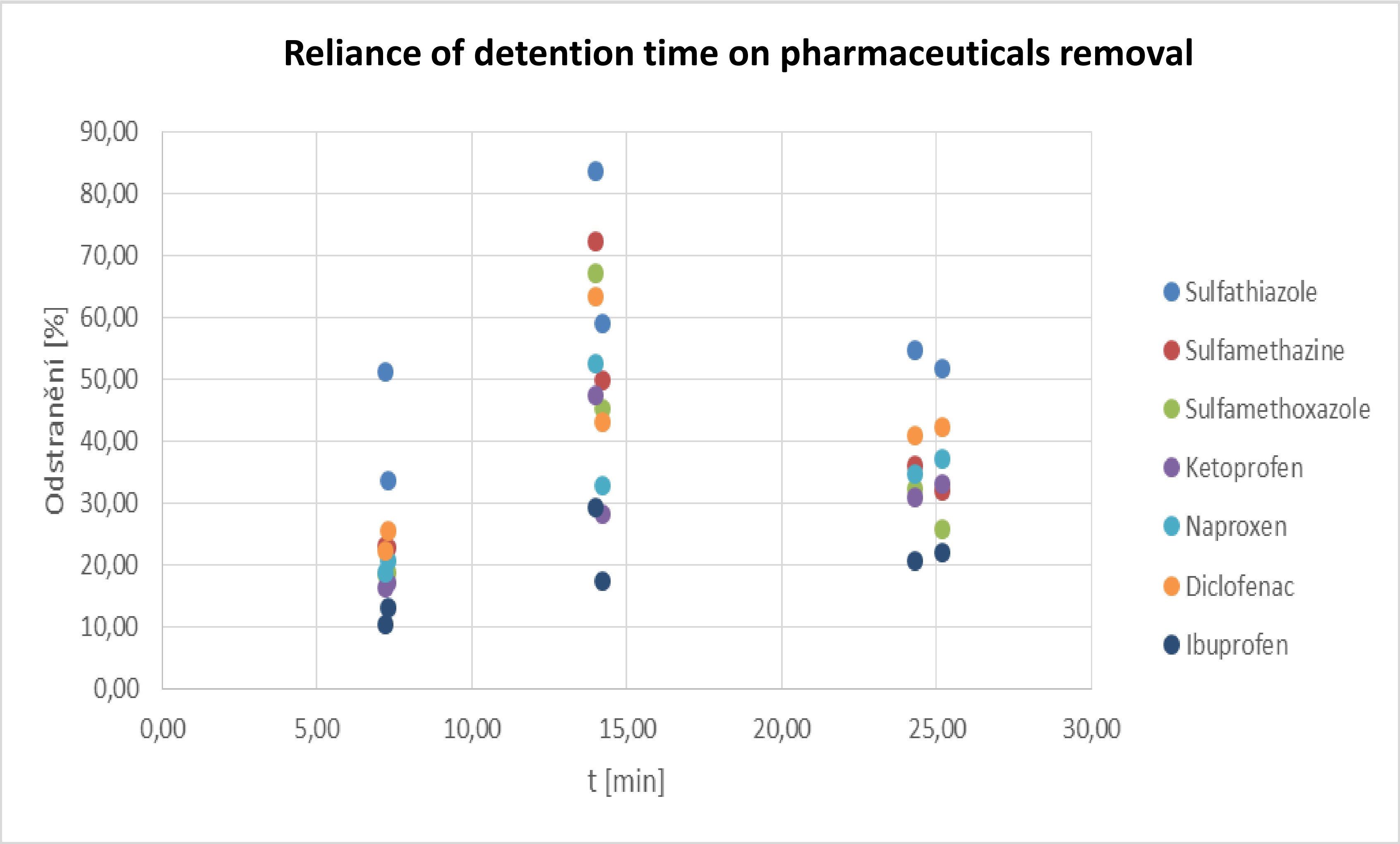
| number of sample | A | B | avg. A,B | C | D | E | F | G | H | - |
|---|---|---|---|---|---|---|---|---|---|---|
| flow (l/h) | | | | 4,89 | 4,94 | 2,57 | 2,48 | 9,62 | 9,83 | l/h |
| contatct time | | | | 14,00 | 14,20 | 24,30 | 25,20 | 7,30 | 7,20 | min |
| Sulfathiazole | 3,00 | 2,67 | 2,84 | 0,46 | 1,16 | 1,29 | 1,37 | 1,88 | 1,38 | µg/l |
| Sulfamethazine | 6,75 | 6,14 | 6,45 | 1,79 | 3,22 | 4,12 | 4,39 | 4,97 | 4,96 | µg/l |
| Sulfamethoxazole | 1,95 | 1,87 | 1,91 | 0,63 | 1,05 | 1,29 | 1,42 | 1,55 | 1,56 | µg/l |
| Erythromycin | 5,97 | 5,30 | 5,64 | | | | | | | µg/l |
| Azithromycin | 16,24 | 16,02 | 16,13 | | | | | | | µg/l |
| Clarithromycin | 15,41 | 15,04 | 15,22 | | | | | | | µg/l |
| Roxithromycin | 12,07 | 12,09 | 12,08 | | | | | | | µg/l |
| Ketoprofen | 71,63 | 69,33 | 70,48 | 37,14 | 50,53 | 48,75 | 47,17 | 58,44 | 59,01 | µg/l |
| Naproxen | 1686,31 | 1630,46 | 1658,39 | 784,60 | 1114,35 | 1082,09 | 1043,80 | 1314,13 | 1346,02 | µg/l |
| Diclofenac | 105,48 | 102,00 | 103,74 | 37,95 | 58,92 | 61,32 | 59,93 | 77,26 | 80,67 | µg/l |
| Ibuprofen | 136,08 | 130,77 | 133,42 | 94,24 | 110,11 | 105,99 | 104,14 | 115,87 | 119,56 | µg/l |

# Results

removal (%)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sulfathiazole | 83,74 | 59,06 | 54,59 | 51,88 | 33,78 | 51,18 | % |
| Sulfamethazine | 72,31 | 49,98 | 36,10 | 31,90 | 22,94 | 22,99 | % |
| Sulfamethoxazole | 67,27 | 45,19 | 32,23 | 25,78 | 18,76 | 18,55 | % |
| Erythromycin | | | | | | | % |
| Azithromycin | | | | | | | % |
| Clarithromycin | | | | | | | % |
| Roxithromycin | | | | | | | % |
| Ketoprofen | 47,30 | 28,30 | 30,84 | 33,07 | 17,08 | 16,27 | % |
| Naproxen | 52,69 | 32,81 | 34,75 | 37,06 | 20,76 | 18,84 | % |
| Diclofenac | 63,42 | 43,21 | 40,89 | 42,23 | 25,52 | 22,24 | % |
| Ibuprofen | 29,36 | 17,48 | 20,56 | 21,95 | 13,16 | 10,39 | % |

# Results


Reliance of detention time on pharmaceuticals removal
90,00
80,00
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
Odstranění [%]
0,00
5,00
10,00
15,00
20,00
25,00
30,00
t [min]
Sulfathiazole
Sulfamethazine
Sulfamethoxazole
Ketoprofen
Naproxen
Diclofenac
Ibuprofen

# CONCLUSIONS

- Biochar can be an environmentally-sustainable substitute for activated carbon in treating organic contaminants.
- The treatment of organic and microbial contaminants using granular biochar filters is feasible. Microbes such as E. Coli can be retained on biochar surfaces during filtration, while organic contaminants in water can be sorbed by removal mechanisms such as pore-filling, aromatic-p interactions, and H-bonding.
- Low density biochar may be problematic in filtration applications due to poor settleability during backwashing.
- The implementation of biochar in specific unit operations for water treatment presents major opportunities for further research.

# Thank you for attention

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FAKULTA STAVEBNÍ

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