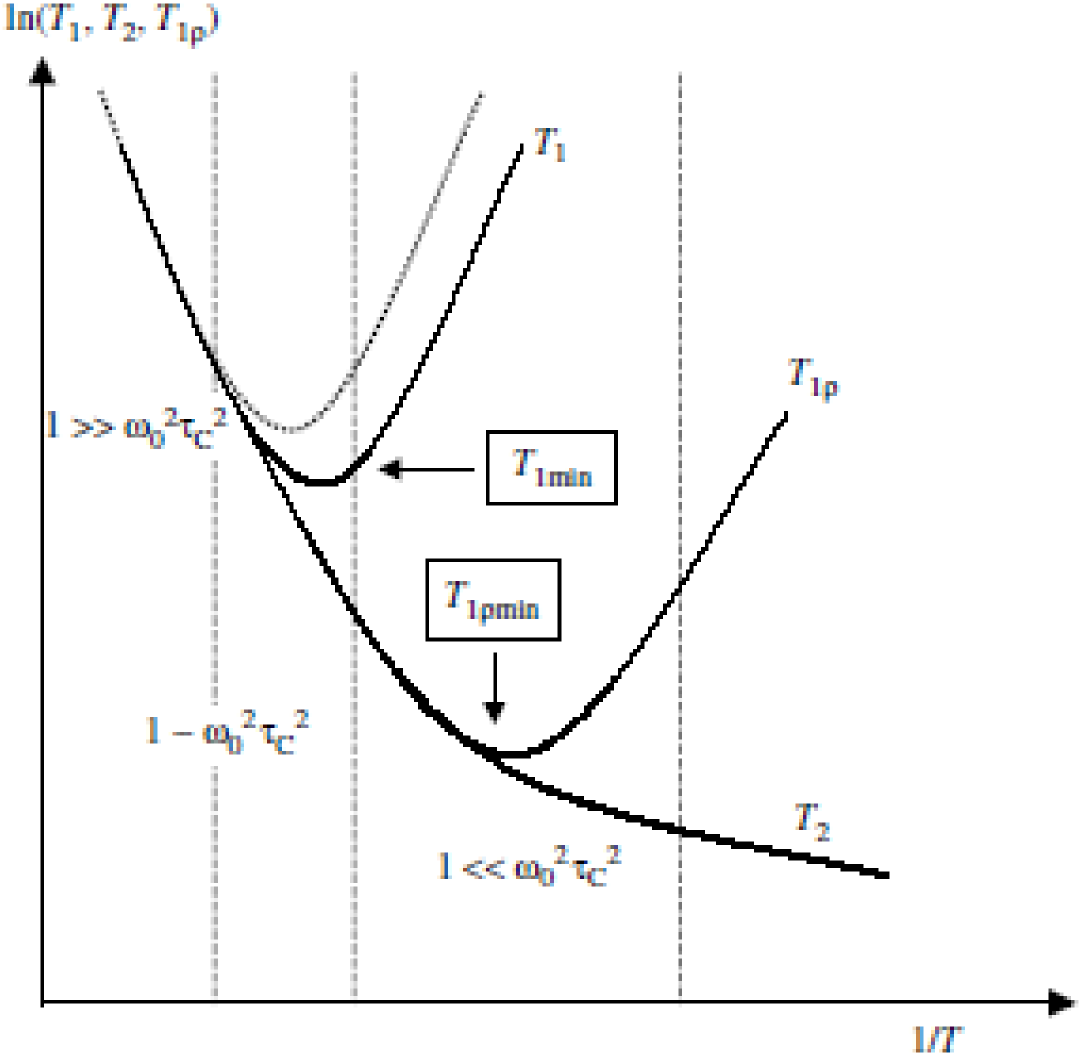
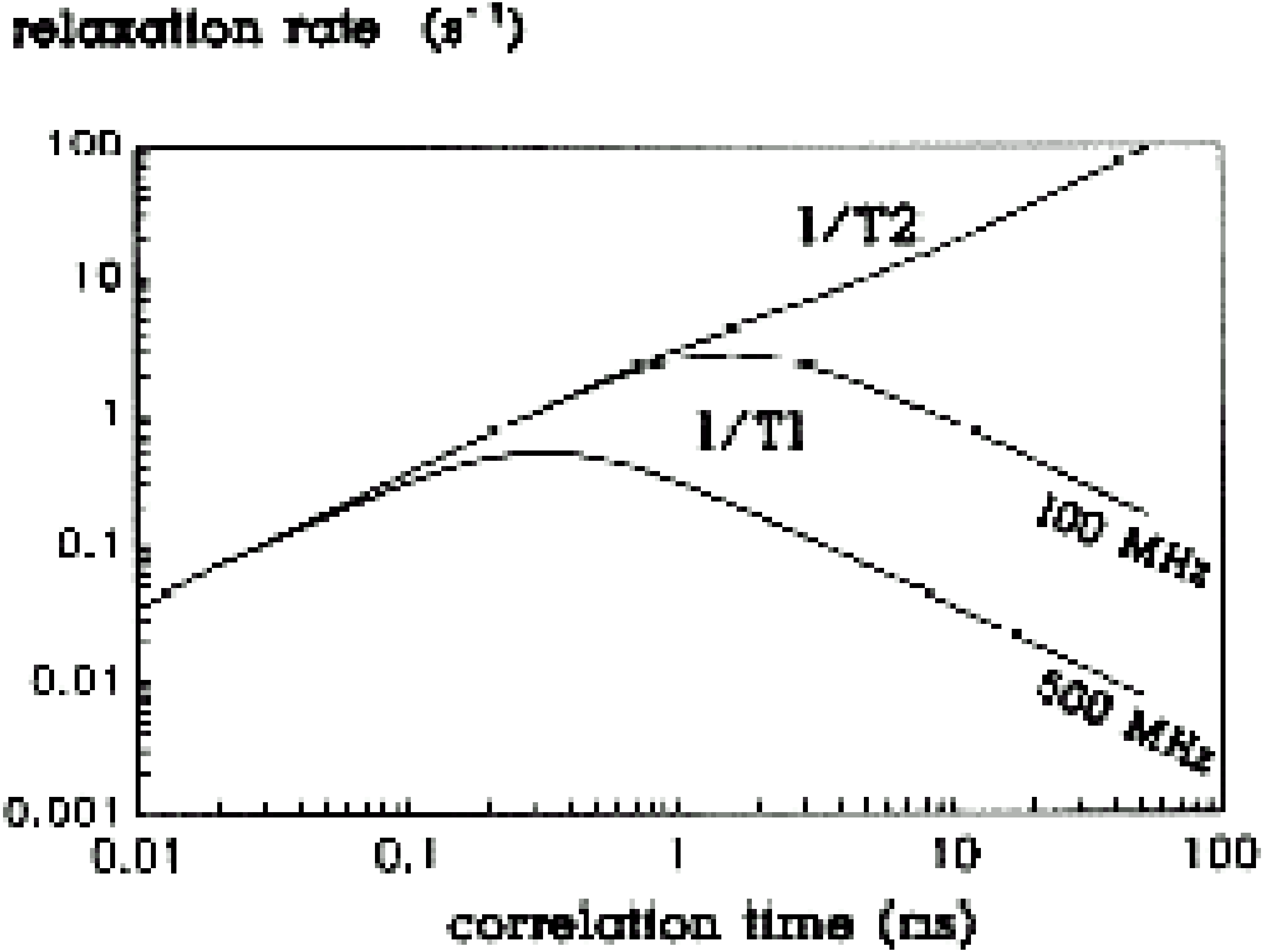
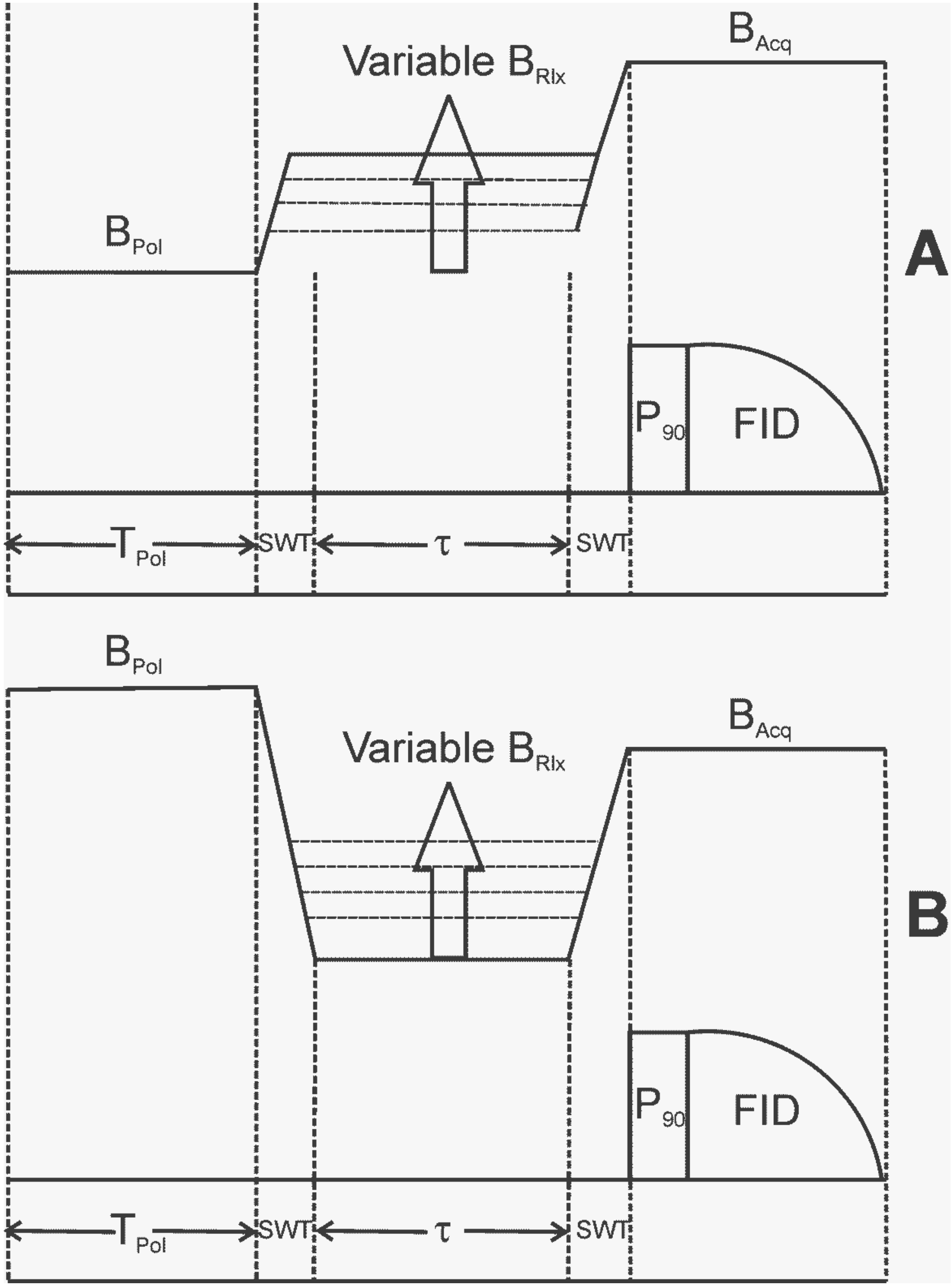
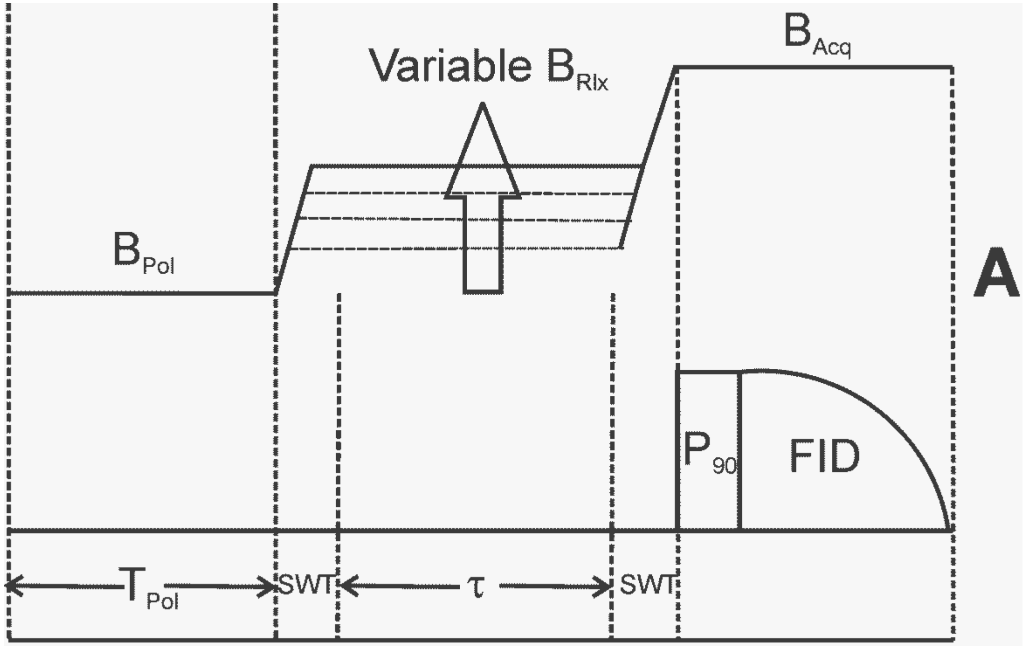


Figure 4.2 Temperature dependences of the dipolar T_1, T_2 and $T_{1\rho}$ relaxation times in semilogarithmic coordinates at the Larmor frequency ω_0. The dashed T_1 curve corresponds to a higher Larmor frequency than ω_0. The regions with $1 \gg \omega_0^2\tau_C^2$, $1 \sim \omega_0^2\tau_C^2$ and $1 \ll \omega_0^2\tau_C^2$ correspond to fast, intermediate and slow molecular motions on the frequency scale of NMR


relaxation rate (s⁻¹)
100
10
1
0.1
0.01
0.001
1/T2
1/T1
100 MHz
500 MHz
0.01
0.1
1
10
100
correlation time (ns)

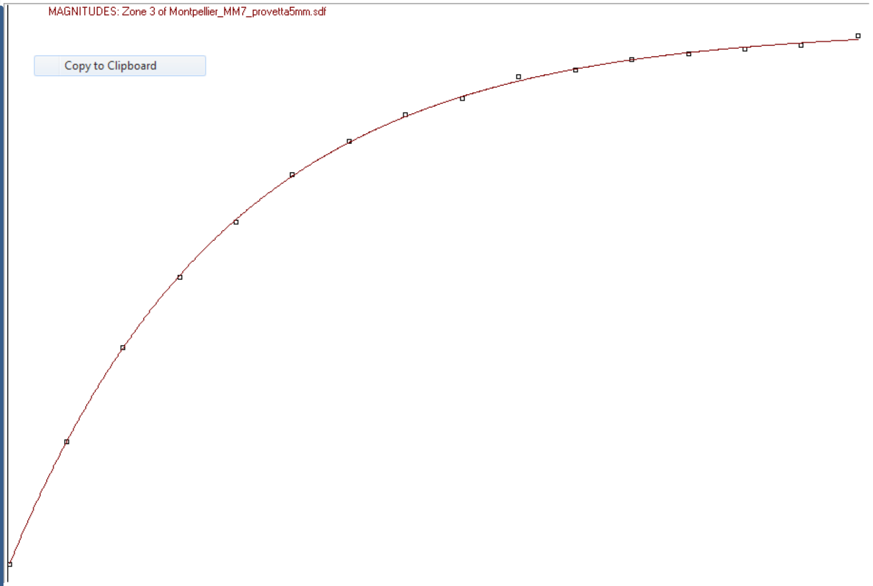


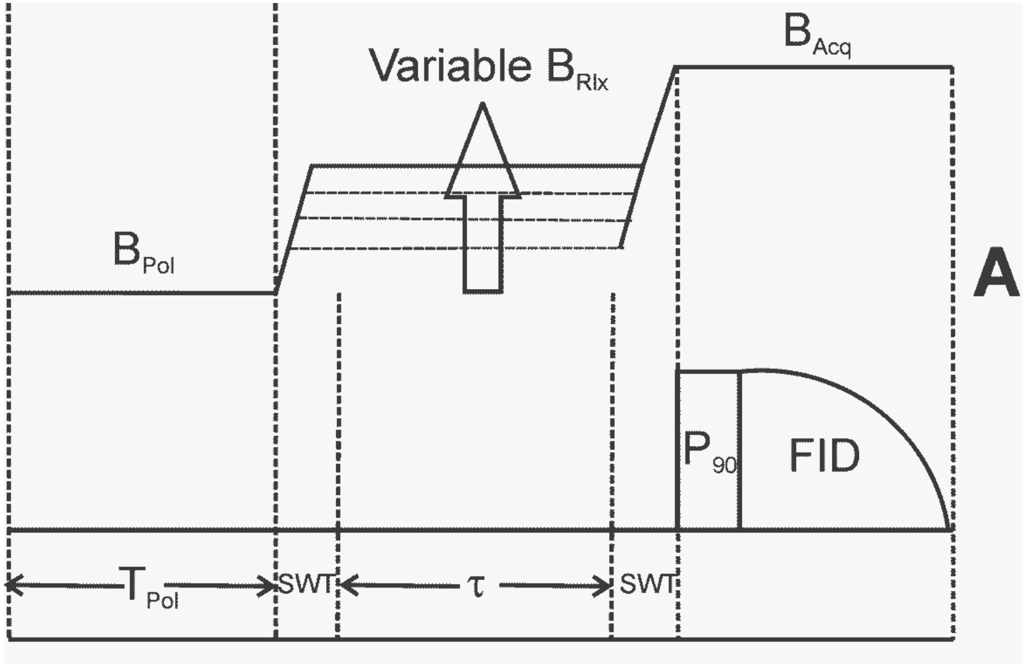
Variable B_{Rlx}
B_{Acq}
B_{Pol}
A
P_{90}
FID
T_{Pol}
SWT
τ
SWT
B_{Pol}
B_{Acq}
Variable B_{Rlx}
B
P_{90}
FID
T_{Pol}
SWT
τ
SWT

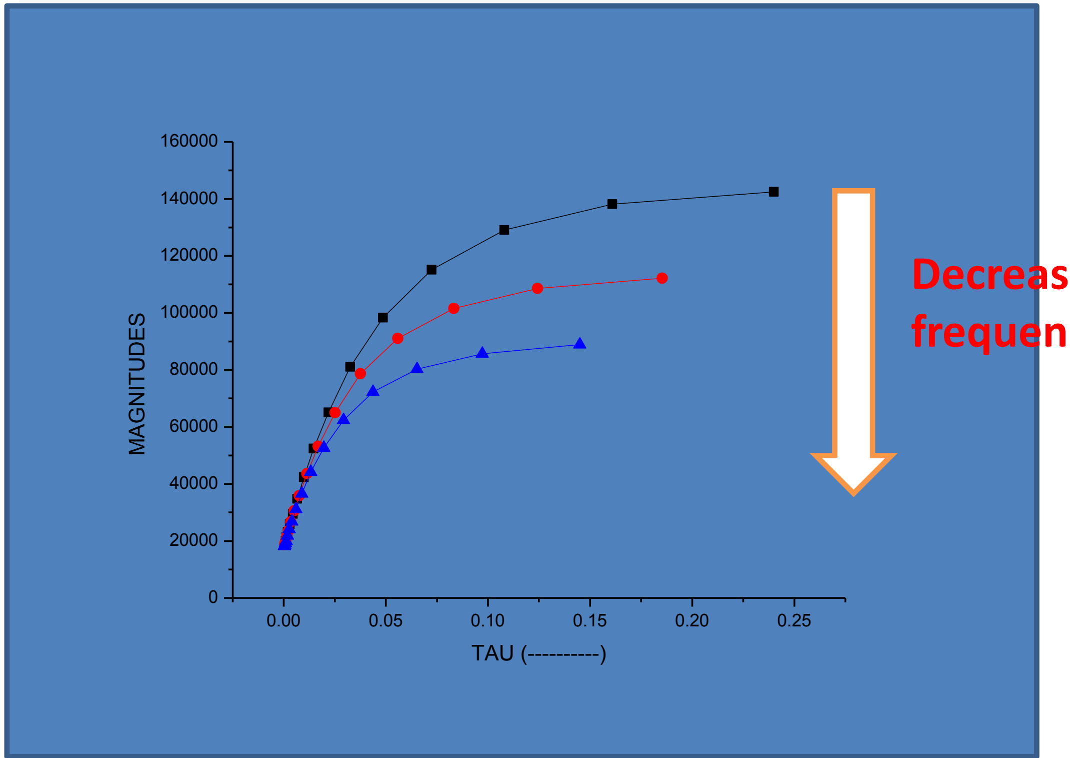


Increasing τ values

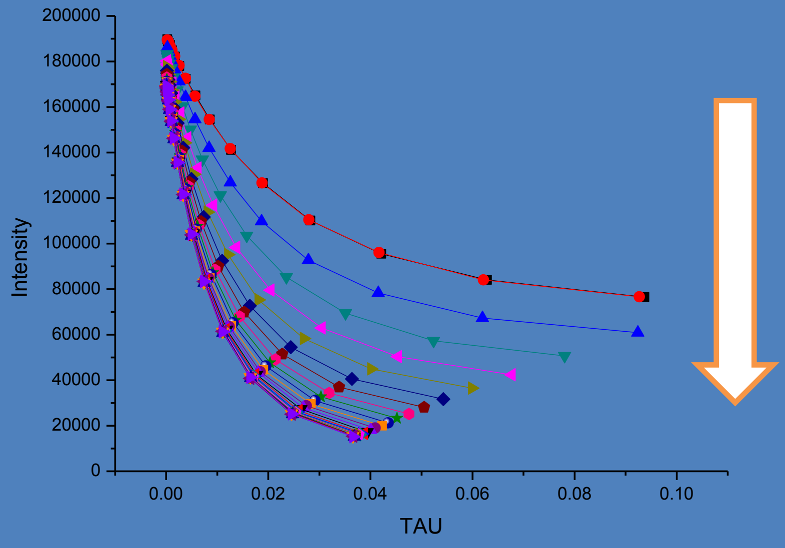
TAU	MAGNITUDES
4.0000e-02	4.8868e+03
3.7340e-02	4.8476e+03
3.4680e-02	4.8303e+03
3.2020e-02	4.8122e+03
2.9360e-02	4.7851e+03
2.6700e-02	4.7408e+03
2.4040e-02	4.7134e+03
2.1380e-02	4.6201e+03
1.8720e-02	4.5530e+03
1.6060e-02	4.4407e+03
1.3400e-02	4.2962e+03
1.0740e-02	4.0933e+03
8.0800e-03	3.8614e+03
5.4200e-03	3.5633e+03
2.7600e-03	3.1630e+03
1.0000e-04	2.6401e+03


MAGNITUDES: Zone 3 of Montpellier_MM7_provetta5mm.sdf

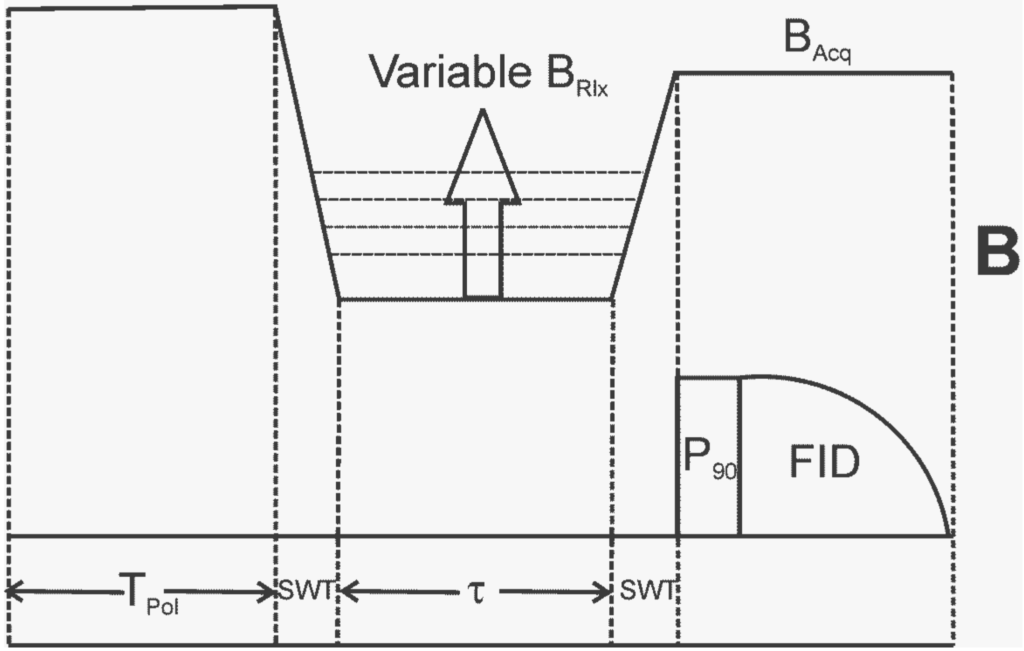


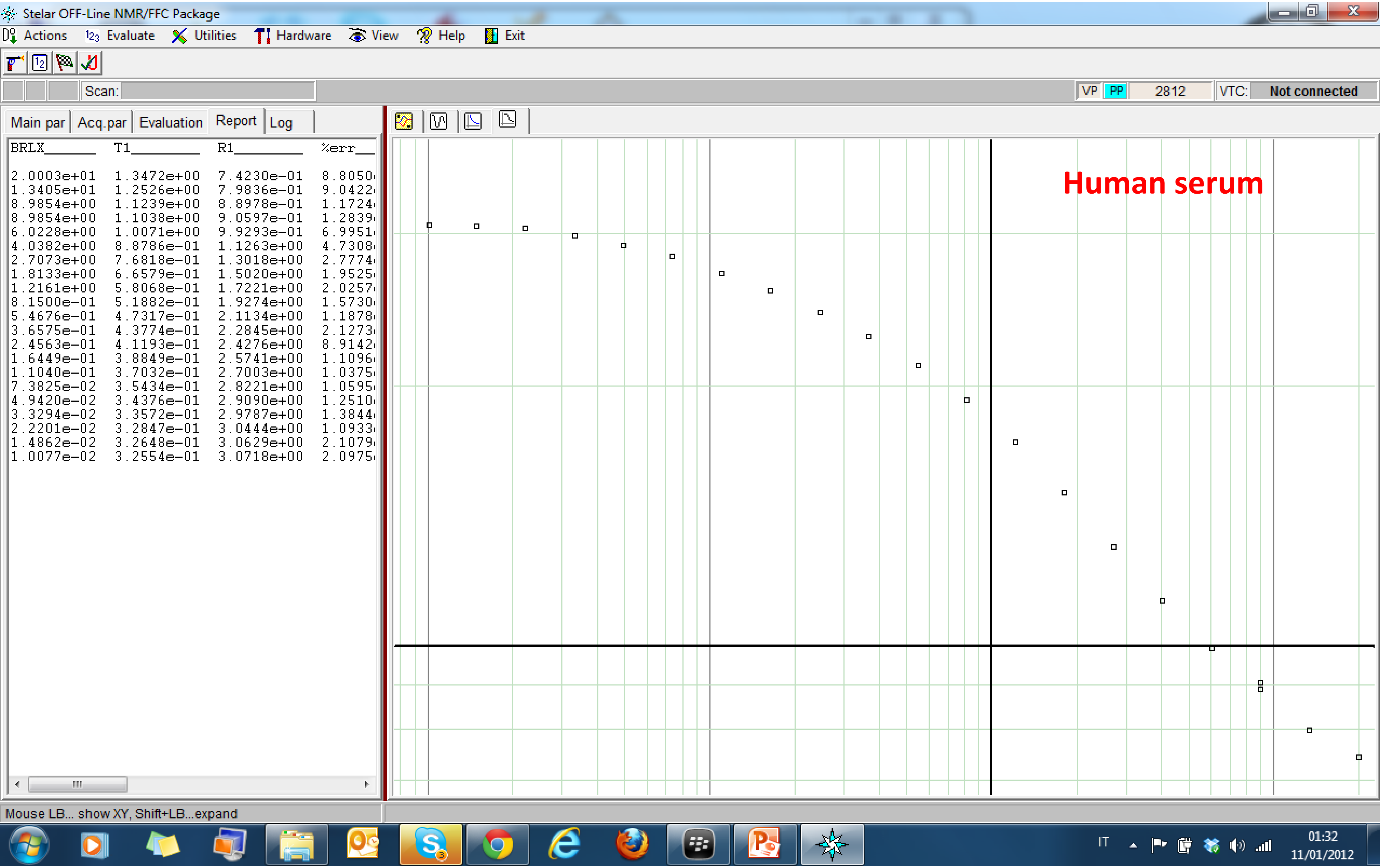


Decreasing proton Larmor frequency



Decreasing proton Larmor frequency



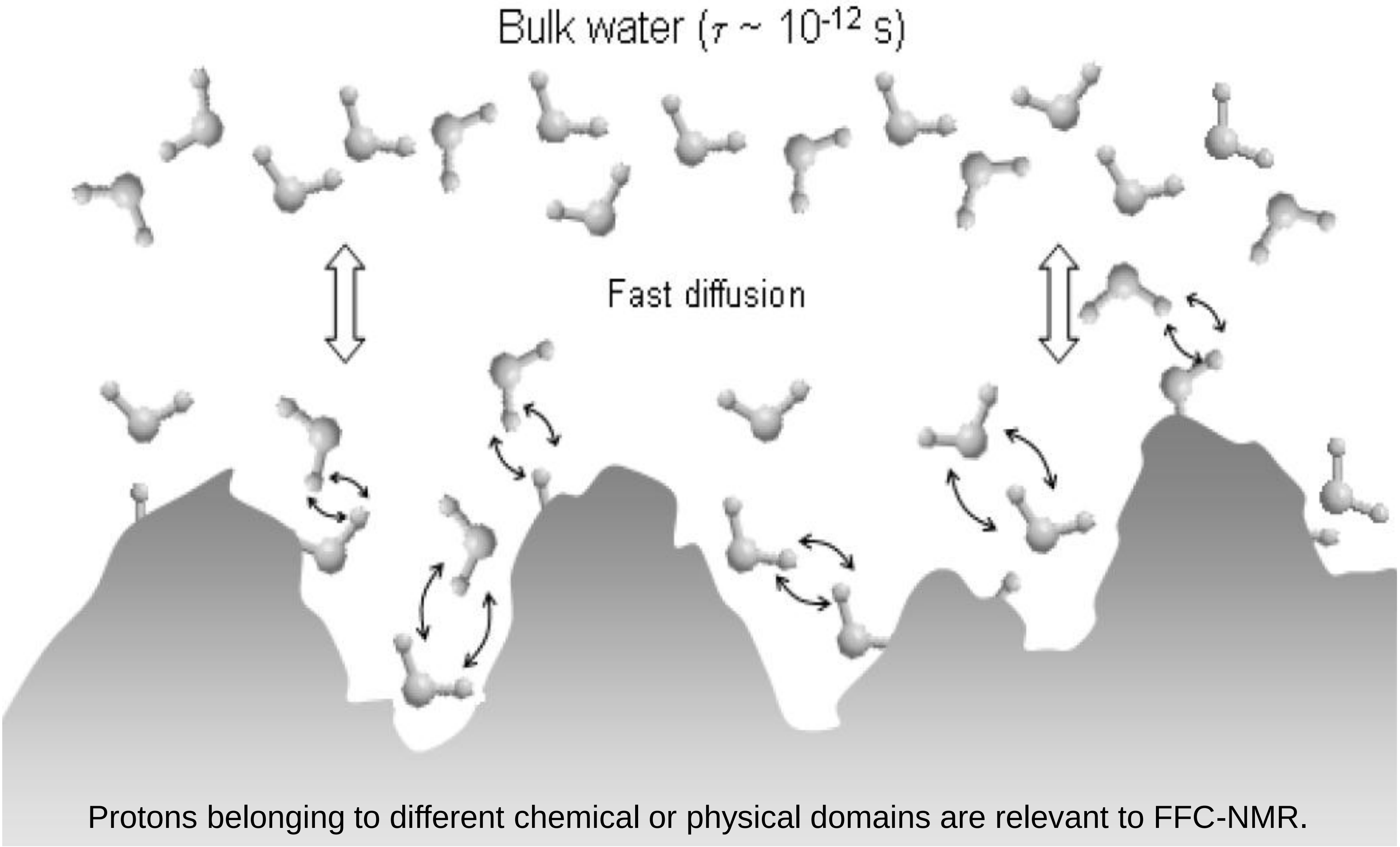


Human serum

```
BRLX______   T1________   R1________   %err__

2.0003e+01   1.3472e+00   7.4230e-01   8.8050
1.3405e+01   1.2526e+00   7.9836e-01   9.0422
8.9854e+00   1.1239e+00   8.8978e-01   1.1724
8.9854e+00   1.1038e+00   9.0597e-01   1.2839
6.0228e+00   1.0071e+00   9.9293e-01   6.9951
4.0382e+00   8.8786e-01   1.1263e+00   4.7308
2.7073e+00   7.6818e-01   1.3018e+00   2.7774
1.8133e+00   6.6579e-01   1.5020e+00   1.9525
1.2161e+00   5.8068e-01   1.7221e+00   2.0257
8.1500e-01   5.1882e-01   1.9274e+00   1.5730
5.4676e-01   4.7317e-01   2.1134e+00   1.1878
3.6575e-01   4.3774e-01   2.2845e+00   2.1273
2.4563e-01   4.1193e-01   2.4276e+00   8.9142
1.6449e-01   3.8849e-01   2.5741e+00   1.1096
1.1040e-01   3.7032e-01   2.7003e+00   1.0375
7.3825e-02   3.5434e-01   2.8221e+00   1.0595
4.9420e-02   3.4376e-01   2.9090e+00   1.2510
3.3294e-02   3.3572e-01   2.9787e+00   1.3844
2.2201e-02   3.2847e-01   3.0444e+00   1.0933
1.4862e-02   3.2648e-01   3.0629e+00   2.1079
1.0077e-02   3.2554e-01   3.0718e+00   2.0975
```

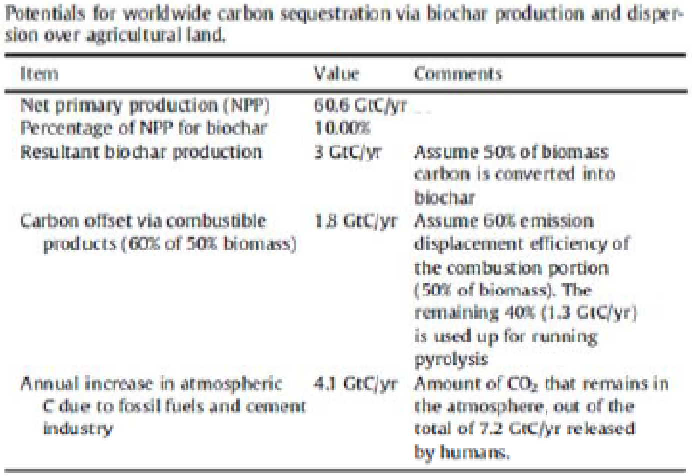
Surface interactions



Protons belonging to different chemical or physical domains are relevant to FFC-NMR.

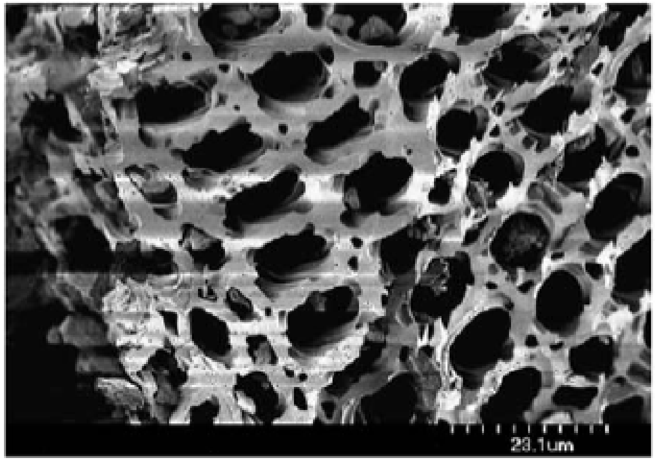
A case study: char analysis

Biochar is a type of charcoal with specific properties obtained from gasification/pyrolysis of biomass. Instead of burning standing biomass from cleared forest, the resource is charred.



Potentials for worldwide carbon sequestration via biochar production and dispersion over agricultural land.

Item	Value	Comments
Net primary production (NPP)	60.6 GtC/yr	–
Percentage of NPP for biochar	10.00%	
Resultant biochar production	3 GtC/yr	Assume 50% of biomass carbon is converted into biochar
Carbon offset via combustible products (60% of 50% biomass)	1.8 GtC/yr	Assume 60% emission displacement efficiency of the combustion portion (50% of biomass). The remaining 40% (1.3 GtC/yr) is used up for running pyrolysis
Annual increase in atmospheric C due to fossil fuels and cement industry	4.1 GtC/yr	Amount of CO_2 that remains in the atmosphere, out of the total of 7.2 GtC/yr released by humans.



An electron micrograph of charcoal collected from a ponderosa pine forest in Northern Idaho, U.S., which was exposed to fire 79 years prior to collection.

Matovick D. Biochar as a viable carbon sequestration option. Energy 2010 in Press

The two pillars that make biochar revolutionary are:

- the affinity of nutrients and water retention (adsorption)
- the high persistence (stability).

Gasification

© Pacific Pyrolysis

Slow Pyrolysis (retort)

Slow pyrolysis (kiln)

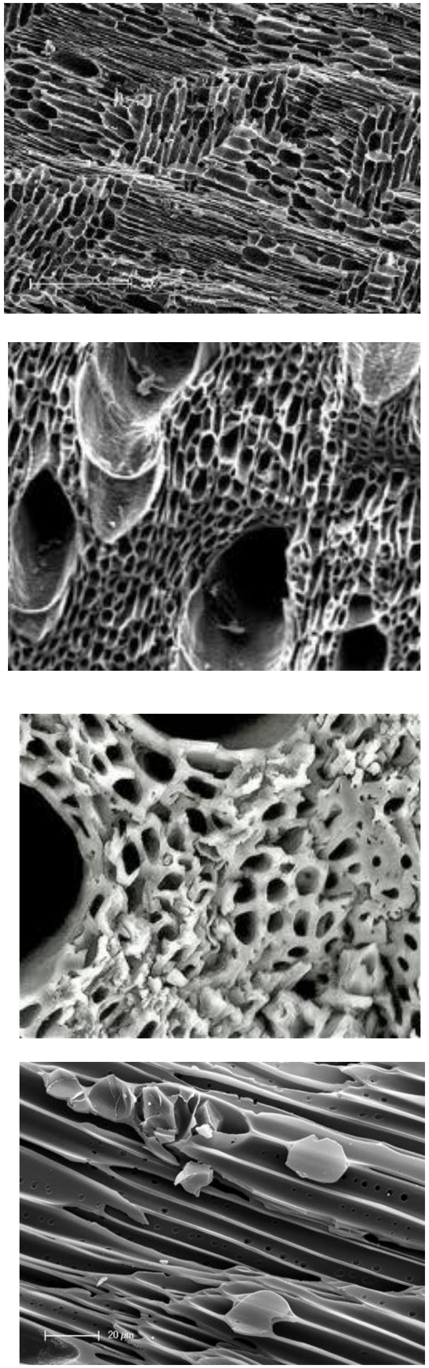
AMAZONIAN DARK EARTH SOILS (TERRA PRETA)

Recognised hypothesis

- ✓ Agricultural activity of ancient populations;
- ✓ Deposition of plant residues;
- ✓ Deposition of ashes and coal produced from use of fires;
- ✓ All those factors contribute to the formation of dark soils in Amazonia basin. These soils result very fertile due to the large amounts of C, P, Ca, Mg, Zn and Mn.

Available research and trials mainly show that biochar amendments result in appreciable improvements of soil fertility:

1. soil cation exchange capacity is increased.
2. soil microbial functions are enhanced; the porous structure of biochar forms a safe haven for microbes that make nutrients available to crops.
3. nutrient retention capacity of soils is improved thus preventing leaching and erosion; this allows farmers to reduce organic and inorganic fertilizers.
4. water retention capacity of soils is improved; the porous structure of biochar holds water and prevents the moisture from evaporating.
5. biochar variously affects soil pH depending on inorganic and organic soil constituents.



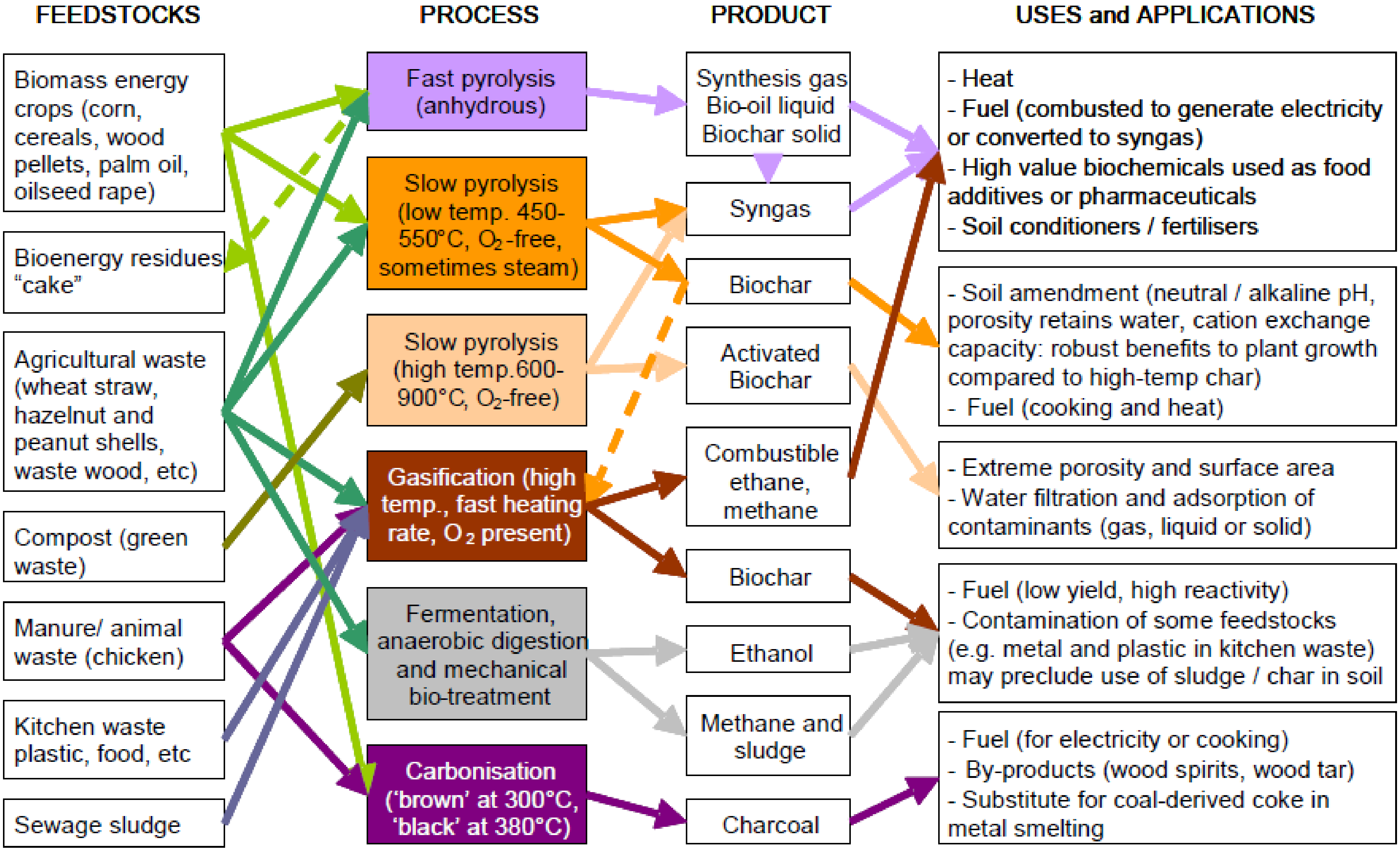
Biochar persistence

It is undisputed that biochar is much more persistent in soil than any other form of organic matter that is commonly applied to soil. Therefore, all associated benefits with respect to nutrient retention and soil fertility are longer lasting than with alternative management.

The long persistence of biochar in soil makes it a prime candidate for the mitigation of climate change as a potential sink for atmospheric carbon dioxide.

1. biochar soils are stable manageable and measurable carbon sinks; they can be built up over time and remove CO_2 from the atmosphere; soils can accumulate hundreds of tonnes of C while improving soil functions;
2. biochar systems halt slash-and-burn agriculture, and thus slow deforestation;
3. biochar produced in efficient pyrolysis plants offers clean, renewable electricity without polluting emissions.

Summary of pyrolysis processes in relation to their common feedstocks, typical products, and the applications and uses of these products



FEEDSTOCKS

- Biomass energy crops (corn, cereals, wood pellets, palm oil, oilseed rape)
- Bioenergy residues "cake"
- Agricultural waste (wheat straw, hazelnut and peanut shells, waste wood, etc)
- Compost (green waste)
- Manure/ animal waste (chicken)
- Kitchen waste plastic, food, etc
- Sewage sludge

PROCESS

- Fast pyrolysis (anhydrous)
- Slow pyrolysis (low temp. 450-550°C, O_2-free, sometimes steam)
- Slow pyrolysis (high temp.600-900°C, O_2-free)
- Gasification (high temp., fast heating rate, O_2 present)
- Fermentation, anaerobic digestion and mechanical bio-treatment
- Carbonisation ('brown' at 300°C, 'black' at 380°C)

PRODUCT

- Synthesis gas
Bio-oil liquid
Biochar solid
- Syngas
- Biochar
- Activated Biochar
- Combustible ethane, methane
- Biochar
- Ethanol
- Methane and sludge
- Charcoal

USES and APPLICATIONS

- Heat
- Fuel (combusted to generate electricity or converted to syngas)
- High value biochemicals used as food additives or pharmaceuticals
- Soil conditioners / fertilisers

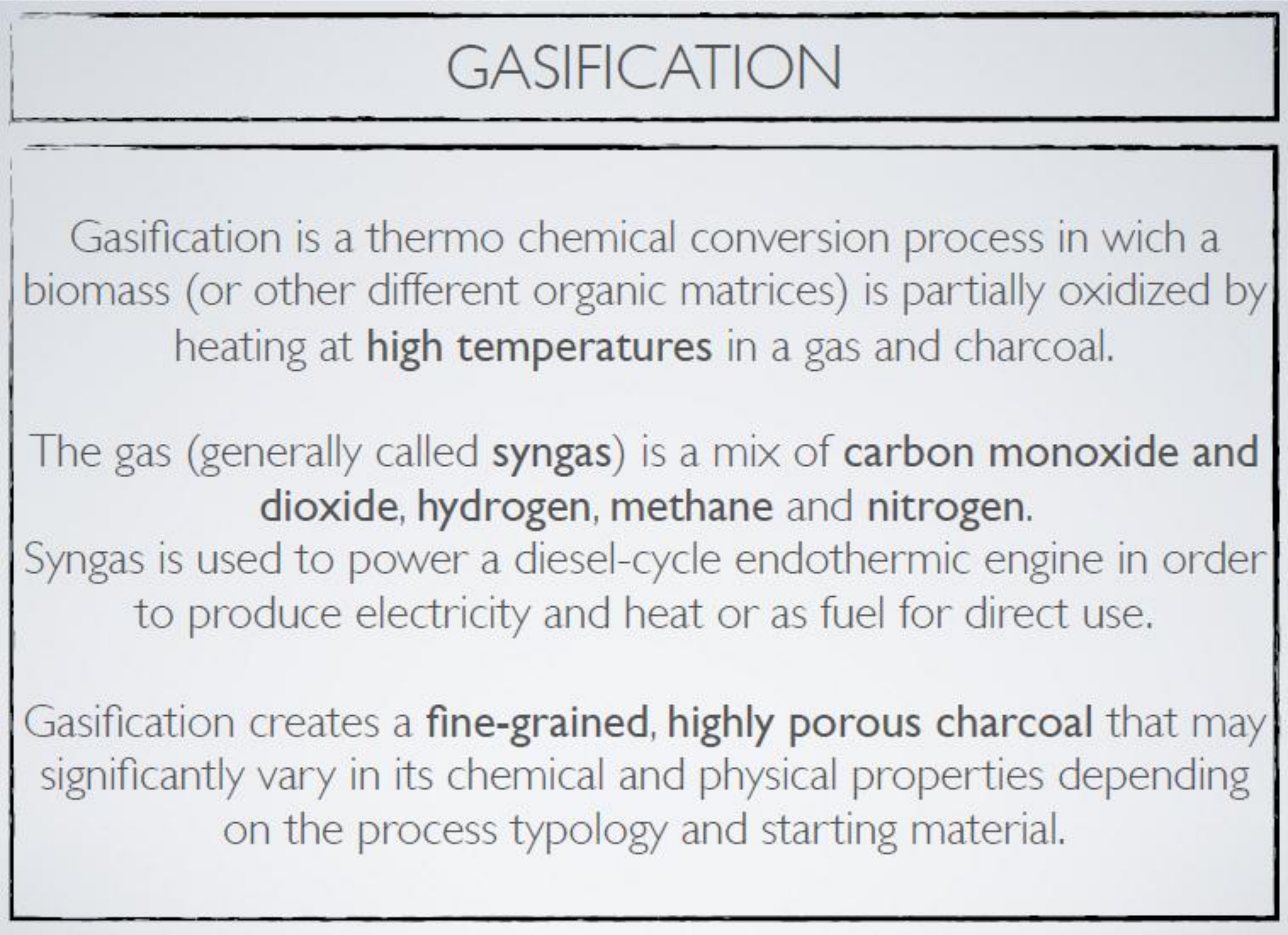
- Soil amendment (neutral / alkaline pH, porosity retains water, cation exchange capacity: robust benefits to plant growth compared to high-temp char)
- Fuel (cooking and heat)

- Extreme porosity and surface area
- Water filtration and adsorption of contaminants (gas, liquid or solid)

- Fuel (low yield, high reactivity)
- Contamination of some feedstocks (e.g. metal and plastic in kitchen waste) may preclude use of sludge / char in soil

- Fuel (for electricity or cooking)
- By-products (wood spirits, wood tar)
- Substitute for coal-derived coke in metal smelting

Industrial gasification process: *biochar is only a by-product*



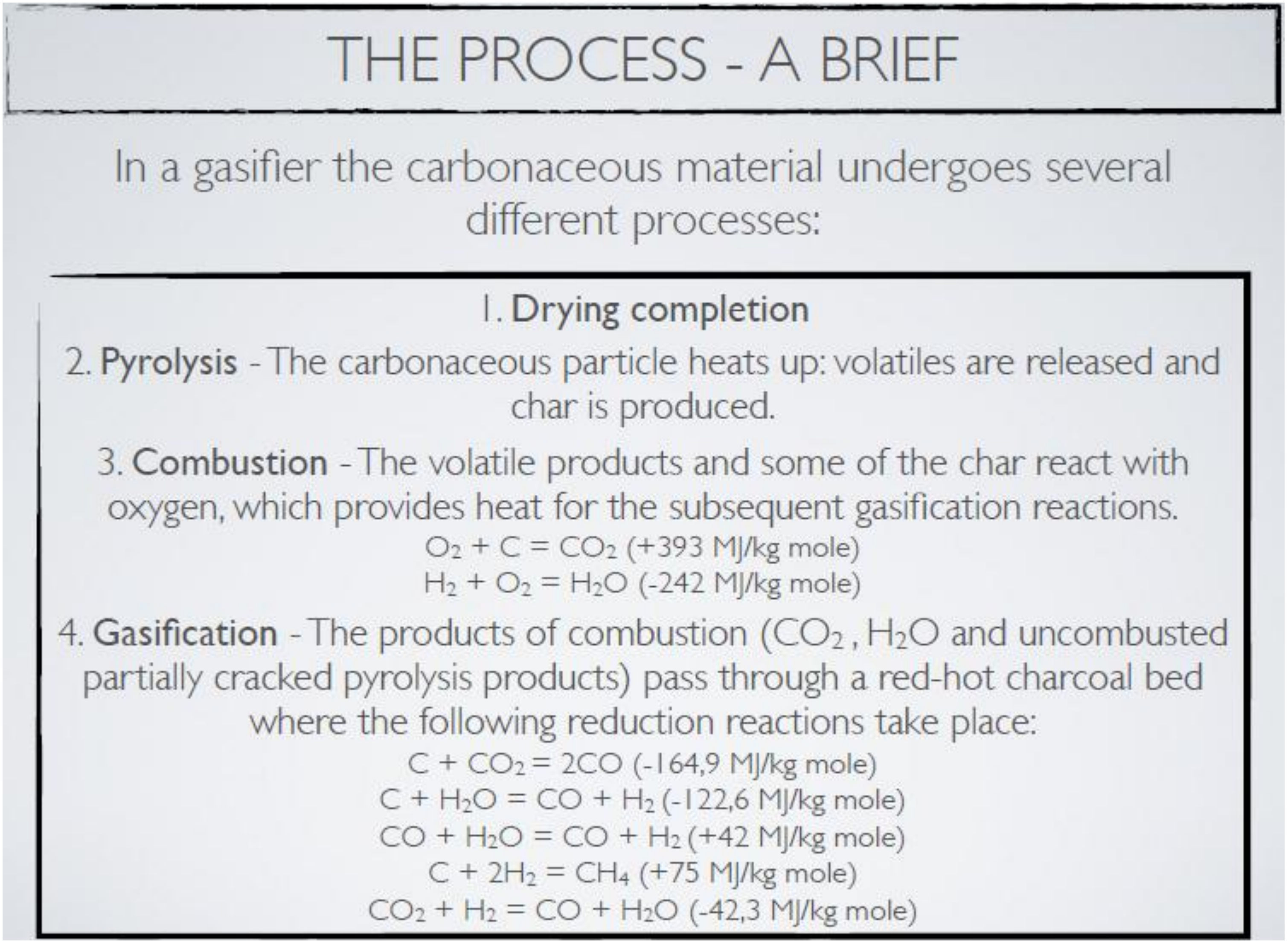
GASIFICATION

Gasification is a thermo chemical conversion process in wich a biomass (or other different organic matrices) is partially oxidized by heating at **high temperatures** in a gas and charcoal.

The gas (generally called **syngas**) is a mix of **carbon monoxide and dioxide**, **hydrogen**, **methane** and **nitrogen**.
Syngas is used to power a diesel-cycle endothermic engine in order to produce electricity and heat or as fuel for direct use.

Gasification creates a **fine-grained**, **highly porous charcoal** that may significantly vary in its chemical and physical properties depending on the process typology and starting material.

Industrial gasification process: *biochar is only a by-product*



THE PROCESS - A BRIEF

In a gasifier the carbonaceous material undergoes several different processes:

1. **Drying completion**

2. **Pyrolysis** - The carbonaceous particle heats up: volatiles are released and char is produced.

3. **Combustion** - The volatile products and some of the char react with oxygen, which provides heat for the subsequent gasification reactions.

$O_2 + C = CO_2$ (+393 MJ/kg mole)

$H_2 + O_2 = H_2O$ (-242 MJ/kg mole)

4. **Gasification** - The products of combustion (CO_2, H_2O and uncombusted partially cracked pyrolysis products) pass through a red-hot charcoal bed where the following reduction reactions take place:

$C + CO_2 = 2CO$ (-164,9 MJ/kg mole)

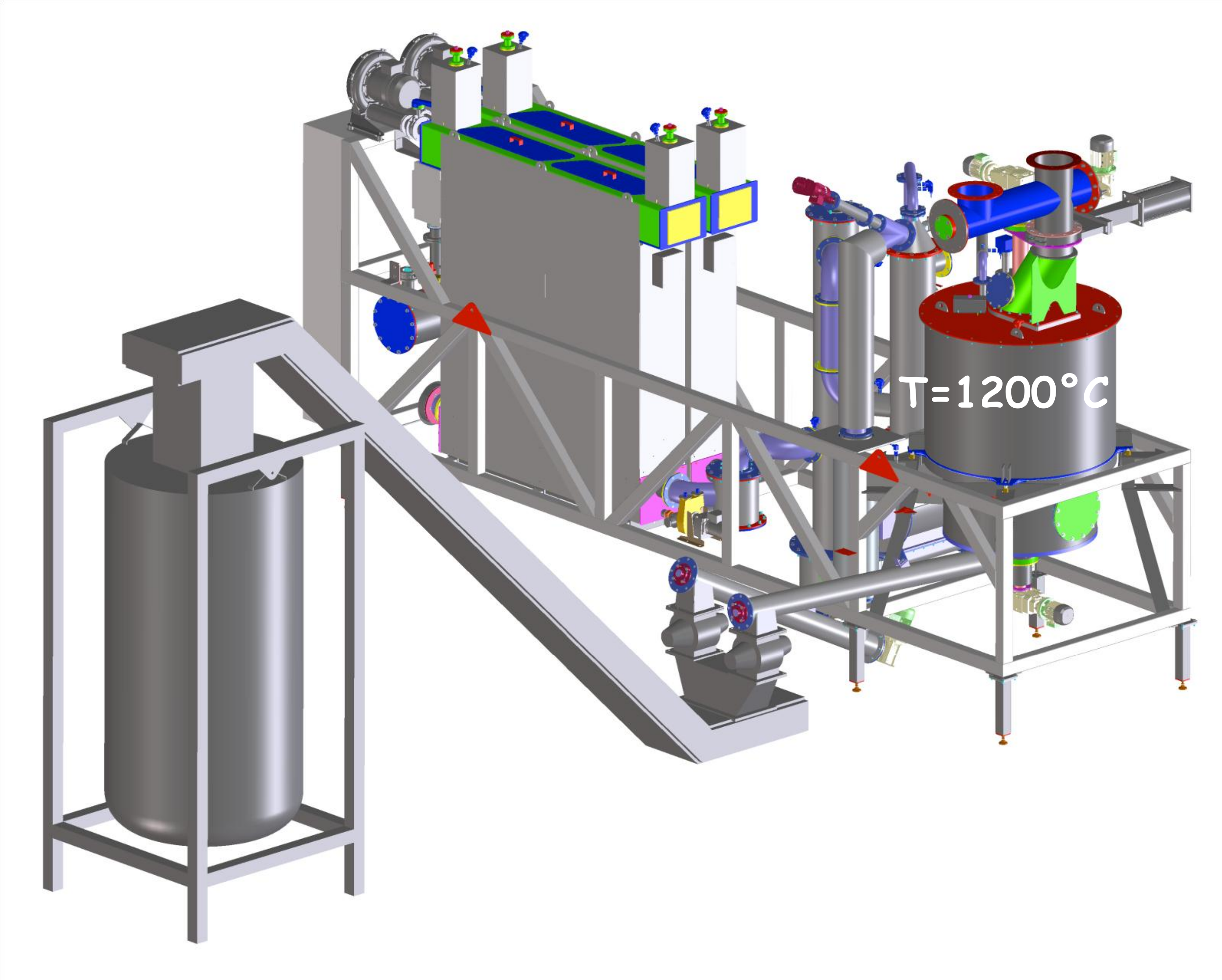
$C + H_2O = CO + H_2$ (-122,6 MJ/kg mole)

$CO + H_2O = CO + H_2$ (+42 MJ/kg mole)

$C + 2H_2 = CH_4$ (+75 MJ/kg mole)

$CO_2 + H_2 = CO + H_2O$ (-42,3 MJ/kg mole)

Industrial gasification process: *biochar is only a by-product*



Eight key questions:

1) Is all biochar the same?
2) How stable is it?
3) Is it safe to use?
4) What are the agronomic benefits?
5) Is it economically viable?
6) What are the environmental and societal benefits?
7) Are the benefits of biochar in mitigating greenhouse gases widely accepted?
8) What are the research gaps and future challenges?

Biochar produced from gasification of

1. Poplar residues
2. Residues from coniferous trees
3. Marc residues

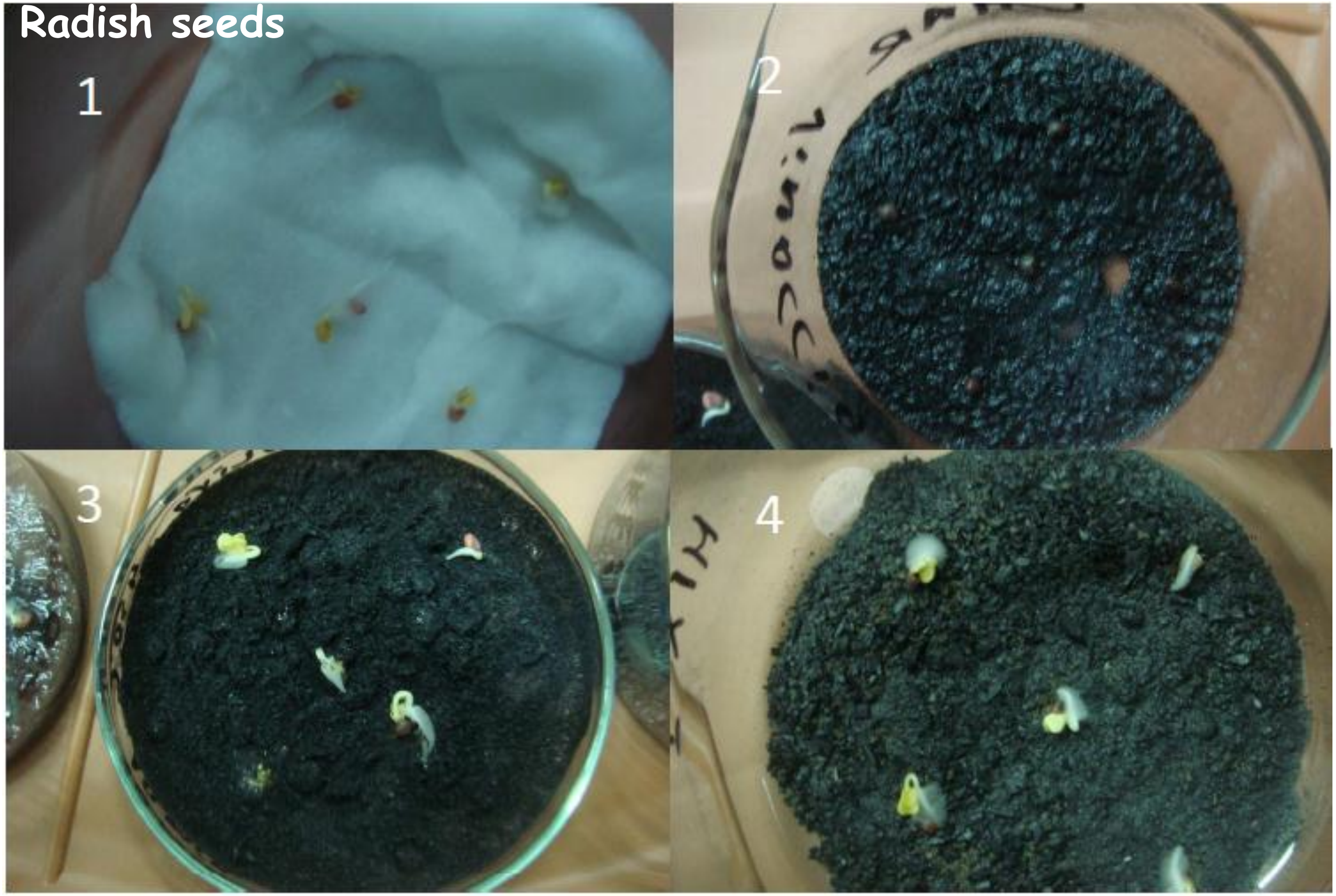
Experimental design

Seeds on wet cotton

Seeds on a soil

Seeds on biochar

Seeds on a mixture Biochar/soil (1:5)



1) cotton; 2) marc; 3) poplar; 4) conifer