Freie Universität Bozen
Libera Università di Bolzano
Free University of Bolzano

Valorisation of char residues from biomass gasification in adsorption applications

V. Benedetti, E. Cordioli, F. Patuzzi, M. Baratieri

Heraklion, 27.06.2019

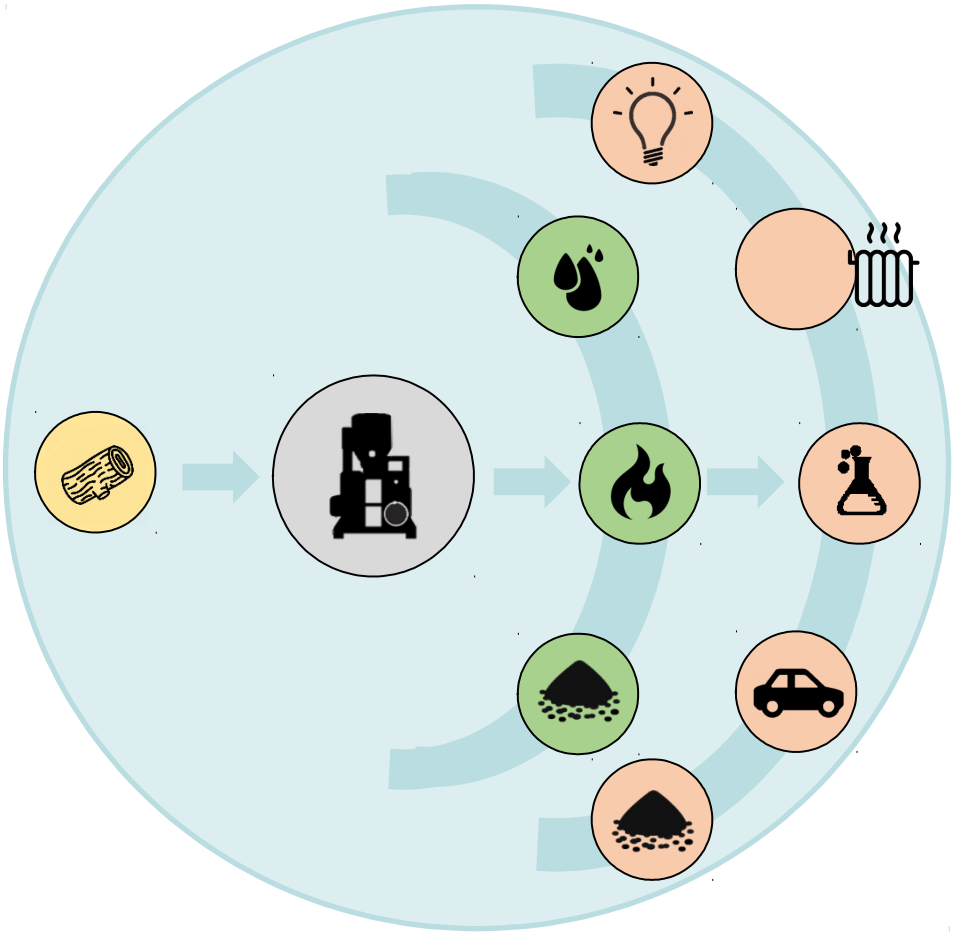
Background

Biomass gasification

- Gas
- Tar (liquid)
- Char (solid)

South Tyrol: about **1300 tons/year** of char disposed of as industrial waste with a high cost for disposal (140 - 150 €/ton)

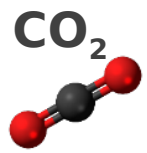
Valorization



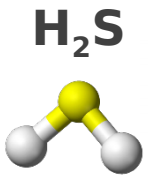
Char valorization at UNIBZ

Catalysis

Agriculture



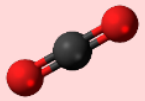
Adsorption



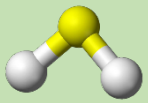
Tar removal

Outline

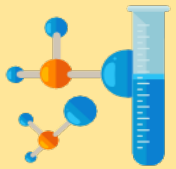
Char collection and characterization



CO_2 adsorption



H_2S adsorption

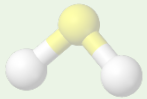


Other applications

Outline

Char collection and characterization

CO_2 adsorption

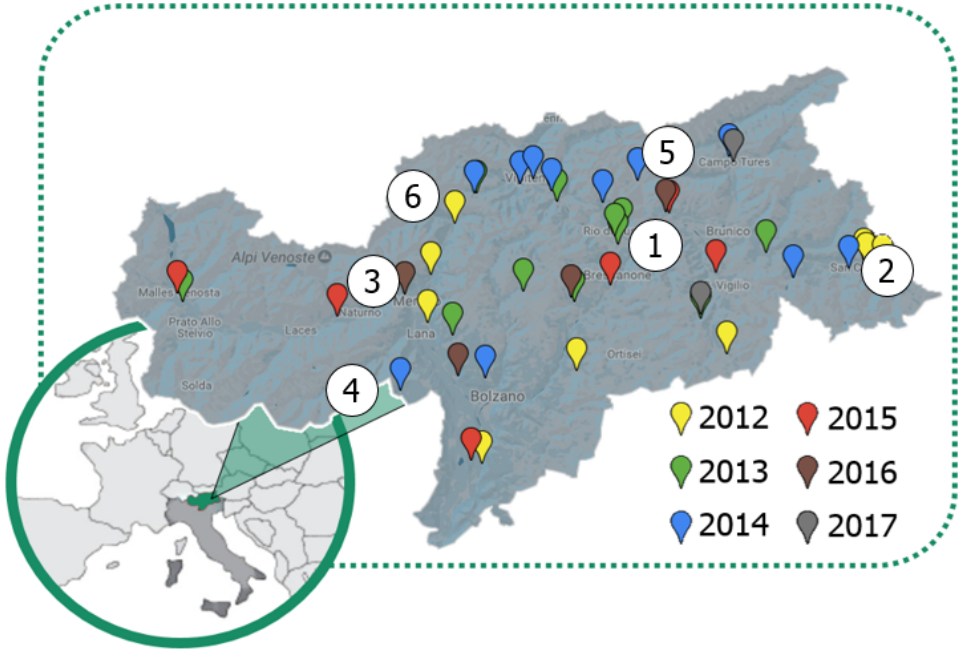


H_2S adsorption

Other applications

Gasification technologies

	Feedstock	Technology	Electric power kW_{el}	Thermal power kW_{th}	T °C
1	Wood chips	Dual-stage	50	110	~900
2	Wood chips	Dual-stage	280	540	~850
3	Pellets	Rising co-current	180	270	~700
4	Wood chips	Downdraft	150	260	~650
5	Wood chips	Downdraft	296	550	~800
6	Wood chips	Downdraft	45	120	~650

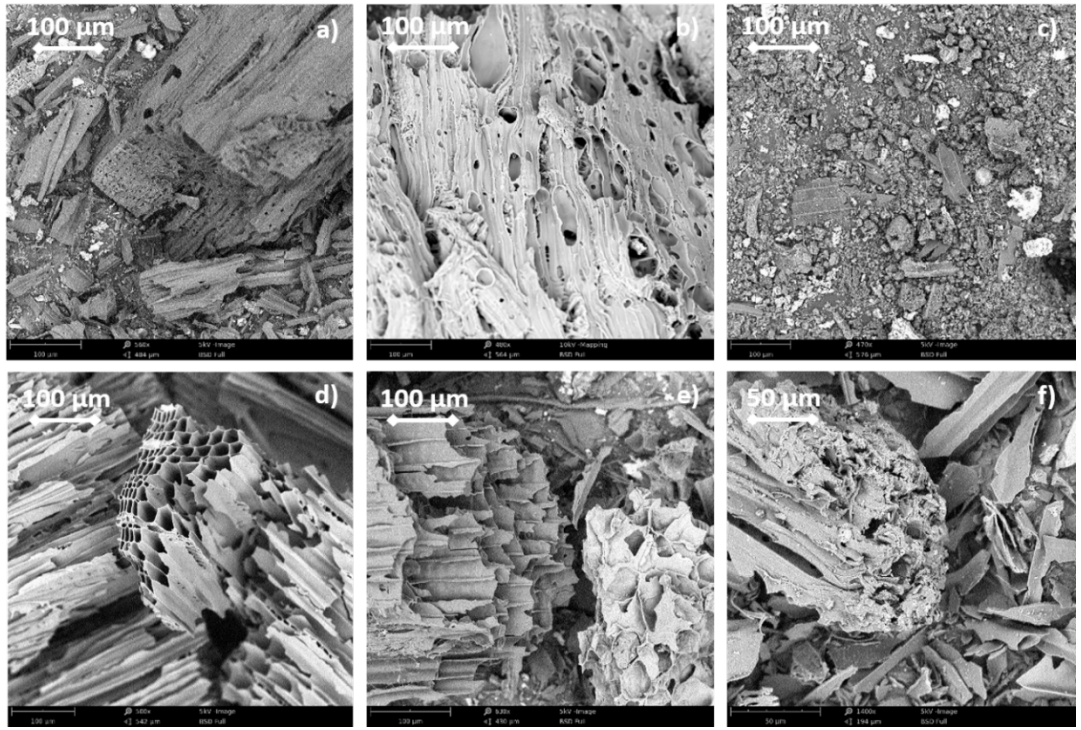


- Scanning electron microscopy
- Small angle X-ray scattering
- Thermogravimetric analysis

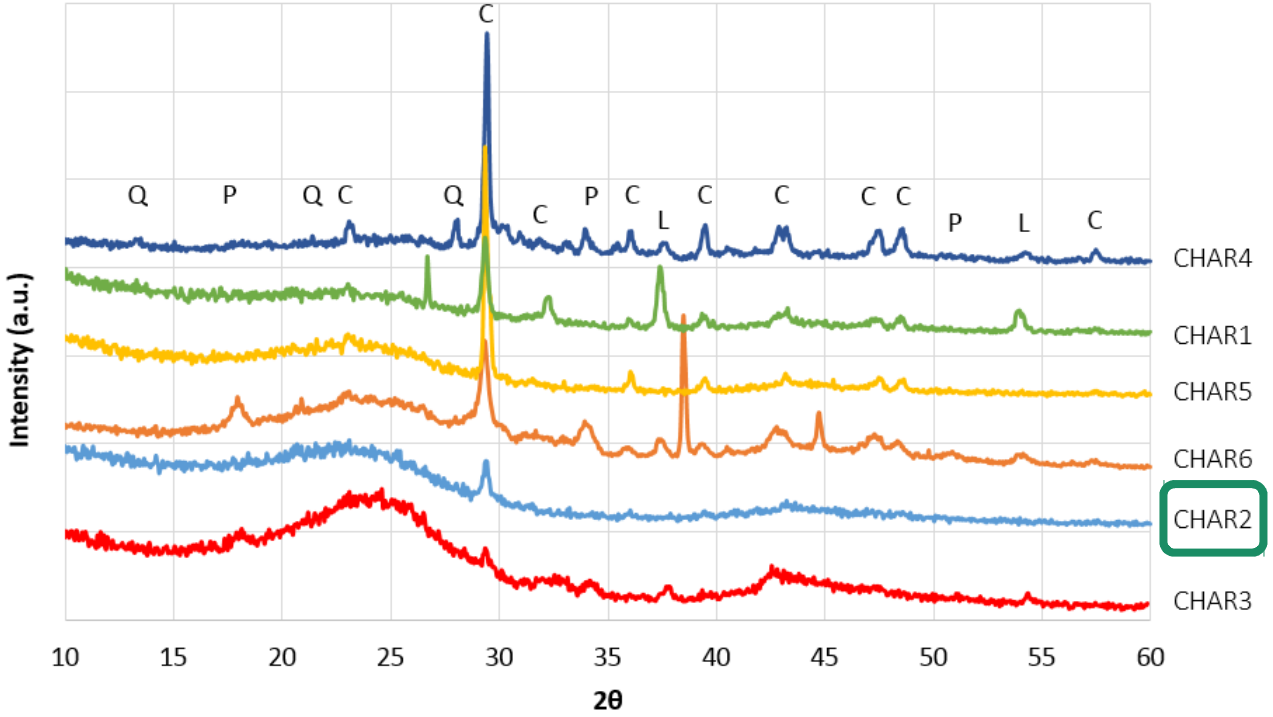
V. Benedetti et al., Characterization of char from biomass gasification and its similarities with activated carbon in adsorption applications, Appl. Energy, 227 (2018) 92-99.

Differences among chars

SEM



XRD



Q: quartz (SiO_2), P: portlandite ($Ca(OH)_2$), C: calcite ($CaCO_3$), L: lime (CaO)

Elemental analysis (% wt_{dry})

Sample	C %wt_{dry}	H %wt_{dry}	N %wt_{dry}	S %wt_{dry}	O %wt_{dry}	Ash %wt_{dry}
CHAR1	81.13	0.23	0.28	0.35	3.74	14.62
CHAR2	91.39	0.72	0.26	0.57	3.43	4.20
CHAR3	81.17	0.25	0.61	0.27	1.89	16.08
CHAR4	48.12	0.49	0.23	0.32	1.64	49.52
CHAR5	80.64	0.55	0.2	0.20	2.79	15.80
CHAR6	68.63	0.33	0.83	0.32	2.05	27.84

1. **Highest surface area**
   Low amount of ash

2. High surface area
   Lowest amount of ash

Surface area

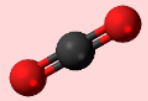
	S_{BET}	pore size	pore volume
	m^2/g	nm	cm^3/g
CHAR1	603	3.88	0.30
CHAR2	297	4.50	0.26
CHAR3	403	4.70	0.50
CHAR4	183	4.90	0.25
CHAR5	427	4.40	0.39
CHAR6	252	4.54	0.24

→ **ADSORPTION**

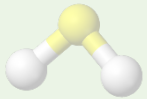
→ **CATALYSIS**

Outline

Char collection
and characterization



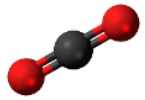
CO_2
adsorption



H_2S
adsorption

Other
applications

Materials and methods

Adsorptive:  CO_2

Adsorbent:


5 pure chars

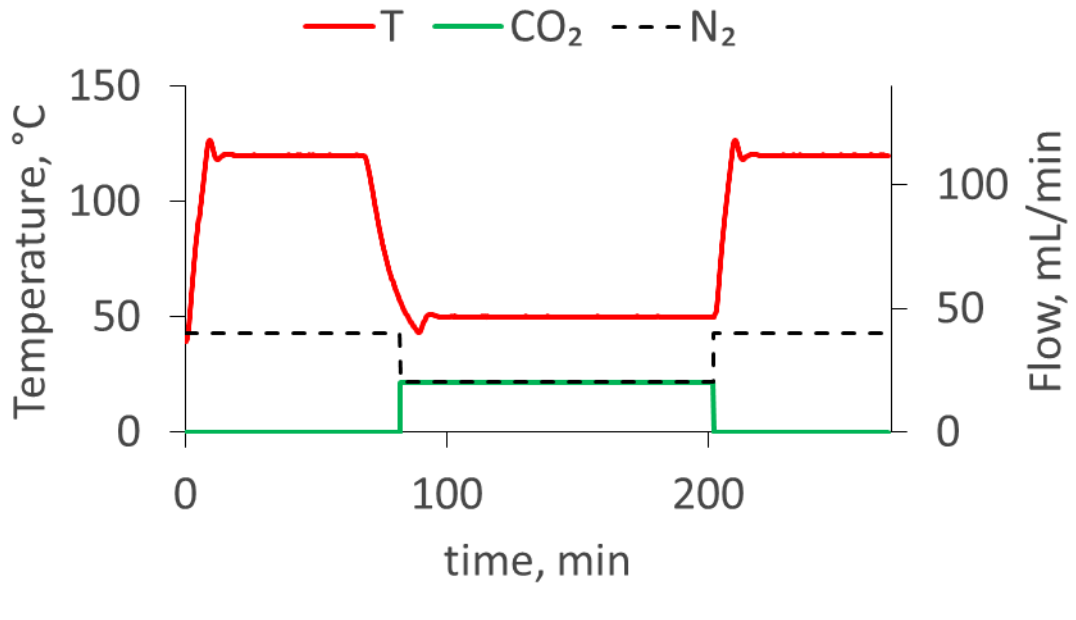

2 activated chars


2 AC

- KOH - $ZnCl_2$
- N_2
- 600 °C
- 1 hour

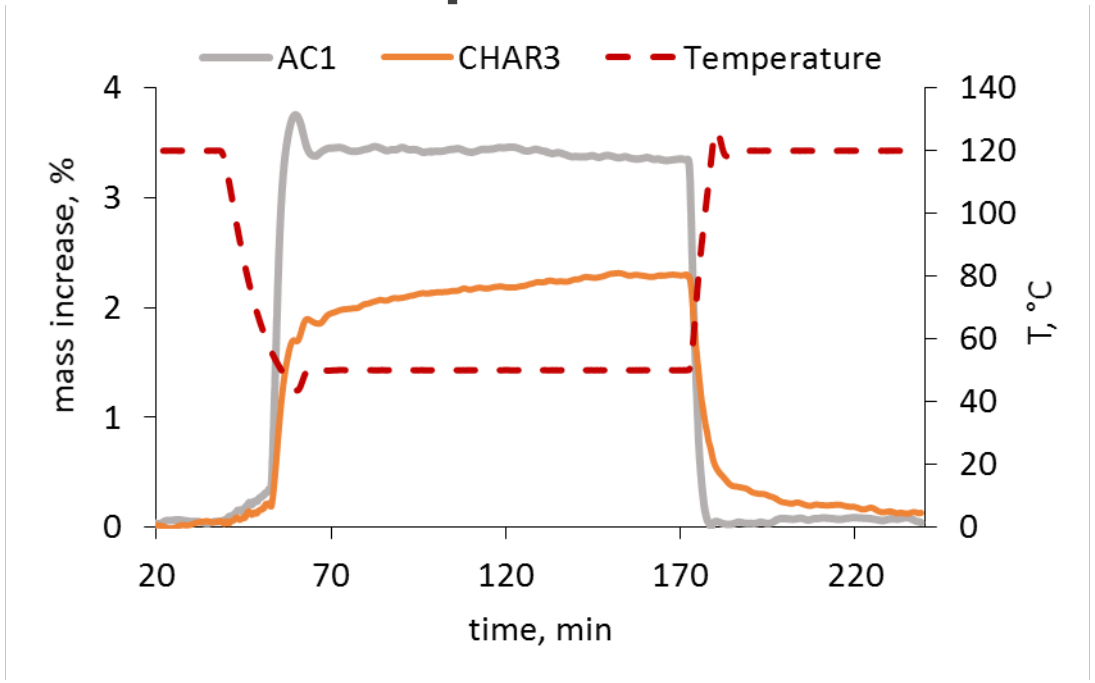
- T_{ads} = 50 - 75 - 100 °C
- CO_2:N_2 = 1:1 - 1:4

Thermo-gravimetric tests
run in a Jupiter STA449-F3 (Netzsch)



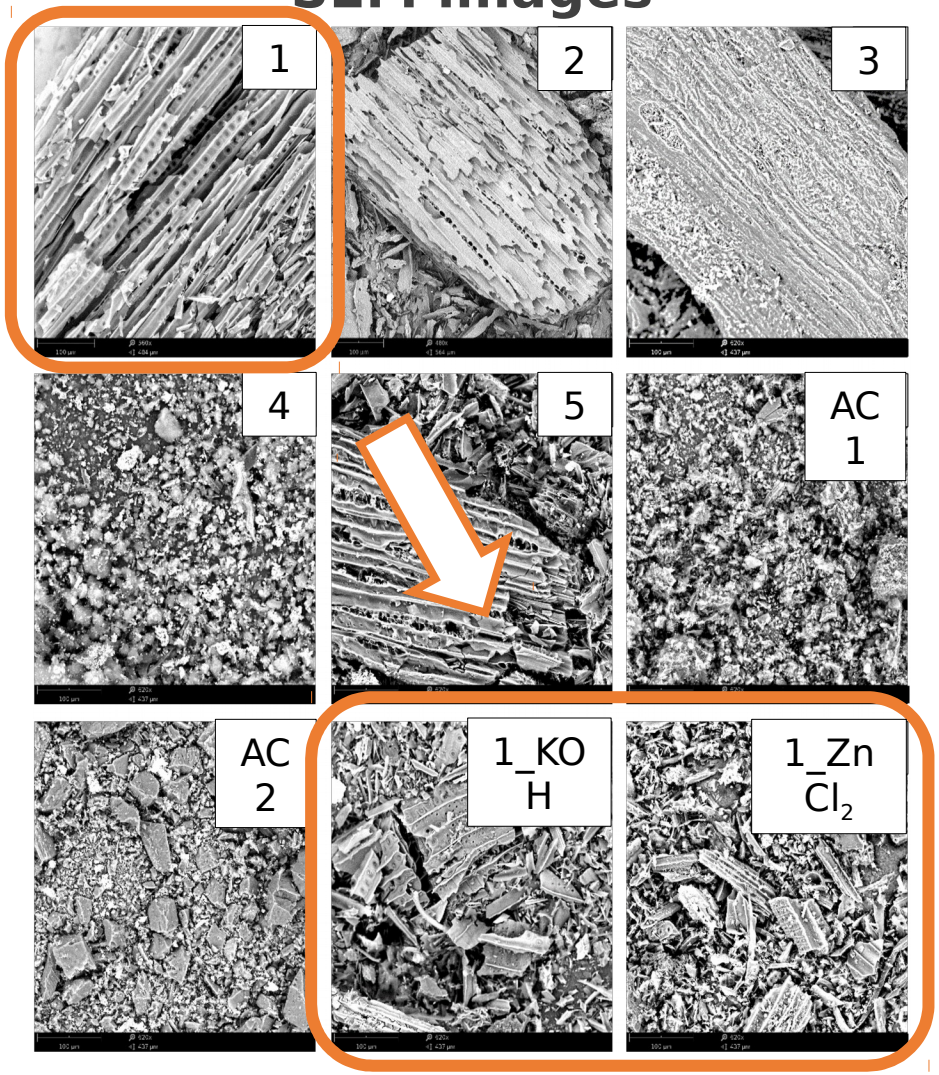
Results

Adsorption curves



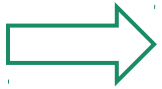
V. Benedetti et al., CO_2 adsorption study on pure and chemically activated chars derived from commercial biomass gasifiers, J. CO_2 util., 33 (2019) 46-54.

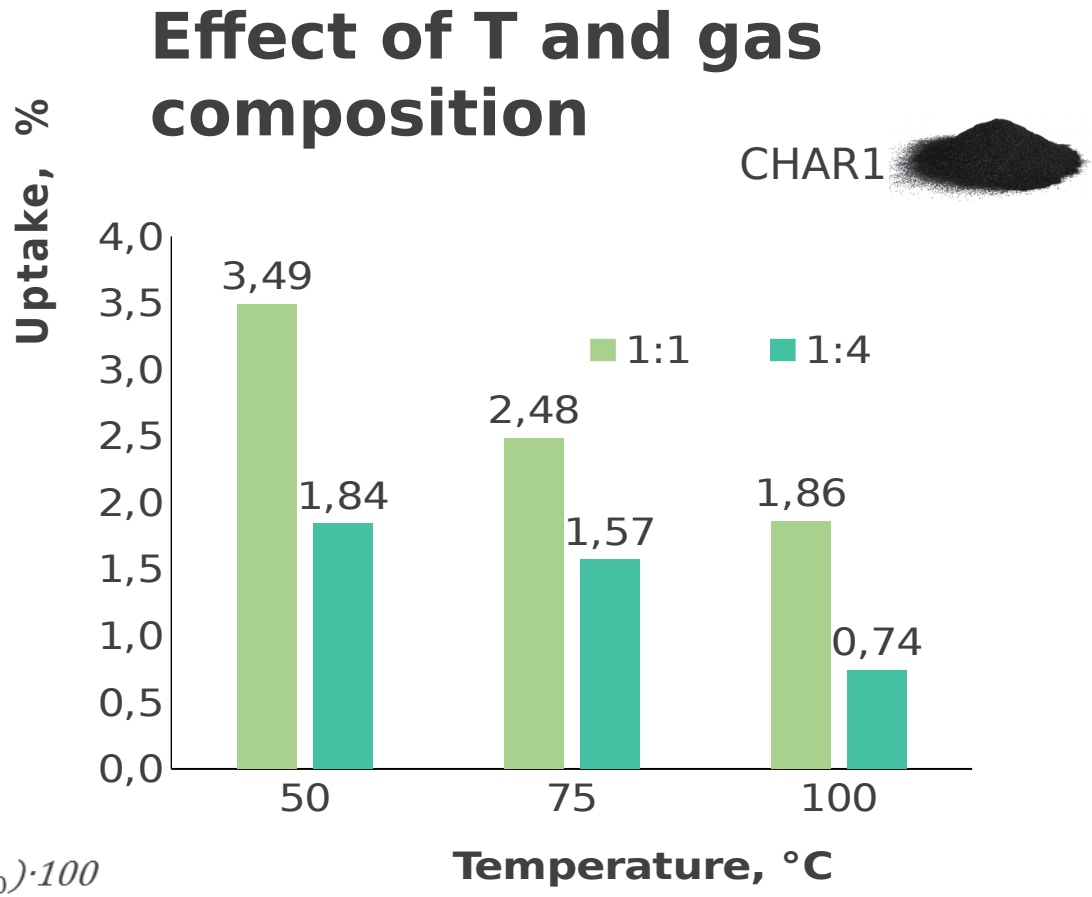
SEM images



Results

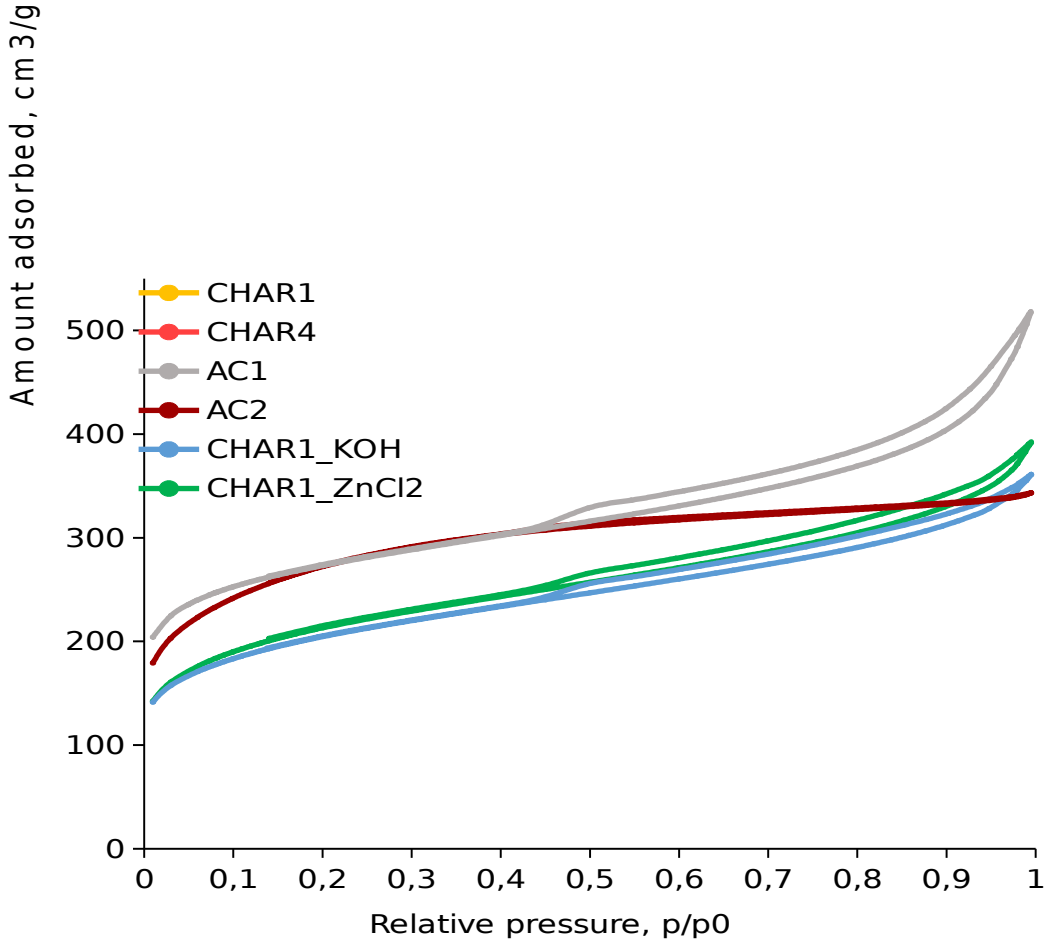
	Sample	Uptake, %	N_2 uptake, %
Pure char	CHAR1	3.49	0.20
	CHAR2	3.04	0.14
	CHAR3	2.09	0.08
	CHAR4	1.69	0.65
	CHAR5	2.75	0.17
	AC1	3.01	0.10
	AC2	2.13	0.07
Activated char	CHAR1_KOH	3.73	0.35
	CHAR1_ZnCl2	3.03	0.13
	Literature	2.50 - 10.70	





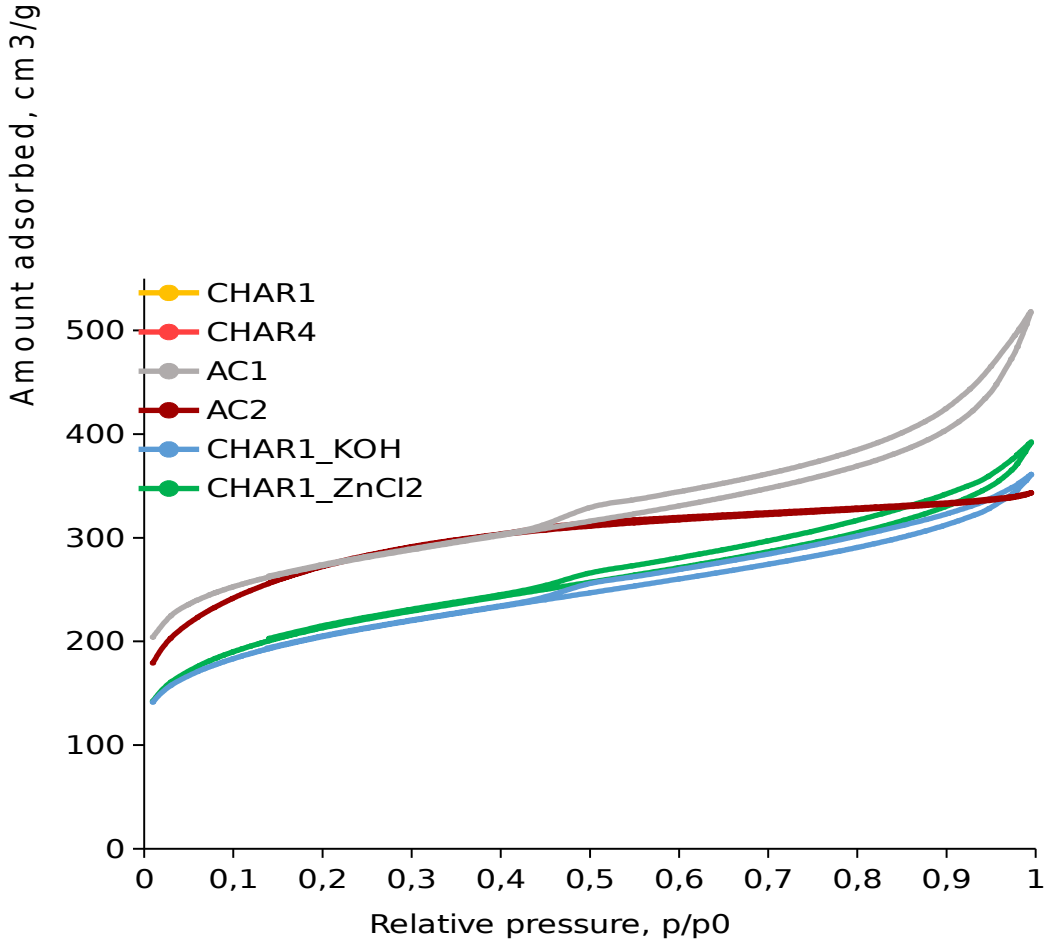
$$Uptake = \frac{(W_{end} - W_0) \cdot 100}{W_0}$$

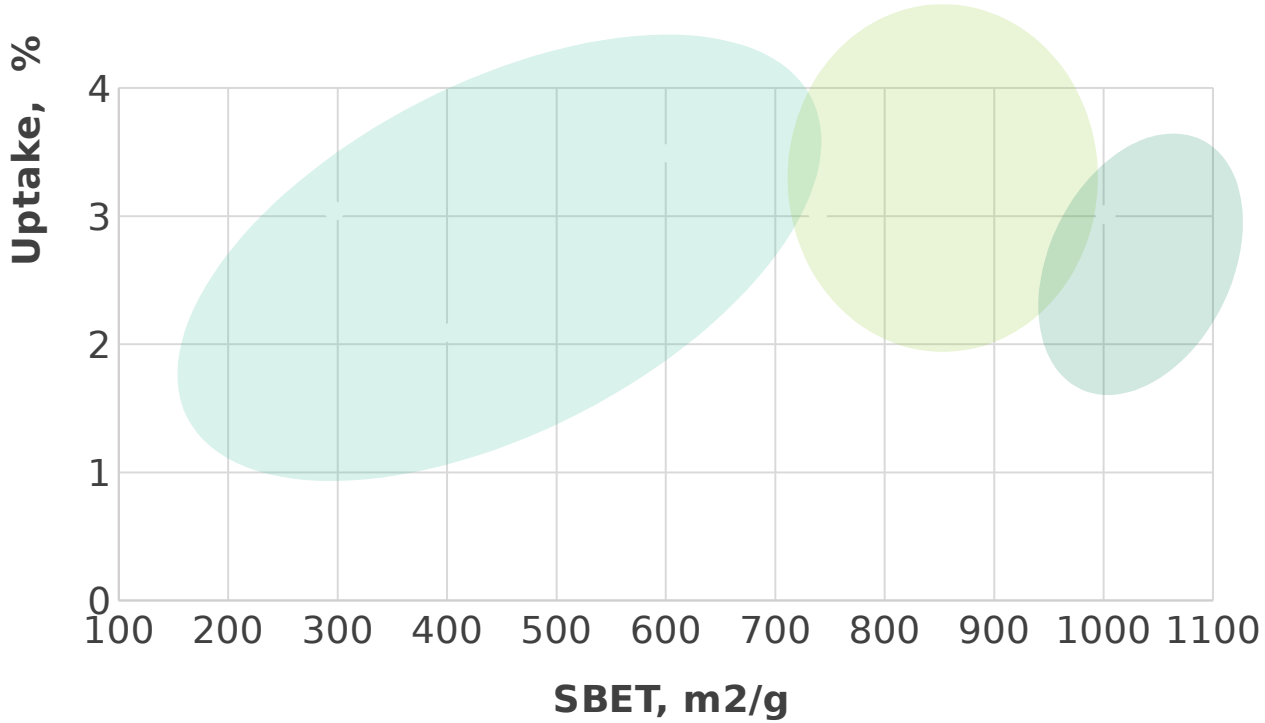
Results - physisorption



	S_{BET} m^2/g	Pore size nm	Pore volume cm^3/g	µ-pore volume cm^3/g
CHAR1	603	3.88	0.30	0.05
CHAR2	297	4.50	0.26	0.02
CHAR3	403	4.70	0.50	0.02
CHAR4	183	4.90	0.25	n.a.
CHAR5	427	4.40	0.39	0.06
AC1	1002	6.10	0.51	0.22
AC2	984	2.90	0.25	0.14
CHAR1_KOH	774	4.57	0.41	0.11
CHAR1_ZnCl2	739	4.85	0.37	0.11

Results - physisorption

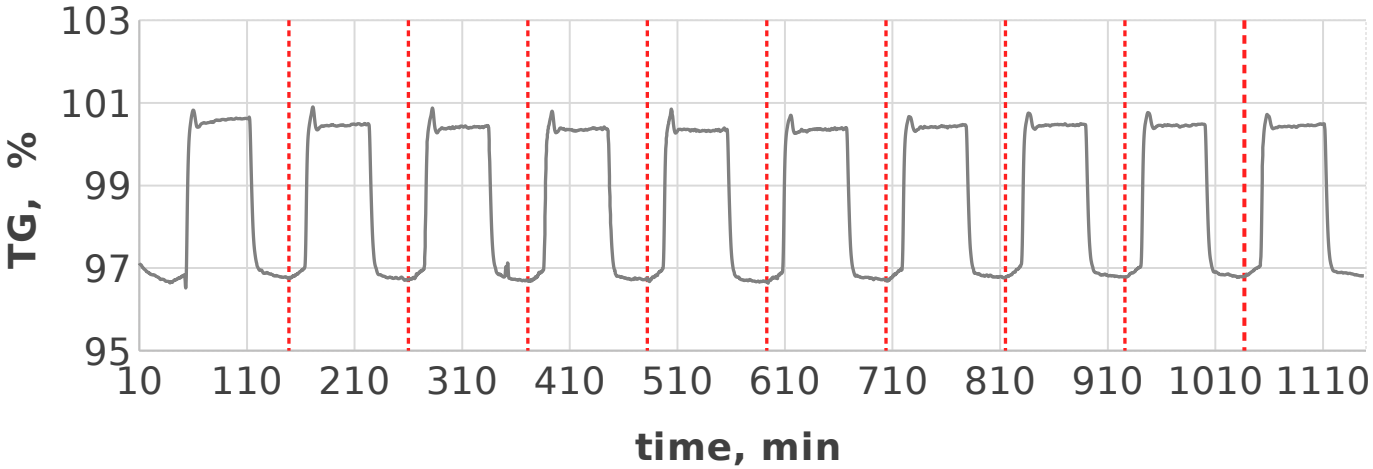


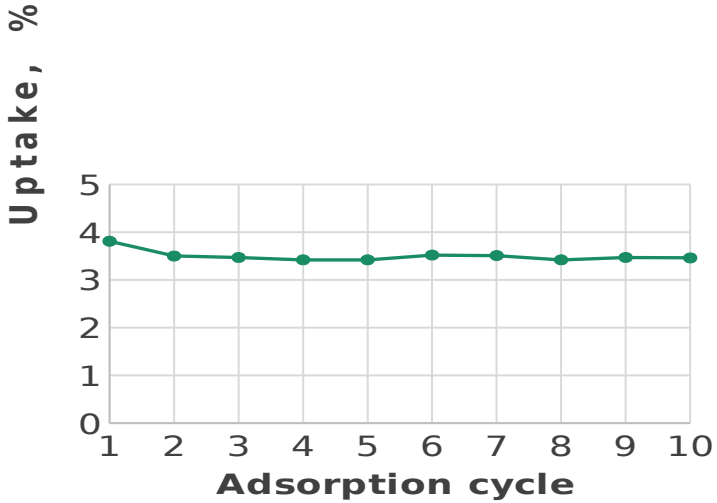


Results

CHAR1_KOH

Adsorption/desorption cycles to test loss of char adsorption capacity





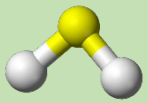
- High selectivity
- High adsorption capacity
- Good adsorption/desorption kinetics
- Stable adsorption capacity after repeated cycles

Effective CO_2 adsorbent

Outline

Char collection
and characterization

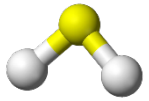
CO_2
adsorption



H_2S
adsorption

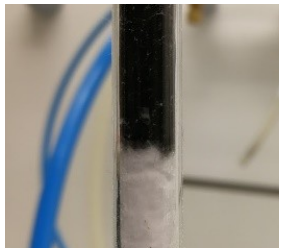
Other
applications

Meterials and methods

Adsorptive:  H_2S

Adsorbent:  5 pure chars

 2 AC

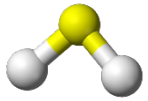


1 - Adsorption capacity

- Fixed bed reactor - quartz
- Char bed height: 2.5 cm (150 - 200 mg)
- H_2S + N_2: 100 NmL/min
- H_2S: 250 ppm
- T_{amb}
- Micro-GC for gas analysis at the

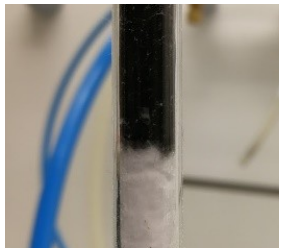
$$m_{ads} = f\frac{M\,P\,Q}{R\,T\,m_{char}}\int_{o}^{t_{fin}}\left(y_{in}-y_{out}\right)dt$$

Meterials and methods

Adsorptive:  H_2S

Adsorbent: 

Best performing char



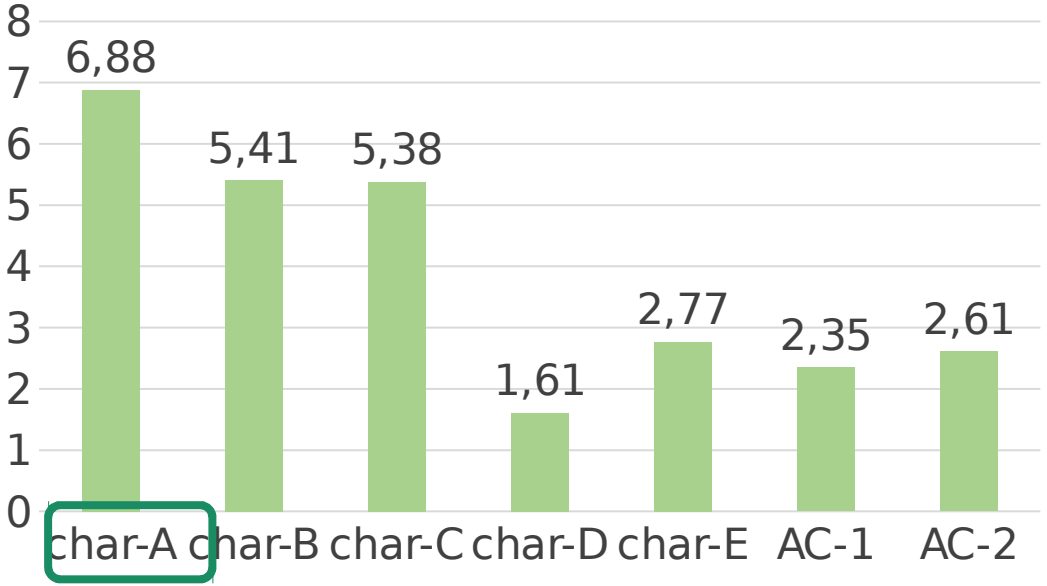
2 - Effect of inlet concentration

- Fixed bed reactor - quartz
- Char bed height: 2.5 cm (150 - 200 mg)
- H_2S + N_2: 100 NmL/min
- **H_2S: 250 -550 -1000 ppm**
- T_{amb}
- Micro-GC for gas analysis at the

$$m_{ads} = f\frac{M\,P\,Q}{R\,T\,m_{char}}\int_{o}^{t_{fin}}\left(y_{in}-y_{out}\right)dt$$

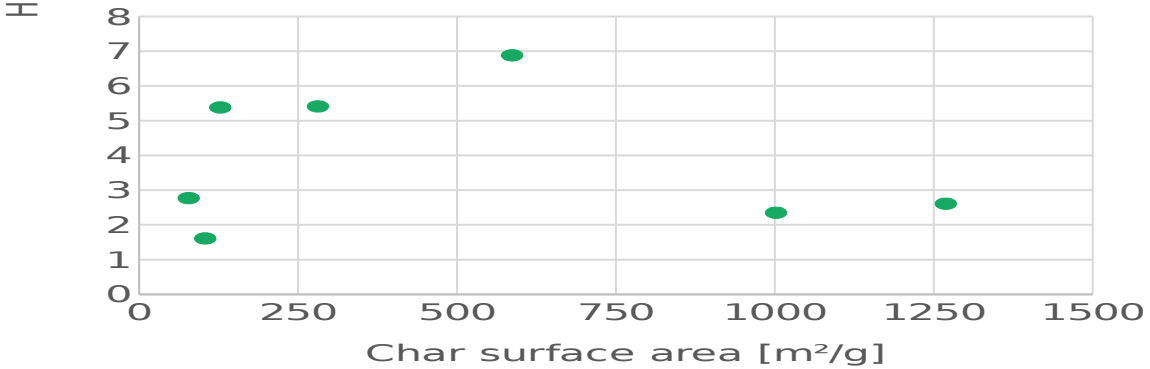
Results

H2S adsorption capacity [mg/g]



Literature 1.71 - 65 mg/g AC
0.04 - 0.22 mg/g char from pyrolysis

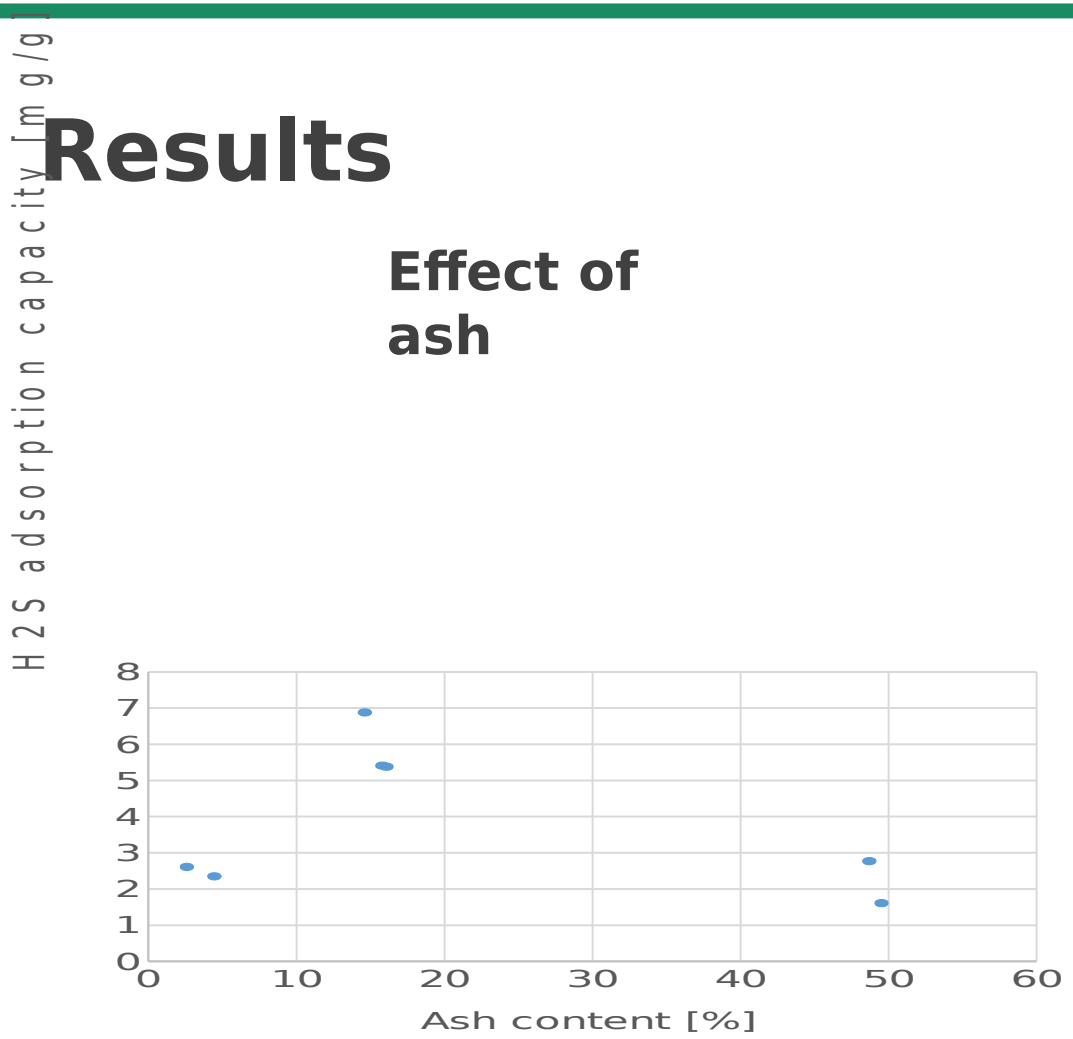
Effect of surface area



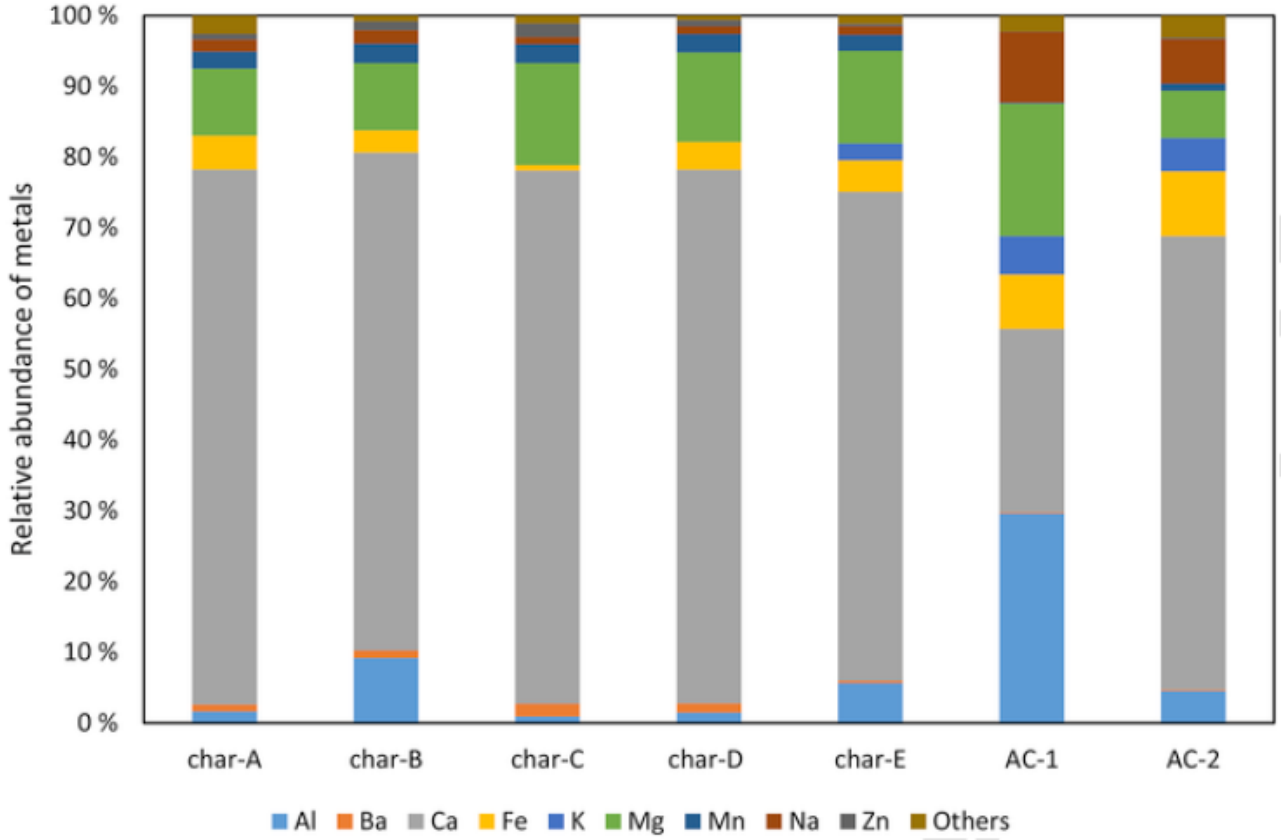
F. Marchelli et al., Experimental study on H_2S adsorption on gasification char under different operative conditions, Biomass Bioenergy 126 (2019) 106 - 116.

Results

Effect of ash



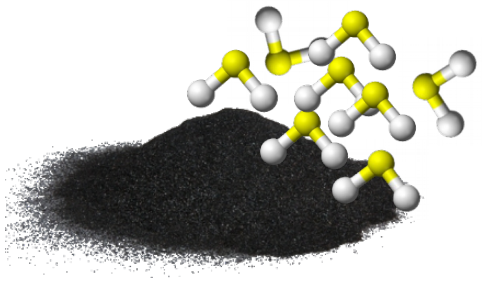
Metal content

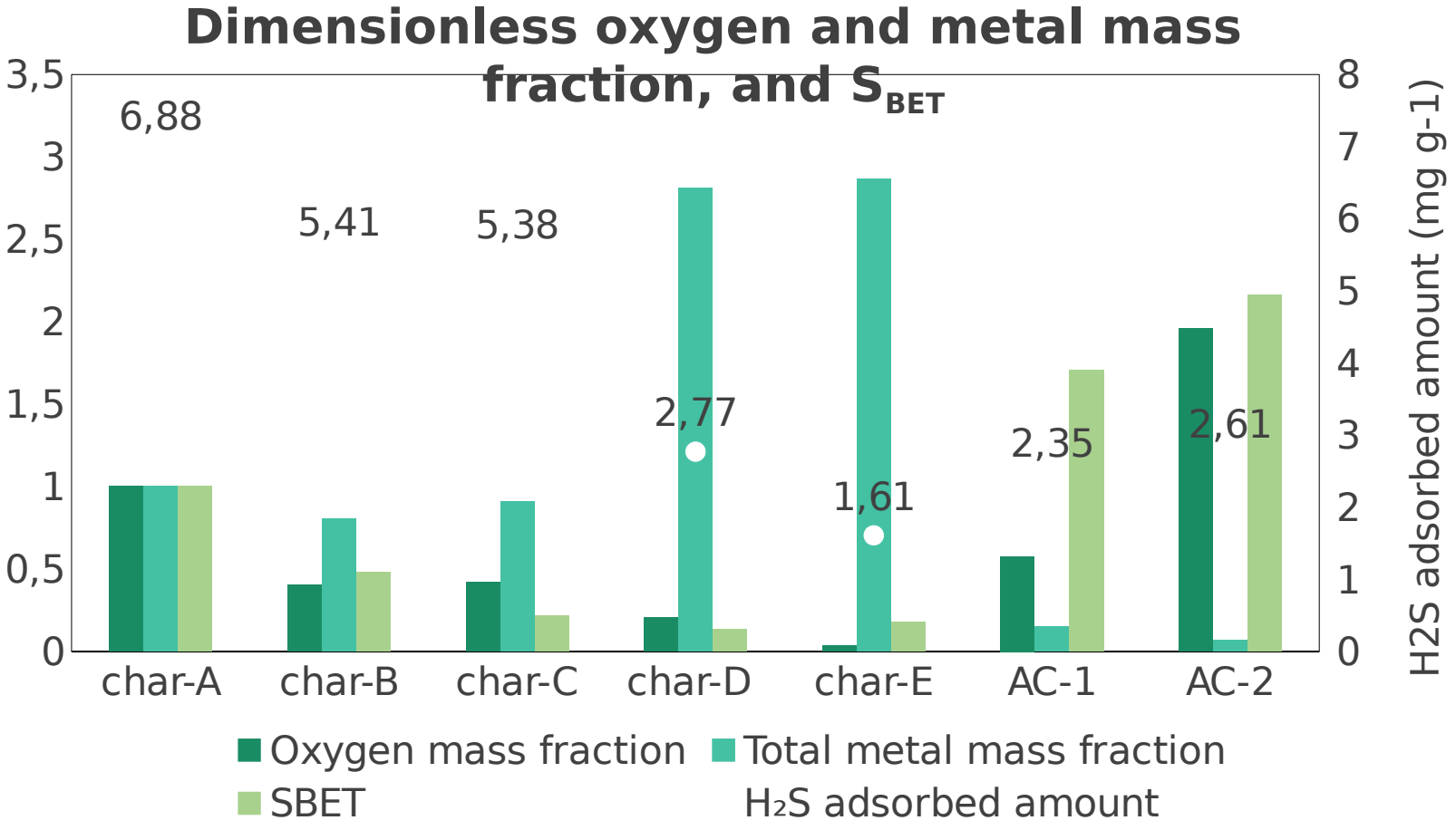


Results

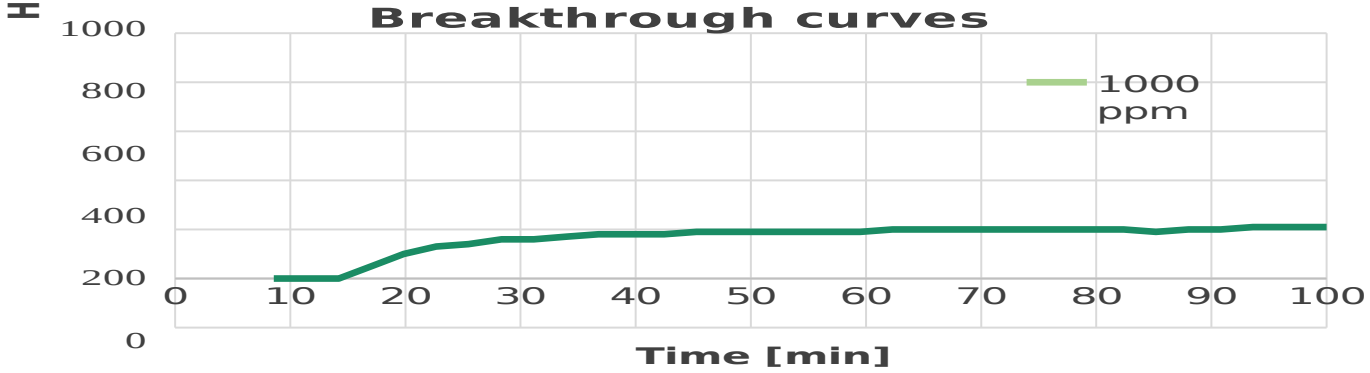
Effects of:

- Oxygen content
- Metals mass fraction
- Surface area





Results - Effect of concentration



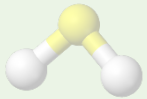
Inlet volume fraction of H_2S, ppm	H_2S adsorption Capacity, mg g^{-1}
250	6.88 ± 0.37
500	7.87 ± 0.70
1000	6.98 ± 0.24

Low concentrations slow down the process, but do not affect the adsorption capacity

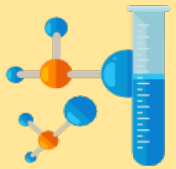
Outline

Char collection
and characterization

CO_2
adsorption

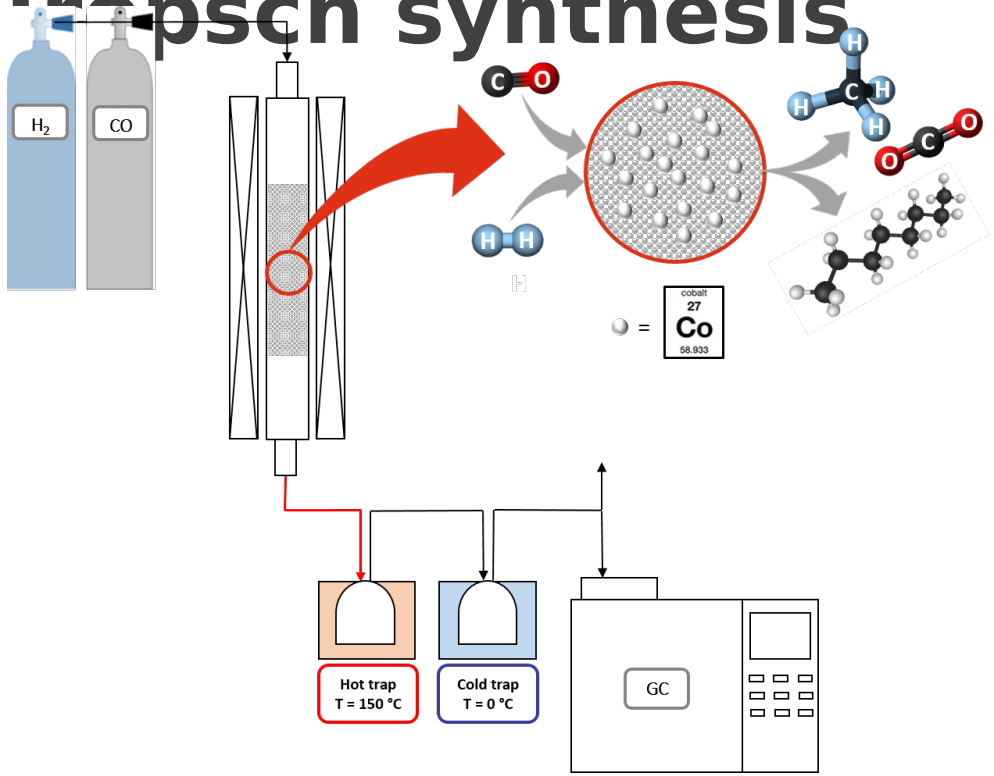


H_2S
adsorption



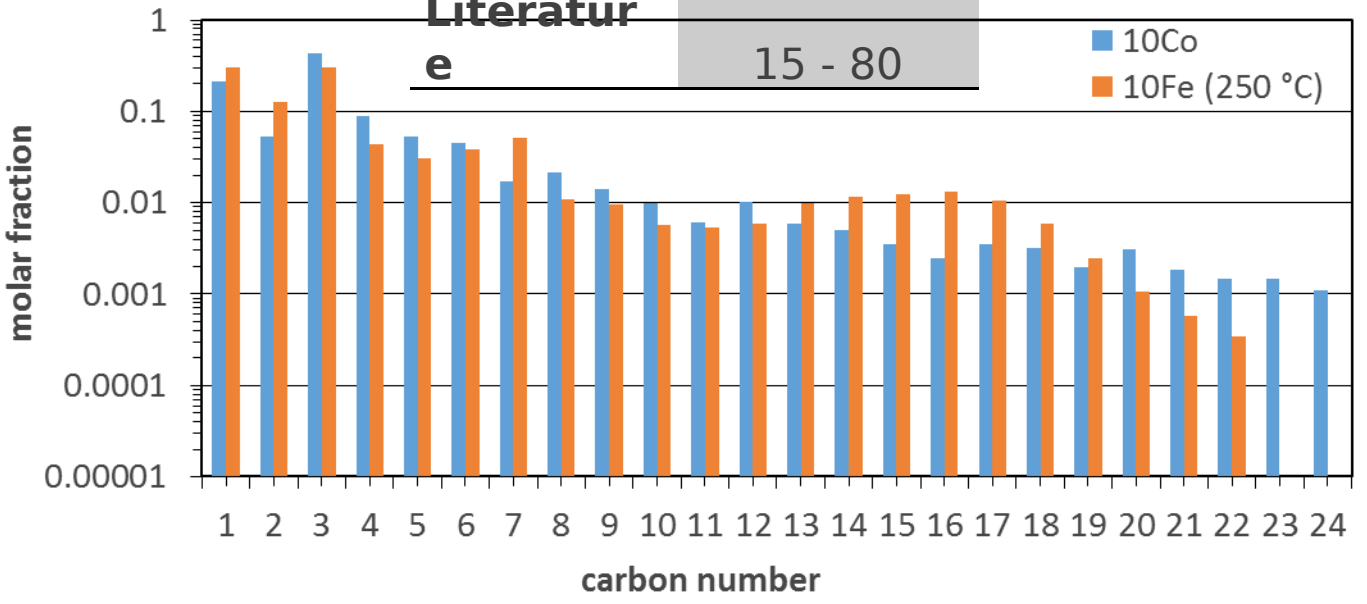
Other
applications

Char as catalyst support for Fischer-Tropsch synthesis



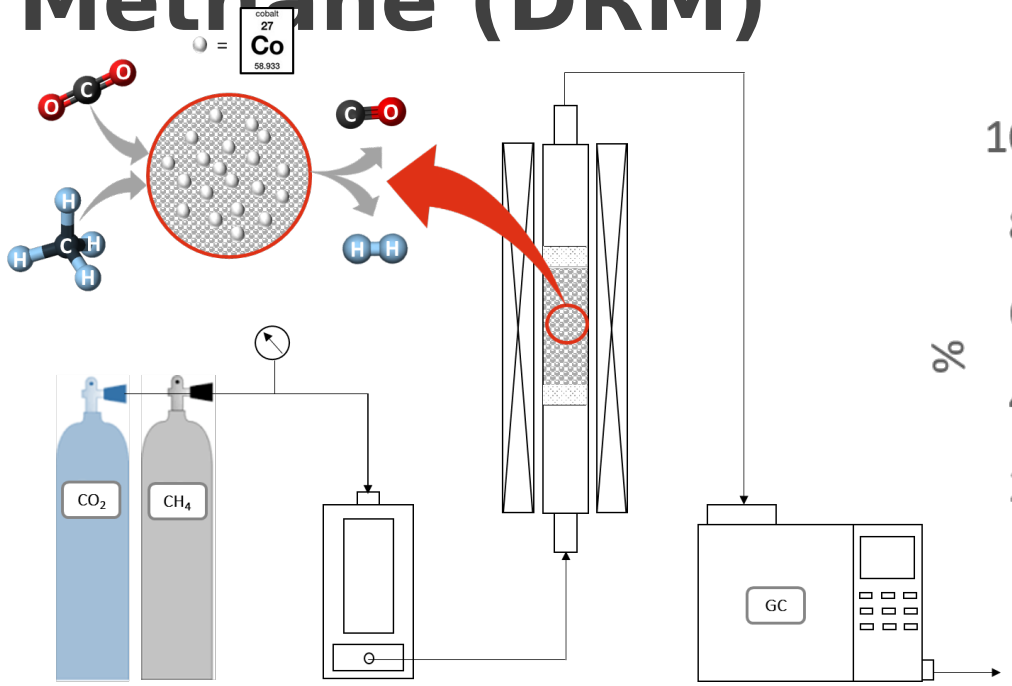
	CO conv., %
Char, 10% Co	8
Char, 10% Fe	26
Literature	15 - 80

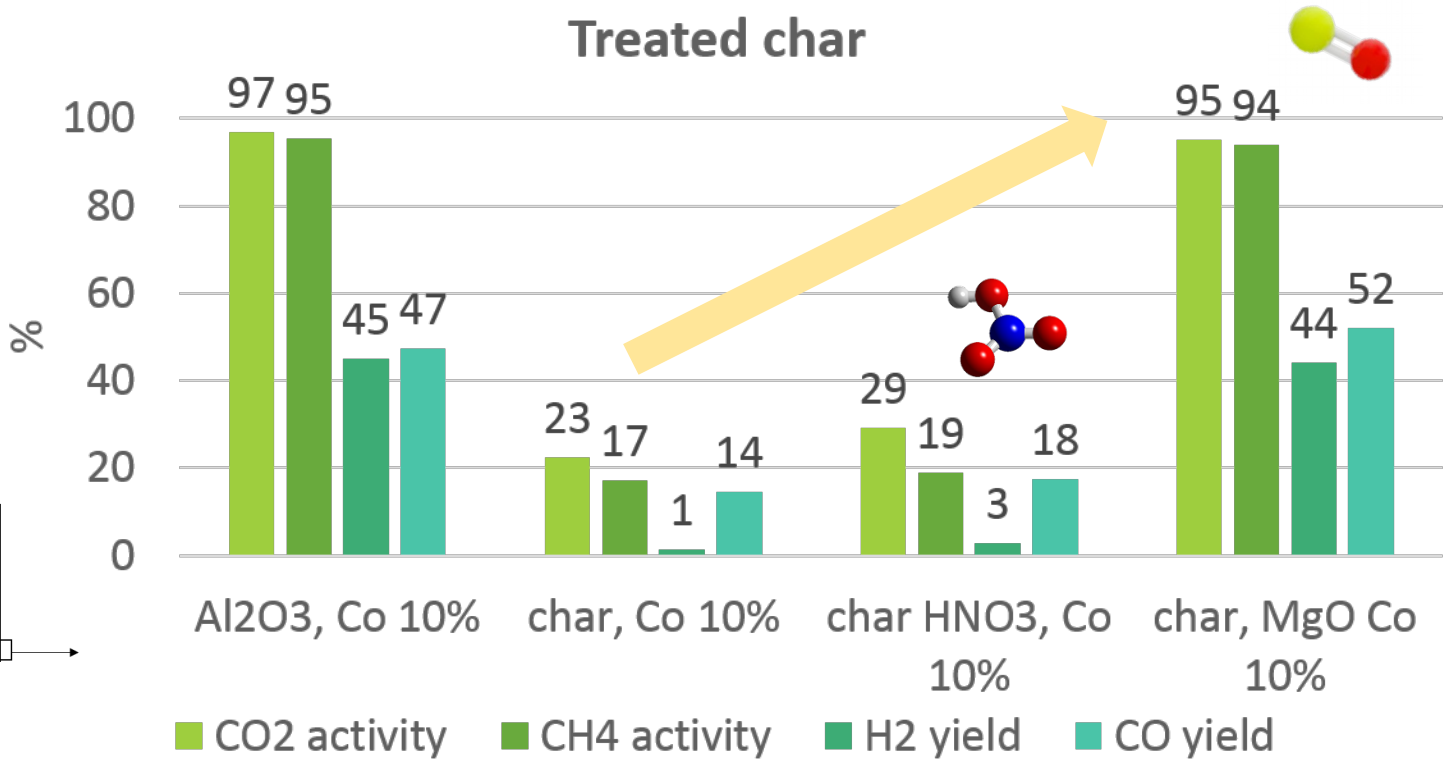
Products distribution



V. Benedetti et al., Investigating the feasibility of valorizing residual char from biomass gasification as catalyst support in Fischer-Tropsch synthesis, under review.

Char as catalyst support for Dry Reforming of Methane (DRM)

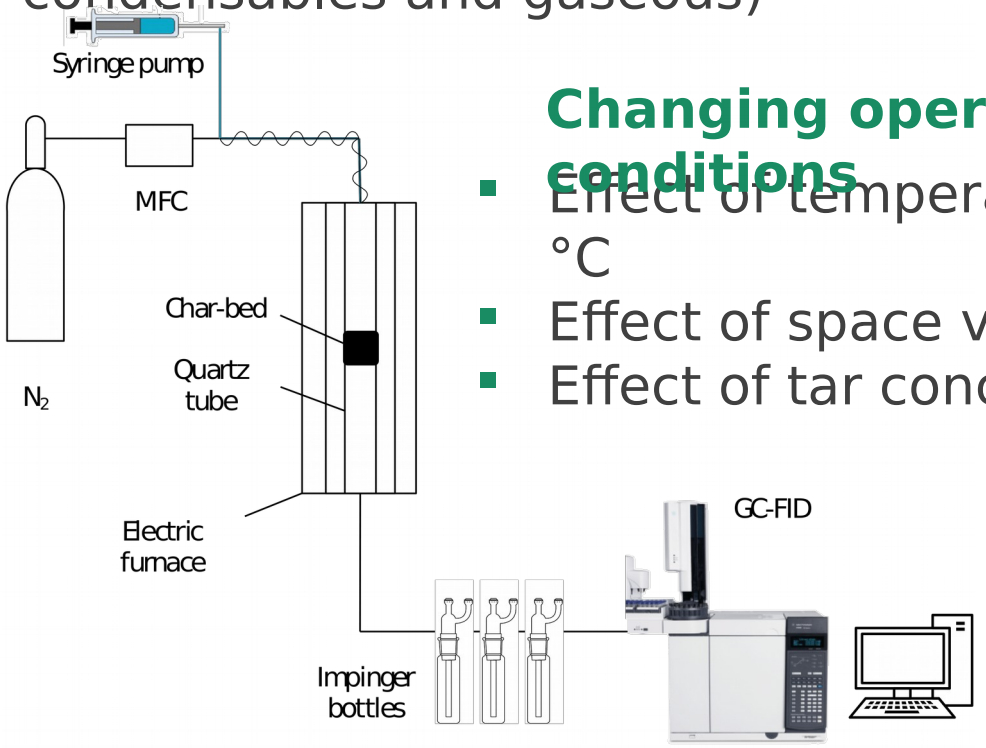




V. Benedetti et al., Valorization of char from biomass gasification as catalyst support in dry reforming of methane, Front. Chem, 7 (2018) 119.

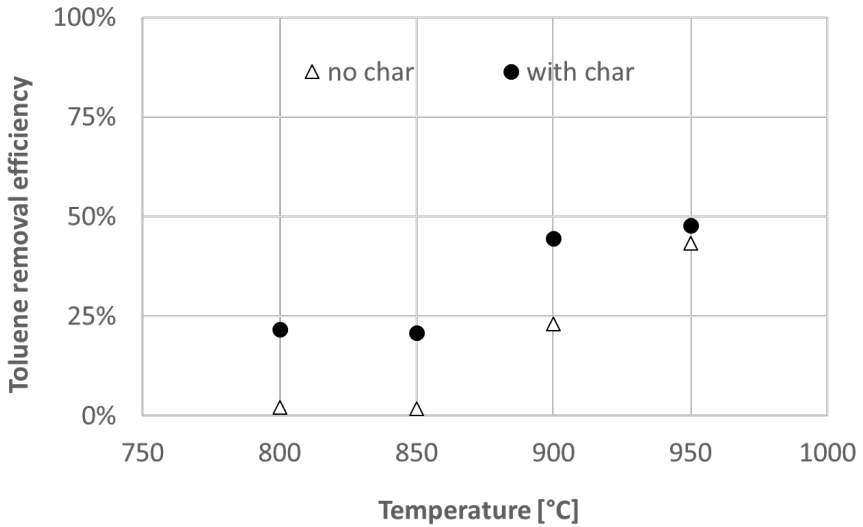
Tar removal by thermal and catalytic cracking

Evaluation of **tar removal efficiency** and analysis of converted products (both condensables and gaseous)



Changing operating conditions

- Effect of temperature 800-1000 °C
- Effect of space velocity
- Effect of tar concentration



First stage

Model tar compounds:
- Toluene
- Naphthalene
- Phenol

Second stage

Other gas mixtures/real tar from lab-scale gasifier

Freie Universität Bozen
Libera Università di Bolzano
Free University of Bolzano

Thank you for your attention

Valorisation of char residues from biomass gasification in adsorption applications

E-mail:
vittoria.benedetti@unibz.it

Website:
https://bnb.groups.unibz.it/