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UNION EUROPÉENNE
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PSYCHE

Avec le soutien du Fonds européen de développement régional
Met steun van het Europees Fonds voor Regionale Ontwikkeling

Syngas purification

08/11/2022

Context

Gasification is a good alternative for the valorisation of different types of carbonaceous materials : biomass, coal, municipal solid waste, plastic waste …

Its composition depends on the feedstock used

H_2	25-30 %v/v
CO	30-60 %v/v
CO_2	5-15 %v/v
H_2O	2-3 %v/v

Some low alkanes

Impurities

Expected contaminants

	Contaminants	Quantity measured/expected after gasification	Acceptable level for FT synthesis*
Particles	Silica (SiO_2)	1%	nd
	Ashes	1,33%	0
Acids	HCl	0,1%	10 ppb
	sulfur compounds	500 ppm H_2S / 500 ppm COS	10 ppb
	Hydrogen cyanide (HCN)	0,1%	10 ppb
	Ammonia (NH_3)	0,1%	10 ppb
Organic compounds	Benzene/Aromatics	1% / 0,1%	nd
	Dioxines	10 µg/Nm³	nd
	Tar	100 g/Nm³	0

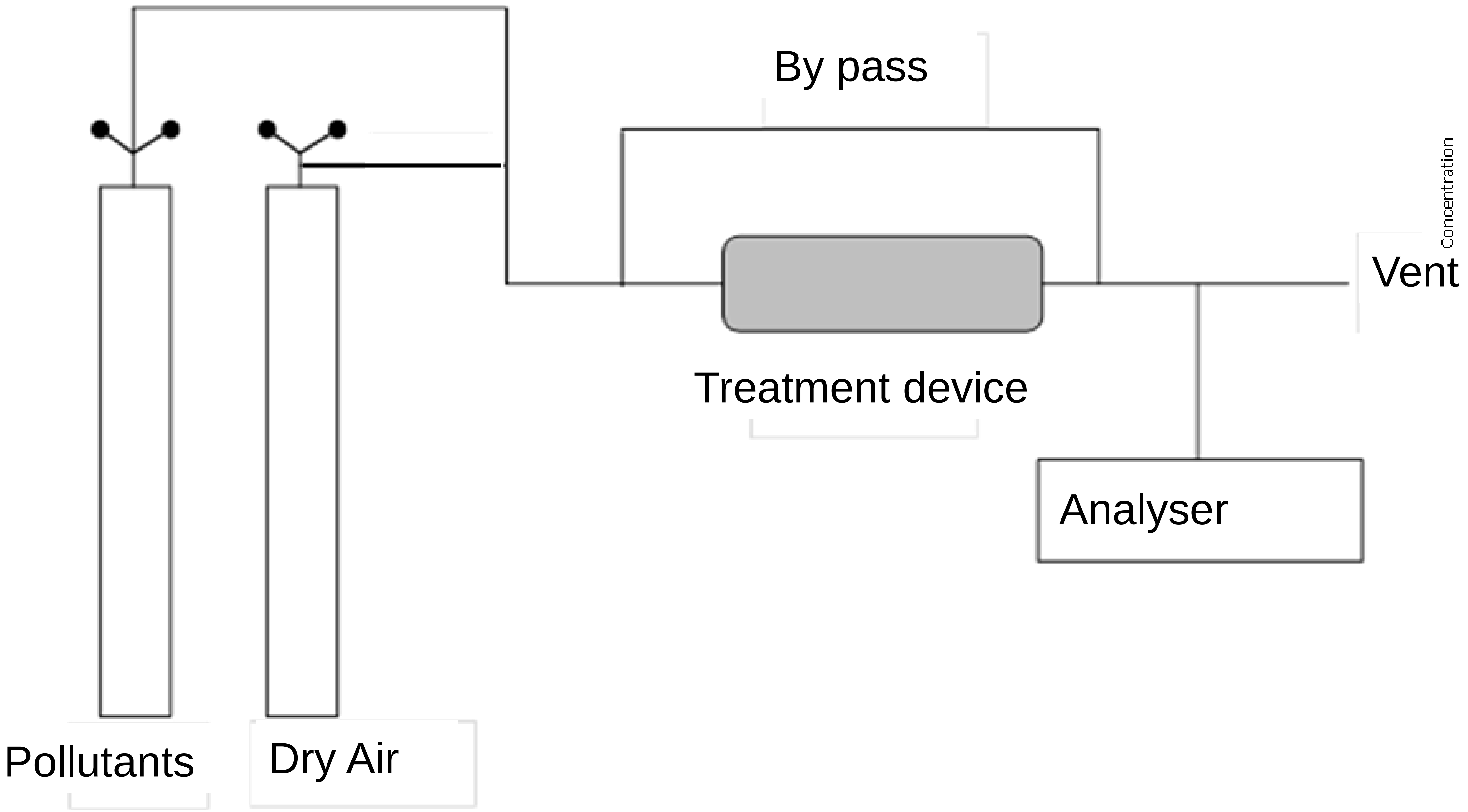
* M.J.A. Tijmensen et al. / Biomass and Bioenergy, 23 (2002) 129 – 152

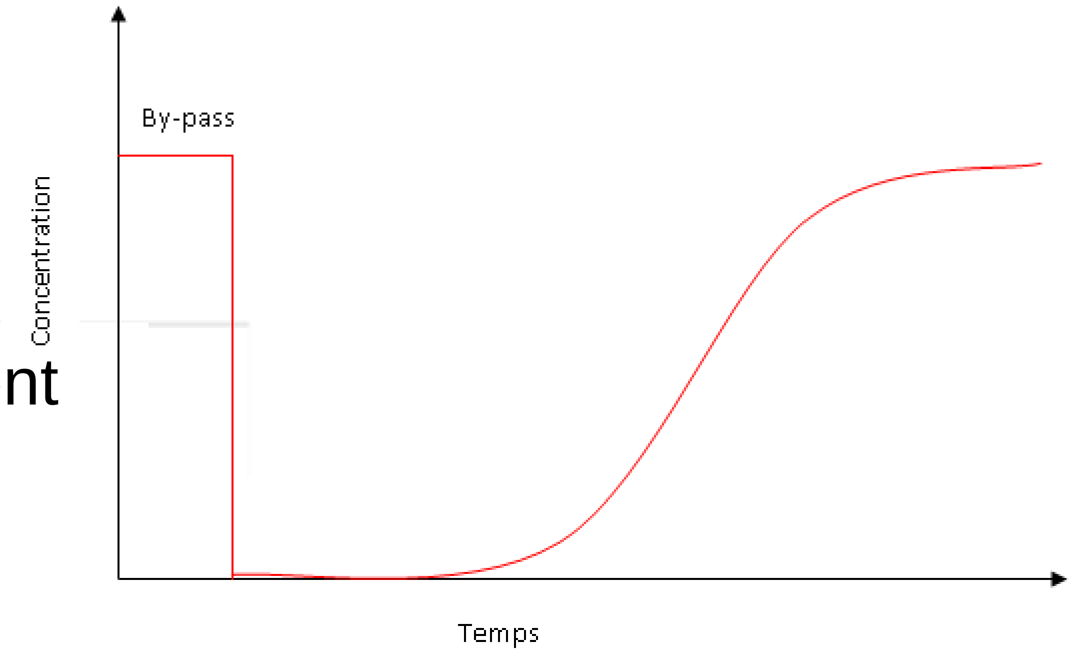
Techniques for syngas purification

Impurities	Cold gas cleaning (needs to add heat exchanger)	Hot gas cleaning/dry gas purification.
Ash, solids particles	low temperature filtration, cyclone, scrubber with solvent	High temperature filtration (ceramic , metallic candle)
Sulfur compounds	Wet process, absorption in amine, cold methanol, dimethyl ethers of polyethylene glycol, … Dry process adsorption on activated carbon (AC) For COS : hydrolysis process Generation of waste to be treated	Reaction with metal oxide, possibility to regenerate the adsorbent.
Hydrogen Halides	Alkali metals, alkaline earth metals (salt: waste)	Alkali metals, alkaline earth metals (salt: waste)
Metal carbonyl	Catalytic decomposition	Catalytic decomposition
Nitrogen compounds	DeNOx process	DeNOx process
Heavy metal	Condensation (Activated carbon a low temperature, CuO for higher temperature)	Condensation (Activated carbon a low temperature, CuO for higher temperature)
Tars	Thermal cracking, catalytic cracking, condensation …	Thermal cracking, catalytic cracking, condensation …

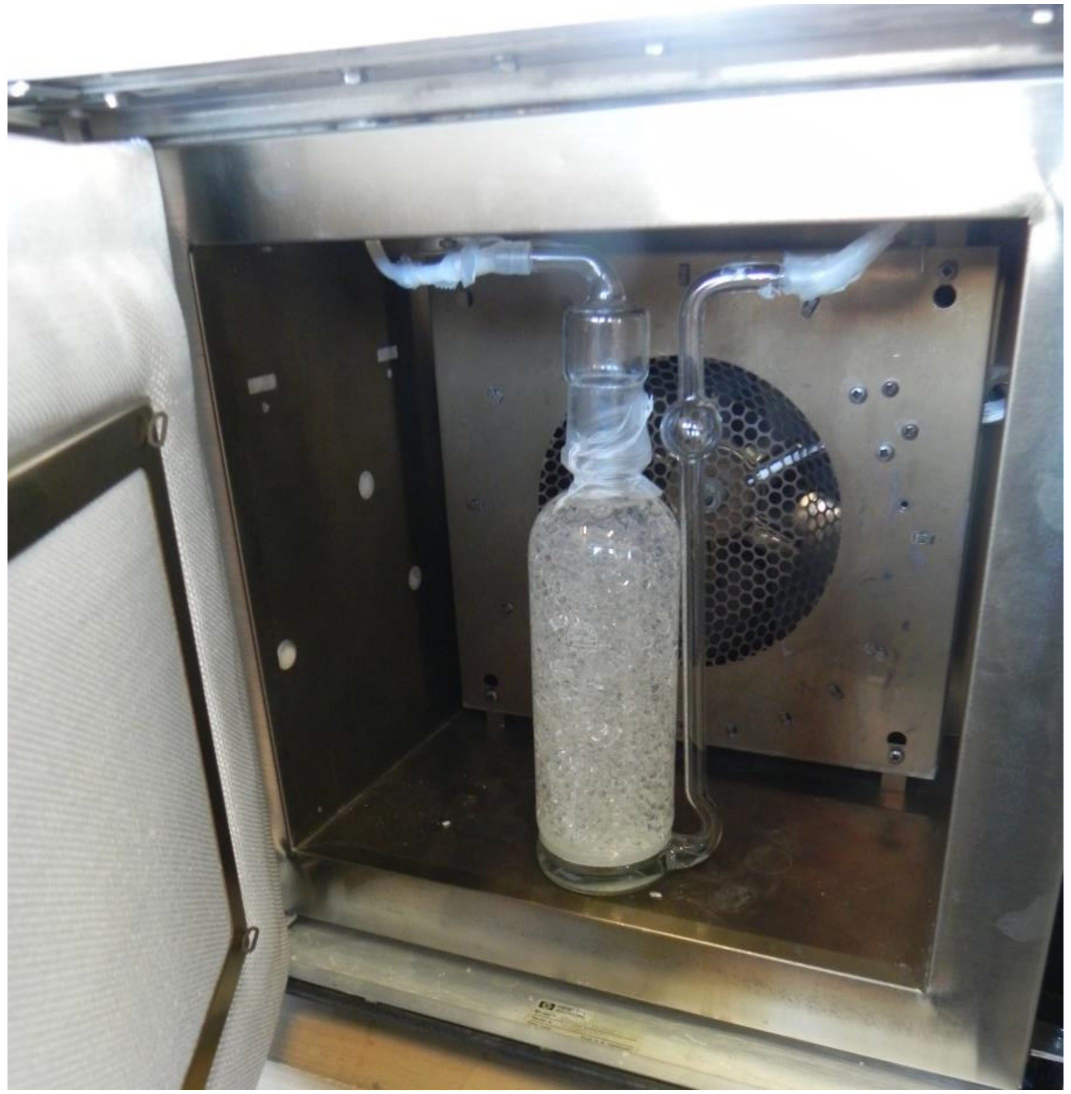
What was done at Certech through Psyche project ?

Experimental setup for the removal of some pollutants at cold gas and hot gas cleaning process





Cold gas cleaning process .

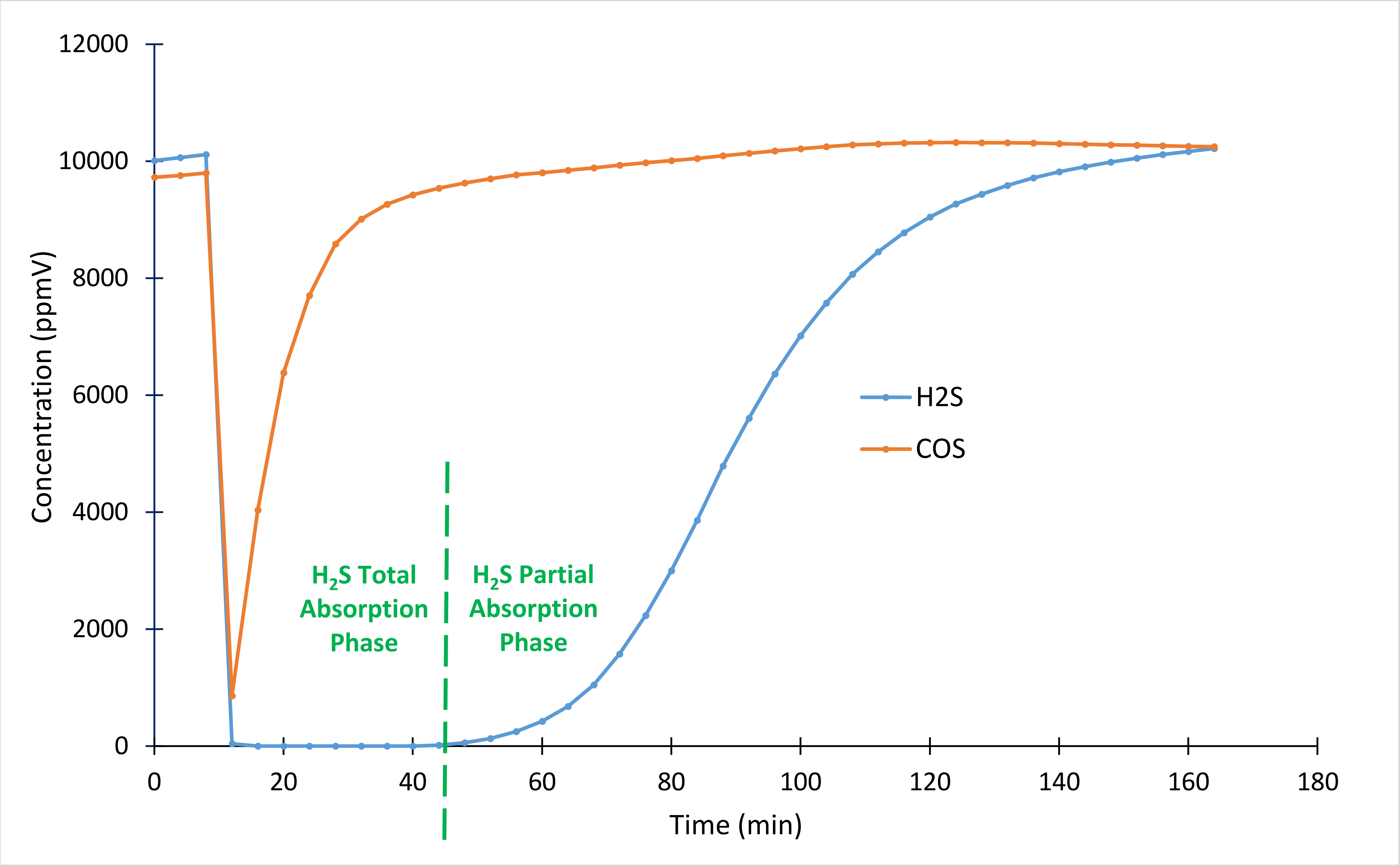


Wet process : absorption on solvent

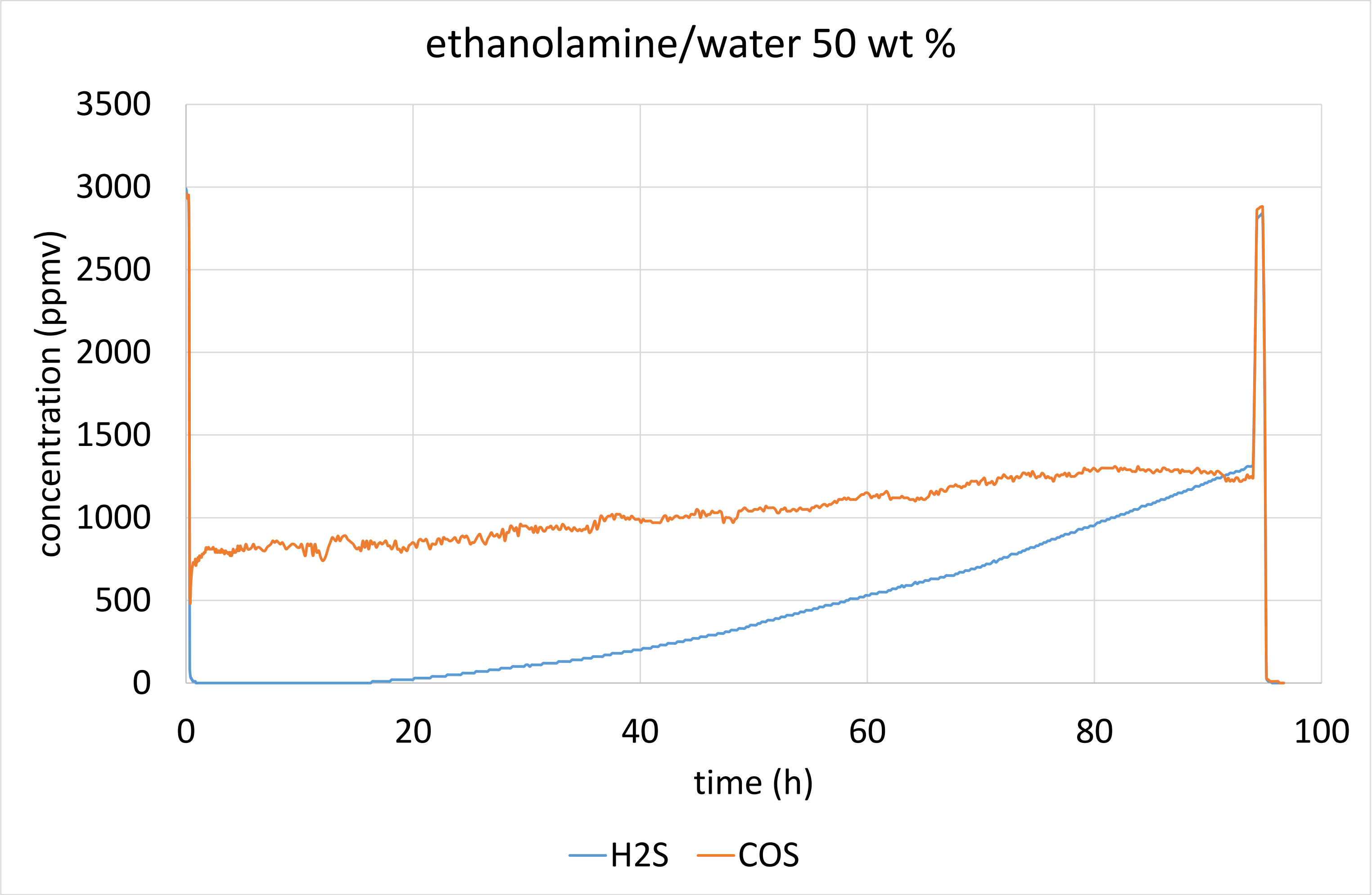
Dry process : adsorption on activated carbon.

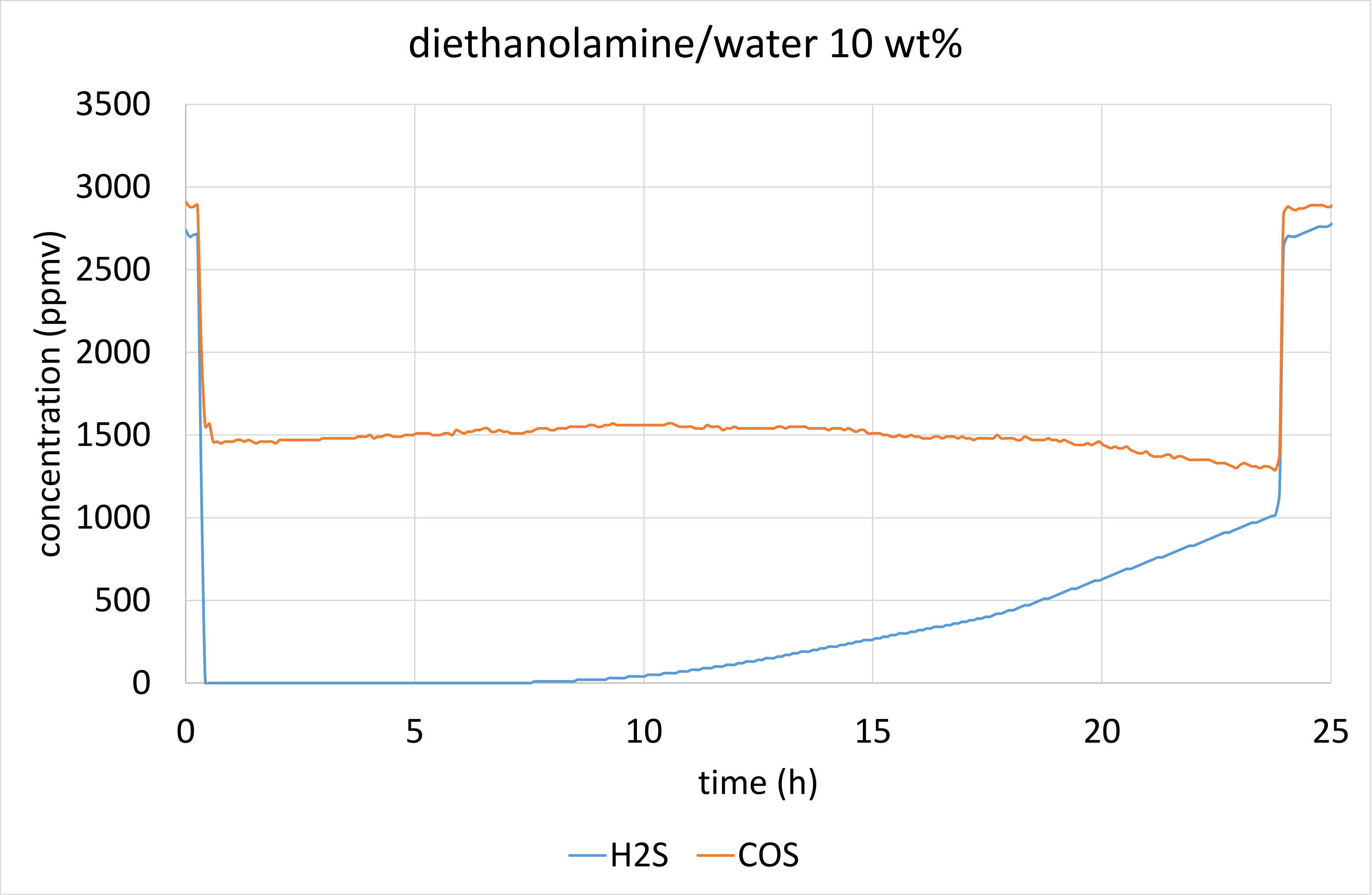
Wet process : basic solutions

Example of H_2S and COS absorption in a NH_4OH solution



Wet process : amine solution.





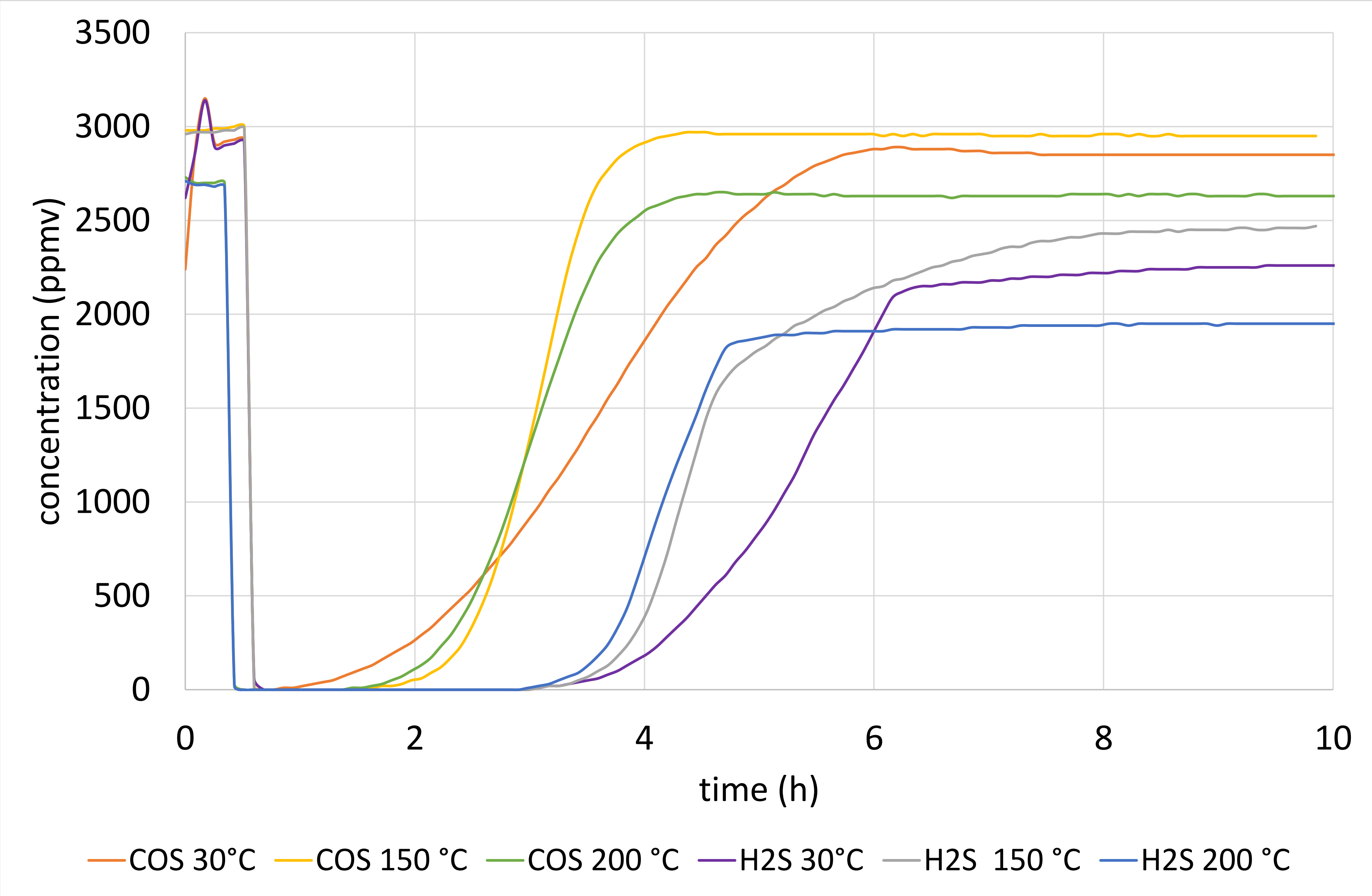
At the breakthrough :

mmole $H_2S/g_{ethanolamine}$: 0,12

mmole $H_2S/g_{diethanolamine}$: 0,29

Dry process : activated carbon (Chemviron)

Influence of the temperature

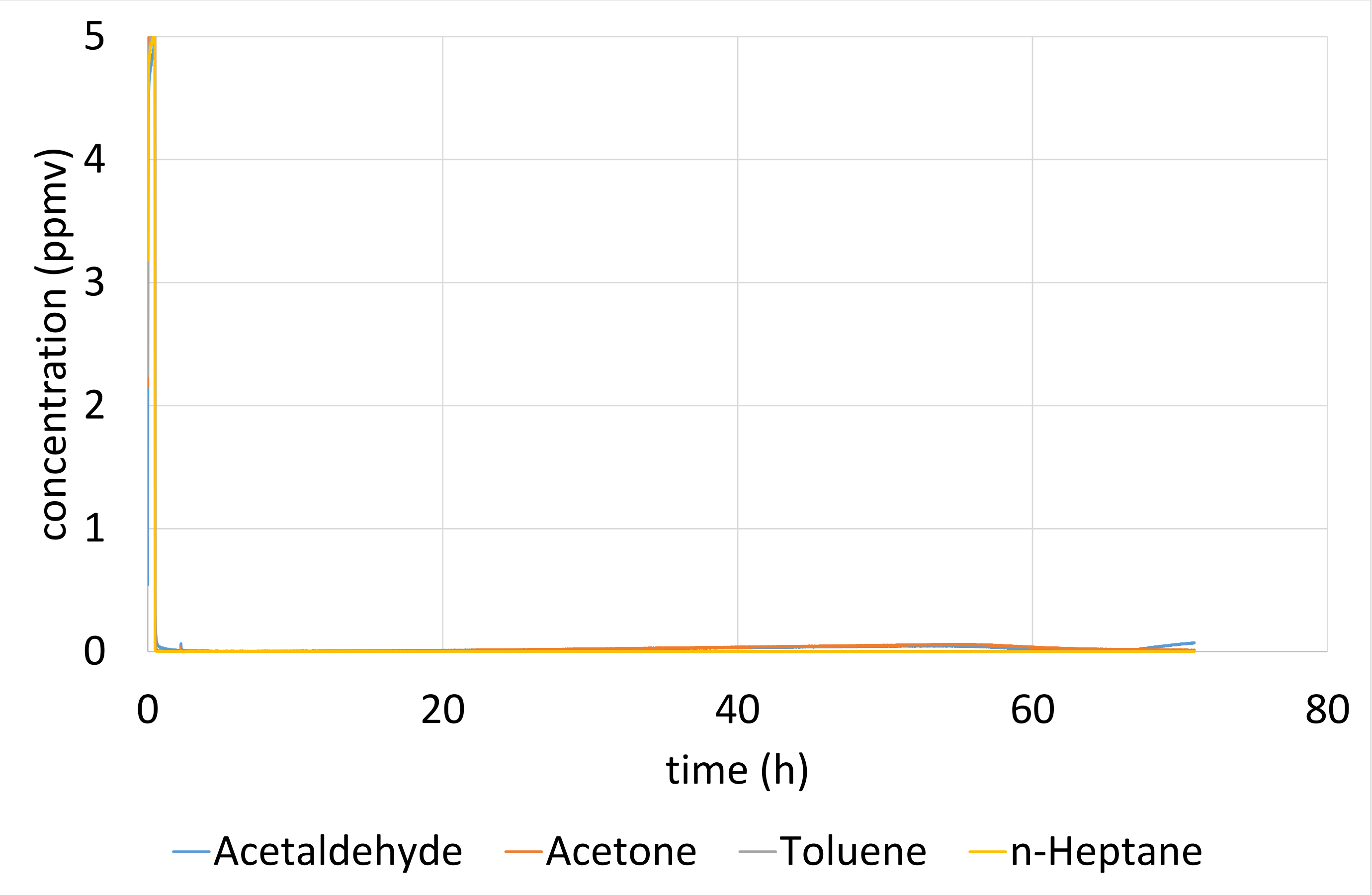


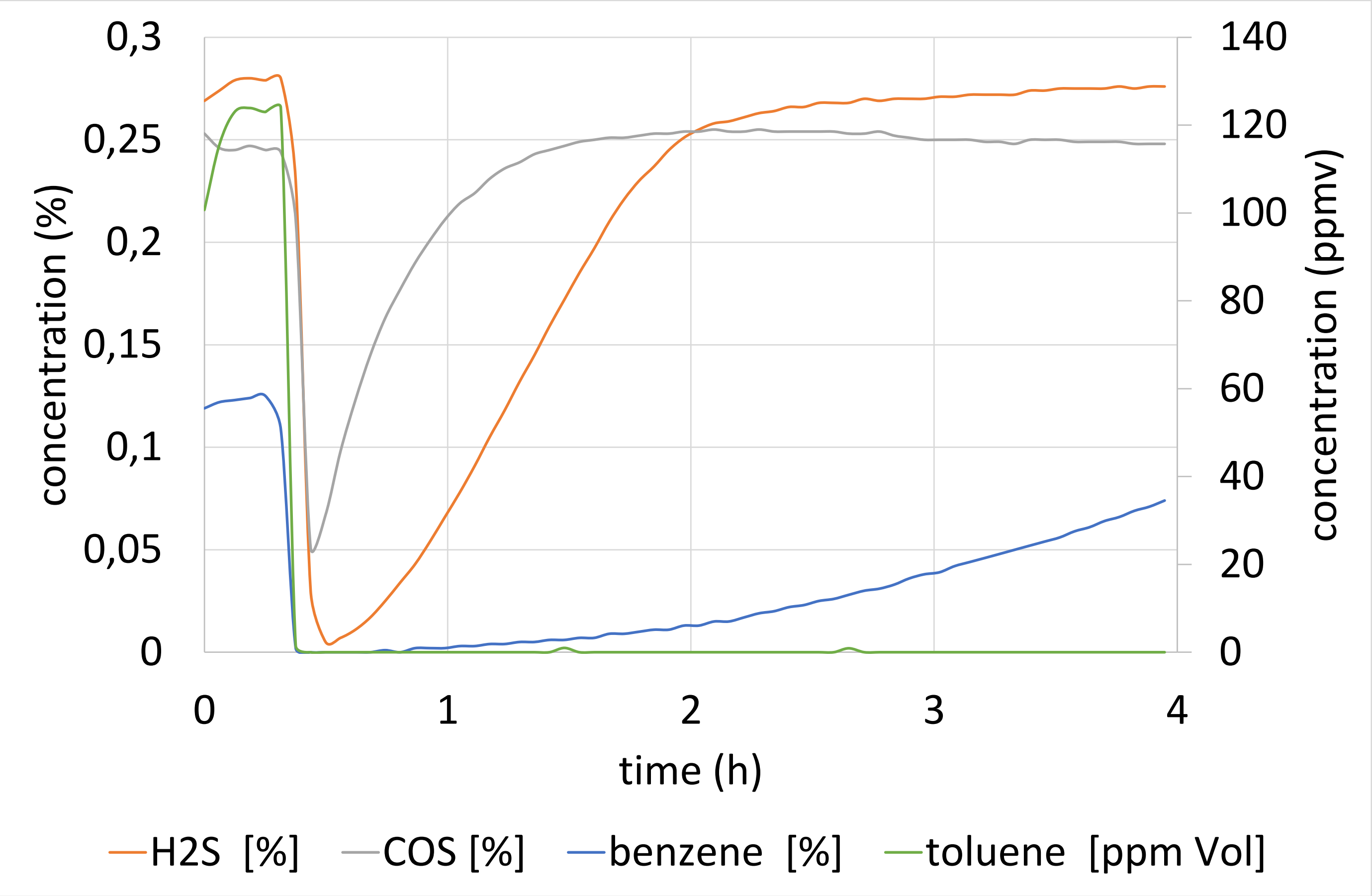
	30° C	150 °C	200 °C
	breakthrough time (min)		
H_2S	148	154	159
COS	21	62	67
	Adsorption capacity of the C3 (wt%)		
H_2S	1,59	1,69	1,52
COS	0,34	1,16	1,14
	Adsorption capacity of the C3 (mmole S/g)		
H_2S	0,50	0,53	0,47
COS	0,11	0,36	0,36

Adsorption tests of VOC on activated carbon C3.

1° test : VOC mixture at 5 ppmv over 4 g of activated carbon C3, flow of 160 ml/min.

⇒ removal of the VOC below 10 ppbv.





2° test : mixture of H_2S, COS, benzene and toluene Over 0,5g of activated carbon C3, flow 100 ml/min.

⇒ activated carbon is also effective to remove VOC.

Kobayashi et al presented a sulfur removal process with mixed oxide : $ZnFe_2O_4$

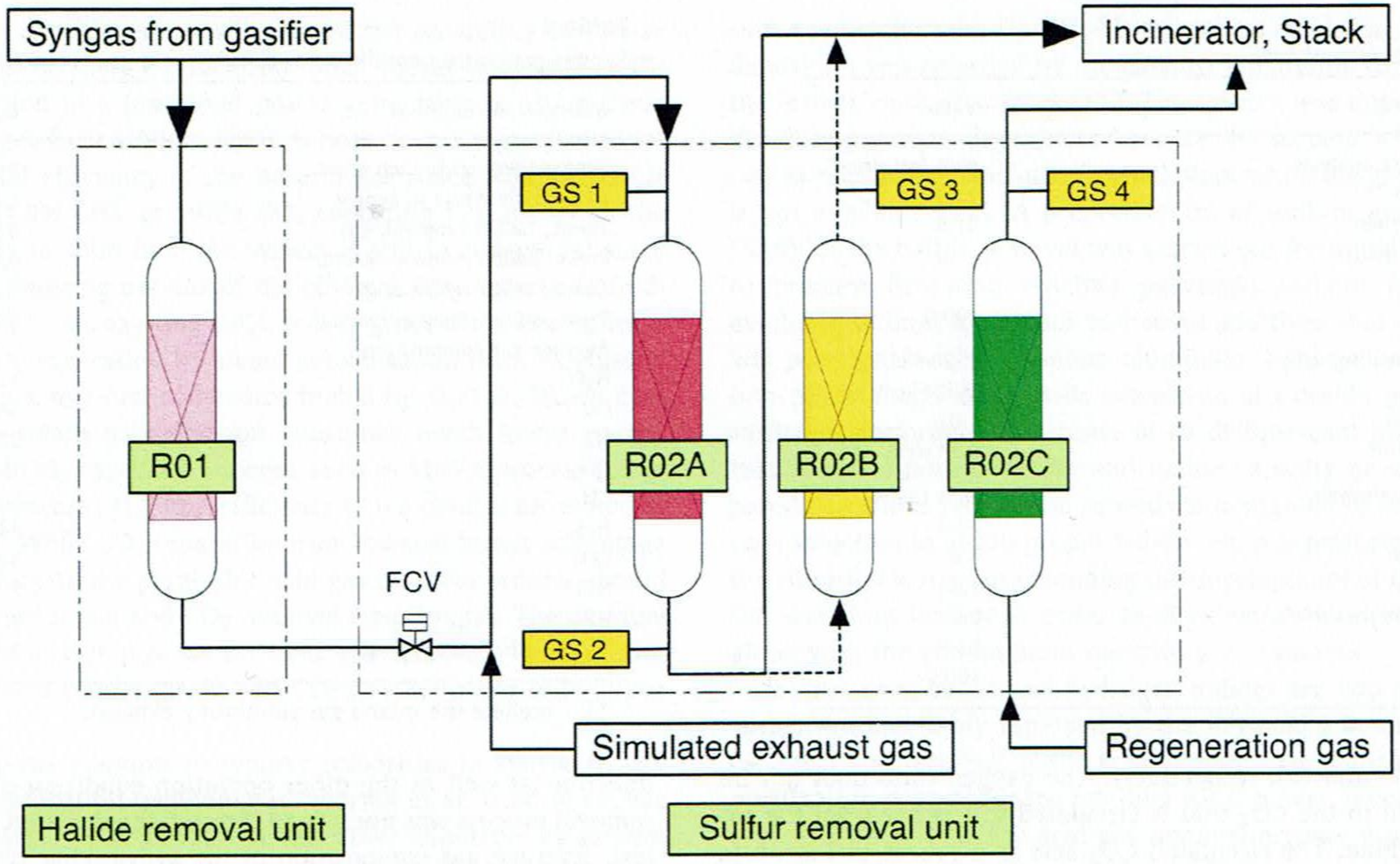


Fig. 2. Dry acid gas removal test facility installed at the O_2/CO_2-blown gasifier test plant.

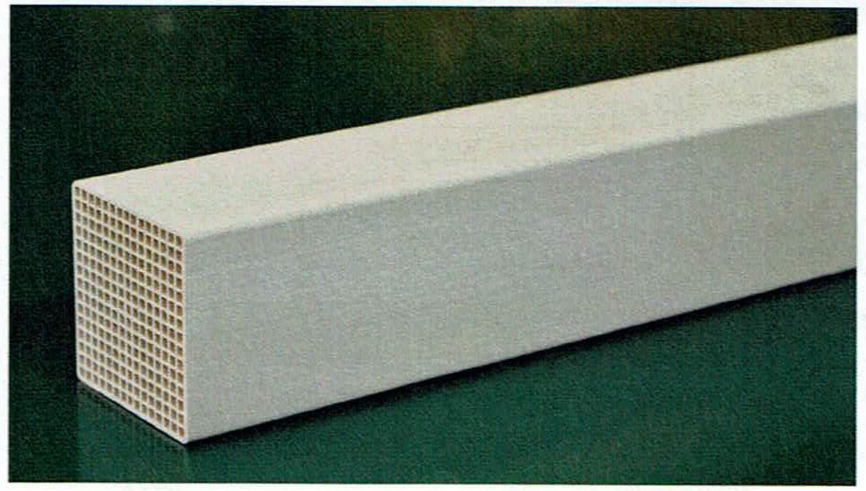


Fig. 5. Honeycomb desulfurization sorbent subjected to the syngas test.

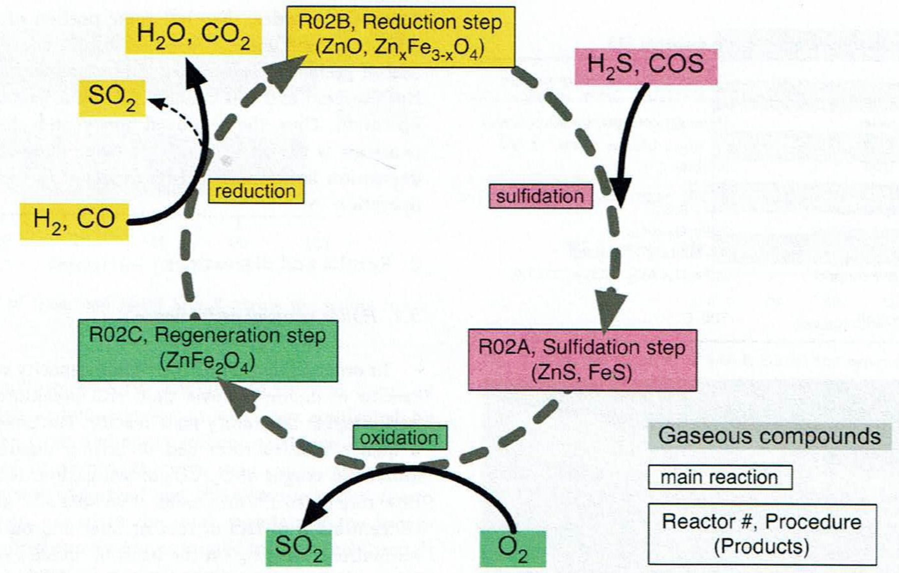


Fig. 3. Schematic diagram of the cyclic operation of the sulfur removal unit.

M Kobayashi et al, Fuel 250 (2019) 144-153

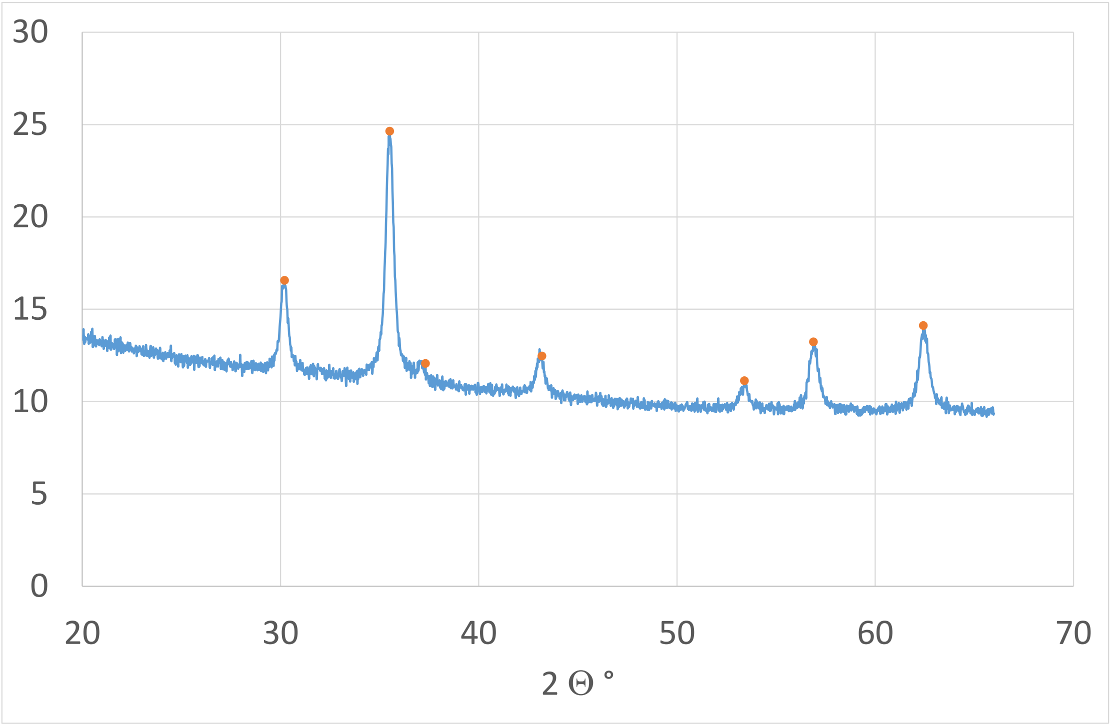
Synthesis of $ZnFe_2O_4$

ZnFe2O4 : synthesis by the citric ways :

$$Zn(NO_3)_2 + 2Fe(NO_3)_3 + 20/9C_6H_8O_7 \longrightarrow ZnFe_2O_4 + 40/3CO_2 + 80/9H_2O + 4N_2$$

120°C

250 °C



Zinc ferrite oxide for sulfur removal

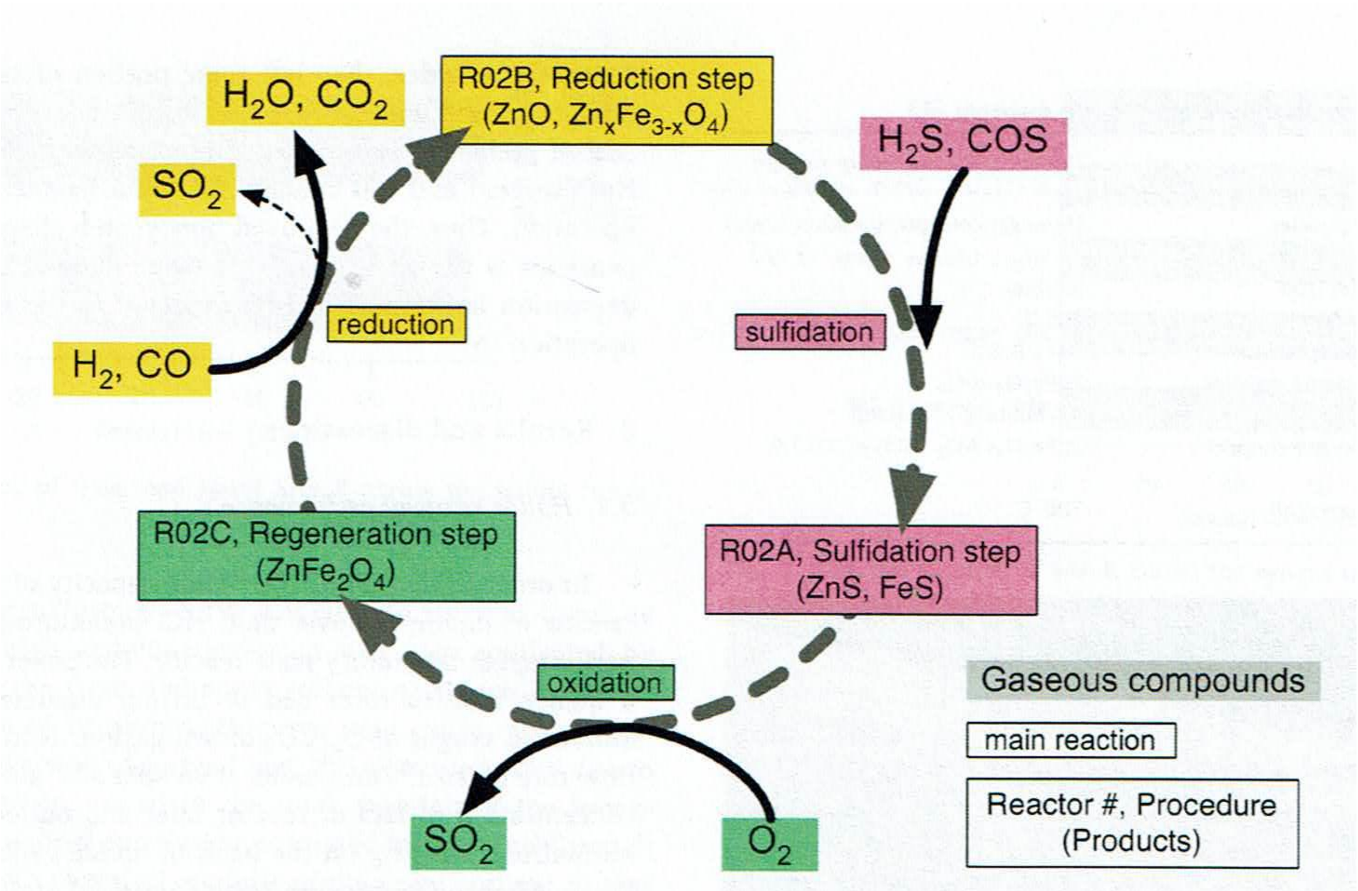
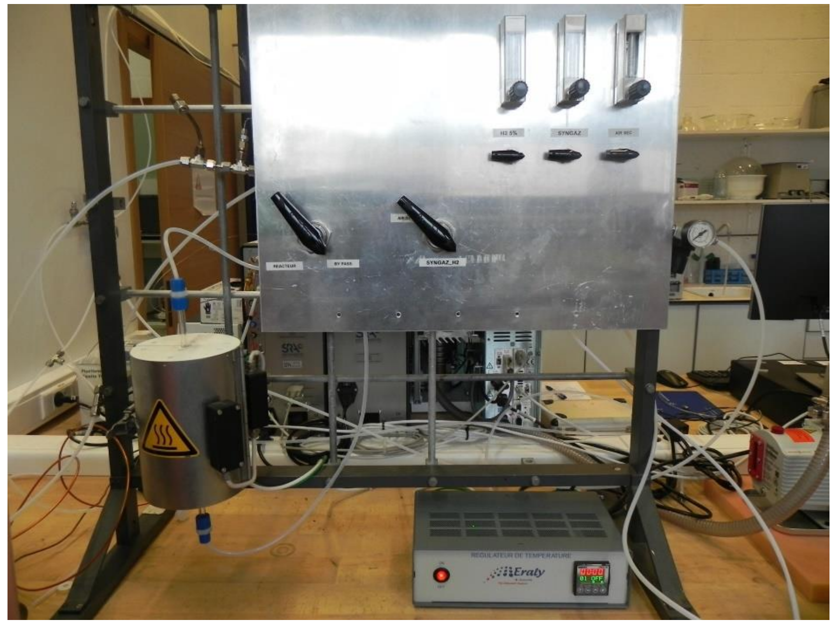


Fig. 3. Schematic diagram of the cyclic operation of the sulfur removal unit.

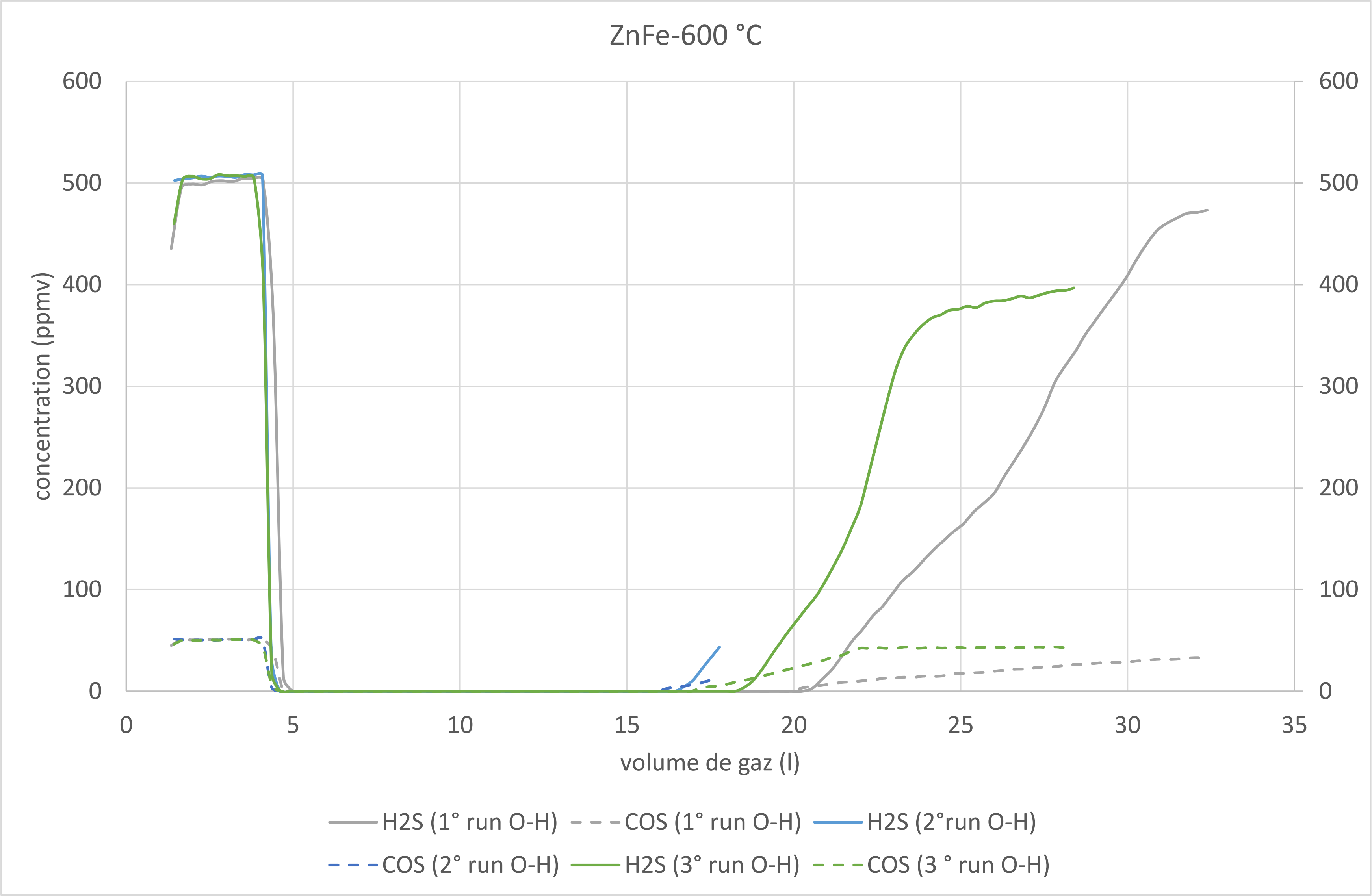


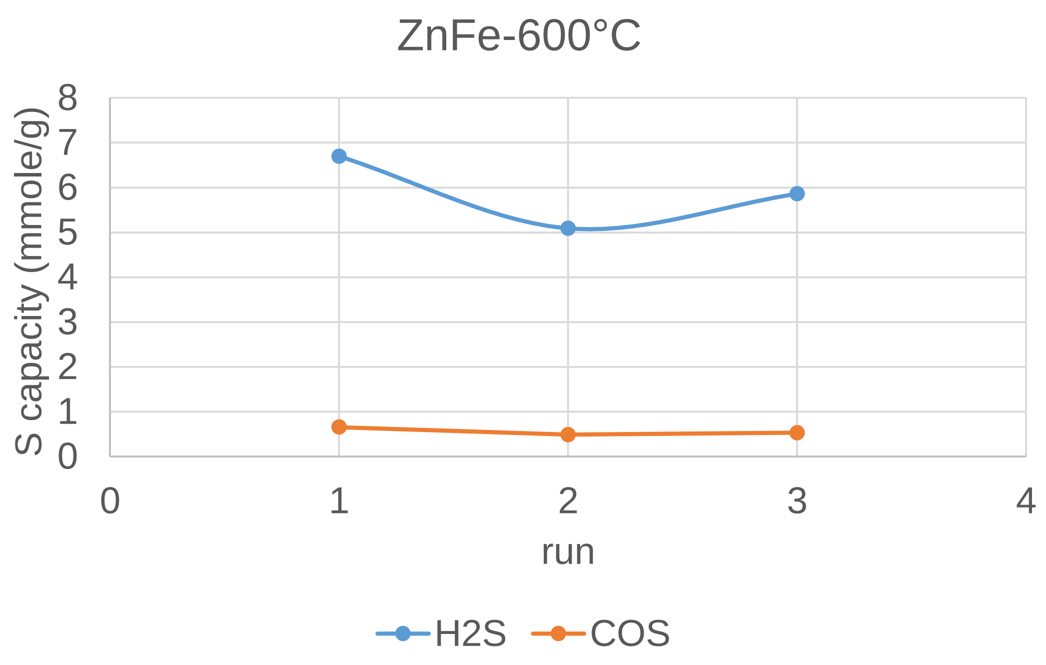
Protocol for cycle tests :

- Catalyst calcination at 600 °C for 1 H
- Reduction under H_2 at 450 °C for 1 H
- Sulfur removal at 400 °C
- Regeneration step under air with a thermal programmed oxidation (TPO) from room temperature until 600°C

Zinc ferrite oxide development for sulfur removal

Example of test with $ZnFe_2O_4$



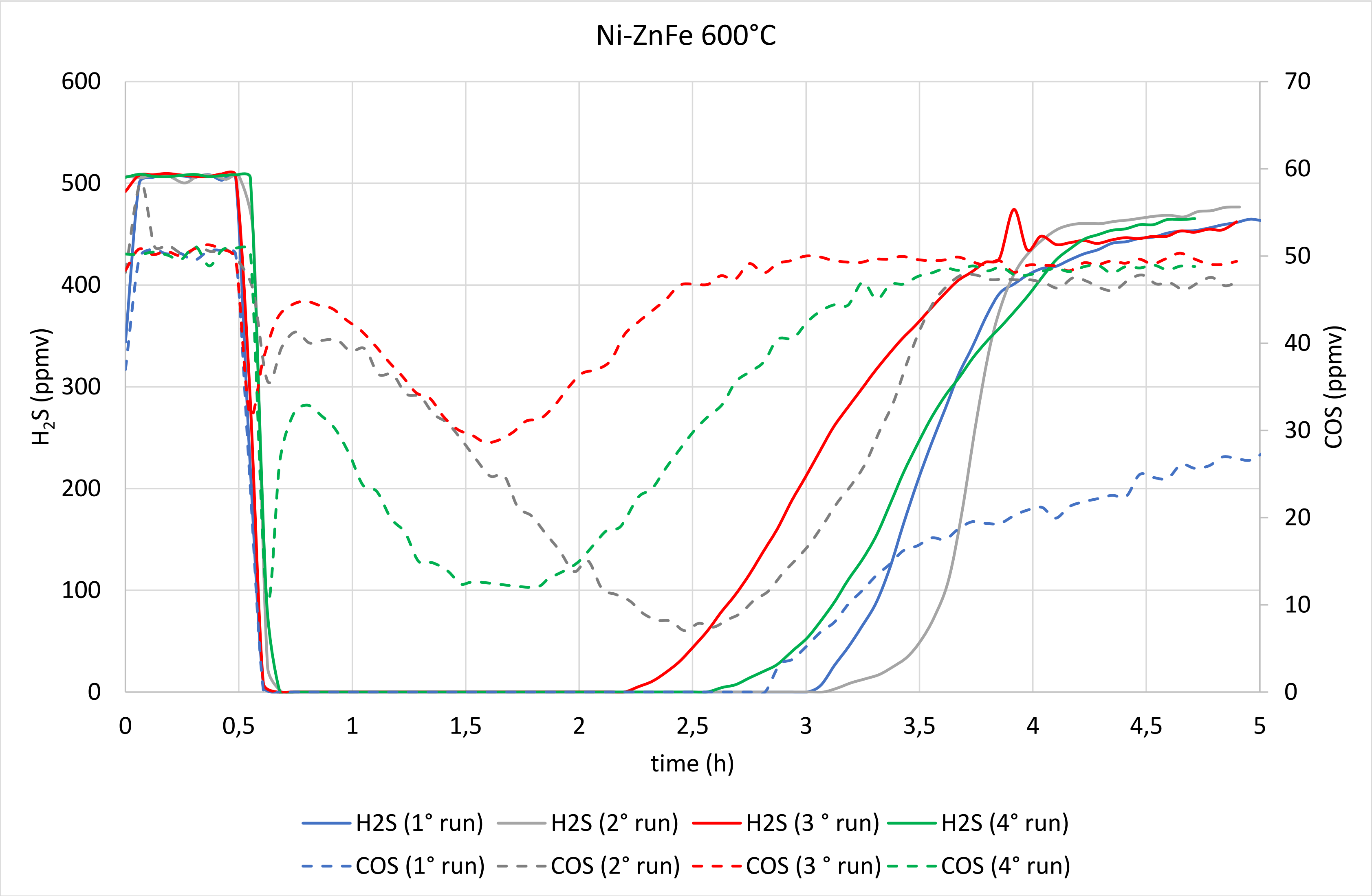


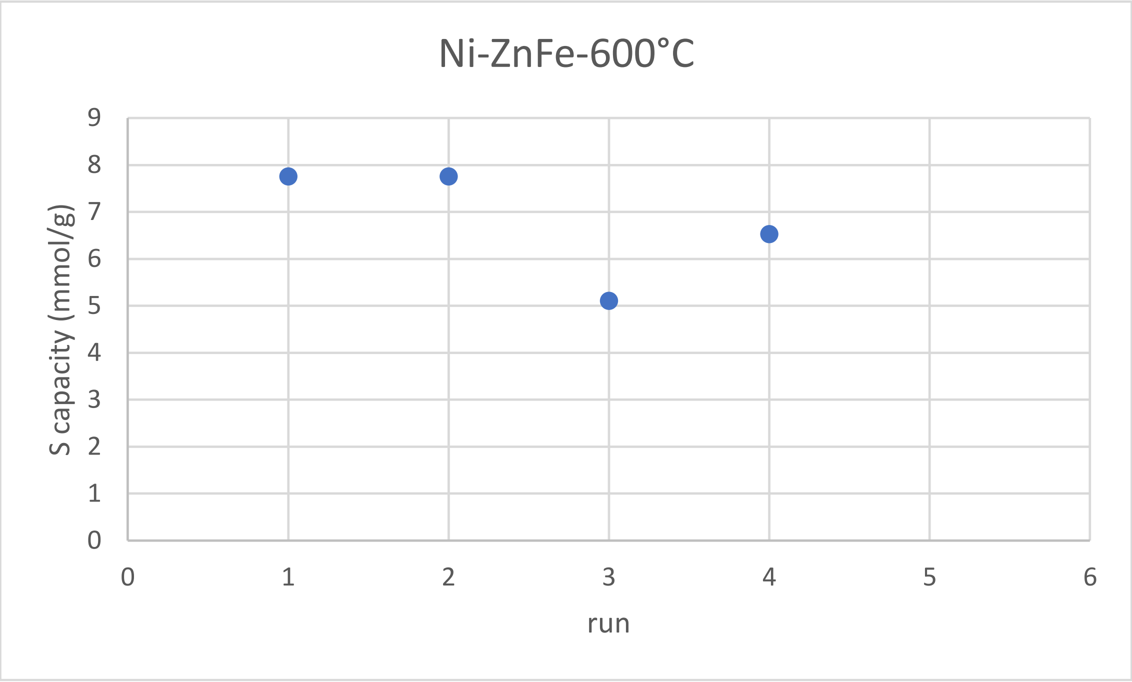
Some lost of activity at second run

COS uptake stable run after run.

Zinc ferrite oxide development for sulfur removal

Tests Ni-$ZnFe_2O_4$ under the new protocol.





Production of COS after the first cycle is due to incomplete regeneration

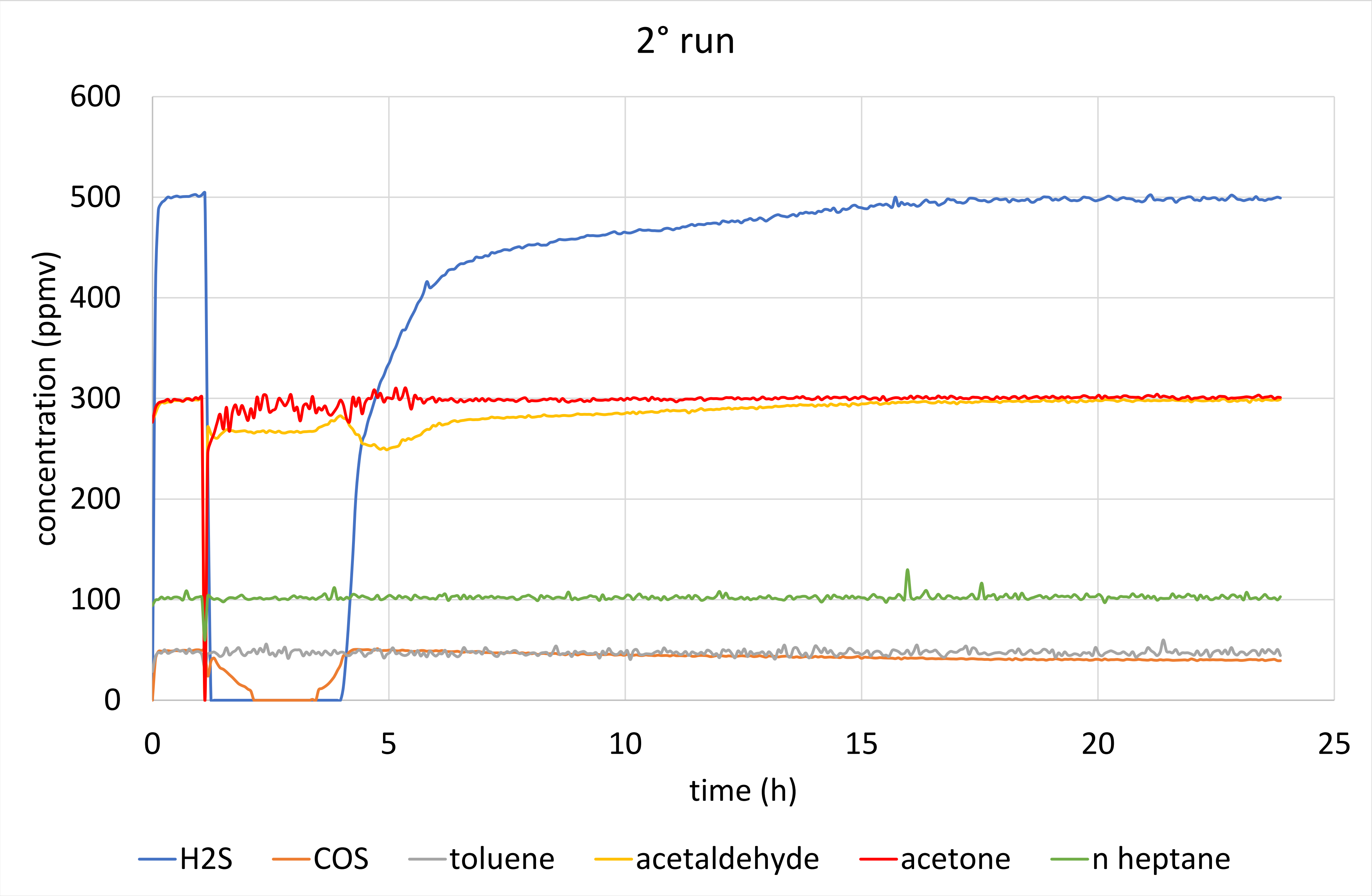
Still presence of NiS formed during the sulfur removal which catalyse the reaction

$$CO_2 + H_2S \longrightarrow COS + H_2O$$

Zinc ferrite oxide development for sulfur removal

Example of test with a mixture of VOC and Sulphur compounds

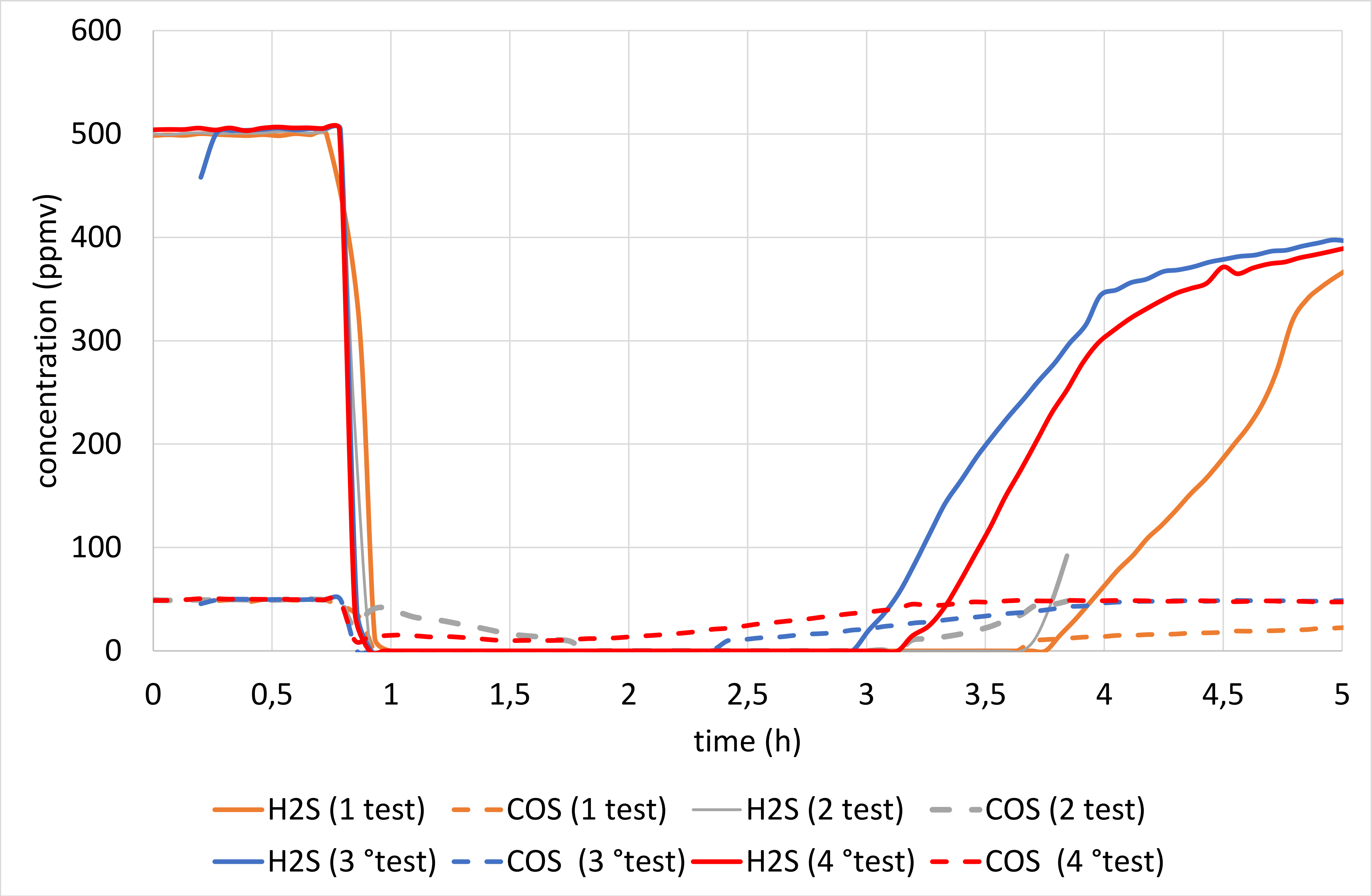
(H_2 8%, CO_2 5%, toluène 50 ppmv, heptane 100 ppmv, acetone 500 ppmv, acetaldehyde 500 ppmv, COS 50 ppmv, H_2S 500 ppmv)

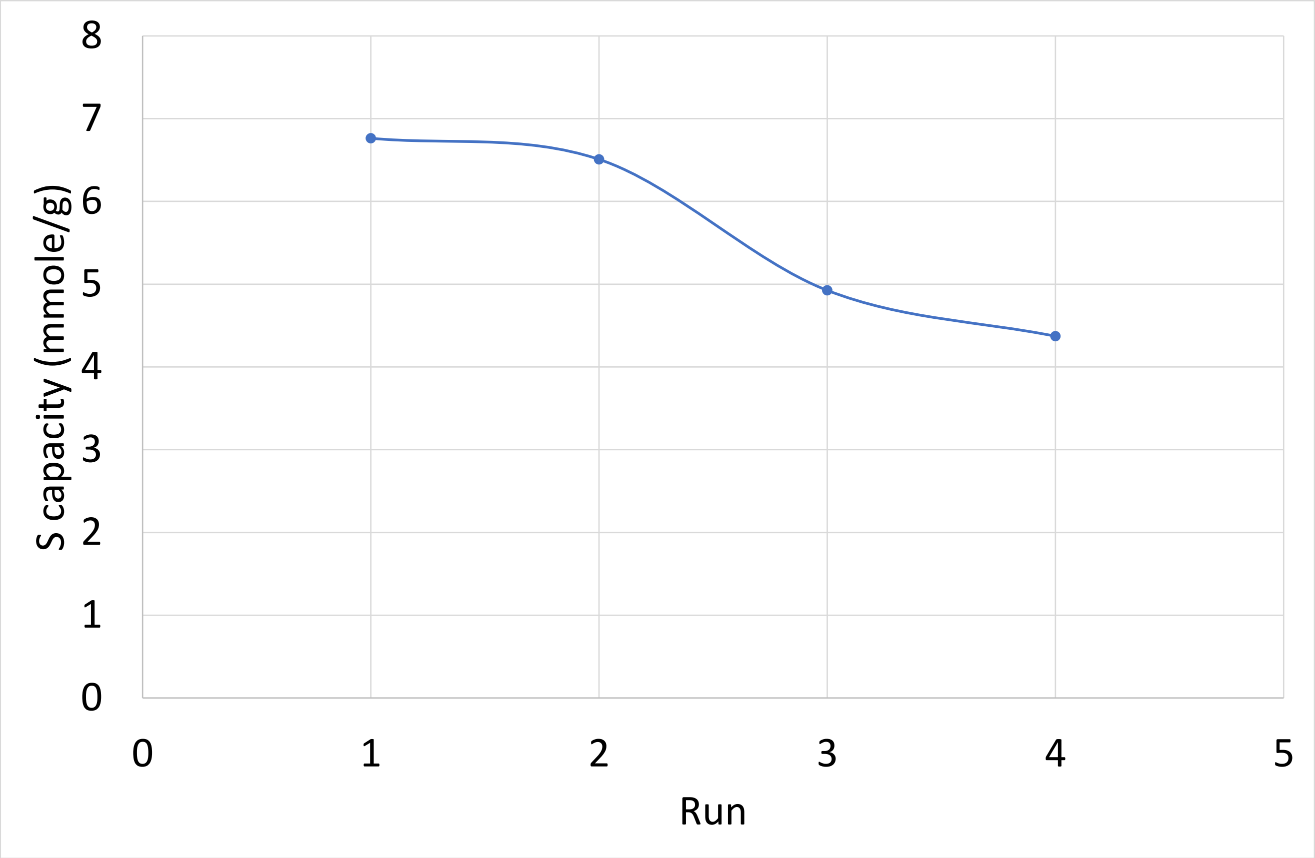


Low activity on COV removal in absence of oxygen

Zinc ferrite oxide development for sulfur removal

Successive runs





Lost of activity on sulphur removal with number of runs.

Needs to removed VOC to keep the activity for the sulphur removal capacity.

Deposition of tars in the outlet of the reactor.

Conclusions

- Complexity of syngas cleaning processes depends on the source of the raw materials for the gasification :
  - Charcoal
  - Biomass
  - Oil
  - Plastic waste
  - …

- It depends also of the final used of the syngas :
  - NH_3
  - H_2
  - Methanol
  - Energy
  - Gas to liquid (Fisher Tropsch process)
  - …

Conclusions

- It depends also on the pollutant to removed

  - Particles/dust
  - Sulfur compounds
  - Nitrogen compounds
  - Tars
  - Heavy metals
  - Hydrogen halides
  - Metal carbonyl

- Needs to carry out a deep gases characterisation to chose the right process.

Conclusions

Two ways can be used to remove impurities from the syngas :

1. **The Cold Gas Cleaning (CGC) process**
   + Well establish wet syngas purification
   But needs to work at low temperature (heat exhanger) and produced by-product which needs to be treated (water, solvent…)

2. **The Hot Gas Cleaning (HGC) process**
   + Work at high temperature, work with regenerable sorbent, less by-product to be treated, no heat exchanger needed.
   Not well establish syngas purification, still needs development.

Acknowledgements

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