RWE

Innovative H2O2-based Sour Gas Cleaning Concept

Basic Ideas and Status

Public Workshop

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Content

1 Background (1/2)

For use of any kind of syngas in syntheses like Fischer Tropsch, Methanol or others, intensive **purification to ppb level** regarding sulfur compounds and other poisons as well as bulk components like CO2 is mandatory.

Mature technologies are well known. In most cases Rectisol® for gas cleaning in combination with Claus® for sulfur recovery is applied. But:

Claus® requests **high H2S concentration in the sour gas** coming from gas cleaning section.

This leads to a selective and **complex design** of Rectisol®.

In addition **refrigeration** of the solvent (Methanol) and **high pressure** operation (gasification and or gas compression) is necessary for effective gas cleaning.

Finally all these aspects lead to very high investment and operation costs.

Scale-up to very large plants is only chance for economical application. In our case for application in biomass gasification, medium scale plants due to fuel logistics are meaningful.

1 Background (2/2)

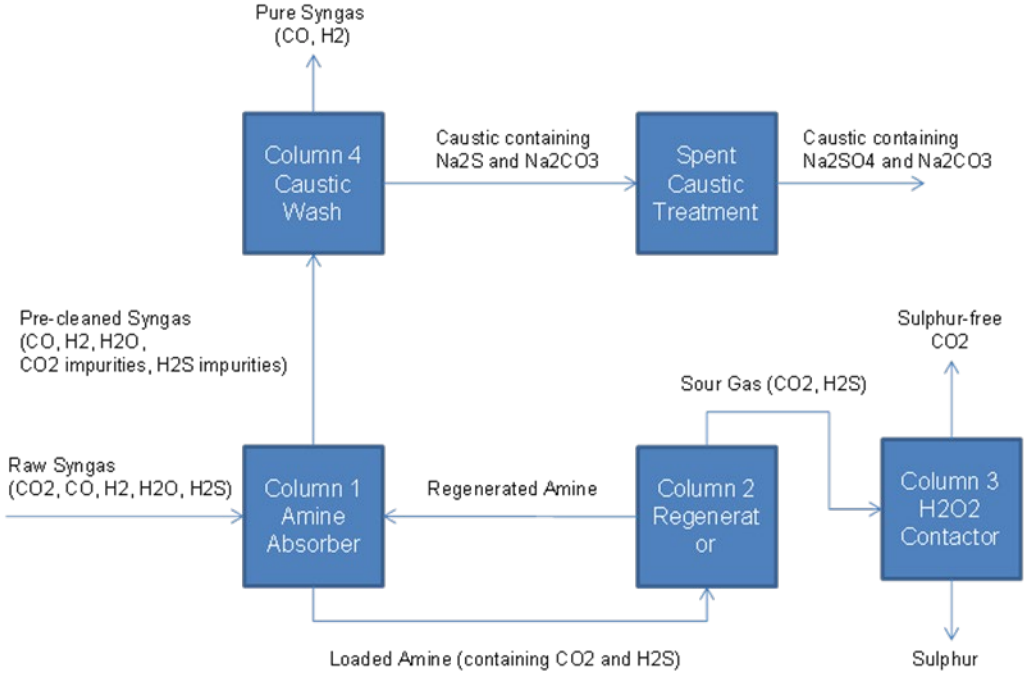
Ideas:

- Use of other solvent without need of gas compression and solvent refrigeration (amine, caustic)
- Use of less complex design with lower H2S in sour gas (simple cycle amine)
- Use of sulfur recovery technology for lower H2S in sour gas (H2O2, KMnO4, …)
- Use of sulfur recovery technology with pure S as main product (H2O2)
- conversion of H2S with H2O2 is known from waste water treatment (low H2S levels already dissolved in large liquid volumes)

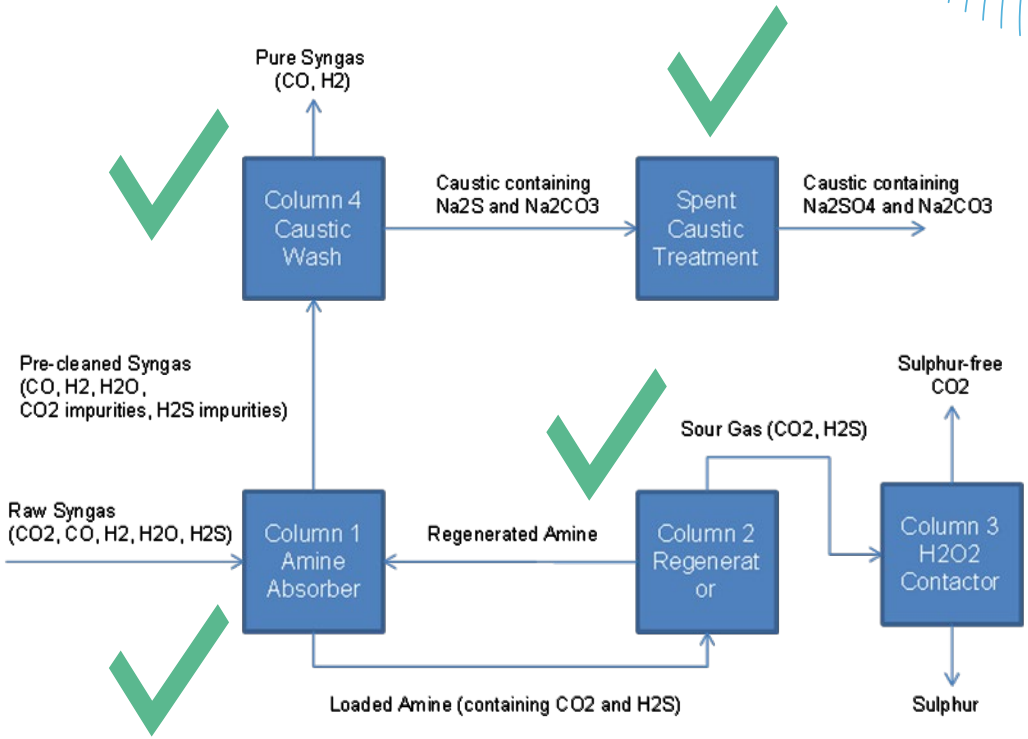
Main question:

- does H2O2 work in a meaningful range for sour gas cleaning (high H2S concentration in large gas quantities)????

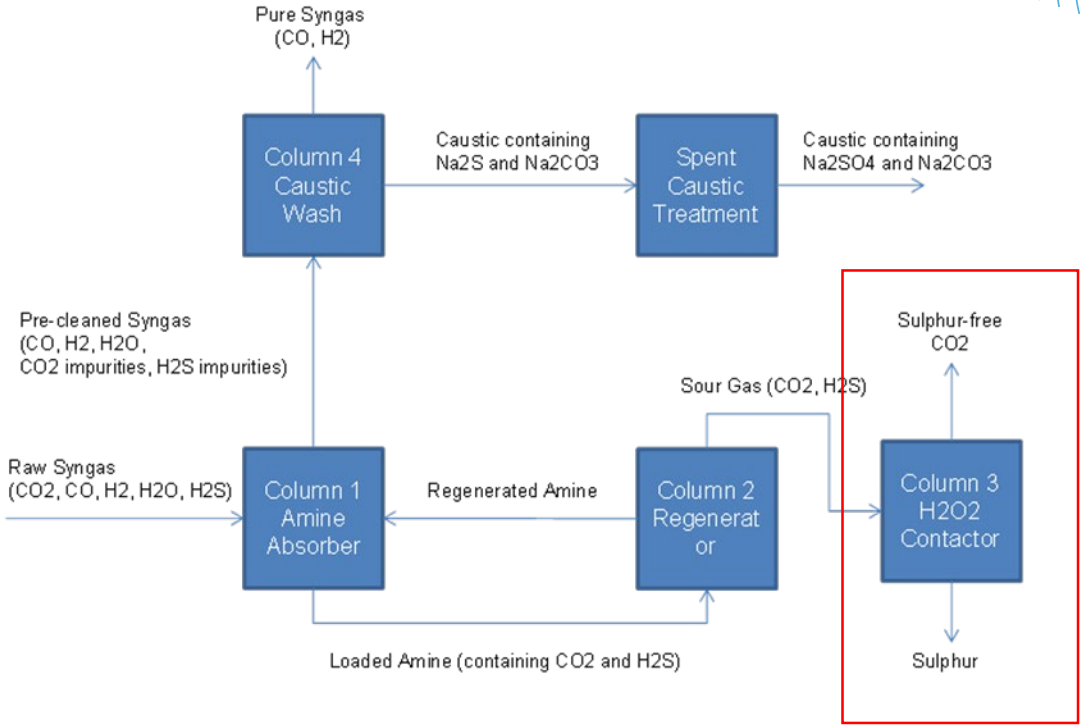
2 Innovative Gas Cleaning Concept



2 Innovative Gas Cleaning Concept



2 Innovative Gas Cleaning Concept



2 Innovative Gas Cleaning Concept Reactions for H2O2 – H2S System

$$H_2S + H_2O_2 \rightarrow S + 2H_2O$$

Desired reaction, leads to pure S to be separated mechanically from liquid phase (water)

$$H_2S + H_2O_2 \rightarrow H_2S + {}^{1}/_{2}\, O_2 + H_2O$$

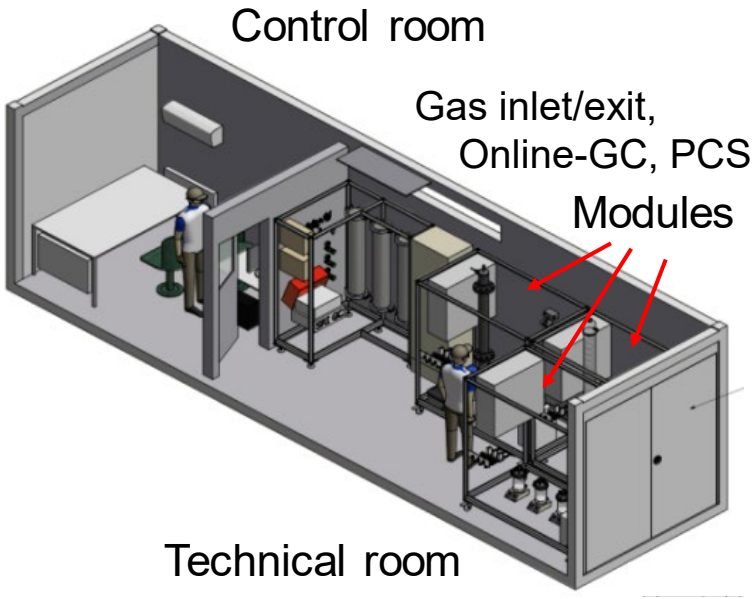
Undesired decomposition of H2O2

$$H_2S + 3H_2O_2 \rightarrow SO_2(g) + 4H_2O$$

Undesired oxidation to SO2

- Few other side reactions are known
- Oxidation potential (Nernst) sufficient to oxidize H2S
- pH value (CO2, H2S in water) justifies oxidation only to pure S, no further oxidation to SO2
- Options to increase kinetics are use of catalyst and increase of temperature

3 Mobile Gas Cleaning Test Rig



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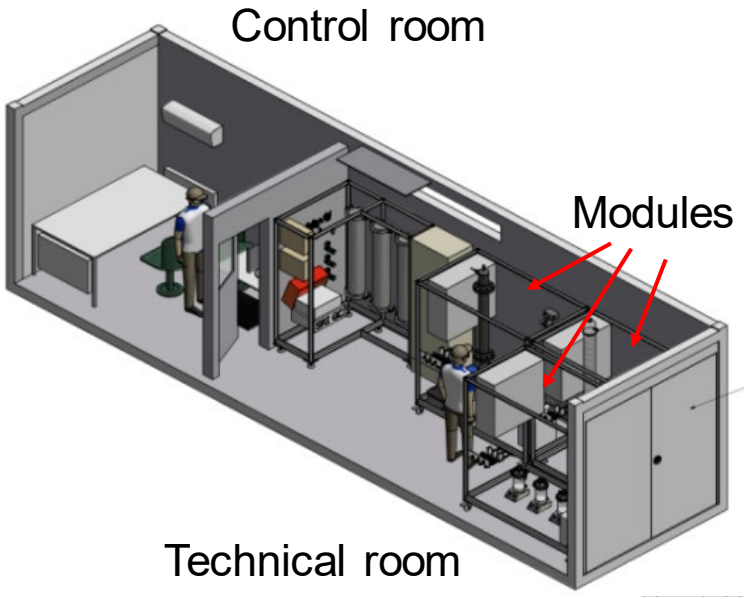


3 Mobile Gas Cleaning Test Rig (Modules for sulfur recovery)

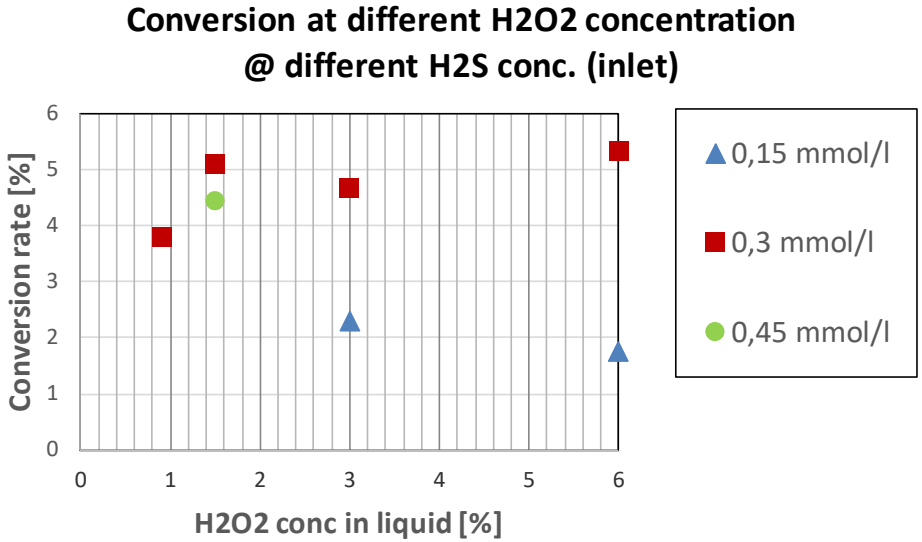
Stirred glass reactors for lab scale basic tests

Glass column for technical scale tests

4 Test Schedule and Results
Stirred glass reactors

- H2O2 in water up to 26 wt%
- Stabilized/unstabilized H2O2
- H2S in feed gas from 10 to 8000 ppmv
- 250 to 1000 (in most cases 500) ml liquid in glass reactor
- 1000 l/h feed gas to stirred glass reactor resulting in
  - ➢ Contact time of 1 to 4 seconds (typical values for columns)
- Stirring velocity up to 420 rpm
- Temperature up to 56 °C
- Use of (Fe(III) nitrate) as catalyst up to 0.45 mmol/l

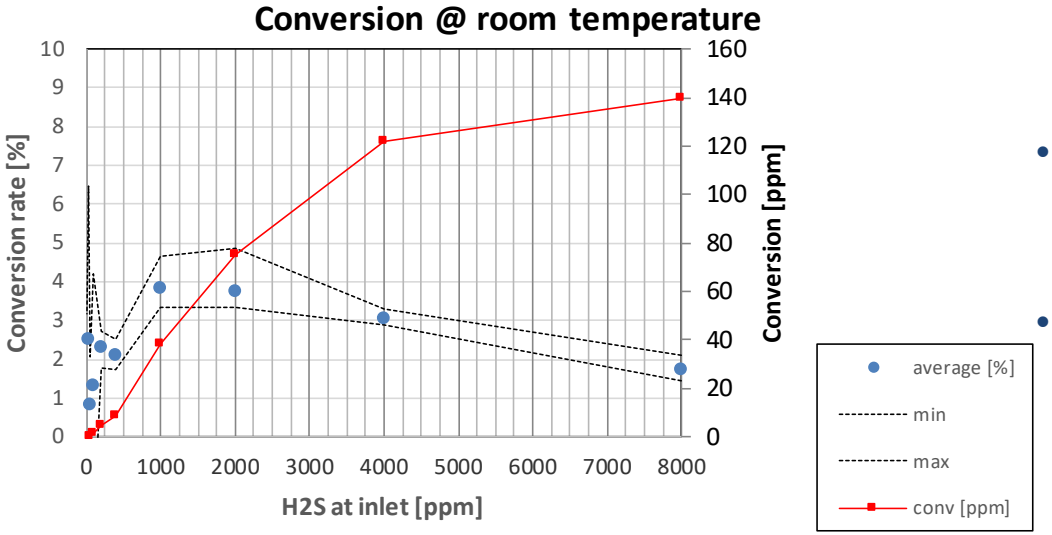
4 Test Schedule and Results
Stirred glass reactors



- No significant effect of H2O2 concentration in the liquid phase
- Little effect of catalyst concentration in the liquid
- Overall level of conversion not very high (sufficient?)

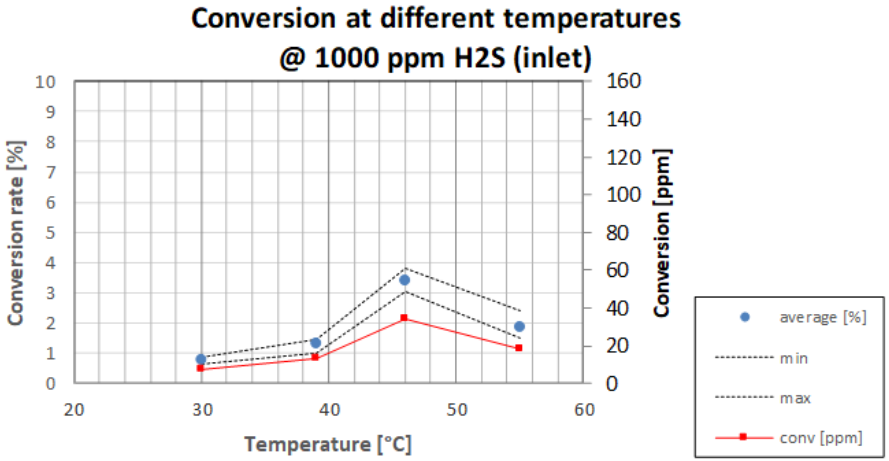
4 Test Schedule and Results

Stirred glass reactors



- very low H2S concentrations in the gas only low conversion (equivalent to top end of absorber column)
- Also very low conversion rates at high H2S concentration in the gas (equivalent to column entrance)
- Asymptotic shape of overall conversion indicates kinetically hindered reaction

4 Test Schedule and Results
Stirred glass reactors



- Temperature increase not sufficient at all
- Absolute level of conversion lower than before, less sufficient

4 Test Schedule and Results
Baffle tray column

- Although contact time was much higher than in stirred glas reactors
- Although catalyst has been used
- Nearly no conversion has been measured

- No diagram at this point

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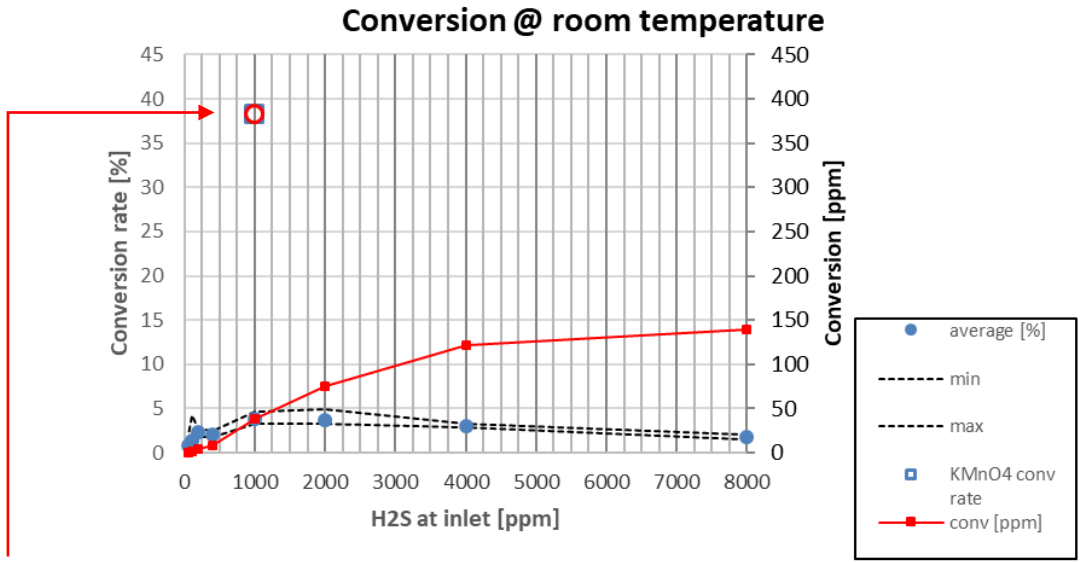
Is this the end??? .....

4 Test Schedule and Results

Stirred glass reactor, alternative reactant



- Significantly higher conversion rate with KMnO4

5 Conclusions and Outlook

- H2O2 is not sufficient for sulfur recovery from sour gas in typical technical equipment
- Promising alternative reactant (KMnO4) has to be investigated further within CLARA (and other projects)
- Subsequent use of experimental data with alternative KMnO4 to complete modeling and technical design / layout of complete gas cleaning section

Thank you very much!

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