Report

on

Gas Cleaning for Synthesis Applications

Work Package 2E: “Gas treatment”

Deliverable: 2E-3

prepared by

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Preface

ThermalNet, supported by the EC through Intelligent Energy – Europe programme, has established a closely integrated cluster of three networks on thermal processing of biomass for fuels and electricity. This includes combustion, gasification and pyrolysis, with a common focus of providing support for more rapid and more effective implementation of all the technologies in the market place by addressing technical, non-technical and commercial issues. The whole chain is considered from biomass production to end-use applications. Information about ThermalNet and the outputs from the project can be found on the website www.thermalnet.co.uk.

Work package 2E within ThermalNet deals with Gas treatment and is lead by TPS Termiska Processer AB. One of the deliverables of this work package is to produce reports of particular items of interest to gas treatment. Included in the WP2E contract was to sub-contract a university for reports to be written by students. The present report by Vienna University of Technology, Inst. of Chemical Engineering, is the product of this cooperation. The report is one of two reports that are produced as Deliverable 2E-3.

I would like to thank the authors for their work and professor Hermann Hofbauer also for the initiative to make this report.

Eva K. Larsson
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Summary

Biomass is beside of hydropower at present the main renewable source of energy. In future it is expected, that biomass is not only used for heat and power applications, but also for the production of chemicals and fuels. For these synthesis applications gasification will be the main conversion technology, as gases from gasification can be used for high efficient CHP or as synthesis gas for production of chemicals and fuels.

There were several gasification systems developed to produce synthesis gas from biomass. They can be classified according to the reactor design, the gasification agent, heat transfer or operating temperature. When the product gas should be used as synthesis gas, only oxygen blown or allothermal gasification systems can be used, as the nitrogen content in the product gas has to be low.

Synthesis gas can be used for production of different products. Ammonia and methanol are at the moment the main products from synthesis gas. In future it is expected, that fuels, like Fischer Tropsch liquids, SNG, DME or chemicals like aldehyds, alcohols or olefins will be produced from biomass.

The synthesis gas reactions have different requirements on the gas composition and the gas quality. Some need a correct ratio of hydrogen to carbon monoxide, like methanol synthesis, others not, like FT with iron catalysts. For some reactions the inert gas components have to be very low (nitrogen content for SNG), other synthesis reaction accept also higher amount of inerts, like FT synthesis in once through concepts. The product gas from the gasifier can be adjusted to the synthesis reaction by conditioning. The main steps here are reforming of hydrocarbons, CO-shift to adjust the H2:CO ratio and removal of CO2.

In general synthesis catalysts are very sensitive to poisoning. Especially sulphur and chlorine components have to be removed completely. But also particles and tars can cause malfunctions due to fouling. As the removal of particles and tars is widely investigated for usage of product gas in CHP this report focuses on the removal of sulphur and chlorine.

Sulphur and chlorine components can be removed either by wet scrubbing or by dry adsorption processes. In wet processes the sulphur can be removed by physical or chemical adsorption or by a combination. An example for physical adsorption is the Rectisol process, which is used at Sasol or at Schwarze Pumpe. Chemical adsorption can be done by amines (MEA, DEA) and this process is widely used in chemical industry. Wet processes are characterised by high investment costs and therefore mainly used at large scale at the moment. Typical examples for dry processes are the adsorption of H2S on ZnO or removal of impurities by activated carbon. Dry processes are used at the moment mainly for low inlet concentrations or as guard beds. Research is going on for dry processes, to use cheaper adsorbents and to include the regeneration step, so that also higher inlet concentrations can be treated.

At the moment there are only some groups, who have practical experience in the whole chain from biomass over synthesis to chemicals and 2nd generation fuels. Most of them use scrubbers as first step and afterwards some fine purification to clean the gas to a level, that it can be used as synthesis gas. It is expected, that with the focus on 2nd generation biofuels, more research will be done in the area of gas cleaning and treatment for synthesis gas applications.
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1 INTRODUCTION

Due to their extensive consumption in the transportation sector, fossil resources will not only reach depletion in the long term but also significantly contribute to greenhouse effects linked with CO₂-emissions [1]. Following recent EU legislation, by 2010 5.75% and by 2020 8% of all transportation fuels will have to be produced from renewables [2]. As a consequence, adequate production facilities are required in the near future.

In order to meet these goals, numerous alternatives are currently assessed to secure biofuel supply for both private and industrial use. 2nd generation biofuels have been identified to have great potential, since they do not rely on plant oils or sugar/starch as raw material but can be made from lingo-cellulosic material. Initially invented for the production of fuels and chemicals from coal [3], the application of the Fischer-Tropsch technology, for instance, has now been successfully adopted for other carbonaceous resources, such as natural gas [4]. Furthermore, due to the similarities of biomass, especially wood, and coal, in that carbon is chemically bound in both, current activities are directed towards the production of high quality fuels from biomass.

Cost effective and efficient gas cleaning is maybe the biggest bottleneck of advanced gasification applications. Before the gas can be used in chemical synthesis prior purification steps are necessary. To increase the overall efficiency the gas cleaning unit should be operated at high temperatures as well. The main impurities are particles, tars and H₂S and a number of secondary contaminants like HCl and alkali metals. This report should give an overview of possibilities for upgrading a product gas from biomass gasification to synthesis gas quality, especially focussing on H₂S and HCl removal.

The overview in the following chapters (2-6) are taken mainly from the Handbook Biomass Gasification (chapter 10.6.2) [5] and updated where necessary as one of the authors contributed also essentially to this book chapter.
2 GASES FROM BIOMASS GASIFICATION

2.1 Definitions

Gasification is the key conversion technology in all processes for the production of energy, fuels, and/or other products from biomass [5]. In electricity production biomass is thermally converted by gasification into a combustible gas that can be used in a gas engine or turbine with electricity as well as heat as products. The advantage of the gasification route is the higher overall electric efficiency compared to the alternative of using direct biomass combustion (e.g. steam process, ORC process). In order to produce fuels and chemicals the combustible gasification gas is used in a catalytic process to synthesis the desired product.

In the discussion on the utilisation of gases from biomass gasification it is important to understand that gas specifications are different for the various gas applications (Figure 1). Furthermore, the composition of the gasification gas is very dependent on the type of gasification process and especially the gasification temperature.

![Gasification and Applications Diagram](image_url)

**Figure 1:** Production of biosyngas and typical applications.

*Product gas* is produced by gasification and contains CO, H₂, CO₂, H₂O, CH₄, CₓHᵧ aliphatic hydrocarbons, benzene, toluene, tars and inorganic impurities (mainly H₂S, NH₃, HCl).

*Biosyngas* (CO, H₂) is chemically similar to syngas derived from fossil sources and can replace its fossil equivalent in all applications. Biosyngas is the gas after gas treatment with the correct composition for the synthesis step.

In this Chapter the major utilisations of both types of gases from biomass gasification will be assessed, i.e. product gas and biosyngas. However, the focus will be on biosyngas applications, as biosyngas utilisation is expected to be dominant on the long term. Whereas for electricity production other renewable options exist (i.e. solar PV and wind turbines), biomass is the only renewable carbon-source.
2.2 Gas Markets

The major application of product gas will be the direct use for the generation of power (and heat). This can be either in stand-alone combined heat and power (CHP) plants or by co-firing of the product gas in large-scale power plants.

Syngas is a versatile building block in chemical industry [6,7]. The total global annual use of fossil-derived syngas is approximately 6,000 PJth, which corresponds to 2% of the total primary energy consumption. The largest part of the syngas is used for the synthesis of ammonia for fertiliser production (~55%), the second largest share is the amount of hydrogen from syngas consumed in oil refining processes (~24%), and smaller amounts are used for methanol production (12%). Figure 2 shows the present syngas market distribution [8]. Today’s, global use of syngas for the production of transportation fuels in the so-called “gas-to-liquids” processes (GTL) correspond to approx. 500 PJ per year, i.e. from the Fischer-Tropsch processes of Sasol in South Africa and of Shell in Bintulu, Malaysia.

![Pie chart showing syngas market distribution](image)

Figure 2: Present world syngas market

In the future, syngas will become increasingly important for the production of cleaner fuels to comply with the stringent emission standards, e.g. methanol/DME, ethanol, and/or Fischer-Tropsch diesel. Also the future fuels will be ultra-clean designer fuels from BtL processes (second generation biofuels) as well as GtL. Transportation fuels of the first generation directly produced from biomass (e.g. biodiesel, pyrolysis oils) are expected to have only very limited application.
3 GASIFICATION

Gasification is the complete thermal breakdown of biomass into a combustible gas, volatiles, char, and ash in an enclosed reactor or gasifier [5]. Gasification is a two-step, endothermic (i.e. heat absorbing) process. In the first reaction, pyrolysis, the volatile components of the fuel are vaporized at temperatures below 600°C by a set of complex reactions. Included in the volatile vapours are hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, tar, and water vapour. As biomass fuels tend to have more volatile components (70-86% on a dry basis) than coal (e.g. 30%), pyrolysis plays a larger role in biomass gasification than in coal gasification. Char (fixed carbon) and ash are the pyrolysis by-products, which are not vaporized. In the second step, the char is gasified through reactions with oxygen, steam, carbon monoxide and hydrogen. The heat needed for the endothermic gasification reactions is generated by combustion of part of the fuel, char, or gases, depending on the reactor technology.

Depending on the temperature of the second and actual gasification step, the process yields a product gas with different components. The choice for the gasification agent (air, oxygen or steam) determines whether the product gas contains nitrogen. There are a large number of gasification processes in development. Within the scope of this Chapter some main types are briefly discussed with the focus on the gas generation.

3.1 Low Temperature Gasification

Product gas is generated by low-temperature (<1000°C) gasification. Gasification processes can be differentiated in direct and indirect (or allothermal) processes. In case of air or oxygen as gasification agent an autothermal (direct) gasification is realized. This means that the necessary heat for gasification is produced by partial combustion of the biomass in the same reaction chamber. A mixture of steam and oxygen is proposed to obtain a nitrogen free producer gas which is normally applied in large scale coal gasification (Fig. 3). To avoid an air separation unit especially for small and medium scale biomass gasification another approach has been established. This process is based on allothermal (indirect) gasification which means that the heat is supplied indirectly via a heat exchanger or a circulating heat carrier. Both types of are currently under investigation and also demonstration plants have been built.

Figure 3: Classification of gasification based on heat supply and gasification agents (CV … calorific value)
For biomass applications the direct processes are typically operated with air as gasification medium. The main direct and indirect processes are:

- Fixed-bed updraft and downdraft;
- Fluidised bed (bubbling and circulating, i.e. BFB and CFB);
- Indirect fluidised bed (steam-blown) and
- Entrained flow

For the more advanced product gas applications, e.g. production of biosyngas, a nitrogen-free product gas is required. A nitrogen-free product gas can be produced by oxygen-blown gasification or alternative by indirect processes. The indirect gasification process is very attractive for N₂-free product gas generation as no oxygen (no air separation unit) is required for the gasification. Furthermore, the conversion is generally complete, whereas, direct gasification processes afford carbon-containing ashes due to incomplete conversion (i.e. typically 90-95%). Pressurised gasification has the advantage that the downstream processes - especially most of the synthesis reactions - require an elevated pressure. Concerning the scale indirect gasification processes have its merits at smaller scale and e.g. pressurized oxygen blown technologies (fluidized bed, entrained flow) at larger scale.

Examples of indirect gasification processes are the Fast Internal Circulation Fluidised Bed (FICFB) process developed by the Vienna University of Technology (TUV) [8], the SilvaGas process based on the Batelle development [9], and the MILENA gasifier developed at the Energy research Centre of the Netherlands (ECN) [10]. Examples of indirect gasification processes, where the heat is transported by heat exchangers, are the MTCI process [11] and the heat pipe reformer [12].

Examples for direct fluidised bed technologies with mixtures of oxygen/steam are the e.g. BIOSYN [13] gasifier, the technology from GTI/IGT RENUGAS [13], the technology from Cutec [14], and VTT-Carbona gasification technology.

### 3.2 High Temperature Gasification

High temperature gasification is normally operated at temperatures above 1200°C. The main reactor type is the entrained flow gasifier (EF) [15]. At these high temperatures the feed is completely converted into product gas, even at the short residence time of only a few seconds. There are two different types of EF:

- Slagging, where the ash is molten
- Non slagging, where the ash remains solid.

Entrained flow gasifier manufacturers are Shell, Texaco, Krupp-Uhde, Future-Energy (formerly: Noell and Babcock Borsig Power), E-gas (formerly Destec and Dow), MHI (Mitsubishi Heavy Industries), Hitachi, Choren (formerly UET), and CHEMREC especially for black liquor.

In most cases, EF gasifiers are operated under pressure (typically 20-50 bar) with pure oxygen and with capacities in the order of several hundreds of MW. Product gas production based on
entrained flow gasification has the technical advantages of higher fuel flexibility and more simple gas cleaning (no organic impurities).

One example of a large-scale entrained flow gasifier is the 600 MW\textsubscript{th} coal-fired Shell gasifier in Buggenum, the Netherlands [15]. It is owned by the utility company NUON and produces electricity with a net efficiency of 43%. Tests have been performed with different kinds of biomass like wood, sewage sludge and chicken manure up to approximately 10% on energy basis (corresponding to 18% on weight basis). It is planned to co-fire 25% biomass on energy basis in 2005. Shell has signed several contracts to make similar coal gasifiers for fertilizer industries in China. Another example is a 130 MW\textsubscript{th} gasifier (25 bar) made by Future Energy, operating on waste oil and sludges on the premises of the Schwarze Pumpe in Germany [16] which was shut down recently.
4 UTILISATION OF BIOSYNGAS

The main application at present of product gas from gasification is found in direct or indirect combustion to generate power with co-production of heat. Due to the typical complex composition of product gases and due to economic reasons, more advanced (synthesis) applications are still in the status of research and development but offer a high potential for product gases from biomass gasification.

4.1 Power Generation

Product gas is a combustible gas and can be used for the production of electricity in all prime movers from steam cycles, to gas engines, gas turbines (combined cycle), as well as fuel cells. Product gas can be used without extensive gas treatment in boilers for steam cycles, while gas engines and gas turbines for power generation require a higher degree of cleaning. Particle separation and tar elimination are the main gas cleaning steps necessary for these applications. In future, if fuel cells would be commercializes more stringent gas cleaning will be necessary.

4.2 Synthetic Natural Gas (SNG)

Whereas high-temperature gasification processes yield product gas with high concentrations of carbon monoxide and little methane, interest in Synthetic Natural Gas (SNG) production is concentrated on gasification processes that yield product gases with high methane contents. SNG is a gas with similar properties as natural gas but produced by methanation of H₂ and CO in gasification product gas upgraded to syngas. Methanation is the catalytic reaction (catalyst: nickel) of carbon monoxide with hydrogen, forming methane and water typically operated at temperatures of 300 – 350 °C and pressures of 1 – 5 bars:

\[ CO + 3H_2 \rightarrow CH_4 + H_2O \] (1)

Consecutive and side reactions (shift conversion, Boudouard equilibrium, and hydrogenation of carbon) make the calculation of equilibrium conditions very complex. The methanation reactions of both carbon monoxide and carbon dioxide are highly exothermic. Such high heat releases strongly affect the process design of the methanation plant since it is necessary to prevent excessively high temperatures in order to avoid catalyst deactivation and carbon deposition. The highly exothermic reaction generally creates a problem for the design of methane synthesis plants: either the temperature increase must be limited by recycling of reacted gas or steam dilution, or special techniques such as isothermal reactors or fluidised beds, each with indirect cooling by evaporating water, must be used.

The methanation process is a very well known and technically important as a catalytic purification step for the removal of trace carbon monoxide (typically below a few vol%) from process gases, especially for hydrogen production. Methanation of gases with a high CO content, like gasification product gas is not well established and there are no commercial catalysts available (i.e. the Dakota coal-to-SNG plant uses a non-commercial catalyst).

For the removal of carbon monoxide from synthesis gases, catalysts with usually <15 wt% nickel are used predominantly. For SNG production, catalysts with high nickel content are
preferred, similar to those used in reforming naphtha to a methane-rich gas. Catalysts based on ruthenium have been tried repeatedly for methanation but have not found the broad application of nickel-based catalysts. Catalytic activity is affected seriously even by very low concentrations of catalyst poisons in gases to be reformed. Such catalyst poisons are sulphur, arsenic, copper, vanadium, lead, and chlorine or halogens in general. Precaution must be taken with nickel-containing catalysts to prevent formation of highly poisonous nickel carbonyl \([\text{Ni(CO)}_4]\). In practical operation of methanation plants, temperatures below 200°C at the nickel catalyst must be avoided [17].

### 4.3 Fischer-Tropsch Synthesis

In the non-selective catalytic Fischer Tropsch (FT) synthesis one mole of CO reacts with two moles of H₂ to form mainly paraffin straight-chain hydrocarbons \((C_xH_{2x})\) with minor amounts of branched and unsaturated hydrocarbons (i.e. 2 methyl paraffins and \(\alpha\)-olefins), and primary alcohols. Undesirable side reactions include methanation, the Boudouard reaction, coke deposition, oxidation of the catalyst, or carbide formation. Typical operation conditions for FT synthesis are temperatures between 220 and 350°C and pressures between 25 and 60 bar [17]. In the exothermic FT reaction about 20% of the chemical energy is released as heat:

\[
CO + 2H_2 \rightleftharpoons -(CH_2)_x + H_2O
\]  

(2)

The Fischer-Tropsch processes can be used to produce either a light synthetic crude oil (syncrude) and light olefins or heavy waxy hydrocarbons. The syncrude can be refined to environmental friendly gasoline and diesel and the heavy hydrocarbons to special waxes or, if hydrocracked and/or isomerised, to produce excellent diesel fuel, lube oils, and naphtha, which is an ideal feedstock for cracking to olefins. For direct production of gasoline and light olefins, the FT process is operated at high temperature (330–350°C), for production of waxes and/or diesel fuel, at low temperatures (220–250°C), cf. Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low-temperature FT</th>
<th>High-temperature FT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Products</strong></td>
<td>Waxes and/or diesel fuels</td>
<td>Gasoline, light olefins</td>
</tr>
<tr>
<td>Temperature [^{°C}]</td>
<td>220 - 250</td>
<td>330 - 350</td>
</tr>
<tr>
<td>Pressure [^{bar}]</td>
<td>25 - 60</td>
<td>25</td>
</tr>
<tr>
<td>CO + H₂ conversion [^{%}]</td>
<td>60 - 93</td>
<td>85</td>
</tr>
</tbody>
</table>

Several types of catalysts can be used for the Fischer-Tropsch synthesis - the most important are based on iron (Fe) or cobalt (Co). Cobalt catalysts have the advantage of a higher conversion rate and a longer life (over five years). The Co catalysts are in general more reactive for hydrogenation and produce therefore less unsaturated hydrocarbons (olefins) and alcohols compared to iron catalysts. Iron catalysts have a higher tolerance for sulphur, are cheaper, and produce more olefin products and alcohols. The lifetime of the Fe catalysts is short and in commercial installations generally limited to eight weeks [17].

Catalysts for Fischer-Tropsch synthesis can be damaged with impurities as NH₃, HCN, H₂S, and COS. These impurities poison the catalysts. HCl causes corrosion of catalysts. Alkaline
metals can be deposited on the catalyst. Tars are deposited, cause poisoning of catalyst and contaminate the products. Particles (dust, soot, ash) can cause fouling of the reactor. The removal limit is based on an economic optimum determined by catalyst stand-time and investment in gas cleaning. But generally, all these impurities should be removed to a concentration below 1 ppmV [17].

### 4.4 Methanol Synthesis

Methanol can be produced by means of the catalytic reaction of carbon monoxide and some carbon dioxide with hydrogen. The presence of a certain amount of carbon dioxide in the percentage range is necessary to optimise the reaction. Both reactions are exothermic and proceed with volume contraction. Therefore, a low temperature and high pressure consequently favours them:

\[
\begin{align*}
CO + 2H_2 & \Rightarrow CH_3OH \\
CO_2 + 3H_2 & \Rightarrow CH_3OH + H_2O
\end{align*}
\]

Side reactions, also strongly exothermic, can lead to formation of by-products such as methane, higher alcohols, or dimethyl ether (DME). The oldest process for the industrial production of methanol is the dry distillation of wood. Methanol is currently produced on an industrial scale exclusively by catalytic conversion of synthesis gas. Processes are classified according to the pressure used:

- High-pressure process 250-300 bar
- Medium-pressure process 100-250 bar
- Low-pressure process 50–100 bar.

Both high- and low-pressure processes are available to hydrogenate carbon monoxide. The high-pressure method was commercialised by BASF. These processes used zinc-chromium oxide catalysts at or above 340°C and required a pressure between 300 and 500 bar to obtain methanol concentrations of about 5-6 vol% in the effluent gases from the reactor, together with significant amounts of methane, dimethyl ether (DME), ethanol, and higher alcohols.

In 1966 ICI introduced a low-pressure methanol synthesis that used a copper-zinc-chromium catalyst at 50 bar. The low-pressure processes differ primarily in operating pressure, catalyst, and reactor design, especially with respect to heat recovery and temperature control. The low-pressure processes are dominant currently and their main advantages are lower investment and production costs, improved operational reliability, and greater flexibility in the choice of plant size [17].
4.5 Ammonia Synthesis

The major share (e.g. 85%) of ammonia is used for the production of fertilisers [17], while the other 15% are used for a broad variety of applications. Each nitrogen atom in industrially produced chemicals is directly or indirectly derived from ammonia (or its derivative nitric acid), e.g. it is used for the production of plastics and fibres like polyurethane, polyamides, and poly-acronitril. Furthermore, ammonia is used for the production of explosives and animal feed. The ammonia synthesis is a catalytic reaction carried out at pressures between 100 and 250 bar and temperatures between 350 to 550°C, according the following reaction:

\[ N_2 + 3H_2 \Rightarrow 2NH_3 \]  

Typically, iron-based catalysts are used for the ammonia synthesis. The reaction is thermodynamically limited and the conversion per cycle is limited to approx. 20 to 30%. To achieve higher conversions the unconverted gas is partly circulated, while the other part is bled to prevent accumulation of inert gases and impurities. The ammonia is recovered from the gas as a liquid by cooling and condensation. In comparison with other syngas-based processes, the ammonia synthesis has two significant characteristics. Firstly, a high concentration of the inert gas nitrogen is acceptable and even required. Secondly, the specifications for oxygen-containing gases (e.g. CO₂, and CO) that typically are present in syngas are very strict, i.e. the sum of the concentrations should be lower than 20 ppmV [17].

4.6 Hydroformylation of Olefins

Olefins react with synthesis gas (carbon monoxide and hydrogen) in the presence of homogeneous catalysts to form aldehydes containing an additional carbon atom. This hydroformylation, also called oxo-synthesis or Roelen reaction, is a commercial-scale process for the production of aldehydes. By catalytic addition of hydrogen and carbon monoxide to an olefin an aldehyde is obtained under chain elongation:

\[ R-CH=CH_2 + CO + H_2 \Rightarrow R-CH_2-CH_2-CHO + R-CH(CH_3)-CHO \]  

Hydroformylation is generally an exothermic, homogeneously catalysed liquid-phase reaction of the olefin with hydrogen and carbon monoxide. The hydroformylation reaction is used on an industrial scale to produce aldehydes and alcohols. The most important oxo products are in the range C₃-C₁₉. With a share of roughly 75 %, butanal is by far the most significant. Propene is the olefin mostly used. The oxo-products are converted to alcohols, carboxylic acids, aldol-condensation products, and primary amines. About 20 commercial processes are state-of-the-art [17].

Up until the mid 1970s only the cobalt-based catalysts were important for industrial applications. The situation changed when Union Carbide and Celanese, independently of one another, introduced rhodium-based catalysts on an industrial scale. Since then, cobalt catalysts for the hydroformylation of propene have been replaced in nearly all major plants by the more advantageous rhodium catalysts despite of the higher price of the noble metal. The catalyst lifetime can be severely diminished by "extrinsic poisons" such as strong acids, hydrogen cyanide, sulphur, hydrogen sulphide, COS, oxygen, and dienes. The feedstock must therefore
be very clean. Next to the efficiency, activity, and selectivity of the catalyst, the catalyst lifetime is the most industrially important reaction parameter.

4.7 Hydrogen

Syngas is one of the main sources for hydrogen. Today, syngas is generally produced by steam reforming of natural gas or in some cases by gasification of heavy oil fractions (“bottom-of-the-barrel”). In refineries, hydrogen is used for hydro-treating and hydro-processing operations. Hydro treating is used to remove impurities (desulphurisation and removal of nitrogen) and for the hydrogenation of olefins. In each refinery several hydro-treating units are present to treat the various product fractions (i.e. gasoline, kerosene, diesel, and heating oil).

Furthermore, the process is used to pretreat the feedstock of catalytic cracking processes. Hydro processing is used to upgrade the heavy oil fractions to lighter products that can be used for the production of transportation fuels. The specifications for hydrogen in the process industry are relatively mild, typical demands for a hydro-cracker are [17]:

- \( H_2 \) content \( \geq 98 \ \text{vol}\% \),
- sum CO and \( \text{CO}_2 \) \( \leq 10 - 50 \ \text{ppmV} \)
- \( O_2 \leq 100 \ \text{ppmV} \)
- inert gases (i.e. \( \text{N}_2 \), \( \text{Ar} \), and \( \text{CH}_4 \)) \( < 2 \ \text{vol}\% \).

4.8 Other Applications

Other applications of syngas have a relatively small market or the processes are still in development phase. Some examples are:

- Mixed alcohols
- Carbon monoxide
- Olefins and aromatics

Mixed Alcohols

Similar to Fischer-Tropsch synthesis in which a mixture of straight chain hydrocarbons is produced with varying chain lengths, a similar mixture of alcohols can be produced in another catalytic syngas process. Various activities on this subject have not yet resulted in industrial developments. However, probably resulting from the large interest in bio-ethanol, the mixed-alcohol synthesis has received renewed attention in the United States. Power Energy Fuels, Inc. in Denver, Colorado plans to commercialise a process that produces mixed alcohols. Their product with the trade name EcaleneTM consists of a mixture of 75 wt% ethanol and the remained being higher alcohols [18].
Carbon Monoxide

The production volume of carbon monoxide (CO) from syngas is very small compared to other syngas applications. The main consumers of CO are acetic acid and phosgene production processes. With the increasing demand of alternative carbon sources (other than crude oil) it is expected that the demand of CO will increase in the future, i.e. the so-called C₁-chemistry [17].

Olefins and Aromatics

Today, the most important classes of base chemicals are olefins and aromatics. Already for several decennia research is ongoing to produce these compounds directly from syngas [17]. So far, these attempts have not been successful; processes in which the chemicals are produced from methanol, i.e. a syngas product, are more promising. Mobil has developed several processes in which methanol is converted using zeolite catalysts. In the methanol-to-gasoline (MTG) process gasoline is produced from methanol. The product contains approx. 15 wt% of aromatics. By applying conventional separation techniques, the aromatics can be recovered and in this way aromatics can be produced from biomass (when the methanol was produced from biosyngas). In a variant of the MTG process, the methanol-to-olefines (MTO) process, olefins are produced from methanol. The processes have been operation on 14,500 bbl/day and 100 bbl/day for the MTG and MTO processes, respectively [19].
5 GAS SPECIFICATIONS

Specifications for biosyngas and product gas are defined by the final gas application and comprise acceptable levels for the concentration of impurities and the required main gas composition.

5.1 Producer Gas Compositions

The producer gas composition is mainly dependent on the type and operation conditions of the gasifier. The main parameters are the gasification agent, operation temperature, operation pressure, and type of reactor. Tab. 2 gives an impression about the typical ranges of three selected reactor types. Allothermal atmospheric steam blown gasifiers lead to a practically nitrogen free producer gas and as further advantage a high hydrogen content can be observed. In case of oxygen blown pressurized fluidized bed and entrained flow gasification the producer gas contains a lower content of hydrogen. At low temperatures (800 - 900 °C) the methane content is high which can be beneficial for SNG (synthetic natural gas) production. High temperature operation (>1200 °C) leads to low methane contents. This gas is well suited for e.g. Fischer Tropsch biofuel production.

Table 2: Typical ranges of producer gas composition for selected gasifiers

<table>
<thead>
<tr>
<th></th>
<th>Low temperature atmospheric steam blown fluidized bed gasifier ¹)</th>
<th>Low temperature pressurized oxygen blown fluidized bed gasifier²)</th>
<th>High temperature pressurized oxygen blown entrained flow gasifier³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ %</td>
<td>35 - 40</td>
<td>23 - 28</td>
<td>29 - 35</td>
</tr>
<tr>
<td>CO %</td>
<td>25 - 30</td>
<td>16 - 19</td>
<td>35 - 44</td>
</tr>
<tr>
<td>CO₂ %</td>
<td>20 - 25</td>
<td>33 - 38</td>
<td>17 - 22</td>
</tr>
<tr>
<td>CH₄ %</td>
<td>9 - 11</td>
<td>10 - 13</td>
<td>&lt;1</td>
</tr>
<tr>
<td>N₂ %</td>
<td>&lt;1</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

¹) Data from Güssing FICFB gasifier
²) Data from Bioflow gasifier
³) Several data from CHOREN and FZ Karlsruhe

The applications of product gas are found in the production of power and/or heat. The utilisation of biomass-based product gas is not (yet) completely established and for the more advanced applications the technologies are still in development. Resultantly, also the technical gas specifications have not yet been defined. More important for heat and power production, however, are the applicable emission regulations that in most cases will results in more stringent gas specifications than required for technical reasons. Typical limits standards apply for emissions of dust, CO and/or CH₄ (indicators for incomplete conversion), NOₓ (from fuel-NH₃ and thermal NOₓ), SO₂ (from fuel S), volatile metals, and PAHs.
5.2 Requirements on Synthesis Gas Applications

Impurities in Biosyngas

The main application of biosyngas is found in catalytic synthesis processes and catalysts are intrinsically very sensitive to small amounts of impurities. In general, the required gas purity specifications depend on economic considerations, i.e. additional investments in gas cleaning versus accepting decreasing production due to poisoning of catalysts or higher maintenance intervals due to fouling of the system. Therefore, there are no “hard” data on maximum levels for impurities in gas. For each plant and also for each catalyst supplier the acceptable levels may be different [5].

A maximum value of less than 1 ppmV is defined for both the sum of the nitrogen-containing and sulphur-containing compounds. Although for low-pressure methanol process a level as low as 0.1 ppmV of total sulphur is required. For the halides and alkaline metals a lower level of less than 10 ppbV is assumed (see Table 2). Solids must be removed essentially completely, as they foul the system and may obstruct fixed-bed reactors. A number of other possible impurities, such as organic acids (e.g. formic and acetic acid) and unsaturated and higher boiling hydrocarbons, are normally not included in purity specifications for synthesis processes because they are already undesirable in upstream process stages of biosyngas production (e.g. compression steps). However, organic compounds present must be below their dewpoint at pressure of the gas application to prevent condensation and fouling in the system [20]. For organic compounds with S or N hetero atoms (e.g. thiophene and pyridine) the additional specification applies that they need to be removed below ppmV level, as they are intrinsically poisonous for the catalyst.

Table 3: Purification level of main biosyngas impurities [20].

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Removal level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum of sulphur compounds (H₂S + COS + CS₂ + organic S)</td>
<td>&lt; 1 ppmV</td>
</tr>
<tr>
<td>Sum of nitrogen compounds (NH₃ + HCN)</td>
<td>&lt; 1 ppmV</td>
</tr>
<tr>
<td>HCl + HBr + HF</td>
<td>&lt; 10 ppbV</td>
</tr>
<tr>
<td>Alkaline metals</td>
<td>&lt; 10 ppbV</td>
</tr>
<tr>
<td>Solids (soot, dust, ash)</td>
<td>essentially completely</td>
</tr>
<tr>
<td>Organic compounds (hydrocarbons, tars)</td>
<td>below dewpoint</td>
</tr>
</tbody>
</table>

Main Gas Composition of Biosyngas

When gasification is followed by downstream synthesis the stoichiometry of that synthesis reaction requires in most cases a very specific gas composition. In addition, economic aspects must be considered concerning the inerts contained in the gas, which unnecessarily reduce the partial pressure of reactants and tend to concentrate in recycle processes so that a considerable amount of purge gas must be branched off [17]. In Table 4 an overview is presented of main gas specifications for the major biosyngas applications [5].
<table>
<thead>
<tr>
<th>Synthesis</th>
<th>H₂ for refinery</th>
<th>Ammonia</th>
<th>Methanol</th>
<th>Fischer-Tropsch</th>
<th>SNG</th>
<th>Oxo alcohols</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>&gt;98%</td>
<td>75%</td>
<td>71</td>
<td>60</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;10-50 ppmv</td>
<td>CO+CO₂</td>
<td>19</td>
<td>30</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt;10-50 ppmv</td>
<td>4-8%</td>
<td>-</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>N₂</td>
<td>-</td>
<td>25%</td>
<td>-</td>
<td>N₂, Ar, CH₄ low</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inert</td>
<td>N₂, Ar, CH₄ balance</td>
<td>Ar, CH₄ as low as possible</td>
<td>N₂, Ar, CH₄ as low as possible</td>
<td>CO₂, N₂, Ar, CH₄ low</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>-</td>
<td>~3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>-</td>
<td>1.0-4.0</td>
<td>0.6-2</td>
<td>1.5-3</td>
<td>1-1.5</td>
<td>-</td>
</tr>
<tr>
<td>H₂/(2<em>CO+3</em>CO₂)</td>
<td>-</td>
<td>1.3-1.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Process pressure</td>
<td>&gt;50 bar</td>
<td>100-250 bar</td>
<td>50-300 bar</td>
<td>25-60 bar</td>
<td>1-20 bar</td>
<td>15-350 bar</td>
</tr>
</tbody>
</table>

Each application has its own specifications, therefore, it is not possible to define one set of biosyngas specifications. However, a general specification is a hydrogen content of >50%. In methanol and Fischer-Tropsch synthesis 10-30% of CO is required, while for hydrogen production and ammonia synthesis the CO must be completely removed. The total content of inerts (e.g. N₂, Ar, and CH₄), which in most cases are not dangerous to synthesis but undesirable for economic reasons, must often be <2% (i.e. as low as possible). The exception is ammonia synthesis, in which 25% of nitrogen is required. In general the required ratio of hydrogen to carbon monoxide offers a simple characterization as the main biosyngas characteristic.
6 GAS CONDITIONING

Gas conditioning comprises all gas treatment steps to adjust the main gas composition of the biosyngas to meet the specifications of the gas application (cf. Table 3). The main issues in gas conditioning are adjustment of the H₂/CO ratio and CO₂ removal. Typically, processes for the manufacturing of syngas from hydrocarbon feedstocks produce mixtures of hydrogen, carbon dioxide, methane, and varying amounts of carbon monoxide. For the majority of industrial processes, the carbon monoxide content is higher than that required for synthesis. The presence of CO₂ is undesired in most processes and this compound should be removed.

6.1 Water-Gas-Shift

To increase the H₂/CO ratio or to (essentially completely) convert CO into H₂ the water-gas-shift reaction is used:

\[ CO + H₂O \rightarrow CO₂ + H₂ \]  (7)

The water gas shift equilibrium among carbon monoxide, carbon dioxide, hydrogen, and steam depends on temperature but is almost independent of pressure in the industrial range (elevated pressures up to 70 bar). Above 950 to 1000°C, the equilibrium is established rapidly enough without a catalyst, but typically the shift is carried out at lower temperatures with a catalyst, since the equilibrium towards H₂ only can be reached at lower temperatures. Temperature ranges used in commercial carbon monoxide shift conversions are:

- High-temperature shift (HTS) at about 300 to 510°C with copper-promoted catalysts
- Low-temperature shift (LTS) at about 180 to 270°C with copper-zinc-aluminium oxide-based catalysts.

Depending on the required H₂/CO ratio the water-gas-shift reaction is carried out in two steps. In the first high temperature (HTS) step the bulk of the CO is converted; the remaining CO concentration is minimum 1-2 vol%. If hydrogen production is aimed at, a second shift LTS step is carried out to reduce the CO content to 0.2-0.5 vol%.

6.2 CO₂ Bulk Removal

Carbon dioxide can be removed from syngas by chemical and physical absorption with a washing liquid or by adsorption with solid absorbentia. The choice for chemical or physical absorption (or a combination of both) depends on the partial pressure in the gas. For chemical absorption in commercial processes substituted amines are used, while solvents like methanol or polyethylene glycol are used for physical absorption. The CO₂ concentration can be removed to values lower than 0.1 vol% by these processes. When the syngas contains significant concentrations of other gases besides H₂ and CO₂, adsorption on solid absorbentia is preferred. Examples of these materials comprise silica gel, active carbon, zeolites, and molecular sieves. The adsorption takes place at low temperatures and high pressures and the regeneration takes place either by higher temperature (TSA; Thermal Swing Adsorption) or lower pressure (PSA; Pressure Swing Adsorption). In these processes also H₂S can be removed.
7 OVERVIEW GAS CLEANING

Each synthesis gas production plant requires gas treatment facilities to purify product gases and also, in many cases, to condition them. Whereas the gas purification system eliminates the components that would affect downstream processing or utilization of these gases, the purpose of a conditioning system is to remove undesired main gas compounds and to adjust gas components to the appropriate ratio. Especially, the ratio of hydrogen to carbon monoxide must be matched to the requirements of downstream synthesis units or gas consumers [5].

Depending on the type and composition of feedstock and the type of gasification process used, the gas purification and conditioning must handle the following impurities and undesired compounds:

- Particulates.
- Sulphur compounds, e.g. hydrogen sulphide, carbonyl sulphide, organic sulphur.
- Nitrogen compounds, e.g. mainly ammonia.
- Halogens, e.g. chlorides.
- Volatile metals, e.g. alkali and earth alkali compounds.
- Tars.
- Hydrocarbons (if removal is necessary for usage), e.g. CH₄, C₂⁺ aliphatic hydrocarbons and aromatics like benzene and toluene.
- Carbon dioxide (if removal is necessary for usage).

For discussion the gas treatment is divided in removal of particulates, organic impurities (i.e. tars and hydrocarbons), and inorganic impurities (i.e. metals, halides, and nitrogen and sulphur containing compounds), and gas conditioning. A good overview about gas cleaning is given in reference [5,17,21], therefore, no detailed description of gas treatment system to remove particulates (including volatile metals after condensation) and tars is given here. In the following chapters the removal of diverse impurities is described shortly and the removal of sulphur and chlorine is described in more detail.
8 PARTICULATES

Particulate removal is required for both product gas and biosyngas. Particulates originate from the ash of the feedstock, dust, unconverted carbon (in product gas from low temperature gasification), soot (typically for high temperature oxygen-blown gasification), and carry-over bed material in the case of fluidised bed gasifiers. There are many different technologies to remove particulates from gases that can be applied to both biosyngas and product gas. To remove particulates from the synthesis gas the following systems can be used: cyclones, barrier filters, electrostatic filters (ESP), and (solvent) scrubbers [5,21].

Particle separation can be carried out at high temperatures (cyclones, moving bed filters, ceramic filter candles) or at low temperatures (scrubbers, wet electrostatic precipitators). Cyclones can be used in a wide temperature range but the separation efficiencies are low. Cyclones are suitable for a first stage particle separation but normally the particle content in the clean gas are still too high. Therefore, for high temperature particle separation moving bed filters or filters containing ceramic filter candles are necessary to meet the clean gas requirements. Fig. 4 shows a filter with ceramic or metallic filter candles.

Figure 4: High temperature filter with ceramic / metallic filter candles (left) and moving bed filter (right).

For low temperature particle separation several additional options can be considered such as fabric filters, wet electrostatic precipitators, and scrubbers. In any case also other impurities have to be taken into account. Tar condensation can be a problem in case of fabric filters and also in scrubbers if water is used as scrubbing liquid. On the other hand, some types of separators can have several functions for gas cleaning. Besides particles separation also tar removal (e.g. in scrubbers with solvent) or NH₃ removal (in case of water scrubbers) can be carried out in one stage.
Table 5 shows different types of scrubbers together with several selected performance data. Similar types of scrubbers are also used for the removal of e.g. sulphur compounds and carbon dioxides (see e.g. chapter 10).

**Table 5: Overview about different types of scrubbers used for gas cleaning.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Tower-Scrubber</th>
<th>Jet-Scrubber</th>
<th>Swirl-Scrubber</th>
<th>Rotation-Scrubber</th>
<th>Venturi-Scrubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separation size in μm for ρ=2,42 g/cm³</td>
<td>0,7 – 1,5</td>
<td>0,8 – 0,9</td>
<td>0,6 – 0,9</td>
<td>0,1 – 0,5</td>
<td>0,05 – 0,2</td>
</tr>
<tr>
<td>Relative velocity in m/s</td>
<td>1</td>
<td>10 – 25</td>
<td>8 – 20</td>
<td>25 – 70</td>
<td>40 – 150</td>
</tr>
<tr>
<td>Liquid/gas in l/m³</td>
<td>0,05 – 5</td>
<td>5 – 20a</td>
<td>-</td>
<td>1 – 3a</td>
<td>0,5 – 5</td>
</tr>
<tr>
<td>Energy consumption in kWh/1000 m³</td>
<td>0,2 – 1,5</td>
<td>1,2 – 3</td>
<td>1 – 2</td>
<td>2 – 6</td>
<td>1,5 – 6</td>
</tr>
</tbody>
</table>

a per stage

Table 6 contains a summary of performance data for different types of particles separators together with possible operations temperatures.

**Table 6: Comparison of different particle separators.**

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature in °C</th>
<th>Particle reduction in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone</td>
<td>20 – 900</td>
<td>45 – 70</td>
</tr>
<tr>
<td>Sandbed filter</td>
<td>20 – 900</td>
<td>80 – 95</td>
</tr>
<tr>
<td>Bag filter / candle filter</td>
<td>150 – 750</td>
<td>90 – 99</td>
</tr>
<tr>
<td>Scrubber</td>
<td>20 – 200</td>
<td>40 – 65</td>
</tr>
<tr>
<td>Wet electrostatic precipitator</td>
<td>40 – 50</td>
<td>95 – 99</td>
</tr>
</tbody>
</table>
9 ORGANIC IMPURITIES

Organic compounds can only be present in product gas generated gasification processes operated at temperatures below 1000°C, such as in fixed or fluidized gasification processes. The main organic compound is methane. Other organic compounds are the aliphatic C$_2$+ hydrocarbon higher than methane, with the most important representative being ethylene (C$_2$H$_4$), the mono aromatic compounds benzene and toluene, and “tars”. At the high temperatures of entrained flow gasification all organic material is completely destructed and converted into H$_2$ and CO (with CO$_2$).

Methane, the C$_2$+ hydrocarbons and benzene are not considered as impurities in most product gas applications. Complete removal of the tars or at least the larger part of them, however, is necessary. A lot of research and development is ongoing on tar removal and a good overview is given in reference [21], therefore, only the main concepts are discussed here:

**High Temperature Destruction**

Upon increasing the temperature of the raw product gas by oxygen injection all organic compounds are 'cracked' and destructed. The effect is similar to direct gasification at a high temperature (i.e. an entrained flow gasifier can be used as tar cracker). As the methane, C$_2$+ hydrocarbons, and benzene are destructed, which is unnecessary or even undesired, this approach is not preferred.

**Catalytic Destruction**

Catalytic tar reduction is typically performed in the raw gas after the gasifier at elevated temperatures (400-900°C) in most cases with nickel-based catalysts. With this method a large part of the tars can be destructed, while the methane and benzene remain intact for the major part. Major disadvantage of this concept is the sensitivity of the catalysts for (inorganic) impurities in the raw product gas.

**Physical Removal**

The most promising tar removal concepts are based on physical removal with organic washing liquids. In the FICFB plant in Güssing biodiesel is used to clean the product gas to meet gas engine specifications (tar dewpoint of ~40°C) [8]. ECN has developed the OLGA process that is capable of removing all aromatic organic components to very low levels (i.e. tar dewpoints below 15°C). Additional advantage is that the tars are removed prior to water condensation to prevent pollution of process water and related costs for wastewater treatment.
10 SULPHUR REMOVAL

Even though the sulphur content of the product gas from biomass gasification is much lower than from coal gasification sulphur represents a major problem. While sulphur removal by wet scrubbing is a well proven technology and used in large scale applications high temperature desulphurization is still under development. On the other hand the production of biosyngas and the applications of biosyngas are also still under development. Therefore, the requirements to gas composition and gas purity are unclear. The exact limit of an acceptable H$_2$S concentration in the gas is not determined yet and has to be investigated and optimised (investment costs versus operating costs). Generally, the published limits are very low (<1ppm for H$_2$S and HCl). But it is still fact that sulphur is harmful to catalysts and that H$_2$S removal to some extent is necessary for the utilization as biosyngas.

In the following the state of the art is presented divided into wet and dry processes.

10.1 Wet Processes / Absorption Processes

Physico-chemical absorption is based in the combination of a physical solvent with a chemical one. It usually allows working with the advantages of both kinds of solvents. However, it usually means more complexity in design and operation. Sulfinol and Amisol are examples of this kind of absorption processes. Physical solvents are effective for high acid gas partial pressure feed, whereas chemical solvents are very effective at low partial pressures.

The following chapter displays several scrubbing processes, focusing on chemical solvents and physical-chemical solvents, which can achieve a higher gas loading at lower pressures, i.e. they can deeply clean gases with low content of H$_2$S or HCl.

10.1.1 MEA (Monoethanolamine) and DEA (Diethanolamine) Processes

All the amine processes have a similar reactor configuration, which can be seen in Figure 5 as simplified flow sheet.

The amine reacts with the acid compounds in an absorber (usually a counter-current packing tower; however, jet scrubbers are also used). The rich solution leaves the bottom of the absorber and goes to the regenerator, where it is heated by saturated steam in a reboiler. The absorption process takes place at low temperature and atmospheric pressure. Monoethanolamine (MEA) is a good agent to absorb H$_2$S as well as CO$_2$. It forms a very stable compound with these two species, as shown in reactions (8) to (11).
Figure 5: Basic flow diagram for amine processes (a - Absorber, b - Solvent cooler, c - Solvent pump, d - Heat exchanger, e – Regenerator, f – Condenser, g – Reboiler)

Reaction of amine and water (protonation):

\[ R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3NH^+ + OH^- \]  \hspace{1cm} (8)

Sulphide formation:

\[ H_2S + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+ + HS^- \]  \hspace{1cm} (9)

Carbamate formation:

\[ CO_2 + 2R_1R_2R_3N \leftrightarrow R_1R_2NCOO^- + R_1R_2R_3NH^+ \]  \hspace{1cm} (10)

Bicarbonate formation:

\[ CO_2 + OH^- \leftrightarrow HCO_3^- \]  \hspace{1cm} (11)

Corrosiveness could create a problem if COS is present. The amine can react with it, which leads to a loss of solvent and the occurrence of undesired compounds that can damage the equipment [22], [23]. Another disadvantage is that MEA has a very high vapour pressure, which means that a large part of the solvent can be discharged together with the gas. It would be necessary to put an amine vapour recovering system just after the scrubber [24]. These disadvantages can be avoided respectively minimized if DEA is used instead of MEA. DEA has a slightly higher price than MEA and DEA cannot be used at low pressure, since it decomposes under its boiling point [25]. Regeneration takes place in a stripper, which needs heat supply in the reboiler. A usual value for the need of saturated steam is 2.4 kg steam/kg acid.

MEA is usually present in a concentration approximately of 15-20 wt% in water. Due to the strong chemical bonds between the solvent and the acid gases, the absorption of H₂S and CO₂ is very effective. The obtainable results in the clean gas are as follows:

\[ H_2S < 3 \text{ ppm and CO}_2 <50 \text{ ppm} \]

There is only little data about HCl absorption, but since it is a strong acid, it is obviously
absorbed completely. The problem comes at the desorption stage, because of the strength of the bond. Thus, the required energy for the desorption step will higher.

One important advantage of using amine is that the reaction in case of H₂S absorption is very fast. That leads to a small size of the absorbers. Also, the heat transfer coefficient is high, which leads to a minor surface necessity in the heat exchanger.

Hydrogen sulphide reacts instantaneously with all amines to form sulphide. Carbon dioxide can only react with primary (like MEA) and secondary (like DEA) amines to form carbamate, whose reaction rate has a moderate velocity. The bicarbonate formation is slow. The different reaction rates of hydrogen sulphide and carbon dioxide with the amines are the basis for selective hydrogen sulphide absorption, as will be shown in the case of the MDEA.

In Table 7 some operating data of a plant in Worland, USA [25] are presented. This plant has a low pressure and a high pressure absorber. As can be seen, at higher pressure the product gas has lower concentration of acid gases.

<table>
<thead>
<tr>
<th>Operating Data</th>
<th>MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean amine concentration</td>
<td>14.7wt %</td>
</tr>
<tr>
<td>Circulation rate</td>
<td>High P Absr. 267 m³/h</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. 33 m³/h</td>
</tr>
<tr>
<td>Gas flow</td>
<td>High P Absr.31398 Nm³/h</td>
</tr>
<tr>
<td></td>
<td>Low P Absr.611,75 Nm³/h</td>
</tr>
<tr>
<td>H₂S inlet</td>
<td>High P Absr. 2.3 %</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. 1.2 %</td>
</tr>
<tr>
<td>CO₂ inlet</td>
<td>High P Absr.23.7 %</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. 58.0 %</td>
</tr>
<tr>
<td>H₂S out</td>
<td>High P Absr. 3 ppm</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. 6 ppm</td>
</tr>
<tr>
<td>CO₂ out</td>
<td>High P Absr. N/A ppm</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. N/A ppm</td>
</tr>
<tr>
<td>Total rich loading</td>
<td>0.66 mole/mole</td>
</tr>
<tr>
<td>Approach to equilibrium at absorber bottom</td>
<td>High P Absr. N/A</td>
</tr>
<tr>
<td></td>
<td>Low P Absr. N/A</td>
</tr>
<tr>
<td>Total steam to reboilers</td>
<td>33656 kg/h</td>
</tr>
</tbody>
</table>

Typical circulation rate values are about 10 m³ solvent/1000 Nm³ of raw gas.
10.1.2 MDEA (Methyldiethanolamine) Processes

The flow sheet is very similar to that of MEA, as well as much of the explanations given in the last paragraph. However, the reactions are quite different. The CO$_2$ reaction can only occur after the CO$_2$ dissolves in water to form a bicarbonate ion which undergoes in the following an acid-base reaction with the amine:

\[
CO_2 + H_2O + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO_3^-
\]  

(12)

According to Polasek [25], at least six different mechanisms for the CO$_2$-MDEA reaction have been proposed. MDEA can react with H$_2$S by the same proton transfer mechanism of primary and secondary amines:

\[
H_2S + A\text{min} e \leftrightarrow [A\text{min} e]H^+ + HS^-
\]

(13)

MDEA has a higher selectivity compared to primary and secondary amines since no carbamate is formed with tertiary amines, and carbon dioxide can only be absorbed via the slow bicarbonate reaction. In order to utilize this selectivity based on the reaction kinetics, the absorber must provide sufficient mass transfer area for complete hydrogen sulphide removal in combination with short residence time to suppress carbon dioxide absorption.

When absorption of CO$_2$ is not very important, the use of MDEA offers as a big advantage its selectivity for H$_2$S. That means that with lower circulation rates than with MEA or DEA all the hydrogen sulphide can be absorbed. Another advantage is that in case of a peak increase of the H$_2$S concentration in the flue stream, it will be absorbed preferential to the CO$_2$, allowing the total removal of hydrogen sulphide without an increase of the solvent loading. Additionally, the obtained H$_2$S is present in a concentration that allows its recovery in a Claus plant (this option is not suitable for small and medium plants like the biomass CHP in Guessing).

The energy requirement is lower than for wet scrubbers using MEA. However, it is high in comparison with physical solvents. In addition to that, the absorber must work at high pressures (up to 70 bars). The results obtainable are:

H$_2$S < 2ppm and CO$_2$ < 1000ppm

Usual concentration of MDEA in water ranges from 20% to 50% weight [25]. In Table 8 the data of a MDEA plant operated in Signalta, USA are shown [26].

<table>
<thead>
<tr>
<th>Table 8: Data of the Signalta MDEA plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pressure</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Solvent rate</td>
</tr>
<tr>
<td>Gas rate</td>
</tr>
<tr>
<td>Feed H$_2$S conc.</td>
</tr>
<tr>
<td>Feed CO$_2$ conc.</td>
</tr>
<tr>
<td>Flue H$_2$S conc.</td>
</tr>
<tr>
<td>Flue CO$_2$ conc.</td>
</tr>
</tbody>
</table>
Usually the absorber operates at high pressure (from 7 to more than 70 bar), and the desorber at atmospheric pressure. The absorption temperature is lower than 60°C. Even lower concentrations of H2S reached are reported for a plant in North Carolina, USA, with levels below 0.1 ppm [25], as can be seen in Table 9.

<table>
<thead>
<tr>
<th>Table 9: Performance of North Carolina plant with MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDEA operating data</td>
</tr>
<tr>
<td>Amine concentration 33 wt%</td>
</tr>
<tr>
<td>Circulation rate 33.55 m³/ h</td>
</tr>
<tr>
<td>Gas flow 36000 Nm³/ h</td>
</tr>
<tr>
<td>H₂S inlet 55 ppm</td>
</tr>
<tr>
<td>CO₂ inlet 3.5 %</td>
</tr>
<tr>
<td>H₂S out &lt;0.1 ppm</td>
</tr>
<tr>
<td>CO₂ out 1.13 %</td>
</tr>
<tr>
<td>Rich loading 0.45 mole/mole</td>
</tr>
</tbody>
</table>

There is little evidence of problems with corrosion, since MDEA does not react with COS, if there is no oxygen. Usually rates between 0.6 and 1 m³ solvent per 1000 Nm³ of treated gas are used in commercial applications. It should be mentioned that COS does not get absorbed in any amine absorption process.

Small amounts of ammonia can cause large problems in amine sweetening units under certain conditions. These problems are usually traceable to a complex of ammonia with CO₂. If large amounts of CO₂ are present, this effect may either cause an increasing of CO₂ and ammonia in the circulating amine or rob the lower section of the stripper of CO₂ which is needed to displace H₂S in the lean amine. In MEA, and it is to be expected with DEA and other secondary amines as well, ammonia tends to push CO₂ into the reboiler, increasing the CO₂ and ammonia in the lean amine.

Using MDEA, the ammonia appears to be beneficial with high volume fractions of CO₂, decreasing CO₂ residuals and by inference increasing the H₂S in the stripper bottoms. Other effects of ammonia contamination may be excessive water loss, increased condenser temperature, reduced reboiler temperature or high acid gas residuals in the lean amine. Depending on the operational problem observed, ammonia contamination can possibly be corrected by increasing the reboiler load, decreasing the condenser load, or using a sour water stripper on the reflux water [27].

Using mixtures of several amines could improve the results in the H₂S and CO₂ removal. One example is a mixture of DEA or MEA with MDEA which allows the increase of amine concentration without corrosion problems, therefore, reaching lower concentrations of acid gases. This allows lower pressures, at which MDEA is not able to dissolve CO₂. These mixtures usually contain a maximum of 55wt% of MDEA, and the primary or secondary amine usually below 20wt% [25].

The use of amines allows a decrease of the absorption temperature down to 25°C [28]. Low H₂S concentrations can be reached. However, CO₂ separation efficiencies will be lower than normal. In addition to that, choosing a special configuration (see potassium carbonate processes) might improve the operation of the process.
10.1.3 Alkaline Hydroxide Processes

Since alkaline hydroxides are very strong bases, they can remove completely H\textsubscript{2}S, HCl, and CO\textsubscript{2} (purity levels can reach <0.1 ppm). The system consists of an aqueous absorber (e.g. packing tower) which is fed with the acidic-gas.

However, the regeneration of the solvent is very difficult. Therefore, the process works in batch configuration and the alkaline waste is usually disposed. It can also be used in an oxidative process in order to obtain elementary sulphur [29]. In this process the sulphide is oxidized at high pH by electrodes to sodium polysulfide and then crystals of sulphur precipitate. The filtrate is recycled to the absorption chamber.

Although NaOH works good, slightly better results are obtained with potassium, due to its higher solubility [22]. A typical value for NaOH concentration, in order to reach proper solubility of acid compounds is 2-normal [22]. Beyond this value the absorption capacity decreases due to an increase of viscosity [29].

10.1.4 Alkaline Carbonate Processes

Two main substances are counted among this group: potassium carbonate and sodium carbonate.

**Potassium Carbonate:**

One of the best known processes is the absorption in hot potassium carbonate. The process consists of an absorption in a contactor at high temperature in which the following reactions take place:

\[ CO_2(g) \leftrightarrow CO_2(l) \]  
\[ CO_3^-(l) + H_2O \leftrightarrow HCO_3^- + H^+ \]  
\[ HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \]

H\textsubscript{2}S absorption, sulphide formation:

\[ H_2S(g) \rightarrow H_2S(l) \]  
\[ H_2S(l) + H_2O \rightarrow HS^- + H_3O^+ \]

HCl absorption, chloride formation

\[ HCl(g) \rightarrow HCl(l) \]  
\[ HCl(l) + H_2O \rightarrow Cl^- + H_3O^+ \]

And from the alkaline solution:
\[
H_2O + CO_3^{2-} \leftrightarrow HCO_3^- + OH^- \tag{21}
\]

Neutralization
\[
H^+ + OH^- \rightarrow H_2O \tag{22}
\]

The reactions can be written shortly as:
\[
K_2CO_3 + H_2S \leftrightarrow KHCO_3 + KHS \tag{23}
\]
\[
K_2CO_3 + CO_3 + H_2O \leftrightarrow 2KHCO_3 \tag{24}
\]
\[
K_2CO_3 + HCl \leftrightarrow KHCO_3 + KCl \tag{25}
\]

There are several configurations, as shown in Figure 6.

Figure 6: Typical configurations for hot potassium carbonate removal (A - Single stage, B - Single stage with splitflow, C - Two stage process)

The first configuration is very simple: the gas is absorbed in a hot dissolution of potassium carbonate at a temperature between 75°C and 125°C according to [22]. Thus, there is only little tolerance for the desorption step (in some cases there is not any heat exchanger). Desorption takes place by flashing and steam stripping at 2 psig (=0.138 bar). Due to the relatively high temperature high concentrated carbonate solution is possible, which means less solvent flow rate.

A second configuration is the single stage with split-flow: in this case a part of the lean solution from the regenerator is cooled and fed into the top of the absorber while the major part is added hot at a point below the top (see Figure 6). This modification improves the purity of the product gas by decreasing the equilibrium vapour pressure of CO₂ over the portion of solution last contacted with the gas.

In the two-step (two stage) configuration the main solution-stream is withdrawn from the stripping column at a point above the reboiler. Thus, only a part of the solution passes down through the bottom of the stripping column to the reboiler. This part is totally regenerated and
is capable of reducing the CO\textsubscript{2} content to a very low value. This completely regenerated part is fed at the top of the absorber while the main stream is fed in at the mid point.

The absorber usually works at high pressure (at the best between 20 and 70 bar). Anyway, experiments with lower pressure (150 psig, i.e. 10 bar) were made, and even at 100 psig (7 bar). The energy needed in the stripper is not as high as in the amine process, while the temperatures are kept in the same range as in the absorption. Sometimes a heat exchanger for the solvent cycle is not necessary [22]. Regeneration of the CO\textsubscript{2} scrubbing solution with steam produces emission of water, NH\textsubscript{3}, CO, CO\textsubscript{2} [30].

The maximum concentration of the carbonate solution at the top of the absorber is 40 wt%. With higher concentration the carbonate starts to precipitate. It also occurs at 30 wt% if the dissolution is cooled. Therefore, the temperature control is very important.

Maybe problems with corrosion could appear, due to alkalinity [22] and high temperature. One available corrosion inhibitor is the potassium chromate, although H\textsubscript{2}S reduces it, making it inadequate. Anyway, the H\textsubscript{2}S can itself inhibit the steel corrosion.

There are several modifications of this process. One of them is the use of carbonate and potassium vanadate as an additive (Benfield process). The Catacarb process uses a combination of carbonate with amines. The presence of amines enhances the mass transfer (thus allowing smaller surfaces and lower sizes) and avoids oxidation.

The Lurgi HP process, with potassium borate as additive and in his high purity version, with two parallel separate absorption systems, achieves a high removal of hydrogen sulphide that leads to a value in the flue gas of 1 ppm [31] and 50 ppm of CO\textsubscript{2}, whereas the two stage hot activated carbonate process (Benfield process) can reach 0.5% of CO\textsubscript{2} and 5-10 ppm of H\textsubscript{2}S.

In the following (Table 10) some operation data of a pilot plant with double stage regeneration are presented [32].

**Table 10: Hot carbonate with double stage regeneration operation data**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pressure</td>
<td>300 psia (=21.41 bar)</td>
</tr>
<tr>
<td>Temperature</td>
<td>108°C</td>
</tr>
<tr>
<td>Solvent rate</td>
<td>42 gph (=0.19 m\textsuperscript{3}/h)</td>
</tr>
<tr>
<td>Gas rate</td>
<td>1204 scd/h (=33.71 Nm\textsuperscript{3}/h)</td>
</tr>
<tr>
<td>Feed H\textsubscript{2}S conc.</td>
<td>1.035 %</td>
</tr>
<tr>
<td>Feed CO\textsubscript{2} conc.</td>
<td>11 %</td>
</tr>
<tr>
<td>Flue H\textsubscript{2}S conc.</td>
<td>5.2 ppm</td>
</tr>
<tr>
<td>Flue CO\textsubscript{2} conc.</td>
<td>0.15 %</td>
</tr>
</tbody>
</table>
**Sodium Carbonate**

In this process, the solvent is an aqueous dissolution of sodium carbonate. The reactions are the same as in the case of potassium carbonate (here only the short expression):

\[
Na_2CO_3 + H_2S \leftrightarrow NaHCO_3 + NaHS \tag{26}
\]
\[
Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2NaHCO_3 \tag{27}
\]
\[
Na_2CO_3 + HCl \leftrightarrow NaHCO_3 + NaCl \tag{28}
\]

The absorber is similar to that in other processes. It can work at 2 psig (1.13 bar, near atmospheric pressure), according to [22]. The carbonate usually is present in a concentration between 3 and 3.5 wt. % [22], [33].

There are different ways to regenerate the solvent:

One of them is to regenerate the carbonate in a vacuum distillation tower (known as actifier) at 0.13-0.3 bar. Steam is used as stripping vapor. Boiling occurs at a temperature of 60°. Some configurations work at 75-85°C. The energy needed in the stripper is not as high as in the amine process, but it is higher than that of physical or physico-chemical sorbents.

Another way is to use air as stripping gas. The air rate is usually 1.5 or 3 times that of the gas. However, it can cause problems due to the oxidation of sulphide to thiosulphate which cannot be stripped, and it leads to loss of solution activity. Thus, a part of the solution must be replaced. If there is HCN in the liquid stream, there are more not-desired reactions such as:

\[
2NaHS + 2O_2 \rightarrow Na_2S_2O_3 + H_2O \tag{29}
\]
\[
2NaHS + HCN + O_2 \rightarrow 2NaSCN + 2H_2O \tag{30}
\]

The process with sodium carbonate permits the following purity in the flue gas for a feed with 20% of CO₂ and 100 ppm H₂S:

Removal efficiency: 85 to 95%
Clean gas concentrations: H₂S 5-15 ppm and CO₂ 1% to 3%

It was found that sodium carbonate processes present, compared to CO₂ absorption, a slightly higher selectivity towards H₂S than that of potassium processes [22].

As in the case of hydroxides, there is a problem of corrosion, because of working at high pH. In addition to that ammonia (NH₃) that could be present in the feed stream is also absorbed, which could be a disadvantage if the clean gas is destined to be used in a fuel cell. The principal advantages of using carbonates are its low purchasing cost.

The little information about HCl removal with this compounds shows that with Na₂CO₃ a fine removal can be reached. The absorption is better at high temperatures.
10.1.5 Rectisol Process

This process (patented by Lurgi and Linde GB713414 GB750399; TM 0953338 and TM 2120948 reg. number) uses methanol at low temperature (from -40 to -80°C) as a physical absorbent for the acid compounds. The specific characteristics of methanol that make it particularly suitable as a physical solvent are listed below [31]:

- High solubility for CO₂, H₂S, and COS – this keeps the solvent circulation rate low and provides low costs for Rectisol plants when the impurities in the raw gas are present in high concentrations.
- High selectivity for H₂S and COS versus CO₂ – a H₂S rich off-gas is obtained even with low H₂S/CO₂ concentrations in the feed gas, which is of importance for economic sulphur recovery
- Low solubility for H₂, CO, and CH₄ – this keeps gas losses at a very low level
- Low vapor pressure under process conditions – solvent losses are very low
- High solubility for water – Rectisol plants can be used for gas dehydration at the same time
- Low viscosity, even at low temperature – this characteristic ensures good heat and mass transfer, even at temperatures just above the freezing point of the methanol
- Optimal chemical and thermal stability – methanol has an extremely high thermal stability, and there is no degradation by acidic components
- Non corrosive – carbon steel can, therefore, largely be used for the equipment
- Good availability of methanol at very low costs – methanol is produced in bulk quantities for use as solvent and as raw material for a great number of industrial applications

A typical flowsheet can be seen in Figure 7.

![Figure 7: Rectisol process (a – Absorber, b - Flash tower, c - Hot regeneration, d – Condenser, e - Methanol – water column)](image)
The gas passes through the absorber in counter current contact with the methanol. Physical absorption takes place, promoted by high pressure (following Henry’s law). Afterwards the gas is washed with water in order to recover the possible methanol losses.

The acid containing solution is sent to a flashing chamber where the pressure is decreased (in this step the possible absorbed hydrogen is removed as well), as well as the temperature. Then the solution is led to the stripper, where the methanol is regenerated by small heat addition (by means of stripping with steam). The regeneration can take place too by means of vacuum or stripping with nitrogen.

The solution must enter a distillation column to recover the methanol from the water. The absorber operates at 300 psig (=21 bar). The rich solution is transported from the absorber to a flash chamber, in order to facilitate desorption. The desorber works at a temperature between 0 and 65° C, and at atmospheric pressure.

The concentration of H₂S and CO₂ could be as low as 0.1 ppm and 2 ppm respectively [23], [22], [31]. This process can also remove trace components such as COS, HCN, mercaptanes, and HCl. The high solubility of HCl in aqueous solutions and in methanol might cause higher costs for stripping due to heating.

In general, the configuration is very flexible. The one presented here represents a standard configuration, for simultaneous removal of H₂S and CO₂, but there are several other possibilities, when a selective removal of H₂S is required (e.g. if a concentrated solution of H₂S is needed for sulphur recovery in a Claus plants).

![Figure 8: Selective Rectisol process for separate removal and recovery of H₂S and CO₂ (a - H₂S absorption, b - CO₂ absorption, c - Flash regeneration, d – Stripper, e – Reabsorber, f - Hot regeneration)](image)
The principal disadvantages of this process are the high complexity (that means high investment costs) and high efforts for refrigerating. However, the heat requirements are very low, since desorption is relatively easy.

10.1.6 Amisol Process

This process (Patented by Lurgi, TM 526383 according to “Madrid Agreement”) uses a mixture of methanol and an amine (could be MEA, DEA, MDEA) as solvent. Thus, the advantages of a good chemical absorbent like amine and that from physical solvents (low vapour pressure and absorption) are combined.

The basic flow sheet is represented in Figure 9 [34].

![Figure 9: Amisol Process](image)

Firstly, the acidic gases remain in the solvent stream. Water is added at the top of the absorber in order to recover the methanol losses similar to the Rectisol process. Then the rich solution is transported to the stripper, where gases are released. The water used to recover the methanol losses is regenerated in a distillation tower in order to take the methanol back to the absorber.

Because of the high capacity of the solvent, the circulation rate is quite low. With this process a high-purity levels can reached [34], [23]:

\[ \text{H}_2\text{S} < 0.1 \text{ ppm and CO}_2 < 1 \text{ ppm} \]

With this process simultaneously trace components such as COS, HCN, mercaptanes, and HCl can be removed.

The temperature in the absorber is in the range of 32 to 38 °C [34]. The pressure during the absorption doesn’t need to be as high as in the Rectisol process. It is enough if the partial pressure in the feed stream reaches 0.1 bars [31]. If the CO\(_2\) content of the feed is between 10
to 20 vol%, the absorber can operate at atmospheric pressure or a bit higher. Anyway, the higher the pressure, the better the absorber works.

The temperature in the desorber after flashing must reach 80°C [34]. Liquid water can be used for heating during the regeneration process. No heat exchanger is necessary between lean and rich solvent since absorption and regeneration temperatures are not far apart.

In this process there are no problems with corrosion of carbon steel, although there is a slow degradation of the amines, therefore, a reclaimer could be required to eliminate the products of that degradation [23]. Typical flow rates for the solvent are 2.4 m³/1000 Nm³ Gasflow. Despite the solvent recovery system, there is a loss of 0.27 kg_solution/1000 Nm³ Gasflow.

Selective removal of both sulphides (carbonyl and hydrogen) versus carbon dioxide is possible by using aliphatic secondary alkylamines such as diisopropylamine (DIPAM) and diethylamine (DETA) instead MEA or DEA [23].

Another possibility is the use of ethanol as solvent (with the problem of higher costs) or glycols, although the latter is supposed to be better in the absorption of hydrocarbons than in the absorption of acid gases (the solubility of H₂S or CO₂ is 20 times less than that in the case of methanol). An interesting possibility is the use of dimethyl ethers of polyethylene glycol [35] as a solvent. Another process uses only DEPG as physical solvent at a temperature of 21°C (TM Selexol), but the results are not so good as with methanol (the concentration ranges from 1 to 20 ppm H₂S) because the maximum solvent loading is lower. In addition to that (as it is true for all the physical solvents) it needs to work at high pressure too.

10.1.7 Sulfinol Process

This system (Patented by Shell) for removal of H₂S is based on the use of a physical solvent (sulfolane, i.e. tetrahydrothiophene dioxide) mixed with amines. These amines are usually diisopropylamine (DIPA) in the case of sulfinol-D; and MDEA for sulfinol M. The flow sheet is similar to that of the Rectisol process.

The operation data found are as follows: Pressure in the absorber: 300-1000 psia (=20-70 bar). The achievable values for acid gas concentration in the flue gas are:

H₂S < 1 ppm [31], [36] and CO₂ < 0.1 vol% [36]

Once more, there are no data for the absorption of hydrogen chloride. It should be mentioned that these values are higher than for the Rectisol process.
10.1.8 Oxidative Processes

These processes are suitable to remove H$_2$S contained in a gaseous stream. They are based on an oxidizing liquid solution able to oxidize the H$_2$S to elemental sulphur.

Two main processes will be discussed in the following:

- Stretford-process, based on the use of vanadates
- Lo-Cat-process, based on the use of iron chelates.

Both are reversible processes.

In the first one, H$_2$S gets absorbed in an aqueous solution containing sodium carbonate and bicarbonate, as well as sodium metavanadate and anthraquinondisulfonic acid (ADA). The Stretford process is no longer in use now. However, for completeness it will be discussed here also shortly. The steps are the following:

1) Absorption of H$_2$S in the alkali solution

\[
H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3
\]

(31)

CO$_2$ should also get absorbed. That gives problems with the selectivity of the process. When the pH value is lowered the removal of H$_2$S is worse. If the pH is high, then problems with carbonate precipitation appear. Adding KOH could solve the problem of precipitation [37].

2) Oxidation of hydrogen sulphide to sulphur

\[
2NaHS + 4NaVO_3 + H_2O \rightarrow Na_2V_4O_9 + 2S + 4NaOH
\]

(32)

3) Reoxidation of vanadate by ADA

\[
Na_2V_4O_9 + 2NaOH + H_2O + 2ADA \rightarrow 4NaVO_3 + 2ADA\text{(reduced)}
\]

(33)

4) Regeneration of ADA by air.

\[
2ADA\text{(reduced)} + O_2 \rightarrow 2ADA + H_2O
\]

(34)

In the iron chelates process (Lo-cat), the iron (III) in aqueous solution oxidizes the hydrogen sulphide. The cation must be complexed in order to keep it in solution at several pH values.

First the absorption takes place:

\[
2Fe^{3+} L + H_2S \rightarrow 2Fe^{2+} L + S + 2H^+
\]

(35)

And then the regeneration with air:

\[
2Fe^{2+} L + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} L + 2H_2O
\]

(36)
The stoichiometric ratio is 2:1 for hydrogen sulphide to iron. Usually the ratio is maintained at 1:1. The advantages of the iron processes over vanadate processes are the use of a non-toxic solvent, a less corrosion rate, more rapid oxidation and improved selectivity [31].

![Figure 10: Lo-cat process](image)

In both processes, at a low pH value, the removal of H$_2$S is not very good. Increasing the concentration of iron chelate (or increasing pH with KOH) can improve the removal. The treated gas can exit the cleaning section with a concentration of H$_2$S much lower than 1 ppm (even smaller than 0.1 ppm).

The SulFerox process differs from the LO-CAT in that way, that the oxidation and the regeneration steps are carried out in separate vessels and sulphur is recovered from the filters, melted, and sent to sulphur storage. Also, the SulFerox process uses a higher concentration of iron chelates (about 2-4 wt% vs. 250-3000 ppmw for the LO-CAT process). This higher solution loading allows lower circulation rates and consequential smaller equipment sizes.

These processes are very good for H$_2$S removal, but they can remove other sulphur compounds only if the residence time is long enough. If they are present, a hydrolysis step before the H$_2$S removal is recommended to convert nearly all the sulphur compounds into H$_2$S.

Another characteristic is that elemental sulphur (S) in solid state is formed. This can be an advantage, because the Claus plant is not necessary, but for the operation it can be also a disadvantage, because it could cause hydrodynamic problems. In this case a packed column may be not the best choice. Instead of that, spray or Venturi absorbers are used although they usually reach less efficiency than a packed tower [23].

These processes work at low pressure (below a partial CO$_2$ pressure of 0.5 atm at a pH of 8) according to [37]. Therefore the problems with precipitation do not appear.

The rates of liquid-oxidative solution are usually high, from 5 to 20 times higher than that one of amine solution in an MDEA (i. e., 3.5-20 m$^3$/solution/1000 L gas).
10.1.9 Selective and Non-Selective Processes

The removal of H$_2$S and CO$_2$ can take place in two different ways. It can be achieved simultaneously, when the absorbent agent takes the two compounds in the same degree, or selective, when it takes most of one and the second one is absorbed in a minor degree.

In the case, if the CO$_2$ should be sold as by-product, it should be of some interest to find a way to remove selectively one of these compounds. In order to obtain a stream of pure CO$_2$ that could be stored and used, and separately, a stream with the other minor acid compounds (H$_2$S, HCl, COS, mercaptans etc.) that could be neutralized with a low consumption of basic compounds.

There are several desirable possibilities, as explained in the following:

I) The first option could be to treat the feed gas with a CO$_2$-selective process, which could yield a pure stream of CO$_2$. The CO$_2$ free product gas could be treated by means of a nonregenerative caustic solution (NaOH or KOH in an absorption tower), in order to deplete the rest of acid compounds, including the CO$_2$ not yet absorbed, till levels lower than 0.1 ppm in the product gas.

However, selective processes for CO$_2$ over H$_2$S are rare. One possibility could be the use of membranes. Some membranes of fluorinated polymers (AF1600) have 8/1 selectivity towards CO$_2$ in certain conditions. The problem is what happens with the other components of the gas; and if this selectivity is enough to separate a big amount of CO$_2$ without reaching the emission limits for H$_2$S. The solution could be to use firstly a selective membrane for simultaneous removal of H$_2$S and CO$_2$ (for example, polydimethylsiloxane PDMS) and then a selective membrane for CO$_2$, leaving the H$_2$S strip.

Since water is not selective (it would also absorb HCl and H$_2$S) and has low loading capacity it is not a preferential absorbent. According to Polasek [25], DGA (i.e. diglycolamine) is a chemical sorbent that reacts preferably with CO$_2$.

Another way to get the selective absorption of CO$_2$ could be based on the configuration, with a split flow regeneration. A semi-regenerated solvent is fed in the lower section of the absorber, getting only CO$_2$, and the fully regenerated in the upper section, absorbing the remaining CO$_2$ and the H$_2$S. If the two sections are different scrubbers, it would be possible to get a stream with only CO$_2$.

![Figure 11: Selective CO$_2$ absorption](image-url)
II) The second option is based on a selective removal of H₂S over CO₂. There is more literature and processes concerning available. This process could be based on the use of MDEA, DIPAM, oxidative processes or even sodium carbonate [22, 38]. Another selective process is the use of a potassium salt of diethyl or dimethylglycine (Alkazyd-dyk solution), that is very selective towards H₂S, CS₂ and HCN.

The gas stream should be freed of H₂S (and possibly of all sulphur compounds), and then it could be treated to remove the CO₂ if necessary (Fischer-Tropsch synthesis) by means of one of the not-deep-removal already studied processes (amine, carbonate, physical absorbent). Additionally a step to remove the HCl (a simple water wash) would be necessary before or after the H₂S removal.

Figure 12: Selective H₂S absorption

III) The third option is, firstly, a simultaneous removal for all the acid gases in order to get a clean gas according to the specifications. This simultaneous removal could be achieved by Amisol Process, Rectisol, MEA or DEA, amine mixture or even carbonate processes. Then, by means of a selective desorption, a stream of CO₂ could be achieved, and another with the rest of compounds (they can get absorbed later in caustic solution).

Figure 13: Simultaneous absorption and selective regeneration
This selective desorption could be made by means of several flash stages. In the case of chemical sorption, the H₂S would be the first to be stripped, since it is a weaker acid and the bonds would be easier to break. The CO₂ would be the last in being stripped (if HCl is removed before). Using a physical solvent, the first to be released would be the CO₂ [38].

IV) Similar to the latter, firstly it is based on a simultaneous removal of the acid gases. The product gas is cleaned of H₂S and CO₂. Then, a selective desorption step takes place, in order to remove selectively H₂S (by means of one of the commented processes). Then a stream of H₂S (and probably other trace sulphur compounds) is generated, that should be treated (can be sent to the caustic cleaning step). After desorption of the other components a new absorption of CO₂ takes place. The other waste stream would contain CO₂, and might be released to the atmosphere.

![Figure 14: Simultaneous and selective H₂S absorption](image-url)
10.2 Dry Processes / Adsorption Processes

Dry processes are based on the adsorption of the sulphur compounds on a solid adsorbent. The most well known adsorbers are based on ZnO or activated carbon and they are widely used in industry, e.g. refineries, as guard beds. One characteristic of dry adsorption processes is that the used adsorbent has to be disposed. Therefore dry adsorption processes are used at the moment only for low sulphur inlet concentrations (normally <50ppm) because of economic reasons.

10.2.1 Adsorption with Metal Oxides

General Process Description

To remove H₂S from a gas a non-catalytic solid-gas reaction with a proper metal oxide takes place. Solid metal sulphide is formed and water is built as by-product.

\[ xH_2S + Me_yO_x \Leftrightarrow Me_yS_x + xH_2O \]  \hspace{1cm} (37)

This reaction takes place in the reducing gas atmosphere of the product gas. Therefore, the sulphidation reaction should be thermodynamically favourable while the reduction reaction of the metal oxide should not be favoured or at least very slow.

A useful tool to predict the stable oxide form under prevailing conditions is the predominant area diagram. In Figure 15 the predominant state of the metal can be seen depending on the gas composition.
Figure 15: Stability of metal oxides as a function of temperature and CO$_2$ to CO ratio [53] (dotted lines represent different coal gas mixtures)

This diagram was also used in many studies to design desulfurization sorbents for coal gas cleaning because it shows a limiting factor for the usability of some metal oxides [39].

A common assumption is that most of the sulphur in the product gas appears as H$_2$S beside small amounts of COS and other sulphur species that can be neglected. Because most interest was directed towards coal gas so far only H$_2$S was considered in these studies. Stinnett et al. predicted the sulphur distribution in a coal gas by thermodynamic calculations [40]. But as the total sulphur content in biomass product gas is lower the situation may be different. Below 1000 ppm H$_2$S the distribution of H$_2$S, COS and SO$_2$ can't be known precisely [41]. Some hints to the sulphur distribution are reported by Towler [42].

The removal of H$_2$S also effects the COS-shift reaction. Most of the transition metal oxides act as catalyst for the shift reaction which means that COS reacts to H$_2$S and would be removed as well depending on the kinetics. A study with ZnO done by Sasaoka et al. confirmed that fact [43].

$$COS + H_2O \rightleftharpoons H_2S + CO_2 $$ \hspace{1cm} (38)

If there is no more capacity for further sulphidation the sorbent has to be regenerated. To rebuild the metal oxide the sulphide is treated with oxygen respectively air. The regeneration reaction is a highly exothermic reaction and needs therefore a tight temperature control.

$$Me_xS_x + \frac{3}{2}xO_2 \rightleftharpoons Me_xO_x + xSO_2 $$ \hspace{1cm} (39)
During the regeneration step a metal sulphate formation is possible but should be avoided. The large sulphate anions cause spalling of the sorbent which leads to capacity and reactivity loss. The presumption of sulphate formation can be predicted with a predominance diagram of the Me-O-S system. The zinc system is depicted in Figure 16.

![Predominance diagram of the Zn-O-S system at 500°C][53]

To make the whole process more economical the formed SO\textsubscript{2} should be used in a further application. Generally this can be done by producing sulphuric acid. But in practice that won't be profitable for biomass gasification. Another possibility is to use SO\textsubscript{2} as regeneration gas. The big advantage is that elemental sulphur is built during this process which can be better handled. Unfortunately not all sorbents can be regenerated with SO\textsubscript{2}. Zeng [44] investigated the utilization of SO\textsubscript{2} for regeneration of Ce-based sorbents. Also iron [45] and manganese based sorbents can be used for direct sulphur process [46]. The utilization will be a bigger topic when it comes to process design and cost calculations of the total process.

**Thermodynamic considerations**

The basic considerations show that thermodynamic calculations are helpful to estimate the sorbent behaviour. With some simple equilibrium calculations the thermodynamic limit of the sulfidation reaction can be obtained. Of course the kinetic factors (diffusion, mass transfer etc.) are limiting and also the actual composition can differ from the calculated one but still it is a useful tool to get more insight. Existing species and achievable limits can be predicted and first decisions can be made. Furthermore the kinetic ought to be fast as the considered processes are taking place at high temperatures. However the results should be examined critically.
An interesting value is the attainable purification limit depending on temperature and gas composition. Therefore, the equilibrium concentrations of H$_2$S are compared for different sorbents using similar concentrations to the product gas of the gasification plant in Güssing as example. Only simple calculations were done here. Thermodynamic calculations of the total gas-solid multi-component system are complex and may be carried out in a later stage of the work.

As a simplification only the sulfidation reaction is considered in this approach. It is assumed that concentrations of other gas components are constant and that their influence to the equilibrium of H$_2$S is small. That implies that changes of the gas composition at different temperatures because of the water gas shift reaction and the methanal reaction are neglected. The sulfidation reaction for H$_2$S removal generally follows equation:

\[ xH_2S + Me_yO_x \leftrightarrow Me_yS_x + xH_2O \]  

(40)

According to equation (41) the free reaction enthalpy for several metal oxides is calculated. The thermodynamic data for the sulfidation reactions is taken from Barin [47]. It is assumed that all gases are ideal gases and that the reaction takes place at a total pressure of 1 bar.

\[ G_R = \sum G_{prod} - \sum G_{ed} \]  

(41)

\[ ZnO + H_2S \leftrightarrow ZnS + H_2O \]  

(42)

\[ MnO + H_2S \leftrightarrow MnS + H_2O \]  

(43)

\[ Fe_2O_3 + 2H_2S + H_2 \leftrightarrow 2FeS + 3H_2O \]  

(44)

\[ Fe_3O_4 + 3H_2S + H_2 \leftrightarrow 3FeS + 4H_2O \]  

(45)

\[ Cu_2O + H_2S \leftrightarrow Cu_2S + H_2O \]  

(46)

\[ 2CuO + H_2S + H_2 \leftrightarrow Cu_2S + 2H_2O \]  

(47)

\[ 2Cu + H_2S \leftrightarrow Cu_2S + H_2 \]  

(48)

Generally the equilibrium constant $K_R$ for reactions is defined by:

\[ K_R = \exp(-\frac{G_R}{RT}) \]  

(49)

($p = p_o$, all gases are ideal, $K_x = K_p$)

With $K_R$ and the equilibrium concentration of the other gas components the equilibrium concentration of H$_2$S can be calculated. In case of heterogeneous reactions only the gas components are necessary for the calculation - it is assumed that the activity of solides is one ($a_s = 1$).
\[ K_R = \frac{\prod p^{v_i}_{\text{prod},d}}{\prod p^{v_i}_{\text{ed},d}} \]  

(50)

**Comparison of equilibrium concentrations**

In Figure 17 the calculated equilibrium concentrations of H₂S for different sulphidation reactions are shown. For the calculation 35% water and 25.5% hydrogen were chosen according to the gasification gas of the biomass CHP Güssing. The desired purity for some synthesis catalysts is shown as the limit line at a H₂S concentration of 1 ppm. It can be seen that at high temperatures only the copper oxides lead to H₂S concentration far beyond this limit. In literature ZnO is handled as thermodynamic favourable but here it is also limited to about 350°C if such a low H₂S content is required. Considering different water contents the result of the equilibrium calculation for ZnO is comparable with the result published by Konttinen [48].

Elseviers [49] made a thermodynamic equilibrium simulation for a multi-phase multi-component system of several sorbents. His results show much lower equilibrium concentrations for ZnO.

Another multi-component calculation for a coal gas done by Westmoreland shows that with ZnO ≈ 99.8% (The actual of gas concentration is relatively high because the ingoing gas contains a few percent of sulphur) of sulphur can be removed up to 700°C [50]. Another interesting fact can be seen in both multi-component studies. Copper is reduced to elemental copper over the whole temperature range which results in higher equilibrium concentrations of H₂S.
The reaction with Ca-based sorbents should be considered separately because of the calcination reaction. Both calcium species CaCO$_3$ and CaO can react with H$_2$S.

Calcination

\[ \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \]  \hspace{1cm} (51)

Sulfidation

\[ \text{CaO} + H_2S \rightleftharpoons \text{CaS} + H_2O \]  \hspace{1cm} (52)

\[ \text{CaCO}_3 + H_2S \rightleftharpoons \text{CaS} + H_2O + \text{CO}_2 \]  \hspace{1cm} (53)

Depending on the water and CO$_2$ content the calcination is shifted. Westmoreland [50] and Elseviers [49] stated that there is no sulfidation possible at all below 600 °C. In [107] it was shown that minimum level of sulphur is achieved at the calcination temperature. Additional to the high sulfidation temperature (above 800 °C for good sulfidation) Ca-based sorbents can't achieve equilibrium concentration down to ppmv levels of H$_2$S. Limestone is primary used for in bed desulfurization [46].
Influence of the H$_2$O content

To see the influence of water in the gas further calculations with modified water concentrations were done. For copper and zinc the results are depicted in Figure 18 and Figure 19. The great influence could be expected because water is a direct product of the sulfidation reaction. Whereby the low H$_2$S concentrations of the copper system can be seen and therefore the influence of water can be neglected.

These simple equilibrium calculations can only show basic tendencies and sorbent behaviour. Still some questions about the whole system remain. Considering the different gas composition of the biomass product gas further calculation would be necessary.

Figure 18: Equilibrium concentration of H$_2$S - reaction with ZnO
Over more than two decades several metal oxides have been tested for hot gas desulfurization. In the late seventies Westmoreland [50] did some thermodynamic calculations to evaluate proper oxides for high temperature desulfurization in coal gasification processes. He found out that 11 candidates have potential from a thermodynamic viewpoint. In a second study Westmoreland compared the kinetic behaviour of some of these oxides and found out that generally the reaction order of the sulfidation is one [51]. Based on his work several materials were tested as sulfidation sorbents by different authors. While early studies concentrate on single metal oxides nowadays several oxide mixtures and supported metal oxides were developed to overcome some problems.

Starting with single iron and zinc oxide today multi oxide systems with Zn, Fe, Mn, Cu, and several support materials are still under development. Not only the materials but also the preparation techniques and the sulfidation conditions changed over the years. The temperature range of interest shifted from high temperatures (800°C) down to temperatures of 350°C to 550°C in recent years. The main advantage is that at lower temperatures more metal oxides are stable or suitable for sulfidation purposes. Zn and Fe (combined with Ti) have reached demonstration scale in the late nineties while other sorbents (oxide mixtures) still remained in laboratory scale [46].

Not only good desulfurization behaviour but also an economic process should be guarantied. To develop high performing sorbents the following requirements should be met:

- selective reaction with H₂S
- favourable sulfidation (thermodynamics and kinetics)
- no favourable or very slow side reactions (reduction, carbide building)
- high capacity for sulphur
- high regenerability
- sufficient strength and durability of the sorbent for many sulfidation / regeneration cycles
- no sulphate formation during regeneration
- low costs (purchase, preparation, etc.)

Depending on the temperature range of the process and the desired H₂S level of the off gas different metal oxides are favourable. In early studies the goal of desulfurization was to achieve environmental requirements. Therefore the obtained H₂S concentrations are too high to meet recent demands. Oxides of iron, zinc, calcium, and copper have been studied extensively considering different aspects. Most attention was given to Zn-based sorbents. But recently also manganese, cerium and some other oxides were investigated. In the following sections some advantages and disadvantages of different metal oxides are pointed out.

**Fe-based sorbents**

The sulfidation equilibrium of iron oxide is relatively low compared to that of other oxides above 550°C. But the reactivity is high and the reaction is fast. Therefore the research especially at medium temperatures is still going on. For moderate temperatures iron oxide sorbents are still favourable candidates. The main advantage is that iron oxides are available at low prices and that the option for regeneration with SO₂ exists.

One main disadvantage of iron oxide is its catalytic nature. Investigations by Zhao et al. [52] showed that especially the Boudouard reaction is influenced by iron oxides which are also well known from the steel industry.

\[ 2CO \leftrightarrow C + CO₂ \]  

(54)

The elemental carbon that is built during that reaction can cause pore plugging and deactivation of the sorbent. Early studies indicated that the reaction system of iron oxide is more complex [53].

Some studies on iron oxide sorbents were carried out in Japan. Sasaoka et al. found out that hematite is more reactive than magnetite during sulfidation but will be reduced to magnetite in the reducing coal atmosphere [54]. Also different binders for iron ores were tested and compared. All showed low reactivity but could be increased by treatment with hydrogen [55]. Patrick et al. reported that Al₂O₃ can stabilize Fe₂O₃ at least to some extent against reduction but the obtained H₂S concentration is still much higher than a few ppm [45]. The regeneration was carried out in this study with SO₂ which should be kept in mind as advantage. Slimane et al. studied some metal oxides at moderate temperatures and found out that no iron oxide based sorbent has sufficient reactivity in the temperature range of 350 to 550°C [56]. However the advantages of iron oxides lead to combinations with other metal oxides. Some studies with zinc ferrites were done.

**Ca-based sorbents**

Calcium based sorbents were one of the first solid sorbents when it came to high temperature desulfurization. For this purpose mainly limestone was used. An advantage of the utilization
of limestone or dolomite is that they are cheap natural materials but probably with less stability. As thermodynamic calculations show CaCO$_3$ can be added directly to the gasification reactor to remove H$_2$S because high temperatures are desired. The downside of this adsorption with limestone is that large quantities of limestone (almost twice the stoichiometric factor) are required and large amounts of waste have to be disposed. The poor sorbent performance can be explained by the different reactivity of CaCO$_3$ and CaO. It was also mentioned that half calcined dolomite compared to CaCO$_3$ could be used in a panel bed filter because of its reactivity [57].

To find out more about the different behavior of CaCO$_3$ and CaO some kinetic studies were done. Ruth et al. [57] found that the reactivity of half calcined dolomite (CaCO$_3$*MgO) is much greater than of the fully calcined dolomite (CaO*MgO) at temperatures up to 800°C. Some further kinetic investigations also at lower temperatures were done by Bogwardt [58], [59]. Influence of particle size and gas composition (particularly H$_2$O, H$_2$, CO$_2$ content) was recognized. At high temperatures sintering reduces the effectiveness of limestone [59], [60].

The reactions of calcium based sorbents are well investigated and some kinetic data is available. In the late nineties also a regenerable desulfurization process with limestone was investigated. A three step process was developed where elemental sulphur is produced during regeneration [61]. Anyway the achievable H$_2$S concentration is not sufficient to clean gas for fuel cells or as synthesis gas.

**Zn-based sorbents**

Zinc based sorbents are handled as thermodynamic favorable but with some restrictions. At the beginning zinc oxide was only used as a nonregenerable guard bed before interest shifted also to regenerable utilization. The investigations started with the single oxide and switched then to zinc ferrite, zinc titanates and other oxide mixtures.

The biggest disadvantage of zinc based sorbents is the reduction to the elemental metal accompanied by vaporization at higher temperatures $T > 700$°C. Also sintering and surface area loss causes sorbent deactivation. Another problem is the sulphate building during regeneration. The much bigger SO$_4^{2-}$-ion leads to spalling above 600°C. Many different approaches with oxide mixtures were done to overcome these problems. Zinc based sorbents still represent a promising solution for high temperature desulfurization.

Zinc ferrites consist of zinc and iron oxides which is a combination of two active sorbents. Advantages of this compound are expected because of the high capacity of ZnO supplemented with the high reactivity of Fe$_2$O$_3$. But still the zinc vaporization appears as a major problem especially over many cycles of sulfidation and regeneration at high temperatures. The following reactions take place:

Reduction

\[
\begin{align*}
\text{ZnOFe}_2\text{O}_3 + \frac{1}{3} \text{H}_2(g) & \rightarrow \text{ZnO} + \frac{2}{3} \text{Fe}_2\text{O}_4 + \frac{1}{3} \text{H}_2\text{O}(g)
\end{align*}
\] (55)
Sulfidation

\[ ZnO + \frac{2}{3} Fe_3O_4 + 3H_2S(g) + \frac{2}{3} H_2(g) \rightarrow ZnS + 2FeS + \frac{11}{3} H_2O(g) \]  \hspace{1cm} (56)

Regeneration

\[ ZnS + 2FeS + 5O_2(g) \rightarrow ZnOFe_2O_3 + 3SO_2(g) \]  \hspace{1cm} (57)

Some kinetic studies were done. Pineda et al. demonstrated that the sorbent performance could be well described with a kinetic grain model [62]. Furthermore in this study was reported that particle size effects exist and depend on the reaction temperature. Gupta et al. compared different preparation techniques in a bench scale fluidised bed reactor. Tests showed big influence of the preparation technique and also that attrition and sorbent loss is a major problem [63].

Portzer et al. developed an advanced hot-gas process which is a direct sulphur recovery process. The idea is to use during ZnS regeneration released SO\(_2\) for iron sulphide regeneration. The achieved H\(_2\)S levels were high. Kobayashi et al. developed zinc ferrite sorbents for coal gas utilization in MCFC [64]. They could achieve concentrations down to < 1ppm H\(_2\)S over 20 cycles at 450 °C (under pressurized conditions).

Another group of zinc based sorbents are zinc titanates. The combination of zinc oxide with titanium oxide should stabilize the ZnO to avoid reduction and vaporization at high temperatures. Since titanium oxide is inactive for desulfurization the capacity of the combined zinc titanates is smaller than the pure zinc oxide because of dilution.

The following reactions take place:

Reduction

\[ Zn_2TiO_4 + 2H_2S(g) \rightarrow 2ZnS + TiO_2 + 2H_2O(g) \]  \hspace{1cm} (58)

Sulfidation

\[ ZnTiO_3 + H_2S(g) \rightarrow ZnS + TiO_2 + H_2O(g) \]  \hspace{1cm} (59)

Regeneration

\[ 2ZnS + TiO_2 + 3O_2(g) \rightarrow Zn_2TiO_4 + 2SO_2(g) \]  \hspace{1cm} (60)

Zinc titanates were the most promising solution to make zinc based sorbents useful for the high temperature range. Therefore a lot of studies were done. It is reported that zinc titanates can stabilize zinc oxide against reduction/vaporization to some extent. Beside the fact that surface area increased over cycles Lew at al. made another interesting observation. From chlorine containing procedures prepared sorbents showed better sulfidation performance [65]. Kinetics of pure zinc oxide was compared with that of zinc titanates by Lew et al. and Woods Et al.. Also different molar rations (Zn/Ti) were compared in these studies and remained to be determined depending on the desired loading and tolerated reduction [66]; [67]. Konttinen et
al. developed a fluidized bed model for scale up. The obtained kinetic data fit to previous results of Lew et al. [68], [48].

Multi-cycle tests and sorbent durability tests in a fluidised bed reactor carried out by Mojtabahedi et al. showed that zinc titanates are attrition resistant and, therefore, physically suitable for fluidized bed reactors. But chemical stability was not satisfactory and also reactivity decreases with the number of cycles [69], [70]. Swisher et al. investigated several zinc titanates with titanium oxide excess and found a good compromise between mechanical properties and chemical reactivity [71].

Due to the idea that the sulfidation is a diffusion controlled process Pinade et al. used graphite as a pore modifier additive [72]. Graphite improved the sorbent's performance. Recently zinc titanates were successfully stabilized with cobalt and nickel oxides against deactivation by Jun et al. [73]. Unfortunately no achievable H₂S concentrations are reported.

**Cu-based sorbents**

In the nineties copper based sorbents were recognized as an effective alternative to overcome well known problems with zinc based sorbents and to achieve much lower H₂S concentrations. From a thermodynamic viewpoint copper oxides are most favorable.

Unfortunately CuO and Cu₂O are immediately reduced to elemental copper in a slightly reducing atmosphere and the sulfidation reaction of elemental copper is significant worse. The total reduction of the copper oxide was also investigated during kinetic experiments by Kyohtani et al. [74]. But still if it is possible to stabilize the copper oxides against reduction these sorbents are most promising to achieve subppm levels of H₂S.

Several support materials and metal oxide mixtures were tested to improve the performance. Manganese oxide which is reactive itself was tested to stabilize copper oxide. Garcia found that MnO can't stabilize the higher oxidation state of copper [75]. Also manganese sulphate formation occurred as a major problem during regeneration. On the other hand no sulphate formation of copper based sorbents was ascertained during regeneration by Abbasian et al. [76]. Al₂O₃ was used as support material by Tamhankar et al. [77]. They found out that it doesn't matter whether the oxides are physically or chemically mixed [78]. Li et al. reported that the decision of a proper support material is crucial because there are many different phenomena at different temperatures [79]. In his tests chromium or cerium oxides were used to support cu-based sorbents.

Abbasian and Slimane developed a regenerable, copper based sorbent with Cr₂O₃ as support material [76]. It was tested successfully at 600 °C. For the medium temperature range (350°C-550°C) Abbasian and Slimane developed further copper based sorbents containing Cu, Mn, Al and Ti oxides. These high attrition resistant sorbents could achieve H₂S levels down to <1ppm [62].

**Mn-based sorbents**

Manganese based sorbents are very stable over a wide temperature range. Above 400°C MnO is the prevailing species. A big disadvantage is that manganese based sorbents should be regenerated at high temperatures (>750°C). Even though the predominance diagram shows
that during the regeneration at 750°C sulphate is stable. Atakül et al. reported successful sulfidation and regeneration cycles at 600°C [81], [82]. To run sulfidation and regeneration at the same temperature would bring lower costs and is therefore favourable.

The big advantage of manganese based sorbents is that no capacity or activity loss occurs even at high temperatures. Manganese based sorbents can also be used at temperatures $T > 900^\circ C$. Due to that fact Slimane et al. investigated manganese based sorbents (combined with $Al_2O_3$) and compared them with zinc based sorbents [83]. In this study also kinetic considerations are reported. In the second part of this study multi cycle tests showed capacity and kinetic improvement due to reduction of diffusion distance. Tests were done at high temperatures $>700^\circ C$ which is necessary mainly for regeneration [84].

The sulfidation reaction is thermodynamically not very favourable and the achievable $H_2S$ levels are many times higher than the desired limits for synthesis gas applications. Even though $MnO$ could be added in an oxide mixture as Garcia et al. investigated [75]. But if the operation temperature is lower the sulphate building combined with sorbent passivity still remains as a problem. However, development of sorbents with additional manganese oxide is still in progress.

**Ce-based sorbents**

Some interesting work on desulfurization with cerium oxide was done. Cerium oxide was tested successfully to stabilize copper oxides by Li et al.. Even though both oxides were reduced low $H_2S$ concentrations were achieved [79]. But cerium oxide itself is also an interesting candidate for desulfurization because of the possibility of direct sulphur production during regeneration. Additional to the mildly exothermic regeneration reaction which makes temperature control easier the sorbent shows no activity loss during some cycles. The sulfidation takes place at high temperatures of about $800^\circ C$.

Zeng et al. [44] presents a two stage process with cerium oxide and zinc oxide sorbents that reaches off gas concentrations of 10ppm $H_2S$ over some cycles. He concluded that cerium oxide is stable enough to be used at higher temperatures ($>600^\circ C$) where it is more effective. The feed gas should be highly reducing for a good performance. Prereduced cerium sorbent turned out to be a suitable alternative for desulfurization with medium reducing and water containing gas at high temperatures [85]. $CeO_n$ is more favorable than $CeO_2$.

**Lanthanum- and Copper-containing Cerium oxide**

As mentioned above, cerium oxide is effective for desulfurization. But this $H_2S$ removal is not enough for the usage of the gas as synthesis gas even if a two stage process with zinc oxide is used. Wang et al. [86] reported the Lanthanum or Cupper contained cerium oxide.
Figure 20 shows the calculated sulfidation equilibrium of CeO$_2$, Ce$_2$O$_3$, La$_2$O$_3$, and copper in a gas mixture of 50% H$_2$, 10% H$_2$O in He. Ce$_2$O$_3$ and La$_2$O$_3$ are superior H$_2$S sorbents that keep the H$_2$S concentration below 30ppm even up to 1200 K in the gas mixture interest.

Based on breakthrough curve, it is obvious that 70wt% lanthanum-doped ceria has the highest sulfidation capacity under all conditions, of the 30wt% lanthanum-doped ceria, CeO$_2$, and 10wt% copper-doped ceria. Ce-70 wt% LaO$_x$ could keep exit H$_2$S concentration below 10 ppm more than 100 min. These reactions are the following:

**Sulfidation**

\[
2\text{CeO}_2 + \text{H}_2\text{S} + \text{H}_2 \rightleftharpoons \text{Ce}_2\text{O}_2\text{S} + 2\text{H}_2\text{O} \quad (61)
\]

\[
2\text{Cu} + \text{H}_2\text{S} \rightleftharpoons \text{Cu}_2\text{S} + \text{H}_2 \quad (62)
\]

\[
\text{Ce}_2\text{O}_3 + \text{H}_2\text{S} \rightleftharpoons \text{Ce}_2\text{O}_2\text{S} + \text{H}_2\text{O} \quad (63)
\]

\[
\text{La}_2\text{O}_3 + \text{H}_2\text{S} \rightleftharpoons \text{La}_2\text{O}_2\text{S} + \text{H}_2\text{O} \quad (64)
\]

**Regeneration**

\[
\text{Ce}_2\text{O}_2\text{S} + \text{SO}_2 \rightleftharpoons 2\text{CeO}_2 + \text{S}_2 \quad (65)
\]

\[
\text{Ce}_2\text{O}_2\text{S} + \text{O}_2 \rightleftharpoons 2\text{CeO}_2 + \frac{1}{2}\text{S}_2 \quad (66)
\]

\[
\text{Ce}_2\text{S}_3 + 2\text{SO}_2 \rightleftharpoons 2\text{CeO}_2 + \frac{3}{2}\text{S}_2 \quad (67)
\]
The regenerability is very important. That is because the adsorption reaction could be controlled to be reversible and it was reported that it could be fully regenerated. If the sulphidation is operated with high space velocity (SV>16000h\(^{-1}\)), it would be possible to limit the reaction to the surface of the sorbent. This surface adsorption is reversible, and thus the sulphided sorbents can be fully regenerated. Regeneration at high space velocities (SV>80000h\(^{-1}\)) can be used to suppress sulphate formation and shorten the total time required for complete sorbent regeneration.

**Ni-based sorbents**

Desulfurization of model gasoline fuels and a real gasoline over a nickel-based adsorbent Ni-Al was studied at a temperature range of 25-200°C under ambient pressure without using H\(_2\) gas in order to evaluate the desulfurization performance of the adsorbent to use gasoline for fuel cells. Including other various sulphurs and hydrocarbons; Thiophene, Benzothiophene, n-hexane, toluene, and so on, gasoline is more difficult for desulfrization than biogas.

Ma et al. [87], [88] shows that the olefins which included real gasoline certainly influence the capability of desulfurization. The breakthrough point volume is decreased about a quarter that if it was not contain 5wt% n-octane.

Figure 21 shows the breakthrough curve of real gasoline. The adsorption capacity is much lower than of different model gasolines, because the real gasoline contains much more olefins and other components.

![Figure 21: Breakthrough curves of real gasoline over Ni-Al at 25 and 200 °C, LHSV 4.8 h\(^{-1}\)](image)

However, it should be discussed that the dramatic improvement of desulfurization performance at high temperature. It was attributed to the fact, that the increase in temperature reduces the adsorption of olefin on the Ni surface, restrains thermodynamically the
hydrogenation of olefin, and/or accelerates kinetically the surface reaction rate of the adsorbed sulphur compounds with the nickel. In biogas case, it doesn’t compound olefin as gasoline does. Then the higher desulfurization capacity could be expected.

**Series sorbents**

Zheng et al. [89] reported a series of Zn-Fe-Ce sorbents supported upon Al2O3 to investigate the effects of different contents of Cerium on the sorbent desulfurization. Desulfurization was performed in the temperature range of 35–90°C. Sorbent regeneration was performed at 200–400°C. Testing different mole ratios of Zn,Fe, and Ce, the sorbent which contains 2:1:0.52 (Zn:Fe:Ce) was most effective.

Interestingly, the regenerability is very high. When adsorption operated at 60°C and 10h^{-1} (liquid; it was researched for gasoline) space velocity and regeneration operated at 250°C and 6.0vol% steam and air, the adsorption capacity (exit sulphur concentration lower than 10ppm) was not decreased, though it was repeated eleven times.

**Other sorbents**

Some other metal oxides were tested with more or less success. Bagajewicz et al. [90] studied vanadium oxides and found that vanadium oxide is not qualified for desulfurization if water is present in the gas. Furthermore, a kinetic study by Westmoreland shows poor intrinsic reaction rate [51]. A process with stannic oxide was developed by Karpuk et al.. Sn-based sorbents do not meet the demands of purity for syngas but the developed process seems to be a low cost alternative [91]. Furthermore, water equilibrium restrictions exist in case of SnO.

**Sorbent properties**

Beside the sulfidation behavior of the oxides also the capacity is an important property especially from an economic point of view. Due to the fact that mostly oxide mixtures are used the capacity varies with different composition. Yumura et al. [53] found that zinc oxide has a high capacity compared to iron and calcium oxide. The capacity of copper based sorbents is low while manganese based sorbents have a high capacity. In Table 11 sorbent characteristics are listed and compared.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Capacity [gS/100g sorbent]</th>
<th>Oxide</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-based</td>
<td>13-22</td>
<td>ZnO</td>
<td>High</td>
</tr>
<tr>
<td>Fe-based</td>
<td>22</td>
<td>Fe_{2}O_{3}</td>
<td>Medium</td>
</tr>
<tr>
<td>Cu-based</td>
<td>9-11</td>
<td>CuO</td>
<td>Very high</td>
</tr>
<tr>
<td>Mn-based</td>
<td>42</td>
<td>MnO</td>
<td>No</td>
</tr>
</tbody>
</table>
Sorbent costs

To develop an economic feasible process also the sorbent costs are an important factor. Natural materials like iron or calcium based sorbents offer a cheap solution but may be excluded because of other reasons. In Table 12 the costs of some metal oxides are listed. Also the costs for the metal oxide are only a small part of the total adsorbent costs, for comparison of different adsorbents it is important to compare also the costs of the raw material. These or similar values were also basic estimates in some sorbent development projects to calculate and compare process costs.

Table 12: Costs of sorbent metal oxides [92]

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cost $/lb</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO</td>
<td>0.5-1</td>
<td>Low</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.5-1</td>
<td>Low</td>
</tr>
<tr>
<td>CuO</td>
<td>2-5</td>
<td>Medium</td>
</tr>
<tr>
<td>MnO</td>
<td>2-5</td>
<td>Medium</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>2-8</td>
<td>Medium</td>
</tr>
<tr>
<td>NiO</td>
<td>3-5</td>
<td>Medium</td>
</tr>
<tr>
<td>CoO</td>
<td>7-10</td>
<td>High</td>
</tr>
<tr>
<td>CeO</td>
<td>8-10</td>
<td>High</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>8-10</td>
<td>High</td>
</tr>
<tr>
<td>MoO₃</td>
<td>8-10</td>
<td>High</td>
</tr>
</tbody>
</table>
10.2.2 Adsorption with Zeolites

Zeolite has remarkably molecular selectivity, because of the pore structure. Generally, it is good to adsorb polar molecular, because it has a polar surface or a hydrophilic surface. H₂S, Thiophene, and other sulphides are polar molecular. Then, zeolite could be expected to have good efficiency for desulfurization.

Xue et al. [93] studied cerium-loaded Y-zeolites for removal of organic sulphur compounds. With the metal ion-loaded zeolites, ion-exchange reactions occur on the surface area. This solid-state ion-exchange method is convenient as a preparation procedure as compared to the conventional ion-exchange method in the liquid phase.

The experiments were accomplished with pre-desulphurized gasoline or diesel oil. The sulphur content was adjusted below 5ppm. From the experiments, it was concluded that the thiophene adsorptive properties are greatly influenced by the Ce content, the Ce valency, and the calcination temperature, as well as the structure of the zeolite framework. The calcination in air had two effects on the adsorbent: oxidation of Ce(III) to Ce(IV) and removal of adsorbed water molecules from zeolite. The increase of Ce content is an effective way to increase the thiophene uptake.

Figure 22 shows the amount of sulphur after adsorption with varied adsorbent. It is shown that CeY–S is a powerful adsorbent for the selective removal of low concentrations of organic sulphur compounds from pre-desulphurized diesel oil, and the combination of the CeY–S and CuO adsorbents can provide a promising desulfurization process for the preparation of clean fuel for biosyngas.

![Figure 22: GC chromatograms of (a) original pre-desulfurized diesel oil, (b) sample after treatment of sample (a) with CeY–S adsorbent, and (c) sample after treatment of sample (b) with CuO adsorbent](image)

Xu et al. put forward the concept of molecular basket. It showed that Molecular sieve Si-MCM-41 loaded Polyethylenimine has the capability of CO₂ also H₂S removal for synthesis gas demands. Polyethylenimine (PEI) has a high density of amino groups to interact with H₂S and, therefore, is expected to show high H₂S adsorption capacity. The PEI in MCM-41 is
expected to show a higher adsorption efficiency for $\text{H}_2\text{S}$ than the bulk PEI particles, because PEI nano-particles can be formed in the channels of MCM-41 that are accessible to gas molecules.

![Figure 23: Comparison of the $\text{H}_2\text{S}$ breakthrough curves of MCM41-PEI and commercial ZnO](image)

Figure 23 shows the $\text{H}_2\text{S}$ breakthrough curves. The conditions for MCM-PEI are as follows:

- **Temperature**: 90°C
- **gas hourly space velocity (GHSV)**: 200min⁻¹
- **$\text{H}_2\text{S}$**: 8ppmv
- **$\text{H}_2$**: 43vol%,
- **$\text{N}_2$**: balance
- **particle size**: 0.5-1.0mm.

Also, the conditions for commercial ZnO were as follows:

- **Temperature**: 400°C;
- **GHSV**: 171min⁻¹
- **$\text{H}_2\text{S}$**: 8ppmv
- **$\text{H}_2$**: 43vol%
- **$\text{H}_2\text{O}$**: 15vol%
- **$\text{N}_2$**: Balance
- **Extrudates**: 3mm.

Although the adsorption temperature was much lower than that for the other adsorbents (such as 400°C for ZnO) the fresh MCM41-PEI adsorbent could effectively adsorb $\text{H}_2\text{S}$ from the gas mixture.
10.2.3 Adsorption with Activated Carbons

Gardner et al. [97] showed H₂S catalytic partial oxidation technology with an activated carbon catalyst to be highly integratable into fuel cell power plant applications. The chemistry behind this process is simple:

\[
H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O
\]  

(68)

In that case three different fuel cell feedstocks were considered. In the case of biomass gasification, the experiments were tested with Texaco O₂-blown coal-derived synthesis. And the activated carbon’s properties showed 13.

Table 13: Properties of activated carbon

<table>
<thead>
<tr>
<th>Trace metals (ppm/g)</th>
<th>Physicochemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum 6332</td>
<td>BET surface area (m²/g) 662</td>
</tr>
<tr>
<td>Calcium 795.4</td>
<td>Particle density (g/cm³) 0.87</td>
</tr>
<tr>
<td>Cobalt 15.73</td>
<td>Skeletal density (g/cm³) 2.07</td>
</tr>
<tr>
<td>Chromium 8.281</td>
<td>Particle size (mm) 3.7</td>
</tr>
<tr>
<td>Copper 24.16</td>
<td>Porosity (%) 60</td>
</tr>
<tr>
<td>Iron 1832</td>
<td>Crush strength (kpsi) 10.7</td>
</tr>
<tr>
<td>Phosphorous 32.49</td>
<td>Loss on attrition (%) 10.5</td>
</tr>
<tr>
<td>Potassium 422.3</td>
<td>Ash (wt%) 4.93</td>
</tr>
<tr>
<td>Magnesium 194.8</td>
<td>Peroxide no. 14</td>
</tr>
<tr>
<td>Manganese 3.800</td>
<td>Iodine no. 800</td>
</tr>
<tr>
<td>Molybdenum 2.387</td>
<td>Sodium 313.7</td>
</tr>
<tr>
<td>Nickel 11.64</td>
<td>Titanium 237.7</td>
</tr>
<tr>
<td>Water (wt%) 4.15</td>
<td>Zinc 16.61</td>
</tr>
</tbody>
</table>

* Provided by manufacturer.

From Figure 24 it can be seen that the outlet H₂S concentration is low enough to use for fuel cells or as synthesis gas and there seems not to be influence temperature regularly. However, it was also shown that the sulphur product began to over oxidize and COS formation became significant, above 145 °C. The activated carbon catalyst was able to reduce total sulphur (H₂S, SO₂, and COS) levels to below 1 ppmv at temperatures less than 145 °C.
Figure 24: The effect of temperature on H$_2$S removal efficiency during H$_2$S catalytic partial oxidation of a Texaco O$_2$-blown gasifier gas
11 HCL REMOVAL

The concentration of HCl in product gas from gasification is much lower than the sulphur contents. Since chlorine contents in the gas are much higher with coal than with biomass gasification (100 to 1000 ppm) more research and development is done for coal. Thus, available literature is focusing on gas cleaning for product gas from coal gasification.

HCl is the stronger acid and therefore easier to get rid of. Thus, more literature can be found on sulphur removal. HCl removal is done mostly with Ca- and Na-based sorbents and will be pointed out in the following in detail.

The reaction of HCl with calcium based sorbents such as slaked lime (Ca(OH)$_2$), limestone (CaCO$_3$), or lime (CaO) to form calcium chloride is of big importance for the removal of HCl from the product gas of biomass or coal gasification plants. The main reactions are displayed in the following:

\[
Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \quad (69)
\]

\[
CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \quad (70)
\]

\[
CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad (71)
\]

At high temperatures CaCO$_3$ and Ca(OH)$_2$ are disintegrated according the following equations:

\[
CaCO_3 \rightarrow CaO + CO_2 \quad (72)
\]

\[
Ca(OH)_2 \rightarrow CaO + H_2O \quad (73)
\]

Weinell and co-workers [98] tested slaked lime and limestone for the adsorption of HCl from the gas phase in the temperature range of 60-1000°C. A maximum between 500 and 600°C were found. Additionally, at temperatures below 150°C slaked lime showed high capacities for bonding of HCl. In both temperature ranges a total conversion to CaCl$_2$ is possible. At temperatures above 500°C the capacity for bonding is limited by the equilibrium between the gas and the solid phase. The reaction kinetic is determined by the diffusion in the solid phase. Kinetic investigations in a fixed bed reactor showed that the treatment of the sorbents (calcination and slaking) showed the same reactivity as measured with pure Ca(OH)$_2$. Thus, these sorbents should be applicable for dry injection, which will reduce significantly the costs [99].

At the Technical University Clausthal (Germany) simultaneous removal of H$_2$S and HCl was tested in a fixed bed reactor in laboratory scale. CaCO$_3$ and CaO were used as sorbents at temperatures between 300 and 700°C. Different residence times and raw gas concentrations of HCl, H$_2$S, and H$_2$O were applied. The results show, that especially CaO acts as excellent sorbent for the simultaneous removal of HCl and H$_2$S. As upper temperature limit the melting point of CaCl$_2$ at 772°C should be mentioned. The bonding capacity of CaO for HCl has a maximum at 600°C. This effect can be explained by the sintering of CaCl$_2$ at about 600°C. The break through behaviour of the fixed bed is influenced of the stability of the particular phase (CaCl$_2$ or CaS). This stability is of course determined by the temperature and gas composition [100].
Duo and coworkers describe a reaction model of sorbents for the HCl removal out of the product gas in a fixed bed reactor [101]. The following chemical reactions are specified in this report:

\[ \text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \] (75)

\[ \text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} \] (76)

\[ \text{Ca(OH)}_2 + 2\text{HCl} \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O} \] (77)

\[ \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2 \] (78)

HCl adsorption with calcium and sodium based sorbents were investigated earlier by this group. As feed for the experiments a model gas, representing typical product gases from gasification with air or oxygen, was used. As expected, the HCl adsorption on Ca-sorbents is influenced by the concentration of carbon dioxide. No influence on Na-sorbents could be detected at temperatures between 300 and 600°C. Figure 25 shows that Na\textsubscript{2}CO\textsubscript{3}*10H\textsubscript{2}O and CaO are significantly better sorbents for air blown fuel gas conditions than NaHCO\textsubscript{3} and CaCO\textsubscript{3}. However, for oxygen blown fuel gas conditions (Figure 26) significant improvement can be accomplished with CaO and Ca(OH)\textsubscript{2}.

Figure 25: Breakthrough curves for air-blown fuel gas conditions
Krishnan and co-workers [103] tested Nahcolite (NaHCO₃), which is a commercial available mineral, in a fixed bed reactor at 400-500°C. A reduction of HCl down from 300ppm to less than 1ppm could be accomplished, if Nahcolite will be injected in the product gas line directly after the gasifier. To reach lower limits than this an external reactor will be needed.

VTT (Finland) reported about removal of halogens at coal and biomass gasification plants. The main part of chlorine can be removed by Ca-based sorbents in the fluidized bed or in a filter cake of a ceramic filter without injection of sorbents in the product gas line. However, more than 60% chlorine removal can be observed, if Ca(OH)₂ will be injected in the product gas line [104].

Duo and co-workers investigated the injection of Na-based and Ca-based sorbents into the feed gas of ceramic filters. The specific surface of the sorbents was found to be important for the adsorption of hydrogen chloride. Improved absorption was observed if the sorbents agglomerated.

Siemens Westinghouse Power Cooperation and the Gas Technology Institute developed jointly an innovative process for hot gas cleaning for IGCC (Integrated Gasification Combined Cycle) plants. The so called “Ultra-Clean Gas Cleanup Process (see Figure 27) is a two step process. Clean gas concentrations of <60ppb for H₂S, <100ppb for HCl, and <0.1ppm for particles can be reached. Based on the thermodynamic equilibrium as well as literature data, transition metals such as zinc, copper, iron, and manganese are favoured for H₂S removal. Na-based sorbents are used primarily for the removal of HCl and are ideal for the described process.

In the first step the fine grinded sorbent particles for the removal of H₂S and HCl are injected in the hot gas flow at 375-600°C. The product gas is then transported to a filter reactor using a moving bed. Thus, the H₂S and HCl concentrations are reduced down to 1-3ppm.

Summarizing it can be stated, that the injection of Na-based sorbents (such as: Nahcolite, Trona, Dawsonite) can reduce HCl concentrations in the clean gas down to values below 1ppm [105].
Figure 27: Representative flow sheet for the Ultra-Clean Gas Cleanup Process [105]
12 CONCLUSION

Biomass will play an important role in the future global energy infrastructure for the generation of power and heat, but also for the production of chemicals and fuels. The dominant biomass conversion technology will be gasification, as the gases from biomass gasification are intermediates in the high-efficient power production or the synthesis from chemicals and fuels.

In the discussion on the utilisation of gases from biomass gasification it is important to understand that the composition of the gasification gas is very dependent on the type of gasification process and especially the gasification temperature. The gas cleaning and treatment, which is the connecting step between gasifier and gas usage, depends also heavily on the type of gasifier and the usage of the gas. In the last years much research has been done on cleaning the product gas from biomass gasification for CHP applications. Here the focus was mainly on removal of particulates and tars. In this area there are already several successful demonstration projects, which shows, that these components can be removed to a level, that gas engines can be operated without any problems.

For synthesis gas applications not only the removal of particulates and tars is necessary, but also the conversion of hydrocarbons and the removal of CO₂, halogens, nitrogen- and sulphur components.

Several studies have shown that many different parameters influence desulfurization. Wet processes, like Rectisol, are complex and have high investment costs. At the moment wet processes are used in coal gasification, (e.g. Sasol or Schwarze Pumpe uses Rectisol) or at refineries (e.g. amine scrubbers for removal of CO₂). In general wet processes are favourable at large scale, because of economy of scale. In the research area, it turned out that recently only metal oxide mixtures of reactive and inactive metal oxides with more or less high capacity were combined and tested. Even though most of the studies were done for coal gas basic knowledge about high temperature desulfurization can be used to choose proper sorbents for biomass producer gas. The operation temperature and the required purity exclude some oxides because of thermodynamic reasons.

Thermodynamic considerations in show that single oxides of Ca, Mn, Fe or elemental copper won't achieve synthesis gas requirements. To get a better insight in equilibrium concentrations of biomass product gas thermodynamic calculations of a multi-component system should be done. The different gas composition of biomass producer gas and the lower sulphur content can show different results. It seems reasonable to start with an experimental approach to get first experience in high temperature adsorption. Based on thermo-dynamical behaviour of coal gas and taking the conclusion of this literature survey into account a preliminary choice of metal oxides can be done. Copper oxides show high potential to reach very low H₂S concentrations.

The halide removal is a technical challenge for the production of a clean product gas via biomass gasification. Most systems use injection of sorbents into the gas flow before the particle separator (e.g. filter, cyclone), which provides sufficient separation efficiencies for standard applications. Sodium carbonate and Nahcolite are mostly used for removal of HCl with gasification processes. Both sorbents are applied between 400 and 600°C. Ca-based sorbents are usually used for high temperature applications and are suitable for simultaneous removal of H₂S and HCl.
For fuel cell and chemical synthesis applications external reactors need to be used since HCl levels below 1ppm are needed.

At the moment there are only some groups, who have practical experience in the whole chain from biomass over synthesis to chemicals and 2\textsuperscript{nd} generation fuels. Most of them use scrubbers as first step and afterwards some fine purification to clean the gas to a level, that it can be used as synthesis gas. It is expected, that with the focus on 2\textsuperscript{nd} generation biofuels, more research will be done in the area of gas cleaning and treatment for synthesis gas applications.
13 REFERENCES

17. Ullmann’s Encyclopaedia of Industrial Chemistry (2002)


