Master Thesis

Solar thermochemical cycle for ammonia production based on aluminium-based redox reactions

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Solar Thermochemical Cycle for Ammonia Production based on Aluminium-based Redox Reactions

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1. Abstract

An alternative way of producing ammonia instead of the known Haber-Bosch process is investigated. The novel two-step cyclic process consists of an endothermic carboreduction of $\text{Al}_2\text{O}_3$ to form $\text{AlN}$ followed by exothermic steam-hydrolysis of $\text{AlN}$ to produce $\text{NH}_3$ and the primal $\text{Al}_2\text{O}_3$. After thermodynamic, kinetic and ecological analyses experiments at the image furnace and the solar simulator both at PSI were conducted to prove theoretical calculations, to state key parameters, close mass balances and to show up problems by employing methane as reducing agent. An autothermic 5kW reactor for the novel cycle was built, successfully tested at the high-flux simulator at ETH, mass balances were closed and efficiencies stated.
2. **Introduction**

2.1 Background

Ammonia was first used on an industrial scale by the Germans during World War I [1], following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain their war effort [2].

Today’s standard (over 90%) in producing ammonia is the 1909 invented and 1910 patented Haber-Bosch process, which we have to owe to “Fritz Haber’s invention and Carl Bosch’s ingenuity” [3]. In 1913, the first Haber-Bosch plant went on stream, representing the first commercial synthesis of ammonia from the elements [4]. Most of the ammonia produced went directly into the industry of fertilizers what permitted also unfruitful regions in the world to develop their agriculture. Today’s global output of ammonia is estimated in the range of 130 million tonnes per year – four-fifths of this goes into fertilizers. With an average net energy efficiency 2003 of 36.8 GJ/t NH₃ [5] this makes up 1.2% of worlds energy consumption.

2.2 Haber-Bosch process

The Haber-Bosch process is often been called the most important invention of the 20th century [3] as it "detonated the population explosion", driving the world's population from 1.6 billion in 1900 to over 6.5 billion in 2006.

As a patriotic German Jew, Haber’s invention also helped Germany to significantly prolong World War I, and to develop the Zyklon B poison gas used in World War II's Holocaust. Therefore, Haber's almost paradoxical biography affected more lives and deaths than anybody else's.

Following the reaction equation

\[ \text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g) \quad \Delta H_{298} = -92.4 \text{kJ/mol}, \tag{1} \]

the reaction takes place on the iron catalyst in order to alter the reaction pathway. Elevated temperatures in the range of 400 – 500 °C (originally up to 600 °C) in order to achieve the activated state and pressures above 100 bar [4] following Le Chatelier are needed. Due to this unfavourable position of the thermodynamic equilibrium, recycling of the unconverted part of the synthesis gas is needed because the equilibrium content of ammonia in the synthesis gas after one step is not more than 20%. Also the separation of the ammonia product needs to be done under high pressure.

Although the synthesis of ammonia is exothermic a lot of energy input is needed in order to overcome the high activation energy of 230-420 kJ/mol without and 103 kJ/mol with iron catalyst [4]. Furthermore the production of the reactants is very energy and carbon intensive: steam-reforming of natural gas and cryogenically separation of nitrogen from air.

Figure 1 depicts the improvements in energy intensity of the Haber-Bosch process within the last 50 years [5]. Today’s average net energy efficiency is 36.8 GJ/t NH₃ where with best available technique it is possible to produce ammonia with 28.4 GJ/t NH₃ [5].
2.3 Solar thermochemical cycle

To overcome these drawbacks, a novel cyclic process has been proposed [6]:

![Scheme of the novel solar thermochemical cycle](image)

The first high-temperature step, performed e.g. in a solar reactor, produces aluminium nitride by carbothermal reduction of alumina. As reductive, either fixed carbon (2a) in the form of charcoal, petcoke etc. or methane (2b) can be used. The hydrolysis (3) is the second step where ammonia and alumina are formed to close the cycle. CO produced in (2a) may be further processed by the water-gas shift reaction to syngas. This synthesis gas, as well as the one from the reaction with methane (2b) can be directly used as fuel or as an intermediate to Fischer-Tropsch products. Products of the cycle can for instance be ammonium and methanol (see 3.2.3).
1st step:
\[ \text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO} \quad \Delta H_{298} = 708.1 \text{kJ/mol} \] (2a)

\[ \text{Al}_2\text{O}_3 + 3\text{CH}_4 + \text{N}_2 \rightarrow 2\text{AlN} + 6\text{H}_2 + 3\text{CO} \quad \Delta H_{298} = 931.9 \text{kJ/mol} \] (2b)

2nd step:
\[ 2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 2\text{NH}_3 \quad \Delta H_{298} = -274.1 \text{kJ/mol} \] (3)

This new process offers 4-fold advantage in comparison to the Haber-Bosch process:
- Elimination of the complication associated with high pressure, minimizing costs and safety concerns
- No need of catalysts; therefore costs for production and recycling are avoided
- Elimination of the need for syngas or hydrogen as feedstock
- Energy source is the sun: thus energy consumption from fossil fuels and greenhouse gas emissions are reduced


For other metals than aluminium, different carbothermal reductions with the aid of concentrated solar energy were already carried out, to be mentioned here is the work of A. Smeets [12] where the solar production of silicon nitride from silicon oxide is investigated in a similar manner as done in this work.
3. **Theory**

3.1 **Reaction extent**

Basic definition of the reaction extent or yield for the first step of the carbothermal reduction:

\[
X_{\text{Al}_2\text{O}_3} := \frac{n_{\text{prod}}^{\text{AlN}} (t, T)}{n_{\text{max}}^{\text{AlN}}} = \frac{n_{\text{react}}^{\text{Al}_2\text{O}_3} - n_{\text{prod}}^{\text{Al}_2\text{O}_3} (t, T)}{n_{\text{react}}^{\text{Al}_2\text{O}_3}} = \frac{n_{\text{prod}}^{\text{AlN}} (t, T)}{n_{\text{prod}}^{\text{AlN}} (t, T) + 2 \cdot n_{\text{prod}}^{\text{Al}_2\text{O}_3} (t, T)}
\]  

(4)

where \(n_{\text{species}}\) is the number of moles of the species, \(n_{\text{max}}\) stays for the maximal achievable amount at total conversion, \(n_{\text{react}}\) is the reactant (at time 0) and \(n_{\text{prod}}\) the product (at time \(t\)). Eq.(4) assumes no loss of any species during reaction.

The number of moles of alumina at \(t=0\) is

\[
n_{\text{react}}^{\text{Al}_2\text{O}_3} = \frac{M_{\text{react}}^{\text{sample}} \cdot f_{\text{Al}_2\text{O}_3}}{M_{\text{Al}_2\text{O}_3}}
\]  

(5)

with \(M_{\text{react}}^{\text{sample}}\) the original mass of the probe, \(f_{\text{Al}_2\text{O}_3}\) the mass fraction of \(\text{Al}_2\text{O}_3\) in the sample and \(M_{\text{species}}\) the molar mass of the species.

A balance of the solids results in the number of moles of alumina after reaction:

\[
n_{\text{prod}}^{\text{Al}_2\text{O}_3} (t, T) = n_{\text{react}}^{\text{Al}_2\text{O}_3} - \frac{M_{\text{prod}}^{\text{loss}} (t, T)}{(M_{\text{Al}_2\text{O}_3} + 3 \cdot M_{\text{C}}) - 2 \cdot M_{\text{AlN}}}
\]  

(6)

\(M_{\text{loss}}\) is the loss of mass in g due to reduction at time \(t\).

Combining eqs. (4), (5) and (6) results in

\[
X_{\text{Al}_2\text{O}_3} = \frac{M_{\text{prod}}^{\text{loss}} (t, T) \cdot f_{\text{Al}_2\text{O}_3}}{M_{\text{react}}^{\text{sample}} \cdot f_{\text{Al}_2\text{O}_3} \cdot (M_{\text{Al}_2\text{O}_3} + 3 \cdot M_{\text{C}}) - 2 \cdot M_{\text{AlN}}}
\]  

(7)

which is the possibility to determine the reaction extent with the aid of a mass balance.

Another way of concluding the yield is a mole balance in terms of the product gases. Following eq.(2a) for each \(\text{Al}_2\text{O}_3\) consumed three molecules of carbon monoxide are produced. Eq.(4) therefore becomes:

\[
X_{\text{Al}_2\text{O}_3} := \frac{1}{3} \int_0^t \dot{n}_{\text{CO}} (t, T) \cdot dt
\]  

(8)

\(\dot{n}_{\text{CO}} (t, T)\) is the molar flow of carbon monoxide at time \(t\) and temperature \(T\) in mol/s, the integral of this gives the total number of moles CO produced during the reaction.

Basic definition of the reaction extent for the second step explicitly the hydrolysis:

\[
X_{\text{AlN}} := \frac{n_{\text{prod}}^{\text{NH}_3} (t, T)}{n_{\text{max}}^{\text{NH}_3}} = \frac{n_{\text{react}}^{\text{AlN}} - n_{\text{prod}}^{\text{NH}_3} (t, T)}{n_{\text{react}}^{\text{AlN}}} = \frac{2 \cdot n_{\text{prod}}^{\text{Al}_2\text{O}_3} (t, T)}{n_{\text{prod}}^{\text{AlN}} (t, T) + 2 \cdot n_{\text{prod}}^{\text{Al}_2\text{O}_3} (t, T)} = 1 - X_{\text{Al}_2\text{O}_3}
\]  

(9)
3.2 Analysis of solar thermochemical cycle

3.2.1 Thermodynamic analysis

Thermodynamic analyses of both alternatives of the first step were done by Gálvez et al.[6].

Figure 3: Equilibrium composition as a function of temperature for reaction (2a)

Figure 3 shows the equilibrium composition for the reaction with solid carbon (2a) at a pressure of 1 bar as a function of temperature. The beginning of the reaction is detected at 1200°C and it is notably accelerated at 1500°C. At 2000°C the conversion of Al₂O₃ reaches 100%, the gas phase contains at this point 94.9% CO, 2.2% N₂ and small amounts of Al(g) and Al₂O(g), 1.3 and 1.6% respectively. At this temperature the solid phase is composed of 2.6% C(gr) and 97.4% AlN.

Figure 4: Equilibrium composition as a function of temperature for reaction (2b)

Figure 4 illustrates the equilibrium composition for the reaction with methane (2b) at 1 bar for different temperatures. Methane cracking is almost completed at 600°C, leading to the formation of C(s) which at higher
temperatures and in the presence of N₂ reacts with Al₂O₃ to AlN. At 1900°C, 100% conversion is reached. The gas phase consists at 2000°C of 31.3% CO, 63.4% H₂, 1.5% N₂ and some small amounts of Al(g), Al₂O(g), H(g), C₂H₂(g), AlH(g) and HCN(g). The solid phase contains 100% AlN.

By applying either C or CH₄ as reducing agents, no formation of Al₆C₃ or oxycarbides (e.g. Al₂O₂C, Al₆OC, Al₆O₃C) is foreseen by the thermodynamic calculations in this temperature range.

The AlN produced is desired to be totally free of Al₂O₃ and C(gr) in order to proceed with the second step of the cycle. Adding a small amount of oxygen in both alternatives of the first step nearly eliminates alumina and solid carbon. The product gas only contains some small amounts of gaseous Al₂O and Al, which however will evaporate in an open reaction system. Reaction (2a) is therefore complemented and rewritten as follows:

\[ \text{Al}_2\text{O}_3 + 3.05\text{C} + 1.1\text{N}_2 + 0.05\text{O}_2 \rightarrow 1.94\text{AlN} + 3.05\text{CO} + 0.13\text{N}_2 + 0.02\text{Al}_2\text{O} + 0.01\text{Al} \]  

(10a)

Table 1 gives the mole fractions in the product and the yield for oxygen-free and oxygen-doped reaction (2a).

<table>
<thead>
<tr>
<th>reactant</th>
<th>product</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (mol)</td>
<td>O₂ (mol)</td>
<td>AlN (s) (mole fraction)</td>
</tr>
<tr>
<td>3.05</td>
<td>0</td>
<td>0.362</td>
</tr>
<tr>
<td>3.05</td>
<td>0.05</td>
<td>0.360</td>
</tr>
</tbody>
</table>

Gálvez et al.[6] also performed heat balances, shown in Figure 5. The enthalpy change is defined as:

\[ \Delta H = H_{\text{products}}^{\text{products}} - H_{\text{reactants}}^{\text{products}} \text{ at } 25^\circ\text{C}, \]  

(11)

where the products are in equilibrium.

For reaction (2a), enthalpy increases slowly up to 1500°C. In this region enthalpy change corresponds to the amount of energy needed to heat up the reactants. Due to reaction starting at 1500°C, it then raises sharply to reach a value of 1147.5 kJ·mol⁻¹.

Table 2 gives the mole fractions in the product and the yield for varying amounts of oxygen according to reaction (2b). Mole fraction “0” means less than 10⁻⁵.

<table>
<thead>
<tr>
<th>reactant</th>
<th>product</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ (mol)</td>
<td>O₂ (mol)</td>
<td>AlN (s) (mole fraction)</td>
</tr>
<tr>
<td>3.05</td>
<td>0</td>
<td>0.176</td>
</tr>
<tr>
<td>3.05</td>
<td>0.02</td>
<td>0.175</td>
</tr>
<tr>
<td>3.05</td>
<td>0.05</td>
<td>0.171</td>
</tr>
</tbody>
</table>

Table 2: Comparison of the thermochemical equilibrium composition products at 1800°C and 1 bar for an initial mixture of 1 mol Al₂O₃ + 1.1 mol N₂ + reactant; (2b).
As expected, the reaction with methane (2b) provokes two changes in the slope of the curve. One between 400 and 700°C due to methane cracking and the second one due to carbothermal reduction of aluminium at temperatures around 1500°C. In this case, the enthalpy reaches a value of 1859.2 kJ·mol⁻¹ at 2000°C.

![Figure 5: Enthalpy change as a function of temperature for carboreduction](image)

The reaction extent is negatively affected by an increase in the total pressure of the system. As shown in figure 6, at 2000°C the yield decreases from 100% to 58.5% for reaction (2a) by increasing the pressure from 1 to 10 bar. Reaction (2b) is less affected by a pressure augment then (2a). This is a purely thermodynamic result and has nothing to do with the principle of le Châtelier although the number of moles in the gas phase is growing in both reactions. But considerably less then one percent of the total gas flow is progressing in the reaction, more then 99% is inert. Therefore a pressure rise during reaction can not be resulting from multiplying the number of moles in the gas phase.

![Figure 6: Influence of the total pressure on the reaction extent of carboreaction](image)
The problem with the hydrolysis (3) is depicted in figure 7: Thermodynamically, \( \text{NH}_3 \) is only favourable at below 350°C while AlN is converted to \( \text{Al}_2\text{O}_3 \) at any temperature. In absence of a catalyst, a considerable amount of \( \text{NH}_3 \) was found in the semester thesis of Tanic and Marketos [13] because of low reaction kinetics. Higher pressure supports thermodynamic stability of \( \text{NH}_3 \) [6].

![Equilibrium composition of the hydrolysis (3) as a function of temperature at 1 bar](image)

**Figure 7: Equilibrium composition of the hydrolysis (3) as a function of temperature at 1 bar**

### 3.2.2 Kinetic analysis

Literature provides a variety of possible reaction pathways for reaction (2a):

- **gas-gas:** \( \text{Al}_2\text{O}_3 \) dissociation into \( \text{Al}(g) \), followed by its reaction with \( \text{N}_2 \), and \( \text{O}_2 \) followed by its reaction with C. Carbon reduces the partial pressure of oxygen to such an extent that alumina-dissociation and \( \text{Al}(g) \)-nitridation become effective [14].
- **gas-gas:** \( \text{Al}(g) \) or \( \text{Al}_2\text{O}_3(g) \) react with \( \text{N}_2 \) and CO [15].
- **solid-solid followed by gas-gas:** \( \text{Al}_2\text{O}_3(s) \) and \( \text{C(s)} \) form \( \text{Al}_2\text{O}(g) \) and \( \text{CO}(g) \) followed by the second step where \( \text{Al}_2\text{O}(g) \) reacts with \( \text{N}_2 \) and CO to result in AlN [16].
- **solid-solid:** A solid state reaction proceeds into and around the alumina grains until the alumina grain is subsumed by aluminium nitride subgrains. A volume reduction of about 2% during the conversion is expected to assist in providing a rapid diffusion path for the carbon, oxygen and nitrogen species down the grain boundaries [17].

O’Donnell and Trigg [17] observed no \( \text{Al}_2\text{O}_3 \)-free AlN nuclei in TEM and NMR spectra. Additionally no weight loss in excess of the theoretical one was detected that would result from the evaporation of aluminium and therefore the solid state reaction mechanism was concluded to be the most probable. This is supported by the detection of a considerable dependency on both particle sizes stated by Chen et al.[18]. Gas-solid reactions show weaker particle size dependencies then solid-solid ones.

Reaction (2b) was never kinetically analysed before, refer to the results and discussion section.
3.2.3 Ecological comparison

A preliminary economic and ecological analysis has been done by Gálvez et al.[6]. An ecological study in a slightly altered form is presented for one cycle with an initial capacity load of 100 kmol (10.2 ton) of Al₂O₃ resulting in 177 kmol (3.01 ton) NH₃ by assuming 90% yield of ammonia per cycle. According to eq.(10a) 110 kmol (3.08 ton) N₂ are needed for each cycle. Note that this is not a complete life cycle analysis because only direct impacts are considered and CO₂-emissions and energy inputs due to construction of the plant or transportation are not included. This is partially supported by Werder et al.[19] stating that for the Zn-cycle impacts from the solar heliostat field can be neglected.

Table 3 compares the conventional Haber-Bosch process with the novel solar thermochemical one without further processing of the product gas (note that CO is assumed to oxidise to CO₂ without any capture of energy). Energy input for the novel technique is only the energy content of the feeding plus energy need for nitrogen separation, solar energy input is not considered at this point because it is assumed to be “for free”. The higher heating value of graphite is 393.5 kJ/mol, with best available technique it is possible to produce ammonia via the Haber-Bosch process with a net energy efficiency of 28.4 GJ/t NH₃ [5], current nitrogen separation is at 0.512 GJₑ/ton N₂ [20]. The world Business Council for Sustainable Development [21] provides specific CO₂-emissions for ammonia produced in different regions in the world from which an average value was taken (1.45 ton CO₂/ton NH₃). UCTE [22] reports for the electricity mix in Europe emissions of 432g CO₂/kWhₑ (=0.12 ton CO₂/GJₑ).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>conventional Haber-Bosch</th>
<th>(10a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C feed (kmol/cycle)</td>
<td></td>
<td>305</td>
</tr>
<tr>
<td>energy input (GJ/cycle)</td>
<td>85.5</td>
<td>121.6</td>
</tr>
<tr>
<td>CO₂ release (kmol/cycle)</td>
<td>99.2</td>
<td>309</td>
</tr>
<tr>
<td>CO₂ release (ton/cycle)</td>
<td>4.4</td>
<td>13.6</td>
</tr>
</tbody>
</table>

Table 3: Ecological comparison of the conventional and the novel cycle by no further processing of the product gas

It makes no sense to employ the solar cycle by no further processing the product gas. The novel cycle shows in this case an enlarged energy input of 42% together with 211% increased CO₂-emissions.

Table 4 compares the conventional technologies (Haber-Bosch process and methane-steam-reforming) with the novel solar thermochemical one with further processing of the product gas to methanol. One complete cycle consists of the formation of AlN according to the thermochemical equilibrium reaction at 1900°C and 1 bar described by eqs.(10a) and (10b) respectively, followed by water-gas shift converting CO to a syngas mixture with H₂/CO molar ration of 2 (see eq.(12)), which then undergoes methanol synthesis. In the second step NH₃ is released by steam reforming (eq.(3)).

\[
3CO + 2H₂O \rightarrow 2CO₂ + CO + 2H₂ \quad (12)
\]

Parameters not stated are the same as for table 3. The higher heating values for methane and methanol are 888 kJ/mol and 713.6 kJ/mol respectively [23]. Specific fuel consumption for methanol is 44.5 GJ/ton CH₃OH [24] and the corresponding specific CO₂ emissions 1.04 ton CO₂/ton CH₃OH [19]. A 90% yield of methanol from syngas is assumed.
Table 4: Ecological comparison of the conventional and the novel cycle with methanol synthesis

The novel cycle with elementary carbon deports in the net energy input (energy input minus energy content of the methanol produced) a 62% reduction and in the carbon dioxide release an augmentation of 23% compared to the conventional technologies. The novel cycle based on methane supply reports a reduction of the net energy input of 72%. The direct CO₂-emissions for this option are coming solely from the production of nitrogen, all the carbon fed to the cycle by methane is stored in the methanol and will be released by the further conversion of the methanol, be it by burning or by feeding to a fuel cell. One has to keep in mind that all the values for the novel cycle are of theoretical nature where the ones for the conventional technologies are practically proven state of the art ones.

Recapitulating, for CO₂ purposes the best way to go for is the carbothermal reduction of alumina with methane. By using elementary carbon as feedstock, more CO₂ is released than with best available technique. One has to bear in mind that generally methane is used to produce the hydrogen for the Haber-Bosch process and not carbon. Therefore two different feedstocks for ammonia production are weighted against. In my opinion this is nevertheless the right way to compare the two technologies because one of the superior goals is to reduce overall CO₂-emissions. The only bottom line out of this is therefore to go either for methane as the feedstock for carbothermal reduction coupled with methanol synthesis or to look for better utilisation possibilities of the CO produced by the novel cycle with elementary carbon.

Adjacent different possibilities for further use of the CO (heating value 305 kJ/mol) resulting from the solar thermochemical cycle with carbon as feedstock (10a) together with their advantages and drawbacks:

- **Methanol synthesis (water-gas shift reaction):**
  The possibility introduced above, will results in a 23% augmentation in CO₂-release compared to conventional technologies.

- **Methanol synthesis (adding H₂):**
  The hydrogen for methanol production is not coming from a water-gas shift reaction but from an external hydrogen production plant. Nowadays hydrogen is mainly produced based on fossil fuels what will lead to an overall increase of the CO₂-release compared to conventional technologies.

- **CO gas turbine:**
  Table 5 gives an ecological comparison for the alternative of a CO gas turbine. The total CO₂-release and the amount of electric energy produced are set equal for both alternatives (alternative 1: novel cycle and electricity generation by burning of CO in a gas turbine; alternative 2: conventional Haber-Bosch and electricity generation with UCTE European electricity mix). With these data, the CO-turbine would need an overall net energy efficiency of at least 83% which is practically impossible (today’s best combined cycles fed by methane show overall net energy efficiencies up to 60%).
### Table 5: Use of CO from reduction for electricity generation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>intermediate CO release (10a) (kmol/cycle)</td>
<td>304</td>
</tr>
<tr>
<td>intermediate total CO release (10a) (GJ/cycle)</td>
<td>92.7</td>
</tr>
<tr>
<td>total CO release novel / conventional (ton/cycle)</td>
<td>13.4</td>
</tr>
<tr>
<td>electricity generation (GJ(_{el})/cycle)</td>
<td>76.9</td>
</tr>
<tr>
<td>efficiency needed</td>
<td>83%</td>
</tr>
</tbody>
</table>

- **CO fuel cell:**
  A fuel cell purely fed by CO and O\(_2\) was not found in literature but would theoretically be imaginable. The energy and CO\(_2\)-balance would be the same as for the CO gas turbine presented above. The key point of a net energy efficiency of 83% remains the same and is not feasible for a fuel cell either.

- **Acetic acid production:**
  The main part of today’s CO produced in industry is used for acetic acid production, called methanol carbonylation [25]:
  \[
  CH_3OH + CO \rightarrow CH_3COOH
  \]  
  (13)
  The reaction to employ in our case would then be
  \[
  4CO + 2H_2O \rightarrow 2CO_2 + CH_3COOH
  \]  
  (14)
  Regrettably no life cycle analysis for acetic acid production could be found and therefore it is not possible to make a comparison. One has to mention that further processing of the product gases from the ammonia cycle helps reducing CO\(_2\)-emissions but also highly complicate the handling of the whole process.

### 3.3 Particle size dependence of the melting point

The dependence of the melting temperature on particle size is described in literature. However this phenomenon describes the behaviour of nano particles, defined by mean particle sizes smaller then 100nm.

One model to explain this observation is based on classical thermodynamics and takes into account the surface/interface energies of a particle when evaluating the total free energy of the system. This model predicts that under equilibrium conditions each particle will consist of two phases (see figure 8) [26]: a solid inner core (with radius r, dependent on temperature) and a liquid outer-shell layer (radius R, constant).

![Figure 8: a) the two phases of a particle in equilibrium conditions. b) solid inner core radius dependence on temperature](image)
At low temperature, the two radii are almost equal \( r(T) = R \). By increasing temperature, the liquid outer-shell layer enlarges, therefore \( r(T) \) decreases where \( R \) remains constant. By further increasing temperature, the solid inner core decreases down to a critical value \( r_m \) where complete melting suddenly occurs. For \( R > r > r_m \) the process is continuous and reversible where for \( r < r_m \) it is discontinuous and irreversible. The temperature at which \( r_m \) or the irreversible melting is reached defines the melting temperature \( T_m \).

For clusters of sizes smaller than 5-8 nm (not engaged in this work), surface melting disappears and the whole melting process is discontinuous [26].

A review of existing models describing this phenomenon is done by Zhao et al. [27]. Unfortunately it was not possible to find literature describing this effect for Al\(_2\)O\(_3\), neither the supplier of the aluminium Alfa Aesar had specific information. Estimation can be done with the aid of melting temperature decrease at particle sizes slightly smaller than 100nm for other metals:

- For spherical lead nano particles embedded in aluminium matrix, a decrease in the region of 15K at 25nm particle size is described [27]
- For spherical Indium nano particles embedded in aluminium matrix, a decline of roughly 20K at 25nm particle size is stated [27]
- Diminish of around 50K for 25nm gold particles [28]
- For silver, a decrease of about 50K is reported for 28nm particles [29]
- A decrease of approximately 15K is reported for 50nm sized lead spheres [26]
- 30nm Aluminium particles weaken the melting point in the order of 10K [30]

### 3.4 Model reaction rate

Based on diverse assumptions there exist different models for the kinetics. What they all have in common is the acceptance of the shrinking core model [31]. The papers indicated refer to the derivation of each model.

Wilhelm Jander [32] formulated 1927 the Jander equation based on the assumption that the reaction of two reactants in powder form is made possible by inner diffusion of the crystals and the liquid state is not compulsory needed. Jander found the reaction rate to be dependent on time:

\[
\frac{dX_{Al_2O_3}}{dt} = k_{Jander} \cdot \frac{3}{2} \left( 1 - X_{Al_2O_3} \right)^{\frac{3}{2}}
\]

\[
k_{Jander} = k_0 \cdot e^{-E_a/RT}
\]

\( E_a \) is the activation energy in kJ/mol and \( R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \) the universal gas constant. In the integrated form this becomes

\[
\left( 1 - \left( 1 - X_{Al_2O_3} \right)^{\frac{3}{2}} \right)^2 = k_{Jander} \cdot t,
\]

where the dimensionless constant obtained from integration obviously vanishes because there is no yield at \( t = 0 \).

All the models presented here are derived by the assumption of an unreacted core model [31] depicted in figure 9. Based on this, a mass balance is applied:

\[
\frac{\partial c}{\partial t} \cdot S_r \cdot \Delta r = J_{r \pm \Delta r} \cdot S_{r \pm \Delta r} - J_r \cdot S_r
\]

\( c \) is the concentration of species A, S, and \( S_{r \pm \Delta r} \) the surface area of a sphere with radius \( r \) and \( r \pm \Delta r \) accordingly and \( J_r \) is the molar flux \( (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) \) at a radius \( r \). \( S_r \) is a commonly used approximation for the volume of the shell.
between radii $r$ and $r + \Delta r$. With the assumption of no dependence of diffusivity of species A ($D_A$) on the radius, dividing eq.(18a) by the volume of the shell and let $\Delta r$ become $dr$ this results in

$$\frac{\partial c_A}{\partial t} = D_A \cdot \frac{1}{r} \cdot \frac{\partial c_A}{\partial r} + D_A \cdot \frac{\partial^2 c_A}{\partial r^2}$$

(19a)

Figure 9: Simplified scheme for the unreacted core model

However the Jander model [32] is mistakenly derived from a simplified 1D-model of a planar shell with a constant cross-sectional area for the diffusion, irrespective of the laps of time. Eq.(18a) then becomes the equation known for rectangular coordinates:

$$\frac{\partial c_A}{\partial t} \cdot S_r \cdot \Delta x = J_x \cdot S_c$$

(18b)

Solving this yields

$$\frac{\partial c_A}{\partial t} = D_A \cdot \frac{\partial^2 c_A}{\partial r^2}$$

(19b)

This is a serious mistake in the derivation process of the Jander equation by expressing the material balance with eq.(19b) instead of eq.(19a). Irrespective of criticism by several authors [33] the Jander model is most commonly used for reactions such as gas-solid reactions.

The Ginstling-Brounshtein-equation considering the true mass balance of eq.(19a) is proposed [33]:

$$\frac{dX_\text{Al}_2\text{O}_3}{dt} = \frac{3}{2 \cdot \left(\frac{1-X_\text{Al}_2\text{O}_3}{1} \right)^{\frac{3}{2}} - 1}$$

(20)

$$1 - \frac{2 \cdot X_\text{Al}_2\text{O}_3}{3} \cdot \left(1 - X_\text{Al}_2\text{O}_3\right)^{\frac{3}{2}} = k_{\text{Ginstling-Brounshtein}} \cdot t$$

(21)

$k_{\text{Ginstling-Brounshtein}}$ can be expressed as $k_{\text{Jander}}$ and the dimensionless constant from integrating vanishes as well.

Another simple approximation was done by Levenspiel [24]:

$$1 - \left(1 - X_\text{Al}_2\text{O}_3\right)^{\frac{3}{2}} = k_{\text{Levenspiel}} \cdot t$$

(22)

where $k_{\text{Levenspiel}}$ and integration constant treated as done by Jander.

A more complicated rate law considering the concentrations of the different species is stated by Chen et al. [16].

Experimentally derived kinetics where grain sizes of carbon and alumina, initial bulk densities and a couple of other parameters are accounted is presented by Chen et al. [18].
4. **Experimental**

4.1 Setup image furnace

The main part of the setup shown in figure 10 is the ellipsoidal aluminium reflector {a} that forces the light of the 1kW short arc lamp to converge in the fixed focal point of the reflector [34]. The lamp, whose radiation intensity is controlled by the power controller {b}, is cooled by distilled water, the sample support is connected to the cooling loop of PSI. The lamp was first heated up until the power indicated by the power controller reached a steady state at around 1120W.

![Experimental setup of the image furnace at PSI](image)

- The inlet gas is controlled by flow meters {c} (N\textsubscript{2}: Bronkhorst, 20 l N\textsubscript{2}/min) and (CH\textsubscript{4}: Bronkhorst, 2 l N\textsubscript{2}/min) and merged together 1m before entering the reaction zone.

- The tube of the outlet gas is directly connected to the pump {d}. The only way to vary the pressure inside the dome is to diversify the inlet gas flow because the delivery rate of the pump is not variable. Right after leaving the reaction zone and before entering the pump, the outlet gas is analysed by a filter, gas chromatography (GC) and mass spectroscopy (MS){e}:
  - A filter placed before the connection of all other analyse devices is collecting solid products of the outlet gas. Afterwards the filter can directly be analysed with XRD.
  - The gas chromatography uses a flow-through narrow tube known as the column, through which the different components of the product gas pass in a gas stream (carrier gas). These fractions flow at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). By exiting the end of the column the chemicals are detected electronically and identified corresponding to the time they needed to pass through the column.

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**Figure 10: Experimental setup of the image furnace at PSI**

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GC is a reliable measurement technique for measuring hydrogen, oxygen, carbon monoxide and methane in parts per million. For one run the GC needs about two minutes while the reaction is proposed to take place within a few seconds.

- Mass spectroscopy is a qualitative analytical technique for online measuring the mass-to-charge ratio of ions. Online means that one measurement of the entire input gas is done in less then 1s. The output of the MS is ion-currents for the different molar masses. By measuring molar mass 32 e.g. this indicates directly the qualitative tendency of oxygen in the gas. For a quantitative analysis the MS needs to elaborately be calibrated (see appendix A). The drawback with this technique is the difficulty in measuring CO in a nitrogen flow because both CO and N$_2$ have the same molar mass.

The GC was operated only in the early stages of this thesis to determine leakages within the whole setup. For all experimental runs at the image furnace, an online measurement was indispensable and therefore MS was utilized.

- The distance from the sample to the focal point determines the heat flux (see 4.2) delivered to the sample and can be tuned in by a stepping motor which varies the sample height. The software and the computer piloting the motor were both updated. Figure 11 explains the driving profile. Starting from origin, the motor is driving with a velocity $v_a$ (to declare in increments per second) to z-coordinate a and continuing with different velocity $v_b$ to coordinate b. After waiting at position b for t seconds, the sample support drives back to the origin with velocity $v_c$.

![Figure 11: Driving profile of stepping motor at the image furnace PSI](image)

The distance d referred to as from now is the absolute difference between focal point of the concentrator (with copper screw and Sigradur disc 166.02 mm) and position b of the driving profile.
- A digital camera \(g\) is placed on the top of the aluminium concentrator in order to record the experiments. A couple of darkening lenses have to be placed between experiment and camera to reduce brightness to a recordable range.

- The sample support \(h\) illustrated in figure 12 is fixed on a small wagon. To facilitate better sealing the “Hammer” was deactivated. Gas flows in through six circumferencally located intakes \(A\) and is leaving the reaction zone through the exit ring \(B\). The sample holder \(C\) is pointed up in figure 13. The flow pattern within the dome presented by Guesdon [34] is simply considering forced convection and is therefore only valid for cold runs viz without heating. In hot environment forced and natural convection are interfering each other and the flow pattern looks completely different. Regrettably the CFD-code used at PRE (Ansys CFX) has some problems by superposing forced and natural convection and because both modes are indispensable I did not try to compute the flow pattern.

![Figure 12: Setup of the sample support at the image furnace PSI](image)

A copper screw fixes a self-made and modified copper washer \(\alpha\) to the water cooled copper sample holder \(\beta\). The modified copper washer retains a Sigradur C disc \(\gamma\). This device separates materially and isolates the cooled copper from the hot sample. The Sigradur C discs are hard and persistent in inert gas up to 3000°C and were ordered from HTW Hochtemperatur-Werkstoffe GmbH, D-Thierhaupten, www.htw-germany.com. In oxidizing media such as oxygen the carbon burns at 600°C. In order to always put the same amount of reactant at exactly the same position the sample \(\delta\) is placed with the aid of a commercial washer M4 (note that after reaction the products will be spread over the Sigradur disc as shown in figure 13).
For the whole setup leaks were looked for and repaired such that for a pressure in the dome of 1 bar less than 50 ppm of oxygen was detected.

Figure 14 illustrates a schematic of the setup used at the image furnace.
4.2 Temperature and heat flux profiles image furnace

4.2.1 Routine

By reasons of not having a pyrometer available the diploma thesis of Christine Guesdon [34] and [35] was accessed with the intention of being able to estimate the operation temperature in the image furnace. These experiments were done in the same configuration of the solar furnace as the experiments in this work but the xenon short arc lamp is not able to radiate the same power over its entire lifetime. On account of this, a routine to determine the temperature profile along the z-axis (the vertical axis through the lamp where the focal point is defined as zero) was shaped up.

The routine consists of melting metals with well known melting temperatures and measuring the distance from focus at which the metals begin to melt.

The metals and conditions to apply together with their melting points are the following:

- Iron powder (Fe) in pure nitrogen (N$_2$) atmosphere, melting at 1808K
- Platinum sheet (Pt) in pure nitrogen (N$_2$) atmosphere, melting at 2045K
- Titan dioxide powder (TiO$_2$) in air, melting at 2123K
- Perovskit powder (CaTiO$_3$) in air, melting at 2248K
- Alumina (Al$_2$O$_3$) powder in air, melting at 2319K

It is also possible to use other materials but one has to take care that they do not reduce or oxidise before melting (e.g. NiO and BaO changed their faces in air and nitrogen before reaching their melting temperatures).

One has to take care that the fundamental working conditions do not change within a calibration. The melting points are pretty independent of pressure. But the material and the cooling of the support is doubtless influencing the temperature of the probe and therefore has to be chosen in the same way as during the experiments.

4.2.2 Execution of the routine

The routine described above was applied the 23 October 2006. Lamp power was adjusted to 1120W, the dome applied and the probe was put on a Sigradur C glassy carbon which itself was fixed on the cooled copper screw with a copper sheet (see 4.1). The power of the lamp had significantly diminished, so it was not possible to melt alumina (Fluka Nr. 06285, median particle diameter measured to 100µm) anymore like reported by Guglielmini [9] in spring 2006. However a fine-grained alumina powder (Alfa Aesar Nr. 042573, denoted mean particle size 0.35 – 0.49µm, measured median particle size 0.29µm) melted in the focus. A literature review about particle size dependence of the melting point (refer to 3.3) lead to the assumption that this fine-grained alumina has its melting point about 20K less than bulk alumina. Therefore the temperature in the focus is assumed to be 2299K, 20K less than the melting point of bulk alumina.

The metered distances for the different melting points measured 23 October 2006 together with a polynomial fit are reported in figure 15.
The quality of a fit is usually described by the root mean square error, defined as:

$$rms = \sqrt{\frac{1}{N} \sum_{i=1}^{N} x_i^2}$$  \hspace{1cm} (23)

The polynomial fit 4th degree with a root mean square error of 18.1K is described by

$$T(x) = -3.4 \cdot 10^{-3} x^4 - 4.1 \cdot 10^{-17} x^3 - 2.3 \cdot x^2 + 2.2 \cdot 10^{-14} x + 2321.8$$  \hspace{1cm} (24)

where $x$ the distance from focus in mm and $T$ the temperature in K.

The corresponding heat flux can now be determined by applying a heat balance on the sample as depicted in figure 16:

$$Q_{rad,in} = Q_{rad,out} + Q_{conv} + Q_{cond}$$  \hspace{1cm} (25)
For incoming radiation and convection, the cylindrical sample with height 1mm and diameter 5.5mm is simplified to a two-dimensional circle with a surface area of $A = 2.4 \times 10^{-5}$ m$^2$. The powdery sample is assumed to have a uniform temperature $T_{\text{sample}}$ (neglecting internal heat conduction and convection). $Q$ are heat fluxes in W.

- $Q_{\text{rad,in}} = A \cdot \alpha \cdot q_{\text{rad,in}}$ 
  is the radiation heat flux coming directly or indirectly (by reflections of the aluminium concentrator) from the xenon arc with $\alpha$ the absorptivity of the sample ($\alpha = 1$, carbon within the sample behaves like a black body) and $q_{\text{rad,in}}$ the incoming radiation heat flux per area (W/m$^3$), to be determined.

- $Q_{\text{rad,out}} = A_{\text{out}} \cdot \varepsilon \cdot \sigma \cdot T_{\text{sample}}^4$ (26) 
  are the radiation losses of the sample with $\varepsilon$ the emissivity of the sample ($\varepsilon = 1$, carbon within the sample behaves like a black body), $\sigma = 5.67051 \times 10^{-8}$ W m$^{-2}$ K$^{-4}$ the Stefan-Boltzmann constant and $A_{\text{out}} = 4.1 \times 10^{-5}$ m$^2$ the relevant surface area including shell and top circle.

- $Q_{\text{conv}} = A \cdot \bar{h} \cdot (T_{\text{sample}} - T_{\infty})$ (27) 
  are heat losses due to convection with $T_{\infty}$ the surrounding temperature ($T_{\infty} = 293$ K, equal to the incoming gas temperature) and $\bar{h}$ the mean heat transfer coefficient, averaged over the surface $A$. Lienhard [36] and Raithby and Hollands [37] suggest for horizontal plates

\[
\overline{Nu_{L^*}} = \frac{0.560Ra_{L^*}^{1/4}}{1 + \left(0.492/Pr\right)^{9/36}}^{1/3},
\]  
where Nusselt

\[
\overline{Nu_{L^*}} = \frac{\bar{h} \cdot L}{k},
\]  
Prandtl

\[
Pr = \frac{\mu \cdot c_p}{k}
\]  
and Rayleigh

\[
Ra_{L^*} = \frac{g \cdot \beta \cdot \Delta T \cdot L^3 \cdot Pr}{\nu^2}.
\]  
Lloyd and Moren [38] propose the characteristic length scale in Nusselt and Rayleigh to be

\[
L^* = \frac{A}{P}
\]  
For all fluid properties, the temperature of the boundary layer is important, which can be approximated by $(T_{\text{sample}} + T_{\infty})/2$, which becomes for the focal point equal to 1300 K. The relevant properties of nitrogen at 1 bar and 1000°C are thermal conductivity ($k = 0.072$ W m$^{-1}$ K$^{-1}$), dynamic viscosity ($\mu = 4.61 \times 10^{-5}$ N s m$^{-2}$), heat capacity at constant pressure ($c_p = 1223$ J kg$^{-1}$ K$^{-1}$) and density ($\rho = 0.268$ kg m$^{-3}$) [39]. Kinematic viscosity ($\nu = 1.72 \times 10^{-4}$ m$^2$/s) can be calculated out of this data. The acceleration of gravity $g$ is equal to 9.81 m/s$^2$, for ideal gases $\beta$ becomes the inverse of $T_{\infty}$, $\Delta T$ is the difference between surrounding and sample temperature and $P$ is the perimeter equal to 0.017 m.

The mean heat transfer coefficient $\bar{h}$ for $T_{\text{sample}} = 2299$ K then becomes 33.2 W m$^{-2}$ K$^{-1}$.

- $Q_{\text{cond}} = A_{\text{contact}} \cdot \kappa_{\text{disk}} \cdot \Delta T \Delta z$ (33) 
  is an approximation of the conduction losses through the sample holder. The parameters are the thermal conductivity of the Sigradur G ($k_{\text{disk}} = 6.3$ W m$^{-1}$ K$^{-1}$, manufacturer instruction), the distance $\Delta z$ equal to the disk thickness of 2 mm and the temperature difference between upper (sample) and lower
(cooling water) part of the Sigradur disc. The temperature at the lower part of the disc is set to 473K in order to consider heat conduction within the copper part. The contact area between the copper cooled screw and the disk is a ring with outer diameter of 5.5mm and the inner one of 4.5mm resulting in $A_{\text{contact}} = 7.9 \cdot 10^{-6}$ m$^2$.

In the focal point ($T_{\text{sample}} = 2299$ K) the elaborated terms become
- $Q_{\text{rad, out}} \approx 64.9W$
- $Q_{\text{conv}} \approx 1.6W$
- $Q_{\text{cond}} \approx 42.8W$

what points out the dominance of heat conduction.

Eq. (25) can be rewritten and solved for the incoming heat flux:

$$ q_{\text{rad,in}} \approx \frac{A_{\text{rad}} \cdot e}{A \cdot \alpha} \cdot \sigma \cdot T_{\text{sample}}^4 + \frac{\bar{n}}{\alpha} \cdot (T_{\text{sample}} - T_{\text{a}}) + \frac{A_{\text{contact}} \cdot k_{\text{disc}} \cdot \Delta T}{A \cdot \alpha} \cdot \frac{\Delta z}{\Delta z} $$

Equation (34)

Solving this equation leads to figure 17 showing the calculated data points of the heat flux profile together with a 4th degree polynomial fit valid for the image furnace at 23 October 2006. The root mean square error is concluded to $9.9 \cdot 10^4$ W/m$^2$.

![Figure 17: Heat flux profile image furnace PSI 23 October 2006](image)

4.3 Determination of the yield with XRD

The calibration of aluminium nitride/oxide with the XRD presented by Guglielmini [9] turned out to be wrong. The general way of proceeding did not change much: Probes of totally 1g aluminium nitride (Aldrich Nr. 24190-3) and oxide (Fluka Nr. 06285) with different molar ratios are well mixed in the pebble mill for 3 minutes on level 80 (from maximal 100). The corresponding yields are calculated with eq.(4).

The alumina from Fluka and the one used in the 1st step with methane (Alfa Aesar Nr. 042573) where both determined to $\alpha$-$\text{Al}_2\text{O}_3$, the most common one.
Figure 18: XRD spectrum from 40 to 60° of a sample consisting of aluminium oxide and -nitride

A run in the X-ray diffractor in the analysing spectrum from 40 to 60°, as shown in figure 18, is done. This is adequate because both $\text{Al}_2\text{O}_3$ ($2\theta = 44.6°$ and 55.3) and AlN ($2\theta = 42.1°$ and 45.8°) have two different detached peaks in this range. Around $2\theta = 48°$ both of the substances have not distinguishable peaks which are therefore not considered. The areas under the relevant peaks are read out by the software “Profit”, a ratio defined as

$$XRD = \frac{A_{42.1} + A_{45.8}}{A_{42.1} + 2 \cdot A_{44.6} + A_{45.8} + 2 \cdot A_{55.3}}$$

(35)

is being calculated. $A_{20}$ is the area of the peak at 20 where the dimension is not important since only the ratio of them is matter of interest.

Figure 19: Calibration curve of the reaction extent
Figure 19 describes the dependency of the yield from XRD. The cubic approximation of the calibration points has a root mean square error of 1.24% and is described as follows:

\[ X_{Al_2O_3} = 3.87 \cdot 10^{-5} \cdot XR^3 - 1.40 \cdot 10^{-2} \cdot XR^2 + 2.02 \cdot XR - 2.00 \]  

where both XRD and yield in %.

The procedure for determine a yield from a probe is simply the following:

1. run XRD and read out the areas under the peaks at \(2\theta=42.1^\circ\) (AlN), 44.6° (Al\(_2\)O\(_3\)), 45.8° (AlN) and 55.3° (Al\(_2\)O\(_3\))
2. calculate XRD with the help of eq. (35)
3. read out the yield from figure 19 or calculate it with eq. (36)

4.4 1st step with activated carbon at the image furnace

Refer to the setup (4.1), only the differing settings are stated here.

All the runs with activated carbon were performed with a molecular compound of \(\alpha\)-aluminium oxide (Fluka Nr. 06285) and activated charcoal (Fluka Nr. 05105) of 1:6, this is double the stoichiometric ratio. The compound was milled in the ball mill for 3 minutes leading to a median particle size of 9\(\mu\)m.

The first runs were performed with the sample placed on a zirconium oxide tablet which itself was directly placed on the copper screw of the supports head. The ZrO was first put into the furnace (15 minutes at 500°C) to eliminate any organic matter and then compressed with a hydraulic press. As an isolation layer the tablet avoided the outermost part of the sample to be chilled from the cooling cycle of the copper screw [9].

By performing a few runs the tablet turned out not to be inert but to change its face during the runs. Also the method for determine the yield with XRD described in 4.3 was affected by the tablet in two ways: The XRD-pattern of ZrO shows a peak slightly before the one of Al\(_2\)O\(_3\) (at 2\(\theta = 44.6^\circ\)) and the pattern of ZrN has a peak mildly after the one of AlN (at 2\(\theta = 45.8^\circ\)). With the tablet, the method was not well-defined and therefore not applicable anymore. Due to these reasons a Sigradur C disc was placed instead (see 4.1).

The direct and fast driving into the focus practised in the first runs turned out not to be adequate. The camera showed a small “explosion” and some black charcoal particles were detected on the inner side of the dome. By fast driving in the upper part of the sample was not able to react firstly, the reaction commenced at the lower part of the sample. The incoherently placed sample has some gaseous nitrogen also on the bottom. By fast driving in the temperature arises within less then half a second from 300K to 2300K which leads with the ideal gas equation to a jump of the nitrogen density of a factor of more then 7. This can easily catapult a significant amount of the sample out of the reaction zone.

Together with Peter Haeberling the software of the stepping motor was adapted in such a way that it is now possible to drive a profile with two points and to appoint the velocity for each section. The profile is explained in section 4.1. The reaction extent rose from about 50% up to 90% by slowly driving in.

The parameters for the runs performed are presented in table 6 where d is the distance between focal point of the concentrator and sample position.
### Table 6: Parameter variation charcoal image furnace PSI

<table>
<thead>
<tr>
<th>d (mm)</th>
<th>T (K)</th>
<th>I (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2111</td>
<td>3.9·10⁶</td>
</tr>
<tr>
<td>7.5</td>
<td>2180</td>
<td>4.2·10⁶</td>
</tr>
<tr>
<td>6</td>
<td>2234</td>
<td>4.5·10⁶</td>
</tr>
<tr>
<td>0</td>
<td>2299</td>
<td>4.7·10⁶</td>
</tr>
</tbody>
</table>

The pressure in the reaction zone was 1 bar, the driving profile (see 4.1): a = 156mm with \(v_a = 400\text{inc/s}\), \(v_b = 13\text{inc/s}\), \(v_c = 400\text{inc/s}\).

#### 4.5 1\textsuperscript{st} step with methane at the image furnace

Different materials and compounds were used:

- coarse-grained alumina: raw \(\alpha\)-aluminium oxide with median particle diameter measured to 100\(\mu\)m (Fluka Nr. 06285)
- fine-grained alumina: raw \(\alpha\)-aluminium oxide with mean particle diameter denoted 0.35 – 0.49\(\mu\)m and measured median size of 0.29\(\mu\)m (Alfa Aesar Nr. 042573, purity 99.95%)
- C-doped alumina 1:1: molecular substoichiometric compound of \(\text{Al}_2\text{O}_3:\text{C} = 1:1\) (fine-grained alumina and activated charcoal Fluka Nr. 05105 with median particle size of 16\(\mu\)m), mixed by hand
- C-doped alumina 1:0.5: molecular substoichiometric compound of \(\text{Al}_2\text{O}_3:\text{C} = 1:0.5\) (fine-grained alumina and activated charcoal Fluka Nr. 05105), mixed by hand
- 6.3% Fe-doped alumina: molecular compound of 6.3% Fe (Merck Nr. 1.03819, corn size 10\(\mu\)m) in fine-grained alumina, mixed by hand
- 6.2% Ni-doped alumina: molecular compound of 6.2% Ni (Fluka Nr. 72220) in fine-grained alumina, mixed by hand
- 1.3% Ni-doped alumina: molecular compound of 1.3% Ni (Fluka Nr. 72220) in fine-grained alumina, mixed by hand

By not indicating any differing settings, the following standard setting was used:

- driving profile (see 4.1): \(a = 145\text{mm}\) with \(v_a = 400\text{inc/s}\), \(b = 155\text{mm}\) with \(v_b = 13\text{inc/s}\), waiting time \(t = 240\text{s}\), \(v_c = 400\text{inc/s}\)
  - with this \(d\) becomes 11\(\text{mm}\) what corresponds to 1991\text{K} or \(3.4·10^6\text{ W/m}^2\).
- inlet gas: 12 volume-percent CH\(_4\) in N\(_2\)
- pressure: 1 bar

#### 4.6 1\textsuperscript{st} step with activated carbon at the solar simulator

The aim of this run was to prove that a big tablet of alumina-carbon mixture is able to react 100%.

The solar simulator at PSI in Villigen [40] was adapted to achieve the solar TG. The principle is the same as the solar furnace described in 4.1 but the power is 50kW instead of 1kW and therefore a few grams of sample can be applied. The second difference is the scale that allows recording an online reaction extent on the basis of the weight loss. Output gas was measured by a GC (CO, CO\(_2\) and O\(_2\)), a calorimeter (fast detection of CO, CO\(_2\) and O\(_2\)) and an oxymat (fast detection of O\(_2\)), where the GC is the most accurate method.
A stoichiometric molecular compound of α-aluminium oxide (Fluka Nr. 06285) and activated charcoal (Fluka Nr. 05105) of 1:3 milled in the ball mill for 3 minutes was pressed to a tablet of 20mm in diameter weighting 2.343g. The probe was dehumidified for 12h at 180°C in order to get rid of the water added to facilitate consistency. The C_{fix} fraction of the activated charcoal is 82.7% (share of elementary carbon without compounds of C), C_{tot} (total carbon, including compounds) is 86.3% [41]. This means that the maximal achievable reaction extent is 86.3% (and not 100% because there is not enough C available). A run with the same reactant conducted at the electrically heated TG at 1700°C resulted in a yield of 89% measured by XRD. The stoichiometric mixture leads to a mass fraction of alumina f_{Al2O3} = 0.739. The nitrogen gas flow was 2 l/min in the aperture, 4 l/min in the box and 6 l/min for the window, overpressure within the reaction chamber was 3 mbar. At these conditions the oxygen fraction in the reaction chamber due to leakage is about 120 ppm. The sample was placed on a sample holder made out of ZrO. This ZrO-disk was fixed with the aid of a piece of aluminium oxide on the bar coming from the balance what can be seen in figure 36. The choice of alumina for this fixing device was not best because at the temperatures reached alumina begins to sinter, therefore the piece changes his shape, the connection becomes waggly and the sample is in danger to fall down. Moreover the alumina from the sample holder may start to decompose at these temperatures and lead to an additional weight loss detected by the scale.
5. **Results and discussion**

5.1 General remarks image furnace

The filter paper placed right after the reaction zone of the image furnace showed traces of solid products within outlet gas, unmistakably there was some black activated charcoal on it. Unfortunately it was not possible to analyse it by XRD, the layer of particles was too thin also after a couple of experiments.

5.2 1\textsuperscript{st} step with activated carbon at the image furnace

The elementary model of Jander (see 3.4) was chosen to model the experimental data because it is widely applied and accepted and it fits measured data best.

Performing the runs described in section 4.4 pointed out that after certain time constant conversion was reached. Figure 20 displays the data points considered for the determination of the rate law where \( f(X) \) is

\[
 f(X) = \left[ 1 - \sqrt[3]{1 - X_{\text{Al}_2\text{O}_3}} \right]^3
\]

which becomes according to eq.(17) the Jander parameter multiplied by the time.

For \(3.9 \cdot 10^6 \text{ W/m}^2\) (2111K) and \(4.2 \cdot 10^6 \text{ W/m}^2\) (2180K) data points up to 20s are included where for \(4.5 \cdot 10^6 \text{ W/m}^2\) (2234K) and \(4.7 \cdot 10^6 \text{ W/m}^2\) (2299K) only data up to 10s and 5s respectively were taken into account. Afterwards constant conversion was reached.

![Figure 20: Data points considered for Jander model together with their linear fits; carboreduction](image)

Extrapolations of the fits of figure 20 would not meet the origin. This fact points out that the assumption of 3.4 of zero yield at time zero is not valid here. Because of slowly driving in a certain amount of alumina is already being converted and for that reason a number has to be added to the measured time (irradiation time after driving in) in order to obtain the true reaction time [32]. Figure 21 shows the same data points as figure 20 but by considering the necessary adjustment of time: For \(T=2299\text{K}\) about 7 seconds have to be added to the measured time for getting the true reaction time. With this tuning the y-axis intercept becomes 0 which signifies no yield at time zero.
For 2234K 2s had to be added. The slowly driving of the distance between these two temperatures needs around 5s which matches the correction described before. The correction times for the two other intensities with their corresponding temperatures of 2180K and 2111K are slightly more then 2s what can be explained in terms of not having absolutely the same conditions for each set of runs (see 4.1).

\( k_{\text{Jander}} \) was determined for each radiation intensity by linear regression and then plotted against the inverse temperature in figure 22. The activation Energy was determined to 363 kJ/mol and \( k_0 \) to \( 3.0 \times 10^6 \text{ s}^{-1} \) with a root mean square error of 0.20 s\(^{-1}\). The parameters are in excellent agreement with Lefort et al. [14] who applied the classical unreacted core model eq.(22) (\( E_a = 384 \pm 23 \text{ kJ/mol} \) and \( k_0 = 3.2 \times 10^4 \text{ s}^{-1} \)) and they are smaller then the ones by Gálvez et al. [6] using Janders model (\( E_a = 815.3 \text{ kJ/mol} \) and \( k_0 = 4 \times 10^{17} \text{ s}^{-1} \)).
Figure 23 illustrates all data points and their corresponding model predictions for the range they were employed. Note that reaction time is used in abscissa and not irradiation time after driving in.

![Figure 23: Reaction extent as a function of time. Markers correspond to the experimental data, solid lines to kinetic modeling using Jander rate law.](image)

At 2299K a maximal reaction extent of 0.92, at 2234K and 2180K 0.86 and the maximal yield at lowest temperature measured was 0.64.

Although there was no formation of oxycarbides foreseen by the thermodynamic analysis performed in 3.2.1., traces of Al$_2$OC were found by XRD-analyses of probes with low reaction extent. At maximal radiation intensity Al$_2$OC was detected in the samples radiated up to 3s, at $3.4 \cdot 10^6$ W/m$^2$ up to 10s. Al$_2$OC is assumed to play the role of an intermediate product because at increased irradiation times no more oxycarbides were found.

A few samples had been analysed with scanning electron microscope SEM and energy-dispersive X-ray spectroscopy (EDX). EDX is able to detect elements within the focus such as O or Al but may not state the compound the elements stay in (Al$_2$O$_3$ or Al$_2$O). The deepness EDX is analysing can not be stated exactly but is in the order of micrometers, therefore by analysing small particles the surrounding or the big particle the small one is sitting on may be analysed as well. The sample holder was made of pure copper.
Figure 24 depicts the SEM picture of sample #225 with following conditions: molecular mixture of 1:6, d = 6mm what corresponds to 2234K or $4.3 \times 10^6$ W/m², irradiation time 20s leading to a conversion of 73%.

EDX detects N by analysing the small bright particles (in the order of one micrometer) whereas by analysing the bigger darker particles (crosshairs) more O is detected. Al and C are always detected, the aluminium coming from its nitrides and oxides and carbon in elementary form resulting from the excess in the mixture. Small AlN particles are also detected on bigger $\text{Al}_2\text{O}_3$ filaments.

Aluminium nitride appears in amorphous form and seems to grow on the surface of the alumina particles resulting in a growing layer of AlN around the shrinking $\text{Al}_2\text{O}_3$ particle. This supports the theory of a solid-solid reaction (3.2.2) and also legitimates the assumption of a shrinking core model (3.4).

5.3 1st step with methane at the image furnace

Conclusions of the experiments with the two pure alumina described in 4.6 are the following:

- No aluminium nitride was produced with the coarse-grained alumina.
- By using fine-grained alumina reaction extents of 10% were obtained. The XRD-analysis showed beside some AlN the existence of different intermediate products such as $\text{Al}_2\text{OC}$ (see also 5.2). By driving nearer to the focus then the standard described in 4.6 the alumina began first to agglomerate and then to melt (effect of particle size dependency of the melting point described in 3.3) resulting in one nugget of aluminium oxide.

We assume the initial step for reaction (2b) to be the cracking of methane and the further devolution being identical to reaction (2a). The dome foged up with carbon particles and the hydrogen detection of the MS proved that a lot of methane cracking took place within the reaction zone. Because methane cracking already takes place at temperatures around 500°C it can occur almost everywhere within the dome. The challenge is to force methane to crack within the alumina powder in order to directly provide the carbon particle to the alumina particle. This may be achieved by catalysts placed within the reactant.
Methane cracking preferably takes place on carbon particles, so a few runs with substoichiometric compounds of alumina and activated charcoal were performed.

The results are explained for the C-doped alumina 1:1: Running this compound without methane resulted in a reaction extent of 19%. In section 5.2, the molecular mixture of Al₂O₃:C = 1:6 (double the stoichiometrically needed carbon) yielded in 60% where three times more carbon was available than needed for theoretical complete reaction. Dividing this 60% by three results in an expected yield of 20%. Applying now methane to the C-doped alumina 1:1 results in a yield of 17%.

The carbon particles participated at the reaction according to reaction (2a) but there was no additional alumina nitride produced by the mechanism of cracking methane on the charcoal particles.

Runs with 6.3% Fe-doped alumina yielded in maximum reaction extents of 17%.

Although the melting point of nickel (1728K) is slightly lower than the one of iron (1811K) and therefore the reaction temperature limitation is more restrictive in order not to melt the reactants, nickel shows better catalytic behavior than iron [42]. By the way, nickel applied on the surface of alumina is a very common catalyst in industry. With a highest yield of 46% nickel turned out to be the best supporter for reaction (2b). With reaction extents higher than 20% one can conclude trends for parameter variation whereas this would not have been possible with the compounds presented above.

The best distance to the focus was determined to d = 11mm which corresponds to 1991K or 3.4·10⁶ W/m². Farther away the temperature is too low for reaction taking place and nearer the reactant (firstly the catalyst) melted and liquid reactants do not provide enough surface for reaction to take place.

Figure 25 presents the dependency of the methane fraction in the inlet gas on the reaction extent at constant total gas flow of 3.38 l/min for the 6.2% Ni-doped alumina. The yield remains approximately constant for methane fractions higher than 0.5% whereas it diminishes rapidly for 0.5% or less methane content in the inlet gas. This agrees with the observation of smoke only occurring at methane fractions superior than 0.5% indicating ascending reaction gases.

![Figure 25: Influence of the amount of methane to the reaction extent for 6.2% Ni-doped alumina](image)

The dependency on the total pressure theoretically stated in 3.2.1 can be reproduced with figure 26. Although there is a considerable scattering, the linear fit shows the diminishing reaction extent for higher pressure which can not be explained by le Châtelier but by thermodynamically moving the chemical equilibrium composition. Experiments with lower methane fractions ended with a cleaner dome than runs with more methane because of less methane cracking.
Going to lower pressures then 1 bar leads to rising oxygen fractions in the inlet gas compared to 4.2. At 0.5 bar 250ppm oxygen are measured, at 0.4 bar 400ppm and at 0.3 bar almost 700ppm are detected. Therefore only measurements from 0.5 bar and higher are considered.

The principle of le Châtelier predicts more methane cracking and therefore higher hydrogen shares at lower total pressure. Figure 27 shows the corresponding measured data points (o) together with a linear fit indicating the diminishing tendency where the right ordinate has to be considered. Multiplying the concentration with the total flow results in the total mean hydrogen output in l/min indicated on the left ordinate. Note that by going to lower pressures it is indispensable to reduce the total flow because the delivery rate of the pump is not variable.

Even if the fraction of hydrogen is raised by going to lower pressures, the total amount of hydrogen in moles is lowered.

All the hydrogen measured here is due to methane cracking. The hydrogen released by reaction (2b) plays a minor role and does not appear by measuring with MS.

**Figure 26: Pressure dependency of reaction (2b) for 6.2% Ni-doped alumina**

**Figure 27: Influence of methane cracking due to variation of total pressure**
It has to be mentioned at this point that the MS was calibrated at a pressure of 1 bar. By sucking in at a certain pressure for a specified time, at lower pressure less volume of sample gas is provided then at higher pressure. The MS therefore delivers only qualitative and no quantitative results at different pressures then 1 bar.

SEM and EDX analyses were conducted under the same conditions described in 5.2.
From the first experiment it was clear that a lot of methane cracking occurs within the dome because of the carbon fouling all over the dome and the rest of the setup. But the question was where this cracking is taking place. 
Figures 28 and 29 prove that methane cracking is also taking place on the sample and not only on the dome. Figure 28 depicts pure carbon filaments in the order of 1µm in diameter and lengths of a few up to 100µm. Analysing the brain-like structures in figure 29 existing in dimensions of hundreds of micrometers pure carbon is detected.

Figure 28: SEM picture 1 of sample #221

Figure 29: SEM picture 2 of sample #221
The destroyed brain-like structure in figure 30 makes the inner life visible. Figure 31 is the spectra of the bright inner part of this structure and proves clearly the existence of aluminium, nitrogen and oxygen. AlN appears in amorphous form in the heart of the huge C-structures.

This explains the evolutionary history of AlN: In the beginning of an experiment, methane cracking is occurring on the Al₂O₃ particles resulting in solid carbon and gaseous hydrogen. Now exactly the same situation as in reaction (2a) is achieved: the carbothermal reduction of Al₂O₃ due to a solid-solid reaction.

Figure 30: SEM picture of sample #220

Figure 31: EDX spectra of the bright amorphous part of figure 30
The mechanism that limits carbothermal reduction of alumina is the ongoing cracking of methane resulting in huge layers of C growing around all existing particles (aluminium nitrides and –oxides) what practically blocks the pathway of N to the other reactants. This also explains why the originally white alumina probes left the reaction zone darker although aluminium oxide and -nitride are white powders. This thesis is supported by detecting thermodynamically unfavourable oxycarbides such as Al$_2$OC within the probes by XRD.

If we assume that nitrogen has just a few seconds free route to the other reactants, the yields obtained can be explained pretty well: run #220 (pure alumina with methane and nitrogen gas flow) obtained 10% reaction extent in totally 240s where at the same temperature a molecular mixture of 1:6 of alumina and carbon under pure nitrogen flow also obtained 10% yield within 1s.

The enhancement in the yield by doping the alumina with a catalyst such as nickel or iron is the effect of attracting and consuming methane by the catalyst what is leading to a delayed growing of the carbon layer around Al$_2$O$_3$. Figure 33 is the EDX-analysis of a filament from figure 32. This illustrates that carbon is growing in a different form (in filaments) around Ni particles than C is growing around the alumina and aluminium nitride particles. Because of Ni and Fe being better catalysts than alumina, carbon is first growing around the catalyst particles. Therefore nickel and iron play a passive role by providing nitrogen more time to reach his reaction partner Al$_2$O$_3$.

Figure 32: SEM picture of a sample with Ni-doped alumina
5.4 Mass balance image furnace

The reaction extent may be calculated in three different ways: By XRD (this is the way it is usually done in this work, see eq.(4)), by the weight loss of the probe (see eq.(7)) and by a mole balance of the product gases (underlying eq.(8)).

Unfortunately it was not possible to close the mass balance for the first step with methane because of not being able to measure the output gas composition (see appendix A).

For both the second and third alternative of calculating the yield, the initial number of moles of Al₂O₃ is needed. But also by slowly driving in as conducted a significant amount of the probe is raised dust and lost to the outlet gas even before the reaction set in.

The trick to nevertheless close the mass balance is to first calculate the yield by XRD, then to count back the initial number of moles that would have been on the tablet by not losing any particle and then apply the mole balance of the product gases.

The augmentation of moles in the gas is very small, therefore the outflow was set equal to the inlet gas flow which in the specific experiments #151 and #170 was 56.3 ml/s what corresponds to $2.34 \cdot 10^{-3}$ mol/s at a molar volume of 24 l/mol (at 20°C). Figure 34 shows the concentration of CO in percent of the total outlet gas flow as a function of the relative reaction time for experiment #151. Integrating over the entire reaction time and multiplying by the total outlet flow yields the overall number of carbon monoxide released by the reaction.
The important parameters of the mass balance are summarized in table 7. For experiment #151, the yield from XRD was determined to 74%. After the experiment the product was weighted to 4.09 mg and with the trick described above the original mass of the sample was counted back with the aid of the yield from XRD and eqs. (5) and (7) to 5.37 mg. This corresponds to $3.09 \times 10^{-5}$ mol Al$_2$O$_3$, where $f_{Al2O3}$ for the 1:6 molar mixture becomes 0.59. The measured original mass was 8.8 mg, therefore about 39% of the mass was physically lost during the experiment #151. This can be suspected by looking at the product exiting the solar furnace in figure 13.

<table>
<thead>
<tr>
<th>variable</th>
<th>description</th>
<th>value #151</th>
<th>value #170</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{Al2O3}$</td>
<td>yield from XRD</td>
<td>74%</td>
<td>51%</td>
</tr>
<tr>
<td>$m_{sample,product}$</td>
<td>mass of solid products</td>
<td>4.09 mg</td>
<td>5.50 mg</td>
</tr>
<tr>
<td>$n_{sample,reactant}$</td>
<td>initial moles of reactant calculated</td>
<td>$3.09 \times 10^{-5}$ mol</td>
<td>$3.78 \times 10^{-5}$ mol</td>
</tr>
<tr>
<td>$n_{CO}$</td>
<td>total amount of CO</td>
<td>$7.84 \times 10^{-5}$ mol</td>
<td>$5.32 \times 10^{-5}$ mol</td>
</tr>
<tr>
<td>$X_{Al2O3}$</td>
<td>yield from mole balance</td>
<td>85%</td>
<td>47%</td>
</tr>
</tbody>
</table>

Table 7: Parameters for mass balance to reduction experiments #151 and #170

With eq.(8) the reaction extent from experiment #151 was now concluded to 85% which lies in the same order as the 74% calculated from XRD. In experiment #170 the values of 51% from XRD and 47% concluded from the mass balance prove that closing the mass balance was achieved. The uncertainty of the CO measurement with the mass spectrometer can regrettably not qualitatively be stated (see appendix A).

A total amount of $6.5 \times 10^{-5}$ mol hydrogen was measured for run #151. For interpretation refer to 6.4.1.

5.5 1st step with carbon at the solar simulator

Figure 35 shows on the left axis the weight loss of the sample due to the reaction and on the right axis the temperature measured with a thermocouple in the front of the cavity close to the window. Regrettably the relevant temperature in the reaction zone is not being measured, the temperature indicated is just useful as a guideline. Furthermore the right axis shows the carbon releases by the reaction measured by the GC in form of CO and CO$_2$. Thermodynamic analysed do solely predict CO but as there is a little bit of oxygen due to leakage the CO can easily oxidise to CO$_2$. 
The cavity has to slowly be heated up by switching on one after the other lamp in order to minimise thermal stress, therefore the real reaction starts no more than around 40 minutes after the beginning. The release of CO within this time of heating up is nothing else then burning of the carbon from the sample with the oxygen from leakage. Note that the volatiles contained in the charcoal are responsible for the slight loss of weight within the first minutes. At the temperatures reached (highest measured temperature 1800°C and then the thermocouple was disabled) the sample needed about 30 min to totally react.

Table 8 gives a summary of the run performed.

<table>
<thead>
<tr>
<th>variable</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>theoretical maximum yield (see 4.6)</td>
<td>86.3 %</td>
</tr>
<tr>
<td>initial mass of sample</td>
<td>2.343 g</td>
</tr>
<tr>
<td>final mass of sample</td>
<td>1.522 g</td>
</tr>
<tr>
<td>total release of CO</td>
<td>$8.24 \times 10^{-3}$ mol</td>
</tr>
<tr>
<td>total release of CO$_2$</td>
<td>$3.83 \times 10^{-2}$ mol</td>
</tr>
<tr>
<td>yield from weight loss</td>
<td>86 %</td>
</tr>
<tr>
<td>yield from CO / CO$_2$ balance</td>
<td>91 %</td>
</tr>
</tbody>
</table>

Table 8: Mass balance solar simulator

The achieved yield from weight loss calculated with eq.(7) of 86% and the achieved yield from the mass balance of 91% conducted with the aid of eq.(8) are in excellent agreement with the theoretical calculated maximum yield of 86.3% (see 4.6). The releases of CO and CO$_2$ are achieved by integrating the corresponding flows from $t = 21$ min. All assumption not stated here are the same as used for the mass balance for the image furnace in 5.4. A total of 0.013 mol hydrogen was released. For interpretation refer to 6.4.1.

Figure 36 shows the reaction chamber with the sample holder (aluminium oxide) and the sample.
The sample leaving the reaction chamber was a chapped quite tough pillow. The outermost mantle part was bright pink whereas the inner part was white. Both parts were analysed by XRD and SEM combined with EDX.

The heart of the pillow consists mainly of AlN. Additionally, XRD analysis showed some traces of Al$_{2.667}$O$_4$. SEM pictures show that AlN is growing in the amorphous form of particles and in the form of filaments. The AlN particles appear in the same size as the original Al$_2$O$_3$. Almost no oxygen was detected in the inner part of the pillow.

The outermost mantle part of the pillow consisted of a mixture of the original Al$_2$O$_3$ and AlN with a yield of 9% measured by XRD. Figure 37 gives an idea about how this looked like in detail. The bigger roundished original Al$_2$O$_3$ particles are the main part of this section and the filaments, identified by EDX to be AlN, are in minor quantity.

During heating up the carbon at the surface of the pillow was burned and by reaching the reaction temperature this carbon was missing. This presumption can be confirmed by the observation of a declining oxygen concentration and the detection of CO during this period. For a reactor design oxygen leaks have to be minimised and carbon has to be provided in small excess in order to accomplish a yield of 100%.
Gaseous metals or oxides tend to condense at the first cold surface they meet along their pathway. Powder collected directly at the exit of the reaction chamber as well as material collected by the filter turned out to be a mixture of Zn and ZnO. The reduction of ZnO to Zn performed in previous runs in the solar simulator lead to deposits of its reactants and products within the cavity which release by heating up. Figure 38 depicts the XRD spectra of the powder collected at the inner part of the filter consisting solely of Zn and ZnO.

Figure 38: XRD spectra of the inner part of the filter
6. Reactor design

The task to design a (simple) solar reactor could itself be the topic of a whole master thesis. Palumbo et al. [43] illustrate an iterative process for designing solar thermal chemical reactors. In order to speed up this iterative process and to benefit from earlier experiences a literature review on existing solar reactors was done accompanied by discussions with qualified solar reactor designer such as Prof. Aldo Steinfeld, Lothar Schunk, Daniel Gstoehl or Christian Wieckert. The projects with existing reactors considered together with their publications and the most important features are the following:

- hydrogen production by steam-gasification of petroleum coke [44] and [45], steam gasification of charcoal [46]:
  directly irradiated fluidized bed in a quartz tube, beam down, maximum working temperature 1200°C
- solar carbothermic reduction of ZnO [47], heat transfer model of the reactor [48]:
  two-cavity reactor (indirect irradiation), beam down, maximum working temperature 1300°C
- co-production of zinc and synthesis gas [49]:
  SynMet: directly irradiated gas-particle vortex flow, also together with CPC, maximum operating temperature 1327°C
- solar-thermal production of Zn [50]:
  SLOPE: direct irradiation, use of ZnO as reactant and insulator, temperatures up to 2100°C
  ROCA [51]: rotating conic cavity, secondary concentrator
  ZIRRUS: decoupled arrangement of ZnO as absorber, reactant and insulator, implementation of a diffusion barrier, temperatures around 1700°C
- thermal decomposition of calcium carbonate [52]:
  atmospheric-open cyclone solar reactor, designed for solid-gas reactions, temperature limit of the walls 1260°C
- solar production of lime [53]:
  indirect-irradiated multi-tube rotary reactor, temperature limit absorber tubes 1600°C

This overview already points out that overcoming of the temperature restrictions will be one of the most challenging features. The only existing project that also had to deal with this problem is the solar-thermal production of Zn. Reto Müller [50] describes very well the conclusions of the different steps leading to the present ZIRRUS reactor.

6.1 Conception

The huge number of requirements and wishes to the new reactor were collected, the most important ones sorted out and evaluated leading to the conception process presented in table 9. In this table, f stands for fixed constraints to be fulfilled where d are desires or wishes. The input power of 5kW was the first compulsory constraint, given in the definition of the thesis. Together with an assumed efficiency of 30% and the calculated enthalpy change of 1148 kJ/mol (3.2.1) this leads to 0.13 g Al$_2$O$_3$/s continuous feed or to a sample of 8 g Al$_2$O$_3$ at an irradiation time of 60s in a discontinuous mode. The second constraint defined by the tight schedule of this thesis was to use the existing casing of the rectangular cavity and to adapt the layout of the cavity and the setup to these restrictions. The affinity in the requirements of the reactor design from Giacomo Albisetti (carbothermal reduction of MgO) and my project afforded a very good collaboration.

A continuous reactor would be desirable for a further scale-up but for first runs in order to prove the concept a simple design is indispensable. Purge gas for keeping the window clean is indispensable although there are no condensable gases but the natural convection due to the immediate density jump by heating up from ambient to 1800°C
can easily carry small charcoal particles up to the window (observed at image furnace, see 4.4). In order to provide
greatest contact area between the Al$_2$O$_3$ particles, the C and the nitrogen flow a fluidized bed would be best. But it
is a big deal to stabilize a fluidized bed under direct irradiation leading to huge temperature and density gradients.
Additionally one parameter to be investigated with this reactor is the particle sizes of alumina and coal. For a flu-
idized bed the particle size is restricted to be more than 0.2mm. Another solution for providing more contact area
would be to stir the sample, leading to a much more complicated design of the cavity.

<table>
<thead>
<tr>
<th>#</th>
<th>specification</th>
<th>value / function</th>
<th>f/d</th>
<th>background</th>
<th>impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>input power</td>
<td>5 kW</td>
<td>f</td>
<td>definition of thesis</td>
<td>0.13 g Al$_2$O$_3$/s</td>
</tr>
<tr>
<td>2</td>
<td>reactor type</td>
<td>batch</td>
<td>f</td>
<td>simplicity</td>
<td>operation of cycle after cycle</td>
</tr>
<tr>
<td>3</td>
<td>sample size</td>
<td>order of g</td>
<td>f</td>
<td>consequence of #1 and #2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>beam direction</td>
<td>beam down</td>
<td>f</td>
<td>experiments in ETH simulator</td>
<td></td>
</tr>
</tbody>
</table>
| 5  | beamline                   | direct irradia-
|    | tion                      | f   | temperature requirement, less thermal variation in stress | window protection necessary                  |
| 6  | window protection          | keep clean       | f   | preserve transmissivity                                | purge gas                                   |
| 7  | bed                        | fluidized / fixed| d   | enlarging gas-solid contact                            | regulation of gas flow                      |
| 8  | particle size reactant     | variable         | d   | investigate particle size dependence                   | restricts gas flow in a fluidized or a fixed bed |
| 9  | fluid flow direction       | perpendicular to beam | d | increased heat transfer, fluid passes focal point     |                                             |
| 10 | reactions                  | reduction & hydrolysis | f | request                                           | operation at two different temperature levels required |
| 11 | T reduction                | 1700-2000°C      | f   | reaction kinetics, see 5.2                           | choice of construction materials            |
| 12 | T hydrolysis               | 900-1100°C       | f   | reaction kinetics, see [13]                          |                                             |
| 13 | power input hydrolysis     | autothermic      | f   | request                                               | elaborated time management for hydrolysis to meet required temperatures |
| 14 | casing                     | gas tight        | f   | controlled gas fluxes desired                         |                                             |
| 15 | construction materials     | conventional     | d   | delivery time and costs                               |                                             |

Table 9: Conception process

For the different possible construction materials first thoughts were made in table 10. Glassy carbon (as used in the image furnace, 4.1) and quartz are a priori not feasible.

<table>
<thead>
<tr>
<th>material</th>
<th>objection</th>
<th>price</th>
<th>machinability</th>
<th>disjunction of materials</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sintered Al$_2$O$_3$</td>
<td>M.P. relatively low</td>
<td>ok</td>
<td>ok</td>
<td>may affect mass balance</td>
<td>2054</td>
</tr>
<tr>
<td>SiC</td>
<td>high heat conduction</td>
<td>high</td>
<td>bad</td>
<td>-</td>
<td>2700</td>
</tr>
<tr>
<td>sintered ZrO$_2$</td>
<td>possible reduction to Zr</td>
<td>ok</td>
<td>ok</td>
<td>XRD-peak conflict with reactant (see 4.4)</td>
<td>2710</td>
</tr>
<tr>
<td>quartz (SiO$_2$)</td>
<td>temperature resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glassy carbon</td>
<td>reaction with water vapour from hydrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10: Comparison of construction materials

Friatec (www.friatec.de) offers ZrO$_2$ for maximal temperature of use of 1500°C which is not enough for an appli-
cation in the focus. For this function, the raw material Al23 from Friatec met our requirements best. Table 11 gives
an overview of its principal properties.
The material for insulation of the cavity was selected to be alumina insulation type SALI (product number A18015: 18in. width x 24in. length x 2in. thickness) from Zircar Ceramics (www.zircarceramics.com). Its properties are given in table 12. The plate was cut with a knife.

Table 11: Properties of Al23 from Friatec (www.friatec.de)

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>Al2O3</td>
</tr>
<tr>
<td>density</td>
<td>3.7-3.95 g/cm³</td>
</tr>
<tr>
<td>maximal working temperature</td>
<td>1950°C</td>
</tr>
<tr>
<td>specific heat 20°C</td>
<td>900 J/kg K</td>
</tr>
<tr>
<td>thermal conductivity 100°C</td>
<td>30 W/m K</td>
</tr>
<tr>
<td>coefficient of expansion 20-1000°C</td>
<td>8.5•10⁻⁶ / K</td>
</tr>
</tbody>
</table>

Table 12: Properties of insulation type SALI from Zircar Ceramics

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>80% Al₂O₃, 20% SiO₂</td>
</tr>
<tr>
<td>density</td>
<td>0.48 g/cm³</td>
</tr>
<tr>
<td>maximal working temperature</td>
<td>1700°C</td>
</tr>
<tr>
<td>melting temperature</td>
<td>1870°C</td>
</tr>
<tr>
<td>specific heat</td>
<td>1047 J/kg K</td>
</tr>
<tr>
<td>thermal conductivity 1400°C</td>
<td>0.39 W/m K</td>
</tr>
<tr>
<td>coefficient of expansion 20-1100°C</td>
<td>8.0•10⁻⁶ / K</td>
</tr>
<tr>
<td>linear shrinkage 24hrs at 1700°C</td>
<td>3%</td>
</tr>
</tbody>
</table>

First calculations and discussions pointed out that a fluidized bed would be too complex to realize within the given time and would additionally lead to undesirable constraints in the particle size of the reactant. Therefore a fixed bed was chosen.

Different concepts for arrangement and placing of the sample in the cavity were evaluated and discussed. The idea of an irradiated tube of the Al23 described above was promising because the flow would surround the sample. Although one point of the conception process was to have direct irradiation, one run with a closed tube was performed. The tube broke very early during heating up due to thermal stress. It was decided to cut a window in the upper part of the tube to let the radiation directly in. In order to fix the dimensions of this window the comparison with three different dimensions shown in figure 39 was performed leading to the election of the first option. The power and fluxes were calculated using the program “Simple Flux” at the flux measurement computer of the high-flux simulator at ETH following the idea of Melchior [54]. The underlying assumption was to vertically stay in the focal plane during experiment. As mentioned before the tough nut to crack is the temperature requirement. Therefore a first calculation of the temperature in the focal plane was made following the guideline depicted in 4.2.2 with its underlying eq.(25). This resulted in the following equation to be solved for $T_{\text{calc}}$:

$$Q_{\text{rad,in}} \cdot \alpha = 2 \cdot A_w \cdot \varepsilon \cdot \sigma \cdot T_{\text{calc}}^4 + A_w \cdot \bar{H} \cdot (T_{\text{calc}} - T_{\infty}) + 2 \cdot A_{\text{cond}} \cdot k_{Al23} \cdot \frac{T_{\text{calc}} - T_{\text{Inconel}}}{\Delta z}$$

where $Q_{\text{rad,in}}$ is the total input power and $A_w$ the area of the window due to figure 39. The emissivity $\varepsilon$ and the absorptivity $\alpha$ were both set equal 1, the Stefan-Boltzmann constant $\sigma = 5.67051 \cdot 10^{-8}$ W·m⁻²·K⁻⁴, by a conservative approach $T_{\infty}$ was set to 293K, $A_{\text{cond}}$ is the contact area for heat conduction within the crucible equal to $2.16 \cdot 10^{-4}$ m², $k_{Al23}$ the thermal conductivity equal to 30 W·m⁻¹·K⁻¹, $T_{\text{Inconel}}$ an assumed temperature of the Inconel tube of 1300K and $\Delta z$ the extent between $T_{\text{calc}}$ and $T_{\text{Inconel}}$ equivalent to 0.04m. With eqs.(28)-(32) and the properties of nitrogen at
1300K given in section 4.2.2, the mean heat transfer coefficient was calculated to 21.53 W·m⁻²·K⁻¹. Note that outgoing radiation as well as heat conduction is weighted double in order to consider both directions.

<table>
<thead>
<tr>
<th>Window: 60 x 20</th>
<th>current (A)</th>
<th>tot power (kW)</th>
<th>mean flux (10^3 kW/m²)</th>
<th>min flux (10^3 kW/m²)</th>
<th>max flux (10^3 kW/m²)</th>
<th>T_{calc} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.51</td>
<td>1.28</td>
<td>0.95</td>
<td>1.53</td>
<td>1492</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2.2</td>
<td>1.86</td>
<td>1.41</td>
<td>2.18</td>
<td>1672</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>2.85</td>
<td>2.41</td>
<td>1.88</td>
<td>2.76</td>
<td>1807</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>3.86</td>
<td>3.27</td>
<td>2.58</td>
<td>3.67</td>
<td>1979</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: 60 x 20 mm

Sample: 6cm x 1.5cm x 0.5cm = 4.5cm³; 4.5cm³ x 3g/cm³ = 13.5g → ok

Alternative 1 with window of 80 x 20

<table>
<thead>
<tr>
<th>current (A)</th>
<th>tot power (kW)</th>
<th>mean flux (10^3 kW/m²)</th>
<th>min flux (10^3 kW/m²)</th>
<th>max flux (10^3 kW/m²)</th>
<th>T_{calc} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.99</td>
<td>1.27</td>
<td>0.93</td>
<td>1.5</td>
<td>1498</td>
</tr>
<tr>
<td>400</td>
<td>2.89</td>
<td>1.84</td>
<td>1.34</td>
<td>2.18</td>
<td>1677</td>
</tr>
<tr>
<td>500</td>
<td>3.75</td>
<td>2.39</td>
<td>1.82</td>
<td>2.76</td>
<td>1813</td>
</tr>
<tr>
<td>600</td>
<td>5.08</td>
<td>3.24</td>
<td>2.55</td>
<td>3.67</td>
<td>1983</td>
</tr>
</tbody>
</table>

Table 2: 80 x 20 mm

advantage:
- more total power at similar fluxes
- more space for handling

disadvantage:
- powder in the middle may not be reached by the gas flow
- less effect of cavity, more reradiation losses

Alternative 2 with window of 60 x 25

<table>
<thead>
<tr>
<th>current (A)</th>
<th>tot power (kW)</th>
<th>mean flux (10^3 kW/m²)</th>
<th>min flux (10^3 kW/m²)</th>
<th>max flux (10^3 kW/m²)</th>
<th>T_{calc} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.78</td>
<td>1.2</td>
<td>0.73</td>
<td>1.5</td>
<td>1475</td>
</tr>
<tr>
<td>400</td>
<td>2.61</td>
<td>1.75</td>
<td>1.17</td>
<td>2.18</td>
<td>1656</td>
</tr>
<tr>
<td>500</td>
<td>3.41</td>
<td>2.29</td>
<td>1.57</td>
<td>2.76</td>
<td>1794</td>
</tr>
<tr>
<td>600</td>
<td>4.64</td>
<td>3.11</td>
<td>2.2</td>
<td>3.67</td>
<td>1966</td>
</tr>
</tbody>
</table>

Table 1: 60 x 25 mm

advantage:
- more total power at similar fluxes
- more space for handling

disadvantage:
- less effect of cavity, more reradiation losses

Figure 39: Comparison of different dimensions for the window of the crucible

The crucible was made out of a tube of Al23 with a diamond cutting device following the draft in figure 40. Inconel tubes connected the crucible at both sides to the gas flow. Inconel stands for an austenitic nickel-based superalloy with melting point at 1400°C. These tubes were pluged to the reactor wall with Swagelok connections in order to guarantee tightness. Inside the reactor they were connected to the crucible with a handmade plug out of the insulation type SALI.
In figure 41 the reactor with its insulation and the crucible described above are sketched together with the arc and its radiation cone. Note that the opening of the tube-like crucible coincide with the focal plane of the lamp in order to make use of the maximum radiant flux density. This was achieved by drilling a second pair of wholes in the reactor wall.
Figure 41: Lateral draft of the reactor with the radiation cone

A reactor itself is not able to run experiments, it needs a lot of peripheral components and connections to the existing setup and data acquisition. The claim to employ reduction and hydrolysis within one reactor complicated the design of the peripheral components. The final version of the flowchart is presented in figure 42. Blue colour is indicating reduction, red colour hydrolysis and all the rest is used for both steps. The connections are made with Swagelok.

- The carbothermal reduction needs a controlled amount of nitrogen as a reaction partner. Because of natural convection within the focal point the window needs to be protected by a window purge. This is also nitrogen in order to be able to close the mass balance. The two outlets (one coming from the crucible, one from the window purge) are brought together and directed to the gas analysis unit consisting of a micro fast GC (measuring H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, CO, CO\textsubscript{2}), an Ultramat (fast detecting of O\textsubscript{2}, CO, CO\textsubscript{2}, CH\textsubscript{4}) and a Calomat (fast quantifying of H\textsubscript{2}).
Hydrolysis needs a gas input consisting of steam in a carrier gas. This carrier gas was chosen to be argon. The advantage of argon in comparison to nitrogen is that it is possible to measure nitrogen coming from the dissociation of ammonia. The steam generator unit consists of a pressurised tank of distilled water, a liquid flow meter, a gas flow meter, the steam generator itself and a control unit to set steam temperature and water flow. A three-way valve makes it possible to feed the reactor either from the reduction or the hydrolysis path. In order to continue cooling the window an argon window purge is needed.

At the exit the detection of ammonia already run at the Semesterarbeit of Marketos and Tanic [13] was used. Again a three-way valve permitted to switch gas outlet either directly to the gas analysis unit for reduction or to the titration step for hydrolysis. The detection of ammonia by two parallel titration channels is well explained by Marketos and Tanic [13]. After titrating the gas is fed to the gas analysing unit.

By operating with steam all pipes have to be maintained at temperatures above 100°C in order not to let water condense. This can be achieved by fixing a heating coil along all tubes and connections and wrapping it with an insulation band.

The pressure measurement and the overpressure valve were the same for both reactions as well as the temperature measurement consisting of four thermocouples type K and one thermocouple type S. The thermocouple type S, introduced through the Inconel tube and protected by a small cylinder of Al23, was first put directly under the reactant. But as the maximum working temperature of this device is limited by the melting point of platinum (1772°C) it had to be backtracked to a colder region about 8cm away from the focal point. It therefore indicates not the real temperature in the reaction zone but gives an idea about the gradient. One thermocouple type K was at the gas inlet, one at the outlet of the reactor, one was at the bottom of the reactor in order to get an idea of temperatures exterior the insulation and one was mounted at the three-way valve of the titration step. If at this point gas temperature is still warmer than 100°C no condensation can occur over the whole piping system.

Figure 42: Flowchart ammonia reactor; blue indicates reduction, red hydrolysis
6.2 Implementation

Figures 43 and 44 show the realisation of the conception described in the chapter above:

- a) steam generation controlling unit for setting steam temperature (°C) and water flow (g H₂O/h)
- b) steam generator unit
- c) liquid flow controller for water flow
- d) pressurized water tank containing distilled water for steam generation
- e) water filter
- f) 3-way valve serving as inlet switch to select either reduction or hydrolysis inlet path
- g) reactor inlet
- h) reactor outlet
- i) overpressure valve
- j) 3-way valve serving as outlet switch to select either reduction or hydrolysis outlet path
- k) thermocouple type K for temperature control of the heating coil and the insulation
- l) 3-way valve serving as switch between the two titration channels
- m) Erlenmeyer flask containing 25 ml aqueous solution of hydrochloride acid for titration
- n) 2-way valve for closing the channel during removal of the Erlenmeyer flask
- o) cold water for cooling the solution in the flasks
- p) pressure gauge

Figure 43: Picture of the whole setup of the ammonia reactor
The insulation was cut and fitted with knife and rasp following figure 41. The crucible could easily be cut with the diamond cutting device applying a flow of distilled water for cooling purpose. Figure 45 shows a top view of the reactor with the first setup described above. The black powder is the reactant where the small tube directing into the reactant is the Al23 cylinder protecting the thermocouple from direct irradiation.
6.3 Experimental at high-flux simulator ETH

After a test run without irradiation in order to test the steam generator unit the setup was ready to be run. Data acquisition was arranged following table 13. Note that reactor inlet and outlet denomination for temperature is interchanged. During each run a file with data points for every second was produced in order to reconstruct the experiments. The user interface of the delfin data acquisition program was saved in the file “delfin_oberflaeche_new.grf” what can be found on the data compact disk of this report. The method for the GC “oil_res_gasiﬁcation.met” can be found in the same folder. Data of the GC for \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CO} \) and \( \text{CO}_2 \) collected approximately every 100 seconds were written in another file. One has to bear in mind that GC is analysing an averaged sample for the whole sampling time where the time denoted in the data file represents the beginning of the pumping.

<table>
<thead>
<tr>
<th>Channel</th>
<th>naming data acquisition (unit)</th>
<th>meaning for ammonia reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>T cavity ( ^\circ\text{C} )</td>
<td>T in focus (first runs) respectively 5cm away from focal point (later)</td>
</tr>
<tr>
<td>9</td>
<td>T reactor outlet ( ^\circ\text{C} )</td>
<td>T reactor inlet</td>
</tr>
<tr>
<td>8</td>
<td>T reactor inlet ( ^\circ\text{C} )</td>
<td>T reactor outlet</td>
</tr>
<tr>
<td>7</td>
<td>T outlet switch ( ^\circ\text{C} )</td>
<td>T outlet switch to set reduction or hydrolysis for outlet gas</td>
</tr>
<tr>
<td>1</td>
<td>T reactor bottom ( ^\circ\text{C} )</td>
<td>T reactor bottom outside the insulation</td>
</tr>
<tr>
<td></td>
<td>pressure in ( \text{mbar} )</td>
<td>pressure at outlet of reactor</td>
</tr>
<tr>
<td></td>
<td>Gas CO</td>
<td>CO measurement Calomat</td>
</tr>
<tr>
<td></td>
<td>Gas ( \text{CO}_2 )</td>
<td>( \text{CO}_2 ) measurement Calomat</td>
</tr>
<tr>
<td></td>
<td>Gas ( \text{O}_2 )</td>
<td>( \text{O}_2 ) measurement Calomat</td>
</tr>
<tr>
<td></td>
<td>Gas ( \text{H}_2 )</td>
<td>( \text{H}_2 ) measurement Ultramat (out of order)</td>
</tr>
</tbody>
</table>

Table 13: Data acquisition settings high flux simulator ETH

Gas flow applied is denoted in table 14. For the tests with reduction and hydrolysis the two purge lines are fed together. For hydrolysis argon is applied in order to be able to detect nitrogen resulting from the dissociation of ammonia.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Gas</th>
<th>Description</th>
<th>Reduction (l/min)</th>
<th>Hydrolysis (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{N}_2 )</td>
<td>direct</td>
<td>0.7 (until 19.3.07: 1)</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{N}_2 )</td>
<td>purge 1</td>
<td>3 (until 19.3.07: 4)</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ar</td>
<td>steam generator</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Ar</td>
<td>purge 2</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 14: Gas flow high flux simulator ETH

Temperatures of the heating pipe and the steam generator were both set to 200°C. For hydrolysis the specification of a total flow of 1 l/min with 80% of steam leads to the specific flows of 0.2 l/min argon and 35.32 g \( \text{H}_2\text{O}/\text{h} \). The switching between reduction and hydrolysis is a picky point because it has to be done very fast and in the right sequence. Therefore the sequence attached in C.1 was written. After carbothermal reduction the power of the arc is reduced such that the temperature stays constant. Within this time channel 2 is set to zero and channel 4 to 3 l/min Ar, where channel 1 is set to zero as well. Theoretically one should wait now until gas measurement solely shows argon and no nitrogen anymore, practically this needs a lot of time and therefore we proceeded by still observing nitrogen in the reactor. Therefore it was not possible to detect dissociation of ammonia. After the lamp is shut down the electrodes have to be grounded, the 3-way valve of the inlet gas flow has to be switched, then the flow of chan-
nel 3 has to be set to 0.14 l/min Ar, the hydrolysis path left has to be opened, the 3-way valve of the outlet gas flow to be switched to hydrolysis output and last but not least the water flow feeding the steam generator has to be set to 35.32 g water/h.

Reactant was always fed in a stoichiometric (following $C_n$) molar mixture of 1:3.63. Refer to 4.4 for the description of the raw materials, the procedure of milling and a characterisation of the reactant. The crucible was weighted with and without reactant/product before and after the experiments to facilitate calculation of the reaction extent via weight loss (see 3.1). Unfortunately this was not successful because some powder was always blown away by the gas flow.

The first setup described above did not withstand the experiment. The crucible of figure 40 broke into several pieces and the Inconel tubes totally melted resulting in losing the reactant and the thermocouple being directly irradiated after the destruction of the crucible. The adaptation of the reactor and the lesson learned consisted of mainly three points:

- The Inconel tubes were shortened to end within half way of the Zircar insulation. Al23 tubes connected to these Inconel tubes were placed within the cavity.
- Closed structures of Al23 turned out not to withstand the immense thermal stresses during heating up within the focal zone. Therefore the Al23 tube was firstly axially cut into two (later on into three) pieces and secondly shortened to 90mm. It was placed on a crucible support formed out of the Zircar insulation.
- The ceramic tube (unknown material) supporting the crucible was removed in order to eliminate the over-determination of the forces acting at the crucible. From this point on only Al23 was used as construction material within the cavity because it proved to be resistant.

Figure 46 shows the revised setup of the reactor used for all the experiments. One can observe that the outermost layer of the Al23 was melted indicating that the maximal working temperature of 1950°C was reached. In order not to melt the tubes of the incoming and outgoing gas flows, protective shields made out of zirconium oxide felt were applied (see figure 47). It is indispensable to heat the felts out ($T > 900\degree$C) prior to first use in order to remove carbon compounds which could otherwise affect the CO balance of the reaction. As it can be made out in figure 47 depicting the glowing reactor after an experiment, the bottom of the reactor was also protected with an identical felt against parts falling off.
Four runs investigating solely carbothermal reduction and two complete runs including hydrolysis were performed. The copper cap fixing the window was simultaneously used for this experiment and another one producing carbon. It was not possible to completely remove all carbon from this part, therefore closing the mass balance mostly failed due to CO formed out of carbon coming from this fouling. Nevertheless after a few experiments most of this fouling was gone and the only carbon source was the carbothermal reduction.

6.4 Results and discussion at high-flux simulator ETH

The insulation (Zircar) turned out to be a very good choice, temperatures measured at the bottom of the reactor directly outside the insulation were in the order of 60°C. Overpressure at the outlet of the reactor was always around 34 mbar. During hydrolysis all temperatures measured were significantly above 100°C what made condensation impossible. As mentioned above, the reaction temperature itself was not measured. The temperature indicated is just useful as a guideline for the temperature gradient. In fact maximum temperature for each experiment was around 2000°C what can be proved by melting of the Al23.

Figure 48 plots the CO and CO2 measurements from GC and Ultramat. The methods coincide in the gradient but the values of the GC are permanently higher than the ones of the Ultramat. By testing both devices with calibration gases GC turned out to be more reliable, therefore GC data were used for closing mass balances. The characteristic humps in the CO release can be explained in terms of layer growing: First the outermost layer of the cluster of alumina reacts to aluminium nitride. This thin layer of aluminium nitride acts now as insulation and the reactant lying under this cover is shielded, not reaching the desired temperature anymore. By increasing the input power reaction temperature at the reactant is reached, reaction takes place attested by CO release and another insulating layer of aluminium nitride is formed.
6.4.1 Hydrogen release

Chemically no hydrogen can be produced by the reaction. Nevertheless for the run at the 13.03.07 totally 0.026 mol H₂ were released. Hydrogen production was also observed for the termogravimetric runs, the experiments at the image furnace as well as during the experiments at the solar simulator at PSI.

There are two possible sources for hydrogen: Firstly the activated charcoal consists of 82.7% C₇. The rest are carbon or other compounds that can release hydrogen by decomposing. Secondly water dissociation is occurring in the focal point. Following figure 49 about 1 molar-% of water can be dissociated at 2000K.

Figure 49: Molar fraction of species for the dissociation of water at thermodynamic equilibrium as a function of temperature at a pressure of 1bar [55]
But where is water coming from? Firstly it can come from the reactant where the activated charcoal as well as the aluminium oxide is able to store water. And secondly it can come from the insulation materials in the reactors (in the case of the solar simulator at PSI and the high flux simulator at ETH). Figure 50 depicts the adsorption capacity of commercial alumina. At 40% relative humidity alumina is able to adsorb 10 weight-% of water what corresponds to 57 mol-%. By leaving the reactor open during night, a considerable amount of water can be stored within the insulation.

Figure 50: Static water adsorption capacity of typical commercial activated aluminas at 25°C [4]

Table 15 summarizes the different sources of hydrogen for all the experimental setups used in this work. The fractions of hydrogen resulting from the different sources can not exactly be stated. But doubtless hydrogen resulting from chemical compounds and humidity of the reactant scale with the initial mass of reactant. For the run at the solar TG the reactant was dried out at 180°C during night and therefore no humidity was assumed. The ammonia reactor tested at the high flux simulator at ETH has much more insulating alumina close to the focus where water can be stored. At the solar TG first layers of insulation consist of ZrO$_2$. On the other hand water in the solar TG is likely to react with Zn deposited from earlier experiments to form hydrogen. Beside this, after the experiments of carbothermal reduction with the ammonia reactor at ETH some water could be detected within the tubes from the reactor to the gas measurement unit. By solely conducting carbothermal reduction the tubes are not heated and water coming from the insulation within the reactor can easily condense on the pathway to the gas measurement unit where temperatures are surely less than 100°C.

<table>
<thead>
<tr>
<th>setup</th>
<th>reactant (mg)</th>
<th>totally measured H$_2$ (mol)</th>
<th>hydrogen resulting from</th>
<th>humidity reactant</th>
<th>Al$_2$O$_3$ insulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG</td>
<td>100</td>
<td>9.9·10$^{-5}$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>image furnace</td>
<td>5</td>
<td>6.5·10$^{-5}$</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>solar TG</td>
<td>2300</td>
<td>0.013</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>high flux simulator</td>
<td>1200</td>
<td>0.026</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Table 15: Sources of hydrogen for the different experimental setups; x indicates possibilities
A quantitative analysis of the hydrogen sources should be done in a further work because hydrogen and carbon monoxide / -dioxide releases are in the same order of magnitude.

6.4.2 Carbothermal reduction

The representative run from the 13 March 2007 is summarized in table 16. Reaction extent via weight loss could not be calculated because of losing particles by the gas stream. Initial mass was 1207 mg.

<table>
<thead>
<tr>
<th>yield (%)</th>
<th>XRD</th>
<th>weight loss</th>
<th>CO / CO₂ balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td></td>
<td>-</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 16: Summary of the carbothermal reduction in the new reactor

Figure 51 shows on the left axis outlet gas concentration in % and on the right ordinate the temperature gradient. In the second phase of the reduction carbon monoxide further oxidises to carbon dioxide. This fact, also observed at the image furnace and at the solar simulator, is thermodynamically not foreseen and should therefore be investigated in a further work. For closing the mass balance, it does not matter whether carbon is released in CO or CO₂. Integrating the CO- and CO₂-releases led to a total carbon discharge of 0.024 mol what resulted in a reaction extent for the first reaction of 96%.

Gas concentrations in figure 51 are based on GC data. It looks like there would be CO release even before temperature is increasing. This is misleading because GC provides data points approximately every 100 seconds and the first data point for CO unequal zero is definitely after turning on the lamp.
Figure 52 depicts the driving profile of the high flux simulator. The current was increased with the aim of obtaining a constant temperature gradient. The mean heat flux was measured using “Simple flux” at the flux measurement computer at ETH for the projected area of the sample (80x20mm).

![Graph of driving profile with arcs and temperatures over time]

**Figure 52: Driving profile of the high flux solar simulator at 13.03.07**

XRD analysis of the product was done at PSI. The upmost white part of the product was a little bit sintered and analysed to be composed of 96% aluminium nitride and 4% of the original aluminium oxide. The bottom layer of the sample was grey (containing small amounts of carbon) and showed also 96% of reaction extent. An averaged value of the yield was determined by mixing the whole sample leading to a value of 97% which is in very good agreement with the 96% obtained by closing the mass balance.

6.4.3 Complete cycle

The run of the 21st March 2007 presented in figure 53 and summarized in table 17 was done with an initial mass of 706 mg.

<table>
<thead>
<tr>
<th>reaction extent</th>
<th>XRD</th>
<th>titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrolysis (%)</td>
<td>12</td>
<td>10</td>
</tr>
</tbody>
</table>

**Table 17: Summary of the complete cycle in the new reactor**

The conditions for the carbothermal reduction are the same as described in 6.4.2. After 27.4 min the lamp power was reduced such that the gas flows could be switched at constant temperature. At 38.5 min the arc was shut down, the procedure described in C.1 commenced and within approximately one minute hydrolysis was started.
Unfortunately the reaction extent for the first reaction could not be measured by a CO / CO\textsubscript{2} balance because there was too much carbon release from the copper cap like described in 6.3. For further calculations the yield of the carbothermal reduction was assumed to be 100% viz by starting hydrolysis the sample consisted of 100% aluminium nitride which was obtained in previous runs.

![Graph showing concentration vs. time](image)

**Figure 53: Complete cycle run in the ammonia reactor at 21.03.07**

As described in 6.3 the dissociated ammonia could not be measured, ammonia was only measured by titration. One impinger was applied for the whole hydrolysis starting at 1111°C, lasting 10 min and ending at 569°C. Note that temperature measurement for hydrolysis by no external heat input is accurate because there is no focal zone. The temperature gradient of reactor cooling is in between 100 K/min at the beginning and 28 K/min at the end of the hydrolysis. For only two and half a minute the reactor was in the optimal temperature range of hydrolysis above 900°C [13].

Back titration showed that 0.8 ml of HCl were gone meaning that 0.8 mmol of NH\textsubscript{3} had been captured by the impinger. For calculation of the reaction extent of hydrolysis the total number of aluminium nitride after reduction is needed. By assuming 100% conversion of the first step 9.7 mmol AlN would have been in the reactor. Back calculations by means of measuring the product at the end of the whole cycle resulted in 6 mmol of AlN before hydrolysis. The difference comes from blowing particles away by the gas flow during both reactions. A mean value of 7.85 mmol AlN is taken as input for eq.(9) resulting in 10% reaction extent for the hydrolysis.

**XRD analysis of the totally white product was done**: The upmost part of the sample showed a yield of 26% for the second step where the bottom layer of the product purely consisted out of aluminium nitride. An averaged value of the reaction extent of hydrolysis was determined by mixing the whole sample leading to a value of 12% which is in good agreement with the 10% obtained by titration. No other species like oxynitrides were found.
6.4.4 Carbothermal reduction using air

Based on thermodynamic calculations of M. Halmann from the Department of Environmental Sciences and Energy Research at the Weizmann Institute of Science in Israel the carbothermal reduction proposed in eq.(2a) is likely to run also in air instead of nitrogen. The benefit would be the avoidance of the energy intensive nitrogen separation.

For this reaction a very fast heating up with a steep temperature gradient is indispensable in order to reach reaction temperature before all the carbon already reacted away with the oxygen. Therefore the conventional TG with heating rates of around 20 K/min is no option.

A first run with a double stoichiometric mixture was carried out at the image furnace at PSI by Alwin Frei. XRD analysis proved that all the carbon was just burned with the oxygen from air and no aluminium nitride was produced.

The experimental setup and the conditions for the run conducted in the ammonia reactor at the 22.03.07 were exactly the same as described in 6.3. The only difference was the application of air at all channels instead of nitrogen. Figure 54 visualizes the run. The bend in the temperature curve results from a failure in the lamp which forced us to shortly interrupt the experiment.

Figure 54: Carbothermal reduction in air performed at 22.03.07

Regrettably the mass balance could no be closed by means of a CO / CO₂ balance because there was too much carbon release from the cupper cap like described in 6.3.

Figure 55 illustrates the crucible after shutting down. It was not possible to collect particles for XRD because the entire sample was completely melted. The additional heat input of the combustion of coal (adiabatic flame temperature around 2000K) raised the temperature within the reaction zone to more than the melting point of aluminium oxide at 2046°C.

For a further attempt to prove the theoretical calculations by Prof. Halmann one has to be able to diminish the temperature in the reaction zone. This can either be done by applying less heat input by the arc or by applying
more air flow resulting in a higher cooling rate within the focus. With the current setup it is disappointingly not possible to raise fluid flow because of blowing away the sample.

Figure 55: Picture of the crucible after carbothermal reduction in air

6.5 Energy balance

The results of energy balances performed and detailed in the subsequent chapter are summarized in table 18.

<table>
<thead>
<tr>
<th></th>
<th>$\eta_{\text{total}}$ (%)</th>
<th>$\eta_{\text{reaction}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbothermal reduction</td>
<td>3.7</td>
<td>0.15</td>
</tr>
<tr>
<td>complete cycle</td>
<td>4.2</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 18: Summary of efficiency calculations ammonia reactor

6.5.1 Carbothermal reduction

A simple energy balance with the goal of calculating a solar energy conversion efficiency is done in figure 56. Data of the run from the 13.03.07 presented in 6.4.2 are used where for integration purpose the run was finished by switching off the lamp at 30.4 min what gives a total experimental time of 22.4 min. Gas exit temperatures for calculation purpose are a mean value of real exit temperatures during the whole run.
The enthalpy $H_i^T$ at temperature $T$ of species $i$ is defined as follows:

$$H_i^T = n_i \left[ h_0^i + \int_{298}^{T} c_p^i(T) \,dT \right] \approx n_i \left[ h_0^i + c_p^i \left( \frac{298 + T}{2} \right) \cdot (T - 298) \right]$$  \hspace{1cm} (38)

where $n$ is the number of moles, $h_0$ the enthalpy of formation at 298K and $c_p(T)$ the heat capacity as a function of temperature $T$. The integral can be approximated by the mean value of $c_p$ in the desired temperature range.

Tables 19 and 20 illustrate calculations of the enthalpy for reactants and products [56], [57], [58]. The heat capacities are evaluated at their mean temperatures of 700K except the one of AlN whose mean temperature is 1000K. The change in nitrogen flow during reaction is negligibly small. The reaction extent is rounded to 100% meaning that no carbon is left in the product.

### Table 19: Carbothermal reduction: enthalpy calculation reactants [58]

<table>
<thead>
<tr>
<th>reactant</th>
<th>$T$ (K)</th>
<th>$n_i$ (mol)</th>
<th>$h_0^i$ (kJ·mol$^{-1}$)</th>
<th>$H_i^T$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>298</td>
<td>4.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>298</td>
<td>2.9·10$^{-2}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>298</td>
<td>8.2·10$^{-3}$</td>
<td>-1675.7</td>
<td>-13'740.7</td>
</tr>
</tbody>
</table>

### Table 20: Carbothermal reduction: enthalpy calculation products [56], [57], [58]

<table>
<thead>
<tr>
<th>product</th>
<th>$T$ (K)</th>
<th>$n_i$ (mol)</th>
<th>$c_p^i$ (J·mol$^{-1}$·K$^{-1}$)</th>
<th>$h_0^i$ (kJ·mol$^{-1}$)</th>
<th>$H_i^T$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>1141K</td>
<td>4.7</td>
<td>30.8</td>
<td>0</td>
<td>122'033</td>
</tr>
<tr>
<td>CO</td>
<td>1141K</td>
<td>1.4·10$^{-2}$</td>
<td>31.2</td>
<td>-110.5</td>
<td>-1’178.8</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1141K</td>
<td>9.1·10$^{-3}$</td>
<td>48.5</td>
<td>-393.5</td>
<td>-3’208.8</td>
</tr>
<tr>
<td>AlN</td>
<td>1640K</td>
<td>1.7·10$^{-2}$</td>
<td>48.5</td>
<td>-318.0</td>
<td>-4’299.4</td>
</tr>
</tbody>
</table>

Integration of the mean flux in figure 52 multiplied by the size of the aperture of 80x20 mm results in the total solar heat input $Q_{solar} = 3'437.4$ kJ.
Total solar energy conversion efficiency defined as

\[
\eta_{\text{total}} = \frac{H_{I,\text{products}} - H_{I,\text{reactants}}^{298\text{K}}}{Q_{\text{solar}}} \tag{39}
\]

was concluded to 3.7% for the run of 13.03.07. The reaction efficiency does not include heating up of nitrogen, only the enthalpy changes of Al\(_2\)O\(_3\), CO, CO\(_2\) and AlN are considered. It is computed to 0.15%.

6.5.2 Complete cycle

The energy balance for the whole cycle is presented in figure 57.

As experimentally observed, hydrolysis is assumed to last from 1111°C to 707°C what corresponds to 6 min. The reaction extent of the hydrolysis of 12% is taken from 6.4.3. Heat input during switching from nitrogen to argon which is characterized by the constant temperature in figure 53 is not considered. Calculations of the enthalpy for reactants and products are presented in tables 21 and 22 [56], [57], [58]. All assumptions not stated here correspond to the ones of 6.5.1.

<table>
<thead>
<tr>
<th>reactant</th>
<th>(T) (K)</th>
<th>(n_i) (mol)</th>
<th>(c_P^i) (J⋅mol(^{-1})⋅K(^{-1}))</th>
<th>(h_v^i) (kJ⋅mol(^{-1}))</th>
<th>(H_T^i) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>298</td>
<td>4.7</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>298</td>
<td>2.9⋅10(^{-2})</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>298</td>
<td>8.2⋅10(^{-1})</td>
<td>-</td>
<td>-1675.7</td>
<td>-13’740.7</td>
</tr>
<tr>
<td>Ar</td>
<td>473</td>
<td>8.0⋅10(^{-1})</td>
<td>20.8</td>
<td>0</td>
<td>2’912.0</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>473</td>
<td>1.2⋅10(^{-1})</td>
<td>34.3</td>
<td>-241.8</td>
<td>-28’295.7</td>
</tr>
</tbody>
</table>

Table 21: Complete cycle: enthalpy calculation reactants [58]
Table 22: Complete cycle: enthalpy calculation products [56], [57], [58]

<table>
<thead>
<tr>
<th>Product</th>
<th>T (K)</th>
<th>( n_i ) (mol)</th>
<th>( c_p^i ) (J·mol(^{-1})·K(^{-1}))</th>
<th>( h_0^i ) (kJ·mol(^{-1}))</th>
<th>( H_T^i ) (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>1141K</td>
<td>4.7</td>
<td>30.8</td>
<td>0</td>
<td>122'033</td>
</tr>
<tr>
<td>CO</td>
<td>1141K</td>
<td>1.4·10(^{-2})</td>
<td>31.2</td>
<td>-110.5</td>
<td>-1'178.8</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>1141K</td>
<td>9.1·10(^{-3})</td>
<td>48.5</td>
<td>-393.5</td>
<td>-3'208.8</td>
</tr>
<tr>
<td>Ar</td>
<td>1273K</td>
<td>8.0·10(^{-4})</td>
<td>20.8</td>
<td>0</td>
<td>16'224.0</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>1273K</td>
<td>1.2·10(^{-1})</td>
<td>38.8</td>
<td>-241.8</td>
<td>-24'476.4</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1273K</td>
<td>1.0·10(^{-3})</td>
<td>120.1</td>
<td>-1675.7</td>
<td>-1558.6</td>
</tr>
<tr>
<td>AlN</td>
<td>1273K</td>
<td>1.5·10(^{-2})</td>
<td>46.8</td>
<td>-318.0</td>
<td>-4085.6</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>1273K</td>
<td>2.0·10(^{-3})</td>
<td>51.1</td>
<td>-45.9</td>
<td>7.8</td>
</tr>
</tbody>
</table>

The solar heat input of 3’437.4 kJ remains the same. Total solar energy conversion efficiency is determined to 4.2% whereas the reaction efficiency excluding enthalpy changes of the fraction of gases not participating in the reactions (nitrogen, argon and water vapour) is equal to 0.11%.

A solar energy conversion efficiency of 4.2% for the first run in the first reactor built for this reaction is an acceptable value. This underlines the potential of further work in this subject. Nevertheless this is just a first rough estimate of the efficiency not including energy consumption of the peripheral components such as data acquisition or vaporizer. One could also argue to consider the heating value of carbon in the denominator, to employ the rectangular opening of the insulation as aperture or to exactly integrate enthalpies. This would certainly not change the order of the efficiencies calculated above.

Maximising efficiency will be a subject for further work. The main trade off to consider is the increase in system efficiencies by going to lower temperatures what simultaneously negatively affects the reaction rate.
7. **Conclusion**

After elaborating the temperature and heat flux profile at the image furnace at PSI, experiments identified the activation energy for the carbothermal reduction using activated charcoal to be 363 kJ/mol, based on the kinetic rate law of Jander. Carboreduction using methane was tested at the same site showing up the problem of growing layers of carbon around the alumina particles what hinders nitrogen to reach the reaction zone and thus brings the reaction to an end. Nevertheless reaction extents of 10 and 46% by employing no respectively nickel as a catalyst were reached and the influences of total pressure and methane concentration in the inlet gas have been stated. Using carbon as reducing agent, reaction extent is specified by three independent approaches as depicted in table 23.

<table>
<thead>
<tr>
<th></th>
<th>XRD</th>
<th>weight loss</th>
<th>CO / CO₂ balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>image furnace PSI</td>
<td>74</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>solar simulator PSI</td>
<td>86</td>
<td>86</td>
<td>91</td>
</tr>
<tr>
<td>high flux simulator ETH</td>
<td>97</td>
<td>-</td>
<td>96</td>
</tr>
</tbody>
</table>

**Table 23: Comparison of the reaction extent of the reduction using carbon performed at different sites**

A first upscale from milligrams to grams has successfully been accomplished by the design of the 5kW autothermic reactor. Runs at the high-flux simulator at ETH proved the concept and permitted to solar carbothermal fabricate ammonia out of an autothermic reactor for the first time. The new ammonia reactor showed a solar energy conversion efficiency of 4.2% at achieved spot temperatures of above 1950°C.
8. Recommendations

- Do perform or have a whole life-cycle analysis of the novel cycle made to definitely state its energy- and CO₂-saving potentials. The key point within this analysis will be to find the most adequate further use of the CO.
- Investigate particle size dependence of Al₂O₃ and the different carbon sources. Always keep a future industrial realisation in mind that is unlikely to deal with nano particles because of cost reasons [59].
- Why is it that at all sites CO₂ is produced although thermodynamically only CO is foreseen? Where is this oxygen coming from beside the small amount due to leakage?
- For the new ammonia reactor:
  - Implement temperature measurement in the focus by means of pyrometry.
  - Find optimal fluid flows in order not to blow any particles away.
  - Think about how to provide more time at around 1000°C to complete hydrolysis. The concept of an autothermic reactor may be revised in order to afford further heat input during the second step.
  - Perform more runs by varying different parameters such as carbon source, irradiation time and intensity for the reduction, steam content or temperature level for hydrolysis etc. and study their impact on the target variables (system efficiency, reaction efficiencies and extents of first and second step, operation stability).
  - Try to be able to control the temperature by runs with air instead of nitrogen to learn about its potential.
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>distance</td>
<td>m</td>
</tr>
<tr>
<td>α</td>
<td>absorptivity</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>distance</td>
<td>m</td>
</tr>
<tr>
<td>A</td>
<td>area</td>
<td>m²</td>
</tr>
<tr>
<td>β</td>
<td>coefficient of thermal expansion</td>
<td>1/K</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat capacity</td>
<td>J·kg⁻¹·K⁻¹</td>
</tr>
<tr>
<td>c_species</td>
<td>concentration of species</td>
<td>mol/m³</td>
</tr>
<tr>
<td>d</td>
<td>distance</td>
<td>m</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
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</tr>
<tr>
<td>E_a</td>
<td>activation energy</td>
<td>kJ/mol</td>
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<tr>
<td>ε</td>
<td>emissivity</td>
<td>-</td>
</tr>
<tr>
<td>f_species</td>
<td>fraction of species in the probe</td>
<td>-</td>
</tr>
<tr>
<td>η</td>
<td>efficiency</td>
<td>-</td>
</tr>
<tr>
<td>g</td>
<td>acceleration of gravity</td>
<td>m/s²</td>
</tr>
<tr>
<td>h</td>
<td>convective heat transfer coefficient</td>
<td>W·m⁻²·K⁻¹</td>
</tr>
<tr>
<td>h₀</td>
<td>enthalpy of formation at 298K</td>
<td>J/mol</td>
</tr>
<tr>
<td>H_T</td>
<td>total enthalpy of species at temperature T</td>
<td>J</td>
</tr>
<tr>
<td>∆H₂⁹⁸</td>
<td>enthalpy difference of a reaction at 298K</td>
<td>J/mol</td>
</tr>
<tr>
<td>I</td>
<td>heat flux</td>
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</tr>
<tr>
<td>J</td>
<td>molar flux</td>
<td>mol·m⁻²·s⁻¹</td>
</tr>
<tr>
<td>k</td>
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</tr>
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<td>k_model</td>
<td>constant of model</td>
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<td>M_species</td>
<td>total mass of species</td>
<td>g</td>
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<td>molar mass of species</td>
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<td>-</td>
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<td>ν</td>
<td>kinematic viscosity</td>
<td>m²/s</td>
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<tr>
<td>p</td>
<td>pressure</td>
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<td>perimeter</td>
<td>m</td>
</tr>
<tr>
<td>Pr</td>
<td>Prandtl number</td>
<td>-</td>
</tr>
<tr>
<td>q</td>
<td>specific heat flux</td>
<td>W/m²</td>
</tr>
<tr>
<td>Q</td>
<td>total heat flux</td>
<td>W</td>
</tr>
<tr>
<td>r</td>
<td>radius</td>
<td>m</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant</td>
<td>J·mol⁻¹·K⁻¹</td>
</tr>
<tr>
<td>rms</td>
<td>root mean square error</td>
<td>(different)</td>
</tr>
<tr>
<td>S_r</td>
<td>surface area of sphere with radius r</td>
<td>m²</td>
</tr>
<tr>
<td>σ</td>
<td>Stefan-Boltzman constant</td>
<td>W·m⁻²·K⁻⁴</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
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<tr>
<td>$T_m$</td>
<td>melting temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\theta$</td>
<td>angle in XRD</td>
<td>°</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
<td>inc/s</td>
</tr>
<tr>
<td>$x$</td>
<td>rectangular coordinate</td>
<td>m</td>
</tr>
<tr>
<td>$X_{Al_2O_3}$</td>
<td>reaction extent carbothermal reduction, yield</td>
<td>-</td>
</tr>
<tr>
<td>$X_{AlN}$</td>
<td>reaction extent hydrolysis</td>
<td>-</td>
</tr>
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<td>ratio from XRD-pattern</td>
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<tr>
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</tbody>
</table>
10. Acknowledgement

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The whole staff from the professorship in renewable energy carriers ETH and the solar technology laboratory PSI for discussions and new inputs

The many people who are not mentioned but contributed to this master thesis
11. References

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[50] R. Müller, Reaktor-Entwicklung für die solar thermische Produktion von Zink, Diplomarbeit ETH-Swiss Federal Institute of Technology (2005), Diss. ETH Nr. 16329


[61] M. Haltmann, A. Steinfeld, Aluminum and Syngas Co-Production by Carbothermal Reduction of Alumina Combined with Partial Oxidation of Methane or Coke, in press

12. **Appendix**

A **Calibration of mass spectrometer**

Quadstar 32-Bit (GSD 301) QMS 200 Version 7.02 from 30.11.2004 is the software of the Pfeiffer vacuum Quadrupole mass spectrometer QMS 200 with the product documentation [60].

A calibration first needs some thoughts about which gases should be measured (see A.2). Then for each component to be measured later on one well defined gas (the component to be measured as a known fraction in the carrier gas, see A.1) has to be supplied and measured for calibration purpose. The mixtures were provided by mixing the pure elements with the aid of “Sonymix”, a mixing machine which is also being used for calibrating the GC at PSI.

Note that Balzers, the supplier of the MS, tells it is impossible to measure CO in the carrier gas nitrogen because they have the same masses. Nevertheless a way of doing this (and additionally including methane) is presented. A special thank goes to Juraj Pecho who helped me a lot in this subject.

The error of the measurements after calibrating can not quantitatively be stated here, but one has always to be aware of it.

A.1 **Explanation and method**

The MS needs a carrier gas, the component that makes up the main part of the gas to be analysed. In our case this was nitrogen (molar mass 28). The problem is that CO also has mass 28 and therefore would not be detected separately.

The MS however measures e.g. for O₂ mass 32. With the ion source it besides splits up O₂ into two O⁺. By feeding pure oxygen, masses 32 (O₂) and 16 (O⁺) are therefore measured. The ion current of mass 32 is related 100% to oxygen where the one of mass 16 is only about 16% (meaning that 8% of O₂ is split up into O⁺, leading to 16% O⁺). The factor of 16% is an estimate from [60] and has to be measured and calibrated later on.

Table 24 gives an overview of the crypto fragments resulting of the expected product gas containing H₂, N₂, O₂, CO, CO₂ and CH₄:

<table>
<thead>
<tr>
<th>mass</th>
<th>crypto fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H⁺</td>
</tr>
<tr>
<td>2</td>
<td>H₂⁺</td>
</tr>
<tr>
<td>6</td>
<td>C⁺⁺</td>
</tr>
<tr>
<td>7</td>
<td>N⁺⁺</td>
</tr>
<tr>
<td>8</td>
<td>O⁺⁺</td>
</tr>
<tr>
<td>12</td>
<td>C⁺</td>
</tr>
<tr>
<td>13</td>
<td>CH⁺</td>
</tr>
<tr>
<td>14</td>
<td>N⁺ CH₃⁺ CO⁺⁺</td>
</tr>
<tr>
<td>15</td>
<td>CH₃⁺</td>
</tr>
<tr>
<td>16</td>
<td>O⁺ CH₄</td>
</tr>
<tr>
<td>22</td>
<td>CO₂⁺⁺</td>
</tr>
<tr>
<td>28</td>
<td>N₂⁺ CO</td>
</tr>
<tr>
<td>32</td>
<td>O₂⁺ O₂⁺⁺</td>
</tr>
<tr>
<td>44</td>
<td>CO₂⁺⁺</td>
</tr>
</tbody>
</table>

*Table 24: Relevant crypto fragment ions in MS*
As an example CO₂ can theoretically be detected at the ion currents of masses 44 (CO₂), 28(CO), 22(CO²⁺), 16(O⁺), 14(CO⁺), 12(C⁺), 8(O²⁺) and 6(C⁺). Not all crypto fragments are important, e.g. the fraction of CO₂ split up into CO⁺ is vanishing small and not to be considered. In which fragments elements are actually splitting up can be tested by feeding the gas to be analysed and then executing in the program “Measure” -> scan -> analog -> C:\Q32BIT\PAR\Mess-files\scan0-50.sap where 0-50 stands for analysing only masses between 0 and 50.

Table 24 shows up the main problem: At mass 16 fractions of O₂, CO, CO₂ and CH₄ are measured. The matter of calibrating the MS is to tell it which percentage of the ion current at mass 16 is resulting from CO, which percentage from O₂, CO₂ or CH₄.

One further not considered problem is that the MS always detects some water in the product gas (humidity of the gas and water deposition within MS) which is detected at the masses 18(H₂0), 17(OH⁺), 16(O⁺), 2(H₂) and 1(H⁺). One can reduce this amount by baking the MS (reducing deposition).

A.2 Calibration parameter

Table 25 shows the conclusion of the method described above. Unfortunately pure hydrogen was not available in our laboratory and therefore a known mixture of He and H₂ was used instead. This causes no problems because helium occurs only in mass 4 which is not affected by any other element. The fraction of CO in mass 28 is not considered because the amount of nitrogen will be in the order of 99% and the one of CO around 1000ppm, the same is valid for mass 14. In mass 32 the fraction of O₂⁺ from CO₂ is not considered because it is much smaller then the fraction of O₂.

<table>
<thead>
<tr>
<th>mass</th>
<th>elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>H₂</td>
</tr>
<tr>
<td>4</td>
<td>He</td>
</tr>
<tr>
<td>12</td>
<td>CH₄, CO</td>
</tr>
<tr>
<td>14</td>
<td>CH₄, CO</td>
</tr>
<tr>
<td>15</td>
<td>CH₂</td>
</tr>
<tr>
<td>28</td>
<td>N₂</td>
</tr>
<tr>
<td>32</td>
<td>O₂</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
</tr>
</tbody>
</table>

Table 25: Masses and corresponding elements measured with MS

Four calibration runs are needed to fully calibrate the MS with these settings: One for O₂ in N₂, one for CO₂ in N₂, one for CO and H₂ in N₂ and the last one for CH₄ in N₂. CO and H₂ can be calibrated in the same run because they do not have common crypto fragments in table 24.

The measurement time for one mass is set to 0.1s what leads to a total measurement time for all the 7 masses of less then 1s.

A.3 Software settings

The files created by calibrating with the presented gases are on the CD attached. First a new folder has to be created: C:\Q32BIT\PAR\calibration\nitrogen. For each calibration run (see A.2) one subfolder has to be created and the calibration files (mcd.mcp, gss.gcp, mass.msp and cal.seq) from an older calibration copied into each of them. Now all these calibration files have to be adapted to the new condi-
tions. Open the program “Parset” and execute the following steps for all the calibration runs. The steps are stated for the calibration run of CH$_4$ in N$_2$.

1. open -> measure -> mcd -> C:\Q32BIT\PAR\calibration\nitrogen\CH4\mcd.mcp. This file defines the fraction of the elements in the different fragments. Fill out according to table 26. Leave the numbers in the fields, in all other fields write “0”. The fractions will be adapted during the calibration runs.

<table>
<thead>
<tr>
<th></th>
<th>28</th>
<th>15</th>
<th>14</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ (carrier gas)</td>
<td>1</td>
<td>0</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0</td>
<td>0.8</td>
<td>0</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 26: Adaptation of mcd.mcp for CH$_4$ in N$_2$

Within the same file -> edit -> channel parameter and change in the subfolder mass the measuring time (Dwell) of all to 0.1s.

2. open -> calibration -> gas specific sensitivity -> C:\Q32BIT\PAR\calibration\nitrogen\CH4\gss.gcp. Here you have to declare which elements to consider for the different masses and the composition of the calibration gas. Fill out according to table 27.

<table>
<thead>
<tr>
<th>Component</th>
<th>Conc.</th>
<th>28</th>
<th>15</th>
<th>14</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ (carrier gas)</td>
<td>99%</td>
<td>o</td>
<td>o</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>1%</td>
<td>o</td>
<td>o</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 27: Adaptation of gss.gcp for CH$_4$ in N$_2$

Within the same file -> edit -> channel parameter and change in the subfolder mass the measuring time (Dwell) of all to 0.1s.

3. open -> calibration -> mass-scale -> C:\Q32BIT\PAR\calibration\nitrogen\CH4\mass.msp. This file defines which masses to be measured and the corresponding measuring times. Fill out like done in figure 58.

![Figure 58: Adaptation of mass.msp for CH$_4$ in N$_2$](image)

4. open -> sequence -> editor -> C:\Q32BIT\PAR\calibration\nitrogen\CH4\cal.seq. Reset only the two paths for executing mass.msp and gss.gcp corresponding to where they are saved. Then carry out -> file -> save & compile.

The zerogas has to be defined only once, see [60].
A.4 Routine

1. execute software settings described in 10.1.3 for each calibration run
2. apply calibration gas with composition stated in gss.gcp
3. open program “Measure” and execute the sequence compiled in point 4 in 10.1.3 (for CH₄ in N₂: -> sequence -> execute -> C:\Q32BIT\PAR\calibration\nitrogen\CH₄\cal.sqe)
4. repeat step 2 and 3 for each calibration run
5. create or modify an existing .mcp-file [60] like done for the calibration in point 1 in 10.1.3. but you have to include all the masses and elements you want to measure. The factors are being adapted automatically. Save it to C:\Q32BIT\PAR\Mess-files\myprogram.mcp. Figure 59 illustrates the example file.

![Figure 59: Adaptation of the measuring file myprogram.mcp](image)

A.5 Test and tuning

The calibration described above can be tested by applying a mixture of the gases to be measured in known fractions (test gas). This was done and the result was quite bad, the concentrations measured did not match the ones from the test gas supplier. The explanation is two-folded:

- The concentrations provided by the “Sonymix” are tainted with errors. The conclusion would be to time-consumingly and expensively order test gases for each calibration run with the desired concentration - this was not done.

- The concerns from Balzers, the supplier of the MS, are not unjustified. But tuning the factors in myprogram.mcp can highly improve the measurements. Just apply the test gas, measure it with myprogram.mcp, modify the factors in “Parset” (open -> measure -> mcd -> C:\Q32BIT\PAR\measures\myprogram.mcp) a little bit, measure it with the new myprogramm.mcp and repeat this until the results of the measurements are satisfying. Tip: Air is a good test gas with known composition.

Because no helium will be observed in the product gas, delete He and mass 4 in myprogram.mcp, this leads to a minor error. Also for the runs without methane CH₄ should be taken out of myprogram.mcp. Mass 14 was completely deleted from the measuring program because it just confused.
B Solar carbothermal reduction of alumina to produce elementary aluminium

The aim of this experiment is to trap metallic aluminium in order to provide experimental evidence to the paper of Halmann and Steinfeld [61].

B.1 Theory

The current production of aluminium by the electrolytic Hall-Héroult process is characterised by high energy requirements, the release of perfluorocarbons and vast greenhouse gas emissions. Analogue to the solar thermochemical cycle for ammonia production presented in the main part an alternative less energy-intensive carbothermic reduction of alumina is investigated.

The ideal reaction equation eq.(40) for this process depicts the two main differences compared to the first step of the ammonia cycle, namely the missing of nitrogen (for the reaction an inert gas has to be applied, e.g. argon) and the elevated reaction energy needed.

\[
\text{CO}_32 \overset{323}{\rightarrow} \text{Al}_2 \overset{32}{\rightarrow} \text{CO} \quad \Delta H_{298} = 1344.1 \frac{kJ}{mol}
\] (40)

Eq.(40) is reported to be thermodynamically favourable at above 2320K [62]. Additionally, the reaction is accomplished by formation of the stable aluminium carbide Al\(_4\)C\(_3\). The thermodynamic analysis performed by Halmann and Steinfeld [61] presented in figure 60 repeats the main problem of an experimental verification: Aluminium is formed at above 2300K, Al\(_4\)C\(_3\) is used up at above 2600K and C(gr) is still present even at 2800K.

![Equilibrium composition as a function of temperature at 1bar total pressure, CO is not shown](image)

**Figure 60: Equilibrium composition as a function of temperature at 1bar total pressure, CO is not shown**

At 2500K and 1 bar the equilibrium composition of a substoichiometric mixture is given in eq.(41) resulting in an aluminium yield of 33% (moles of aluminium produced divided by theoretically maximal possible moles of aluminium production).

\[
\text{Al}_2\text{O}_3 + 4C \rightarrow 0.661\text{Al} + 0.342\text{Al}_2\text{O}_3 + 2.658\text{CO} + 0.857\text{C(gr)} + 0.162\text{Al}_4\text{C}_3
\] (41)
B.2 Experimental

A first run was performed by Alwin Frei in the HT TG of PSI Ost. The stoichiometric mixture was exposed 17 hours to a flow of argon at 1766°C. The GC detected CO during the whole run, mass loss was 71.39%. The product, a yellow crystalline powder, was analysed by XRD to consist mainly of Al₄C₃ with some traces of AlN. This AlN is supposed to be the result of the nitrogen content of 150ppm in the argon atmosphere due to leakage. Unfortunately metallic aluminium was detected neither in the solid product nor as a thin film on the crucible or on the TG itself.

A similar run is performed at the solar simulator. Parameters and settings not stated here are the same as stated in 4.6. A molecular mixture of Al₂O₃ (Fluka Nr. 06285) : C (Fluka Nr. 05105) = 1 : 4 is milled in the ball mill for 3 minutes at level 80, pressed to a pillow with the aid of water and then dehumidified for 12 hours at 180°C. The weight of the sample was measured to 7.746g. Figure 61 gives the particle size distribution of the original mixture. The median particle size is 7.9µm and standard deviation 3µm.

Figure 61: Particle size distribution of the reactant

Metallic aluminium is expected to go into gas phase from the sample. In order to provide the Al a place to condense, a water-cooled glass tube was placed directly after the reaction zone. Two effects force the gaseous Al to condense at the cooled surface: Firstly, the hot gases in the middle of the tube are characterised by bigger and faster oscillating Brownian motion compared to the cooler gases close to the surface and therefore Al(g) particles are pushed in direction of the cold surface. The second effect is diffusion due to a concentration gradient (higher concentration in the centerline of the tube than near to the cold surface).

The total flow of 12 l/min argon contents due to leakage around 100ppm of oxygen.

Regrettably the sample fell down after 60 min because of sintering of the fixing device between the bar coming from the balance and the sample holder, like described in 4.6. But nevertheless the run was completely evaluated.
B.3 Results and discussion

On the left axis of figure 62 the weight loss of the sample due to reaction and on the right axis the temperature measured with a thermocouple in the front of the cavity close to the window can be observed. This temperature indicated is just useful as a guideline, the temperature in the reaction zone can not directly be measured with this setup. Furthermore the right axis shows the carbon releases by the reaction measured by the GC in form of CO and CO$_2$. The run was terminated after 60 min because of falling down of the sample.

![Figure 62: Run for the production of elementary aluminium at the solar simulator](image)

XRD analyses of the inner and the outermost mantle part of the sample determined the pillow to be composed of a mixture of Al$_2$O$_3$ and Al$_4$C$_3$. Also carbon (not detectable by XRD) existed due to incomplete reaction. Figure 63 depicts the XRD pattern of a powder collected from the inner part of the filter placed after the cooled glass tube. On the inner as well as on the outermost part of this filter and in the material collected from the cooled glass tube XRD analyses prove a mixture of Zn, ZnO (both coming from deposits from previous runs performed in the same reactor) and (Al$_2$O$_3$)$_{1.333}$. This alumina seems to be in a different form then the original Al$_2$O$_3$. Analyses of probes collected at the same positions for the run with nitrogen instead of argon showed not any trace of alumina (see figure 38).
The SEM picture in figure 64 approves the mean particle size of the original mixture of alumina and carbon stated in B.2 to be in the order of 10µm. The small bright particles are carbon where the roundished ones are the alumina.

The SEM picture of figure 65 gives more detail about the alumina collected from the cooled glass tube. EDX analysis of the huge particle identifies it to consist of Al and O where the smaller brighter particles sitting on the surface of the big one are Zn or ZnO. The alumina particle appears in different form than it appeared in the
original mixture. The production process of the original alumina in figure 64 we do not know but the porous different looking alumina in figure 65 is grown through recrystallisation.

Rapid cooling leads to few big particles whereas slow cooling of the gas leads to the formation of more but smaller particles. This rule for growing of particles can lead to different particle sizes for different compounds. In our case, the gaseous elementary aluminium together with the oxygen coming from the leakage (at the conditions stated above about $8 \cdot 10^{-7}$ mol O$_2$/s) agglomerated to a few big particles where the Zn lead to a huge number of small (in the order of a few micrometers and even smaller) disperse particles.

![Figure 65](image1.png)

**Figure 65:** SEM picture of powder collected from the cooled glass tube

Figure 66 points out the dimensions of these big alumina particles to be in the order of 500µm. The median particle size of the reactant was measured to 7.9µm, the particle size distribution states that not any particle of the original mixture is larger than 26µm. For that reason this alumina particle can not simply be transported from the sample to the filter.

![Figure 66](image2.png)

**Figure 66:** SEM picture of powder collected from the cooled glass tube depicting its dimensions
B.4 Conclusion

Although no metallic aluminium was found by XRD or by EDX, the formation of Al(g) from reaction (40) could be proved by the detection of alumina (formed out of Al(g) and O\textsubscript{2}) on the cooled glass tube and the filter both placed downstream the reaction chamber. These alumina particles were not simply transported from the reactant to its place by the gas flow due to three reasons. Firstly, no alumina was detected at these locations for the reaction with nitrogen instead of argon. The second prove is the size of the alumina particles collected downstream the reaction chamber being at least one order of magnitude bigger then the original ones from the reactant. And thirdly the collected alumina particles appear in different form then the ones from the original mixture.
C Miscellaneous

C.1 Sequence operation of ammonia reactor

before experiment:
- turn heater on (200°C)
- set temperature of vaporiser $T_{\text{vap}} = 200^\circ C$
- hydrolysis switch to path left
- close hydrolysis path left and right
- switch inlet gas flow to nitrogen
- switch outlet gas flow to direct to GC
- apply two Erlenmeyer flasks
- apply ice for cooling the Erlenmeyer flasks

after reducing power of lamp:
1. set gas flow: channel 2 = 0
2. set gas flow: channel 4 = 3 l/min Ar
3. set gas flow: channel 1 = 0

after shutting down:
1. ground electrodes
2. drive reactor out
3. switch inlet gas flow
4. set gas flow: channel 3 = 0.4 l/min until stable, then
5. set gas flow: channel 3 = 0.2 l/min Ar
6. open hydrolysis path left
7. switch outlet gas flow
8. set point water flow = 35.3 g/h

change Erlenmeyer flask:
1. open new path
2. switch to new hydrolysis path
3. close old path
4. remove and recuperate flask