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**Sustainable Production of Carbon Monoxide by
Direct Current Gas Discharge**

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ENERGIE & NACHHALTIGKEIT
Nachhaltige CO₂-Kreisläufe

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by Direct Current Gas Discharge**

Elektrische
Energiespeichersysteme



Nachhaltige
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Elektromobilität &
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Chapter 1

Introduction

The mitigation of climate change due to greenhouse gas emissions as well as the protection of the worlds biosphere are among the major challenges of this time. The manufacturing of chemicals is responsible for 6% of global direct CO₂ emissions, large parts of which could be avoided by the use of alternative feedstock [1]. Additionally, the transport sector emits 21% of CO₂ globally [2]. Both are supplied by the petrochemical sector, which accounts for 7% of global CO₂ emissions and 10% of energy uses [3]. It is not easy to exactly define how these sectors overlap, but simply adding the numbers leads to the conclusion that the industrial manufacturing and use of hydrocarbons as fuel in the transport sector and in production of chemicals contribute 34% of global CO₂ emissions. Unsurprisingly, carbon emissions appear when burning and manufacturing hydrocarbons, which cannot be replaced in either sector: As a fuel in mobile applications hydrocarbons feature the best combination of storability, energy density and non-toxicity. In chemicals, carbon is the very essence of organic chemistry. Without it, there wouldn't be lacquers, solvents, surfactants, or polymers to name just a few. For this reason, the chemical industry objects to the term 'decarbonisation' and instead refers to 'defossilisation'.

Fossil fuels contain the carbon and hydrogen that are used to synthesise hydrocarbons. One might argue that large parts of this carbon end up in products as far as the chemical industry is concerned. But a vast share of these products are not recycled, so carbon still ultimately ends up in the atmosphere. However, the carbon budget humanity has left to emit to keep global warming below 1.5°C is nearing its end [4]. The intergovernmental panel on climate change (IPCC) concludes that the most likely scenario for reaching this 1.5°C goal must reach zero effective emissions by 2050, which is illustrated in fig. 1.1. It must be concluded, that no new carbon

should be dug up in whatever form, and that the industry must shift towards a true circular economy: Alternative carbon sources must be made available, all while not relying on fossil fuels as energy source.

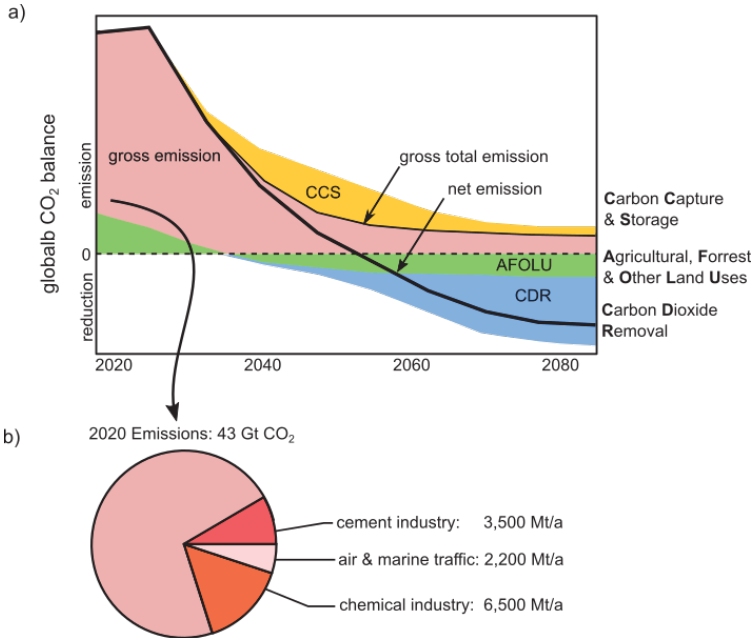


Figure 1.1: a) CO₂ emission goals including carbon dioxide capture (CCS) and removal (CDR) technology to achieve the 1.5°-goal, according to the 2017 IPCC report [5]. CO₂ emissions by sector are shown in b), highlighting the sectors that are addressed in this thesis and their share of global emissions.

Organic sources come to mind first; bio polymers are currently on the rise after all [6, 7]. They cannot compensate for fossil feedstock on their own. Plant feedstock rivals with food production for acreage and water consumption. Land use and eutrophication by agriculture are growing issues [8]. Add to that the fact, that the world produces 2 billion tons of sugar cane annually, the most farmed crop, but in the same time consumes 4 billion tons of oil [9, 10].

Carbon dioxide is gaining attention as a carbon source. Its emission is the main

reason for man made climate change and the gas has become a recognized scourge of humankind on its own. Furthermore, the emission of carbon dioxide is expected to become prohibitively expensive in the near future thanks to mandatory emission certificates, at least in Europe. CO₂ of course is very energy intensive to utilize. After all, it is mainly emitted in energy production, and this would have to be reversed.

Anthropogenic carbon sources are a promising alternative that could offer a compromise between moderate energy requirements and availability. In fact, a lot of waste products created by modern civilization are carbon and energy rich, but some remain untapped until this day: Sewage sludge, scraps, residential and industrial waste end up in landfills or pollute the oceans, river systems and landscapes.

Biogas can be made from sewage sludge, plastics are sometimes recycled or down cycled, but the vast majority of these resources is only used as a low grade energy source, while the contained carbon still ends up in the atmosphere. The material use is still an exception. This is remarkable, considering the energy contained especially in waste plastics: The energy content of dry waste plastics is higher than that of crude oil [11].

After establishing a source of carbon, it must be converted into a useful form. Research is spread across multiple fields to develop technologies that are capable of doing this while using renewable energy sources: Bioreactors use microorganisms which in turn produce enzymes to convert CO₂ directly into useful products [12]. Photochemical processes use light to activate molecules. Electrolyzers can break CO₂ molecules to form more energetic ones like formic acid in a single reactor [13]. Conventional thermochemical processes may be driven by electrical heaters instead of gas fired boilers [13]. Plasma technology can be applied to drive endothermic reactions like the splitting of CO₂ in gas phase reactors [14]. The latter is the topic of this thesis.

1.1 Scope of this Work

The aim of this thesis is to demonstrate sustainable production of carbon monoxide (CO) by plasma. In a broader sense, the goal is to find an economic and ecologic path for carbon utilization. Carbon monoxide is only one out of a range of products that can be made from carbon dioxide, albeit the only one without using a source

of hydrogen. However, it is a stable gas molecule and usually the product of all high temperature plasma processes; albeit not the easiest to work with chemical intermediate. Fig. 1.2 shows various intermediate chemicals with one carbon atom (C1-molecules) alongside Acetylene. Generally, the energy content is higher, if the oxidation state of carbon is lower; ranging from CO_2 at +IV to methane with -IV. Hot plasma can produce selectively only CO from CO_2 or Acetylene from a hydrocarbon source [13, 15]. The other shown compounds require intermediate steps or cannot be made with high selectivity in plasma at all.

Mixing carbon monoxide with hydrogen gives syngas, from which a vast array of chemicals can be manufactured. Plasma based carbon dioxide splitting can be realized with a wide array of plasma technologies [14]. The initial goal of this thesis was the study and optimization of this process using a plasma process. After experimenting with dielectric barrier discharges (DBDs) for nearly two years, gliding arcs (GAs) were picked as more promising technology after an initial experiment surpassed most previously reported performance data for DBDs. Chapter 4 covers the characterization of two GA plasma sources that were constructed. This includes the reactors and electronics to drive them. They are used for the splitting of CO_2 in chapter 5. The results obtained are enticing. However, working on this topic more than three years overall also raised awareness of the problems that plasma-based CO_2 splitting inherently brings: Alongside technical challenges, the process is very energy intensive. For this reason, two alternative processes that build on the gliding arc plasma technology were devised. They are proposed and briefly discussed. The scope of the first process is the production of sustainable cement and carbon monoxide from calcium carbonate, while the second aims at production of syngas from waste plastics. Preliminary experiments and design consideration for future experiments are discussed in chapter 6. The proposed processes are supposed to drastically reduce energy requirements and deliver carbon feedstock at lower cost than the splitting of CO_2 . Before large scale adaption, a process must proof that it is economically viable. Costs of plant, feedstock and energy have to be balanced. This is not only limited to monetary costs, but must also include direct and indirect CO_2 emissions. The sustainability and economic feasibility of the processes when compared to state-of-the-art fossil processes is discussed in chapter 7. To better understand how the presented processes might fit in the future circular chemical industry, a look on the possible resource chains of circular economy is necessary.

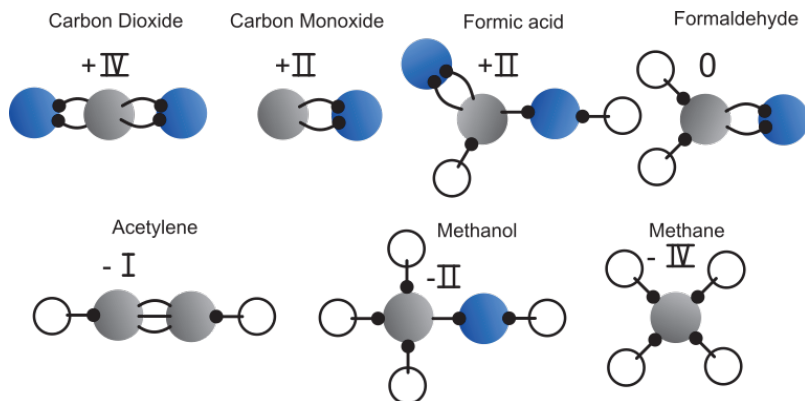
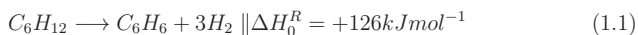


Figure 1.2: Carbon and its oxidation states in different C1-products (also Acetylene) [13, 16].

1.2 Resource Chains of the Circular Economy

Deriving chemicals from fossil feedstock offers a major advantage: The feedstock itself contains a lot of energy, which is emphasised by the fact that carbon is mostly present in oxidation state +IV. Most synthesis performed are either exothermal or only slightly endothermal. For this reason, not a lot of extra energy input is required when synthesizing desired products. This is explained in the following on the example of benzene [17], which is a precursor to nylon, phenol, polystyrenes, polycarbonates and epoxys – a large share of common polymers. Benzene can be obtained from catalytic reforming of hexane, which is the most common process used to date. A quick look at the very simplified reaction equation shows, that the energy requirements are low:



Hexane in turn can be distilled from crude oil at low cost. If benzene were to be made from carbon dioxide and water instead, the required energy is given by its enthalpy of combustion: A staggering 3.3 MJ per mol:



Processes for the production of benzene from biological feedstock like lignin are a topic of current research, however no industrial plant exists yet [18]. The energy

requirement is between the fossil- and carbon dioxide based approach. An electrical process is theoretically possible via the intermediate product ethene – the final synthesis of benzene from ethene is well established [18]. This state is representative of most chemicals that are typically derived from fossil feedstock. The high energy requirement of carbon dioxide utilization methods makes the demand for energy efficient processes all the more apparent.

In contrast, not all chemicals are traditionally derived from fossil fuels. Methods like electrolysis already are well established industrial processes. An example for this is the Chloralkali process, which is utilized widely to produce most of the sodium hydroxide and chlorine used industrially today [19]. Along with the production of aluminum, the Chloralkali process is the most well established electrochemical process in the chemical industry. In contrast to petrochemistry, the energy input is almost exclusively electrical. Thus, these processes have the potential to become green due to the shift to renewable electric energy sources.

The goal of the chemical industry must be to achieve similar processes for organic chemicals. Electrolysis has been the only employed way to introduce electrical energy into chemistry for a long time, except for some niche applications. The developments in the fields of material science and electronics shifted focus towards more fields of research recently: Electrically heated high temperature catalytic reactors, photocatalysis and plasma catalysis. Together, these approaches should be able to offer a suite of renewable precursor chemicals and intermediates that can be used to produce all products desired. The production chain to synthesize these products must be adapted to the new precursors. New synthesis routes become necessary, different intermediates will serve as stepping stones [13]. Economic viability can be increased by valorization of side products. New separation technologies are under development to extract products and side products.

1.3 Carbon Utilization Technologies

Carbon presents some unique challenges, due to its variety of stable oxidation states from -IV to +IV. This is especially challenging in electrolysis and leads to the requirement for highly tuned catalysts to obtain reasonable selectivity [20]. This is unlike water electrolysis, which is an established process: Hydrogen only has two occurring oxidation states, one of which it is already in as feedstock. Furthermore hydrogen as well as oxygen are always gaseous as a product. The equilibrium elec-

trode voltage for water electrolysis is high at 1.23 V, but as long as the electrodes remain stable only the desired products are created. Carbon dioxide, on the other hand, can result in solid products like carbon black. The equilibrium voltage required for splitting carbon dioxide to monoxide is even higher at 1.47 V. For this reason, it is not ideal to utilize carbon dioxide via an electrolyzer. On the other hand, electrolysis can produce a variety of products like methanol or formic acid [13, 20], while plasma based processes usually result in carbon monoxide. A variety of products might be achieved in post plasma catalytic processes, but these did not reach significant success yet [21]. Another drawback of plasma based utilization is that produced oxygen is not automatically separated as it is in electrolysis.

1.4 Plasma Technology in the Chemical Industry

Plasma technology is in use in the chemical industry since the early 1900s. The first commercial application of plasma next to arc lamps were arc furnaces. Siemens obtained a patent for the generation of electric arcs using electrodes that are in principle copper pipes through which a coolant is pumped; other designs were also common [22, 23]. These were first used to produce calcium carbide from calcium oxide. For a long time, this was the primary intermediate in production of acetylene. Acetylene used to be the main source of carbon in organic chemistry and its production from coal hence an important industrial process. This was true especially in Europe. German chemist Walter Reppe was in large parts responsible for the invention of processes that allowed the production of vinyl, carboxylic acids, ethylene compounds and cyclic compounds like benzene [24, 25]. As late as 1980, direct synthesis of acetylene from coal in arc furnaces was implemented in pilot scale plants in West Germany via the Hüls-Process [26]. However, acetylene lost its importance when oil surpassed coal as the cheapest and most utilized feedstock after the second world war. Another example of electrical arcs in the chemical industry is the Birkeland-Eyde process [27], in which air is passed through an arc discharge. The resulting gas contains nitrogen oxides which can be converted to nitric acid in a packed column absorption tower. Birkeland and Eyde combined multiple reactors to multi-megawatt scale in Norway next to a hydroelectric power station to build what would be by today's standards a very sustainable chemical factory. However, the process was also supplanted by the Bosch and Ostwald processes through the

prevalence of cheap natural gas and oil. Both acetylene and nitrogen oxides were manufactured using thermal electrical arcs at very high temperature. Non-thermal plasma in the form of corona discharges, sparks or dielectric barrier discharges saw its first use in the synthesis of ozone, where it is still in use on the multi-kW scale today [28, 29].

Within the 20th century, the production of chemicals by plasma became a niche application: Plasma was far more frequently used in the semiconductor industry and material sciences. However, the processing of semiconductor materials uses plasma generated at very low pressures, less than 1% of atmospheric pressure. The generation of plasma at ambient pressure holds different challenges. To enable chemical processes by plasma, ambient pressure operation is essential for two reasons: Firstly, compressors are expensive and require additional energy. Secondly, the volume of a low pressure plasma reactor would need to be very large in comparison to the mass of chemicals flowing through it [13]. The most prevalent ambient pressure plasma technology today are arc furnaces, which account for roughly a quarter of steel production. Arc furnaces produce a very thin and extremely hot plasma that is used to radiatively transfer heat into the material below. The small volume and extreme energy input make this type of plasma unsuitable for large scale chemical applications, not to mention the fact that the electrodes used degrade rapidly. New methods of plasma generation like inductively coupled and microwave sustained plasma emerged throughout the 20th century [30]. They were in large parts products of the invention of electron tubes and later semiconductor power electronics. These allow the generation of plasma with finely tunable properties. This is a stark contrast to previous arc devices, in which a ballast resistor or inductor often was the pinnacle of control electronics. Computational methods allowed for a deeper understanding of the processes taking place in plasma chemistry [31]. Thus, plasma turned from a way to provide heat to a reaction into a versatile method to introduce energy into a molecule by electron impact. The goal now is the generation of large volume plasma with defined properties, which offers the potential for more efficient chemical processes. Non-thermal plasma has gained attention for its catalytic properties, which can be obtained at moderate energy input. While plasma technology has made significant advances, so has thermo-, bio-, photo- and electrochemistry. Hence the list for chemical processes in which plasma is used on large scale in the chemical industry is no longer than it was decades ago. This might possibly change soon with the overdue electrification of the chemical industry.

Chapter 2

Theoretical Background

To utilize plasma in chemical processes, background knowledge in physics, chemistry and electrical engineering is required; this chapter aims to first define the characteristics of plasma and then give the required background information in each of the three subjects in this order.

2.1 Plasma

A plasma is formed by any gas that contains enough mobile charge carriers to significantly alter its properties. This directly relates to plasma's first observable property: It is electrically conductive. Naturally, charge neutrality requires any macroscopic object to have a net zero charge: The same number of electrons and protons is contained in any volume [32]. This is true in any medium on any length scale exceeding the Debye length, which is less than 1mm in atmospheric pressure plasma. When both are abundant at low temperature, they tend to combine to form stable gas molecules. Thus, no charge carriers are available for charge transport and gas is non-conductive. The transition from a non-conductive gas to a conductive plasma is explained in section 2.1.1. The following section 2.1.2 gives an overview of the particles that can be found in a plasma and their different excited states. To utilize plasma in chemical processes, operation at ambient pressures is favourable. This is contrary to what is widely used and understood in practical applications such as neon lights. The additional effects that need to be considered then are discussed in section 2.1.4. Since magnetic fields were used to address some of the problems that arise from ambient pressure operation, the effect of magnetic fields on plasma are covered in section 2.1.5. Lastly, a few measurement techniques that

were employed to characterize plasma in the scope of this thesis are discussed in section 2.1.6.

2.1.1 Formation

Free charge carriers can be created only when enough energy is put into a gas to liberate them from their bonds. This energy is supplied in one of multiple ways [33]:

- electric fields
- magnetic fields
- ionizing radiation such as UV or X-rays
- high temperature
- microwave or radio frequency radiation

The abundance of charge carriers in a plasma is defining for its behaviour. The relative concentration of charge carriers is given as degree of ionization α [32]:

$$\alpha = \frac{n_i}{n_i + n_n} \quad (2.1)$$

where n_i is the number of ionized particles and n_n the number of neutral particles.

Cosmic rays and background radiation always generate a very small number of charge carriers in the form of free electrons and ions. Their number is so small, that no notable change in properties occurs. A cubic centimeter of air at ambient pressure contains roughly 10^{19} molecules. Only $10^3 \dots 10^4$ of them are ionized due to background radiation, corresponding to a degree of ionization of 10^{-15} [34]. To observe the properties of plasma, a higher degree of ionization is necessary. Ionization by electric and magnetic fields is usually realized in technical applications. The background electrons are accelerated by an applied field. In collisions between electrons and neutral particles, energy is transferred from the electrons to the gas molecules. If this energy exceeds the ionization energy, ionization occurs. This increases the charge carrier density and thus the degree of ionization. A value of $\alpha = 10^{-4}$ is sufficient to generate other typical properties of plasma: Light emission, high chemical reactivity, sensitivity to magnetic fields and conductivity [35]. However, when no external power source is present the plasma quickly loses its properties due to the recombination of charge carriers. During recombination, the
