Plasma for electrification of chemical industry

Citation for published version (APA):

DOI:
10.1088/1361-6587/aa8f7d

Document status and date:
Published: 01/01/2018

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 22. Feb. 2019
Plasma for electrification of chemical industry: a case study on CO$_2$ reduction

To cite this article: G J van Rooij et al 2018 Plasma Phys. Control. Fusion 60 014019

View the article online for updates and enhancements.
Plasma for electrification of chemical industry: a case study on CO₂ reduction

G J van Rooij¹, H N Akse², W A Bongers¹ and M C M van de Sanden¹,³

¹ Dutch Institute for Fundamental Energy Research, DIFFER, PO Box 6336, 5600 HH Eindhoven, The Netherlands
² Traxxys Innovation & Sustainability, Adenauerlaan 17, 3446 HS Woerden, The Netherlands
³ Department of Applied Physics, Plasma and Materials Processing Group, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

E-mail: G.J.vanRooij@differ.nl

Received 3 July 2017, revised 24 August 2017
Accepted for publication 27 September 2017
Published 31 October 2017

Abstract
Significant growth of the share of (intermittent) renewable power in the chemical industry is imperative to meet increasingly stricter limits on CO₂ exhaust that are being implemented within Europe. This paper aims to evaluate the potential of a plasma process that converts input CO₂ into a pure stream of CO to aid in renewable energy penetration in this sector. A realistic process design is constructed to serve as a basis for an economical analysis. The manufacturing cost price of CO is estimated at 1.2 kUS$ ton⁻¹ CO. A sensitivity analysis shows that separation is the dominant cost factor, so that improving conversion is currently more effective to lower the price than e.g. energy efficiency.

Keywords: intermittent renewable energy storage, CO₂ conversion, microwave plasma discharge

(Some figures may appear in colour only in the online journal)

1. Introduction

Concerns about climate change, energy security and depletion of fossil fuels are driving a continuous increase in deployment of sustainable electricity sources, in particular of wind power and solar PV installations [1]. More specific, the 2050 road map of the European Commission projects wind power to become the largest source of power in the EU by 2050 [2]. A well-recognized characteristic of these sources is that their production rate is intermittent (hence ‘Intermittent Renewable Energy Sources’) and inherently not well balanced with the fluctuations in the electricity demand. Firstly, this causes issues in terms of demand response. Presently, conventional fossil based sources supplement periods of shortage in electricity demand. Contrarily, periods in which production exceeds demand causes economical losses due to lowering of renewable energy generation. Sometimes, the renewable energy production becomes so large that it causes real problems in the electricity grid. Such problems are reflected in extremely negative electricity prices. For example, German electricity spot prices dropped in 2012 for short periods of time from an average 40 € MWh⁻¹ to below a negative price of −120 € MWh⁻¹ [3]. We emphasize that this example only illustrates how severe such problems are. This specific example is certainly not the basis for a business case that relies on (better than) free electricity.

It may be clear that reaching even higher degrees of renewable energy deployment requires these intermittency issues to be resolved. Storage of electricity, in particular in the form of electricity (i.e. power-to-power) will therefore be an essential aspect in the development of the electricity grid of the future for demand response and to capitalize the production surpluses [4]. A step further would be conversion of the sustainable electricity into chemical potential energy (yielding fuels and/or chemical feedstocks), which would open up various pathways to integration of different energy sectors [5, 6]. For example, if the power were to be converted to fuel, this would contribute to decarbonization of transport, including aviation. Furthermore, it would become viable to produce these fuels in remote locations, where solar/wind energy potential is optimal, and to use the existing infrastructure for fossil fuels for distribution to the end users. Finally, activation of the thermodynamic most stable molecules such as CO₂, H₂O, and N₂ using sustainable energy
would provide the chemical industry with sustainable raw materials.

The urgency for the chemical industry to find new solutions for reducing their CO₂ emissions is high. Within this sector, it is presently far from clear how to meet the increasingly stricter limits on CO₂ exhaust that are being implemented within Europe [7]. Taking the Dutch industry as example, the goals formulated at the COP21 Climate Conference in Paris imply CO₂ emission reductions of 40%–50% in 2030 and even over 90% in 2050 compared to the 1990 levels. These reductions are stronger than in any of the respected scenario studies [7].

The aim of the present paper is to evaluate a realistic industrial process design for CO₂ activation by plasma for the production of a pure CO stream in order to evaluate the overall costs and hence the economic viability. Such CO stream could serve as renewable input for the chemical industry. Chosen is for microwave plasma, the approach that has been recognized as most favorable for CO₂ dissociation in terms of energy efficiency [8, 9]. It is generally assumed that this is due to a low reduced electric field and hence preferential vibrational excitation that leads to favorable non-equilibrium operating conditions. In effect, the microwave approach also implies a choice for subatmospheric pressures, as otherwise the non-equilibrium advantages would disappear. Costs of integrating a subatmospheric system are thus part of the economics analysis.

2. Promise of plasma chemistry for decarbonization of chemical industry

The plasma phase carries a number of distinct advantages within the context of intermittently available renewable electricity that makes it potentially attractive for activation of the aforementioned stable molecules. Presently, this is well recognized by the international plasma chemistry community and a number of groups is investigating the maximally achievable energy efficiency for the reduction of CO₂ in plasma, both numerically and experimentally, pure and mixed with other molecules, in homogeneous plasma configurations as well as coupled to catalysis [9–24]. The first and most important advantage of the plasma approach lies in the promise of unequivocally high energy efficiency. Experimental results obtained in the 1970s in the former Soviet Union indicate that the net reaction

$$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2, \quad \Delta H = 2.9 \text{ eV/CO}_2 \quad (1)$$

can be driven with energy efficiency in excess of 80% [8]. The results have been explained on the basis of the efficient vibrational excitation that occurs in the interaction between the free plasma electrons and the neutral heavy particles in combination with preferential excitation of higher excited CO₂ molecules by exchange of vibrational quanta with lower excited molecules. In this way, the CO₂ molecules step all the way up the asymmetric stretch vibrational ladder until the point of dissociation. This forms in addition to the desired CO molecule also a triplet O atom, which should react with another CO₂ molecule to produce a second CO molecule in order to achieve the highest energy efficiency for the summarizing reaction (1).

Other advantages of a microwave plasma approach connect to the characteristics of intermittently available renewable electricity. Firstly, this concerns the expectation of low equipment investment costs. Microwave power is very cheap, in essence by virtue of the large market for kitchen microwave sources, so that continuous operation might not be essential for economic viability and intermittent operation can be allowed. Such intermittent operation of course also requires fast switching on and off, which is also provided by microwave plasma as equilibration times are typically on the order of milliseconds. Finally, in view of scalability to the size of the energy market, the absence of scarce materials as well as the high-power density and thus small footprint (i.e. excellent for process intensification) are important characteristics.

The application of plasma in large scale production of chemicals is not new and in fact goes back to the early 1900s when the Birke–Eydeland process was applied for nitrogen fixation [25]. As the plasma process was not yet microwave based but an atmospheric electric arc offering only ~4% energy efficiency [26], it was highly energy intense and required reliable high-power electricity. Therefore, it was not a coincidence that the endeavor took place in Norway, benefitting from hydropower. In hindsight, electricity always having been the most expensive form of energy made plasma chemistry inherently too expensive to be competitive with fossil fuel driven processes. Indeed, after the Haber–Bosch process for ammonia production had been developed and became available as an alternative, it had soon taken over the Birke–Eydeland process within the Norwegian fertilizer industry. It is exactly this pricing hierarchy between fossil fuels and electricity that is currently changing due to the rise of sustainable energy and that is offering new chances for plasma chemistry.

Notwithstanding the opportune electricity pricing developments, it should be noted that technological development is also still required before microwave plasma can become a commercial success. To our knowledge, large scale plasma systems based on microwave generators have not yet been commercialized, despite several attempts over the years. An early example concerns work on microwave plasma dissociation of H₂S [27], which was again inspired by high energy efficiencies in the former Soviet Union, both in terms of the aforementioned performance for CO₂ reduction as well as an increased energy efficiency for nitrogen fixation from ~4% in the Birke–Eydeland process to ~30% in microwave discharges. A recent example concerned full pyrolysis of methane [28] that was pursued by the British/Norwegian company GasPlas and the Canadian company Atlantic Hydrogen Inc. The latter was initiating a 0.4 MW demonstration plant of its CarbonSaver™ microwave plasma concept based on lab experiments at 75 kW scale [29] before its bankruptcy.
produces 20 000 ton yr

In order to arrive at a scale up of the plasma process that

4. Design considerations for scale up

In order to arrive at a scale up of the plasma process that produces 20 000 ton yr⁻¹ of pure CO, three main process steps are to be executed: conversion of CO₂ to CO, removal and recycling of unconverted CO₂, and CO purification. Before discussing in detail the process design, the main considerations for each of these steps as well as for overall plant safety are briefly discussed.

Conversion: It was chosen to design the plasma conversion stage at subatmospheric pressure in order to stay close to the conditions under which best performance was observed in the laboratory scale experiments. This is achieved with an adiabatic expansion valve before and a compressor after the plasma reactor. In order to prevent back reactions, fast freezing of the equilibrium is required after the reactor. This involves a temperature drop from the 3500 K observed inside the plasma down to 2000 K. Unfortunately, adiabatic expansion is not possible in view of the limited available pressure difference given the low reactor pressure of 0.2 bara. Therefore, flash injection cooling is applied. Water is injected at boiling point, which evaporates immediately upon mixing with the hot product gases and cools the reactor effluent due to the high heat of vaporization of water. Subsequently, the water is removed from the product stream before entering the compressor (in view of compressor lifetime) in a drying step.

Removal and Recycle of CO₂: Relyed is upon an existing commercial process to separate CO₂ from the product stream, which is the Benfield process [32]. Amine based systems which are commonly used are not an option due to the high oxygen concentration, leading to excessive amine degradation and make-up.

Purification: Presently, no commercial or mature schemes exist for separation of CO from O₂. A promising process still under development involves Faujasite zeolites [33]. We assume a pressure swing adsorption (PSA) step to become viable for the CO product purification.

Safety: The current process yields a CO₂/CO/O₂ mixture that requires separation and purification. This represents a substantial operational risk (CO/O₂) which is inherent to the current process. Avoiding O₂ formation in the plasma would be the target to go for. If no operating window can be found that meets this target, future process designs will have to go in depth on the issue, how to deal with this effectively.
5. Process description for the 20 000 ton yr$^{-1}$ CO plant

A typical commercial scale size for a CO plant is 20 000 ton yr$^{-1}$. Commercial 915 MHz microwave systems are available up to $\sim$0.5 MW, which sets the maximum single train capacity (76 ton CO/year at 400 mbara reactor pressure and reactor dimensions of 0.124 m height and 0.1 diameter) and translates into a plant with 264 parallel reactor/generator combinations. The process flow diagram shown in figure 2 was constructed for scaling up the plant to fulfill the aforementioned design considerations (showing only four of the parallel reactor/generator combinations). The heart of the plant is formed by the plasma reactor systems (1; numbers refer to the process units in figure 2). These are supplied via adiabatic valves with dry recycle CO$_2$ from the condenser vessel (5). Water is recycled via the flash injection pump (4) and the product gases are further dried in drying bed (16). The raw product gas compressor (8) pressurizes the product stream up to 2.2 bara to compensate for the pressure drop over the two sequential separation steps. First, the CO$_2$ absorber (6) is entered in upflow. Here, a packed bed of Raschig or Pall rings (7) creates interfacial mass transfer area between the liquid and the gas phase. A cool lean absorbent liquid consisting of K$_2$CO$_3$ in water at a pH $>$ 7 enters the absorber in downflow. This countercurrent operation causes the acidic CO$_2$ gas to dissolve completely into the liquid phase by chemically enhanced mass transfer:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2HCO_3^- + 2K^+.$$  

The treated gas consists now of CO and O$_2$ and is sent directly to the PSA beds (19 A, B, and C). One bed adsorbs CO, yielding a contaminated O$_2$ flow that is sent to flare. In the meantime, a second bed is regenerated by desorbing the adsorbed CO, yielding a pure CO flow that is sent to storage (25). A third bed is on standby in case of a malfunctioning in one of the other beds.

Returning to CO$_2$ absorber (6), the unreacted CO$_2$ flow is heated by heat exchange (22) with the still hot absorbent flow coming from surge tank (23). The liquid flow is entering the hot CO$_2$ regenerator (9) in downflow. At the bottom of this regenerator a low pressure steam reboiler (13) is installed.
which evaporates the water phase. The resulting up flowing steam is internally contacted with the down coming liquid absorbent flow which is rich in CO₂. The CO₂ regenerator also contains a packed bed of Raschig or Pall rings (10) to enlarge the liquid/gas interfacial area. The up flowing steam effectively strips the CO₂ out of the liquid phase during the interfacial contact on the packed bed elements. A wet recycle CO₂ flow leaves the CO₂ regenerator (9) over the top. It is cooled in a condenser (11) to remove as much of the water as possible via the condenser vessel (12). The condensed water flow is refluxed back to the top of the CO₂ regenerator (9). The semi-dry recycle CO₂ flow is fed to drying bed (14) before combining with the fresh CO₂ feed flow.

Hot and clean absorbent liquid leaves the regenerator bottom (9) and is pumped by absorbent pump 1 (20) into a surge tank (23). Here, the K₂CO₃ solution is dosed from the make up tank (24) compensate for thermal K₂CO₃ degradation. The reconditioned absorbent is pumped by absorbent pump 2 (21) to the heat exchanger (22) to exchange its latent heat with the cool and rich absorbent flow and finally re-enter cold the CO₂ absorber (6) for the next absorption cycle.

6. CO manufacturing costs and sensitivity analysis

First aspect in the manufacturing costs analysis is the capital expenditures (CAPEX) of the plant. Our estimate for all equipment but the microwave generators is 7.2 M$ USD (USD is referred to throughout this paper). In this part, the compressor is most expensive, estimated at 1.8 M$. Plasma reactor, Silicagel loading, and the CO storage tank with floating roof are other expensive components, costing together ~3M$. The largest part of the CAPEX would however be for the plasma generators. Industrial microwave tubes cost typically 1 $/W (at 915 MHz) and hence we estimate the CAPEX for the plasma generators at 23 M$, giving a total plant CAPEX of 30 M$. Consumer microwave tubes would come much cheaper, however on the expense of shorter lifetime and lower total power. In smaller plant sizes, these would be of course much more interesting in view of much reduced costs at 0.05 $/W. Assuming the future cost level of industrial plasma generators to become around 0.05 $/W (in particular due to rapid developments in semiconductor based microwave generators, a development that is also advantageous in terms of lifetime), overall CAPEX of a 20 000 ton yr⁻¹ CO plant would be in the order of 8 10 M$ which is roughly half of the capital cost required for a CO-plant based on conventional technology and feedstock.

The manufacturing costs of the 20 000 ton yr⁻¹ CO plasma plant are listed in table 2. Performance of the plasma reactor was assumed according to the before defined base case operation. The capital charge assumes that the CAPEX is to be recovered in ten years’ time. Electricity price is set to the present industrial rate of ~50 $ MWh⁻¹. It is evident that electricity represents a large fraction, nearly 50%, of the total costs. The expectation is of course that electricity prices will go down significantly compared to fossil fuel costs or benefit from negative prices in the transition period.

| Table 2. Manufacturing cost sheet 20 000 ton yr⁻¹ CO plant for base case performance. |
|-----------------|-----------------|-----------------|-----------------|
| **Variable costs** |                  | **$ ton⁻¹ CO**  |
| Raw materials    | CO₂             | 31              |
|                  | K₂CO₃           | 9               |
| Miscellaneous    | incl zeolite and silicagel | 7 |
| materials        |                  |                  |
| Utilities        | electricity (0.0147 $ MJ⁻¹) | 603 |
|                  | Cooling and process water, LP steam | 64 |
| **Total**        |                  | **714**         |
| **Fixed costs**  |                  |                  |
| Maintenance (incl materials) | 5.5% of fixed capital | 74 |
| Operating labour and overhead | 2 man/shift, 3 shifts/day | 28 |
|                  | + laboratory, supervision, plant overhead |                  |
| Capital charges and overhead | including insurance, taxes, royalties | 208 |
| **Total**        |                  | **310**         |
| **Sales expenses** |                  |                  |
|                  |                  | **204**         |
| **Total production costs** |                  | **1228**        |

**Figure 3.** Sensitivity analysis for the main cost factors in the plasma CO price. As reference, also an estimate of the present CO bulk and specialty price are shown.

All assumptions in the calculation of the base case CO price were chosen conservatively. More progressive process and commercial parameters will obviously bring the manufacturing cost forecast down. In figure 3 it is shown what the effect of the various possible price reductions and process improvements would be. In the figure, also a present day price for bulk and specialty CO is indicated to judge economic viability of the process. The specialty price is based on various price offers for 40–100 l gas cylinders. The bulk price is an estimate as no bulk market exists for CO in view of safety. It means that bulk CO is only produced for captive use, to be immediately converted into a less hazardous and more valuable end product. As most CO is synthesized from methane and converted into methanol, we estimate the bulk CO price to be in between their market prices, i.e. 228 $ ton⁻¹.
Another way of looking at the plasma CO price is in terms of energy storage, thus per kWh. With the standard enthalpy change of combustion of $-283 \text{ kJ mol}^{-1}$, this gives a stored energy price that ranges between 0.22 (for double conversion) and 0.44 (for the base case) $\text{s kWh}^{-1}$ in CO. This price is to be compared with the input electricity price of 0.05 $\text{s kWh}^{-1}$.

7. Discussion and conclusions

An aspect that became very apparent from the process analysis but has not been put forward yet in the present paper is that there is almost no economy of scale. This is due to the fact that vacuum tube type plasma generators scale up linearly with the plant output. To put it reversely, the strength of the plasma approach would lie especially in small scale local production schemes [34].

The economics of the proposed plasma based process for CO production with electricity is not yet competitive with our estimated bulk CO price. Sensitivity analysis learns that, although generator prices are higher (industrial microwave sources are 20–40 times more expensive than our kitchen microwave) and energy efficiency lower (the literature record energy efficiency of more than 80% has not yet been reproduced) than the horizon that was sketched in the introduction, these are not the dominant factors in the high manufacturing cost. It is the limited conversion that largely determines the manufacturing cost. Obviously, conversion propagates through separation costs as well as capital costs (the same equipment produces less end product). Optimization of conversion should thus be, from an economical point of view, the priority in further research. Alternatively, more optimal separation, quenching (preferably all dry), and probably most importantly, more favorable input raw material and end product combinations (e.g. an easy separable end product such as methanol or pure CO and/or H2 thus requiring no separation at all), would also greatly improve the economics.

Much more optimistic is the business case for situations in which the specialty price would be the reference. In such cases, however, substantial operational risk in CO product handling, storing and shipping would be at play, an aspect that goes beyond the present evaluation.

References

[18] Van Laer K and Bogaerts A 2015 Improving the conversion and energy efficiency of carbon dioxide splitting in a zirconia-packed dielectric barrier discharge reactor Energy Technol. 3 1038
[27] Harkness J B L and Doctor R D 1993 Plasma-Chemical Treatment of Hydrogen Sulfide in Natural Gas Processing GRI-93/0118 Argonne National Laboratory, Gas Research Institute, Chicago, IL
[34] Dahlgren E, Goecmen C, Lackner K and van Ryzin G 2013 Small modular infrastructure Eng. Econ. 58 231