Plasma for electrification of chemical industry

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PAPER

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Plasma for electrification of chemical industry: a case study on CO₂ reduction

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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

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 CarbonSaverTM microwave plasma concept based on lab experiments at 75 kW scale [29] before its bankruptcy.

Figure 1. Technical drawing of the forward-vortex reactor configuration that is the basis of the present process design and evaluation. It shows the stainless steel gas inlet assembly that combines a central axial inlet with two tangential inlets. The assembly is mounted on top of the rectangular microwave waveguide and holds the quartz flow tube that is inserted through the waveguide and contains the plasma.

3. Experimental dataset as benchmark for the process design

The process design takes as starting point the experimental configurations that are in use at DIFFER and the performance data in terms of energy efficiency and conversion that were measured with it. Here, the main elements relevant for the process design and cost evaluation are given. More details can be found in previous publications [30, 31].

Figure 1 shows a technical drawing of the plasma reactor. CO₂ is fed through the axial as well as two tangential inlets. The inlet assembly holds the quartz tube that is inserted through the long side of a rectangular waveguide at 1/4 wavelength distance from its shorted end. The tube contains the CO₂ plasma that discharges on the 0.2–1 kW microwave power launched at 2.45 GHz. The tangential flow prevents the tube from overheating. It however introduces gas slip at an amount that is presently still unknown. For the scope of the present paper it suffices to only regard overall performance data. Future extrapolation to maximum performance in terms of conversion will require deeper knowledge on the amount of slip as it will determine the fraction of input gas that interacts with the plasma discharge.

From the performance data measured in scans of power, gas flow, and reactor pressure [30, 31] the operation parameter set listed in table 1 was selected for the process design in view of its optimal energy efficiency in combination with acceptable conversion. Putting these data in a chemical engineering perspective, it is observed that the reactor volume is extremely small and the gas velocity increases from a modest $\sim 6 \text{ m s}^{-1}$ per nozzle at the inlet to about sonic speed in the plasma region, where it reaches a high temperature of 3500 K [30] in a short gas residence time of 1.5 ms. Defining the energy efficiency and conversion for the base case fixes the specific energy input, which amounts to $1.67 \text{ MJ kg}^{-1} \text{ CO}_2$.

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

Table 1. Base case process conditions and parameters for the plasma reactor on which the process design is based.

Base case process conditions	Units	Value
Reference energy efficiency	%	50
Reference conversion	mol%	15
Pressure plasma reactor	mbara	200
Temperature reactor inlet	K	298
Temperature reactor exit	K	3500
Pressure reactor exit	mbara	200
Temperature exit reactor after quench	K	298
Gas residence time inside plasma	s	1.5×10^{-3}
Plasma height	m	4.7×10^{-2}
Effective reactor diameter	m	2.7×10^{-2}

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 evaporation 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: Relies 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.

Figure 2. Block scheme for scaling up to a plasma plant that produces 20 000 ton yr⁻¹ pure CO. It is noted that the 4 depicted reactors represent a set of 264 parallel reactors to achieve the targeted production rate.

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 ~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 CO₂ from the condenser vessel (14) of the regenerator (9) that is replenished with the fresh CO₂ that enters the plant. The gas compressor (8) located immediately after the reaction section drives all gas flows and control loops (not shown in the diagram) will ensure the optimal reactor pressure by adjusting compressor and gas flow. The reaction products are quenched by flash injection cooling immediately after the plasma reactors. A two stage cooler/condenser (3) prepares the condensable steam and non-condensable product gases for separation in the

condenser vessel (5). Water is recycled via the flash injection pump (4) and the product gases are further dried in drying bed 2 (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 CO₂ 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 K₂CO₃ in water at a pH > 7 enters the absorber in down flow. This countercurrent operation causes the acidic CO₂ gas to dissolve completely into the liquid phase by chemically enhanced mass transfer:

The treated gas consists now of CO and O₂ and is sent directly to the PSA beds (19 A, B, and C). One bed adsorbs CO, yielding a contaminated O₂ 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 CO₂ absorber (6), the unreacted CO₂ 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 CO₂ regenerator (9) in down flow. 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 condensor 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 1 (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 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.

			\$ ton ⁻¹ CO
<i>Variable costs</i>			
Raw materials	CO ₂		31
	K ₂ CO ₃		9
Miscellaneous materials	incl zeolite and silicagel		7
Utilities	electricity (0.0147 \$ MJ ⁻¹)		603
	Cooling and process water, LP steam		64
Total			714
<i>Fixed costs</i>			
Maintenance (incl materials)	5.5% of fixed capital		74
Operating labour and overhead	2 man/shift, 3 shifts/day		
	+ laboratory, supervision, plant overhead		28
Capital charges and overhead	including insurance, taxes, royalties		208
Total			310
<i>Sales expenses</i>			204
<i>Total production costs</i>			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 kJ mol^{-1} , this gives a stored energy price that ranges between 0.22 (for double conversion) and 0.44 (for the base case) $\text{\$/kWh}^{-1}$ in CO. This price is to be compared with the input electricity price of $0.05 \text{ \$/kWh}^{-1}$.

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 H_2 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

- [1] OECD/IEA 2016 *World Energy Outlook 2016* (Paris: International Energy Agency)
- [2] European Commission 2011 *EC EnergyRoadmap 2050-COM* (2011)885/2 European Commission, Brussels
- [3] Kyritsis E, Andersson J and Serletis A 2017 Electricity prices, large-scale renewable integration, and policy implications *Energy Policy* **101** 550–60
- [4] Brouwer A S, Broek M v d, Seebregts A and Faaij A 2014 Impacts of large-scale intermittent renewable energy sources on electricity systems, and how these can be modeled *Renew. Sustain. Energy Rev.* **33** 443–66
- [5] Varone A and Ferrari M 2015 Power to liquid and power to gas: an option for the German energiewende *Renew. Sustain. Energy Rev.* **45** 207–18
- [6] Schiebahn S, Grube T, Robinius M, Tietze V, Kumar B and Stolten D 2015 Power to gas: technological overview, systems analysis and economic assessment for a case study in Germany *Int. J. Hydrog. Energy* **40** 4285–94
- [7] den Ouden B, Lintmeijer N, van Aken J, Afman M, Croezen H, van Lieshout M, Klop E, Waggeveld R and Grift J 2017 *Electrification in the dutch process industry* Berenschot Group B.V. (www.berenschot.nl)
- [8] Rusanov V D, Fridman A A and Sholin G V 1981 The physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules *Sov. Phys.—Usp.* **24** 447
- [9] Kozák T and Bogaerts A 2015 *Plasma Sources Sci. Technol.* **24** 015024
- [10] Spencer L F and Gallimore A D 2011 *Plasma Chem. Plasma Process.* **31** 79
- [11] Spencer L F and Gallimore A D 2013 *Plasma Sources Sci. Technol.* **22** 015019
- [12] Goede A P H, Bongers W A, Graswinckel M F, van de Sanden M C M, Leins M, Kopecki J, Schulz A and Walker M 2013 Production of solar fuels by CO_2 plasmolysis *3rd European Energy Conf.* (Budapest, Hungary)
- [13] Silva T, Britun N, Godfroid T and Snyders R 2014 *Plasma Sources Sci. Technol.* **23** 025009
- [14] van Rooij G J, van den Bekerom D C M, den Harder N, Minea T, Berden G, Bongers W A, Engeln R A H, Graswinckel M F, Zoethout E and van de Sanden M C M 2015 Taming microwave plasma to beat thermodynamics in CO_2 dissociation *Faraday Discuss.* **183** 233–48
- [15] Chen G, Britun N, Godfroid T, Georgieva V, Snyders R and Delplancke-Ogletree M-P 2017 An overview of CO_2 conversion in a microwave discharge: the role of plasma-catalysis *J. Phys. D: Appl. Phys.* **50** 084001
- [16] Ramakers M, Trenchev G, Heijkens S, Wang W and Bogaerts A 2017 Gliding arc plasmatron: providing an alternative method for carbon dioxide conversion *ChemSusChem* **10** 2642
- [17] Berthelot A and Bogaerts A 2017 Modeling of CO_2 splitting in a microwave plasma: how to improve the conversion and energy efficiency *J. Phys. Chem. C* **121** 8236
- [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
- [19] Snoeckx R, Zeng Y X, Tu X and Bogaerts A 2015 Plasma-based dry reforming: improving the conversion and energy efficiency in a dielectric barrier discharge *RSC Adv.* **5** 29799
- [20] Tu X and Whitehead J C 2012 Plasma-catalytic dry reforming of methane in an atmospheric dielectric barrier discharge: understanding the synergistic effect at low temperature *Appl. Catal. B* **125** 439
- [21] Tu X, Gallon H J, Twigg M V, Gorry P A and Whitehead J C 2011 Dry reforming of methane over a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst in a coaxial dielectric barrier discharge reactor *J. Phys. D: Appl. Phys.* **44** 274007
- [22] Tu X and Whitehead J C 2014 Plasma dry reforming of methane in an atmospheric pressure AC gliding arc discharge: co-generation of syngas and carbon nanomaterials *Int. J. Hydrog. Energy* **39** 9658
- [23] Scapinello M, Martini L M, Dilecce G and Tosi P 2016 Conversion of CH_4/CO_2 by a nanosecond repetitively pulsed discharge *J. Phys. D: Appl. Phys.* **49** 075602
- [24] Martini L M, Dilecce G, Guella G, Maranzana A, Tonachini G and Tosi P 2014 Oxidation of CH_4 by CO_2 in a dielectric barrier discharge *Chem. Phys. Lett.* **593** 55

- [25] Hessel V, Wang Q and Lang J 2016 *Chim. Oggi—Chem. Today* **35**
- [26] Patil B S, Wang Q, Hessel V and Lang J 2015 Plasma N₂-fixation: 1900-2014 *Catal. Today* **256** 49
- [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
- [28] Cho W, Lee S H, Ju W S, Baek Y and Lee J K 2004 Conversion of natural gas to hydrogen and carbon black by plasma and application of plasma carbon black *Catal. Today* **98** 633
- [29] Atlantic Hydrogen Inc. CarbonSaver Overview NS Clean Energy R&D Forum 2012 <http://oera.ca/wp-content/uploads/2013/04/Mike-Oliver-Atlantic-Hydrogen-Inc.pdf>, (Accessed: 22 August 2017)
- [30] den Harder N *et al* 2017 Homogeneous CO₂ conversion by microwave plasma: wave propagation and diagnostics *Plasma Process. Polym.* **14** 1600120
- [31] Bongers W *et al* 2017 Plasma-driven dissociation of CO₂ for fuel synthesis *Plasma Process. Polym.* **14** 1600126
- [32] Honeywell-UOP. Benfield process, datasheet on <https://uop.com/?document=benfield-process-datasheet&download=1>
- [33] Nour Z and Berthomieu D 2014 Multiple adsorption of CO on NA-exchanged Y faujasite: a DFT investigation *Mol. Simul.* **40** 33–44
- [34] Dahlgren E, Goecmen C, Lackner K and van Ryzin G 2013 Small modular infrastructure *Eng. Econ.* **58** 231