

# Plasma for Electrification of Chemical Industry: a Case Study on CO<sub>2</sub> 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 CO<sub>2</sub> exhaust that are being implemented within Europe. This paper aims to evaluate the potential of a plasma process that converts input CO<sub>2</sub> 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 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.

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## 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”, IRES) 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 to below -120 €/MWh[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 need 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 decarbonisation of transport, including aviation. Furthermore, it would become viable to produce these fuels in remote locations, where solar/wind energy potential is optimal, and use the existing infrastructure for fossil fuels for distribution to the end users. Or activation of the thermodynamic most stable molecules such as CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> using sustainable energy would provide the chemical industry with sustainable raw materials.

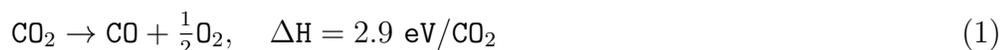
The urgency for the chemical industry to find new solutions for reducing their CO<sub>2</sub> emissions is high. Within this section, it is presently far from clear how to meet the increasingly stricter limits on CO<sub>2</sub> exhaust that are being implemented within Europe[7]. Taking the Dutch industry as example, the goals formulated at the COP21 Climate Conference in Paris imply CO<sub>2</sub> 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 CO<sub>2</sub> 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 favourable for CO<sub>2</sub> 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 favourable non-equilibrium operating conditions. In effect, the microwave approach also implies a choice for sub-atmospheric 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 Decarbonisation 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 CO<sub>2</sub> in plasma, both numerically and experimentally, pure and mixed with other molecules, in homogeneous plasma configurations as well as coupled to catalysis[10, 11, 12, 13, 9, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 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 Sovjet 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 CO<sub>2</sub> molecules by exchange of vibrational quanta with lower excited molecules. In this way, the CO<sub>2</sub> 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 CO<sub>2</sub> 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, based on consumer markets. 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  $\sim 4\%$  energy efficiency[26], it was highly energy intense and required reliable high-power electricity. Therefore, it was not a coincidence that the endeavour 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 H<sub>2</sub>S [27], which was again inspired by high energy efficiencies in the former Soviet Union, both in terms of the aforementioned performance for CO<sub>2</sub> reduction as well as an increased energy efficiency for nitrogen fixation from  $\sim 4\%$  in the Birke-Eydeland process to  $\sim 30\%$  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<sup>TM</sup> microwave plasma concept based on lab experiments at 75 kW scale [29] before its bankruptcy.

### 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. CO<sub>2</sub> gas 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 CO<sub>2</sub> plasma that discharges on the 0.2 - 1 kW microwave power that is launched at 2.45 GHz. The tangential flow ensures that the tube is not overheated. 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.

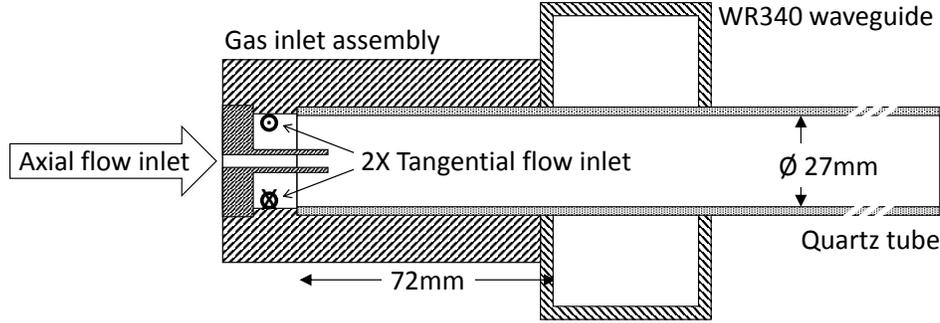


Figure 1: Technical drawing of the forward-vortex reactor configuration that is the basis of the present process design and evaluation. It shows the stainless steel gas inlet assembly that combines a central axial inlet with two tangential inlets. The assembly is mounted on top of the rectangular microwave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

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  $\sim 6$  m/s 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 (SEI), which amounts to 1.67 MJ/kg CO<sub>2</sub>.

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	$1.5 \times 10^{-3}$
Plasma height	m	$4.7 \times 10^{-2}$
Effective reactor diameter	m	$2.7 \times 10^{-2}$

#### 4. Design considerations for scale up

In order to arrive at a scale up of the plasma process that produces 20,000 ton/year of pure CO, three main process steps are to be executed: *conversion* of CO<sub>2</sub> to CO, *removal and recycling* of unconverted CO<sub>2</sub>, 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 sub atmospheric 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 CO<sub>2</sub>:** Relied is upon an existing commercial process to separate CO<sub>2</sub> 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 O<sub>2</sub>. 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 CO<sub>2</sub>/CO/O<sub>2</sub> mixture that requires separation and purification. This represents a substantial operational risk (CO/O<sub>2</sub>) which is inherent to the current process. Avoiding O<sub>2</sub> 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/year CO plant

A typical commercial scale size for a CO plant is 20,000 ton/year. 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

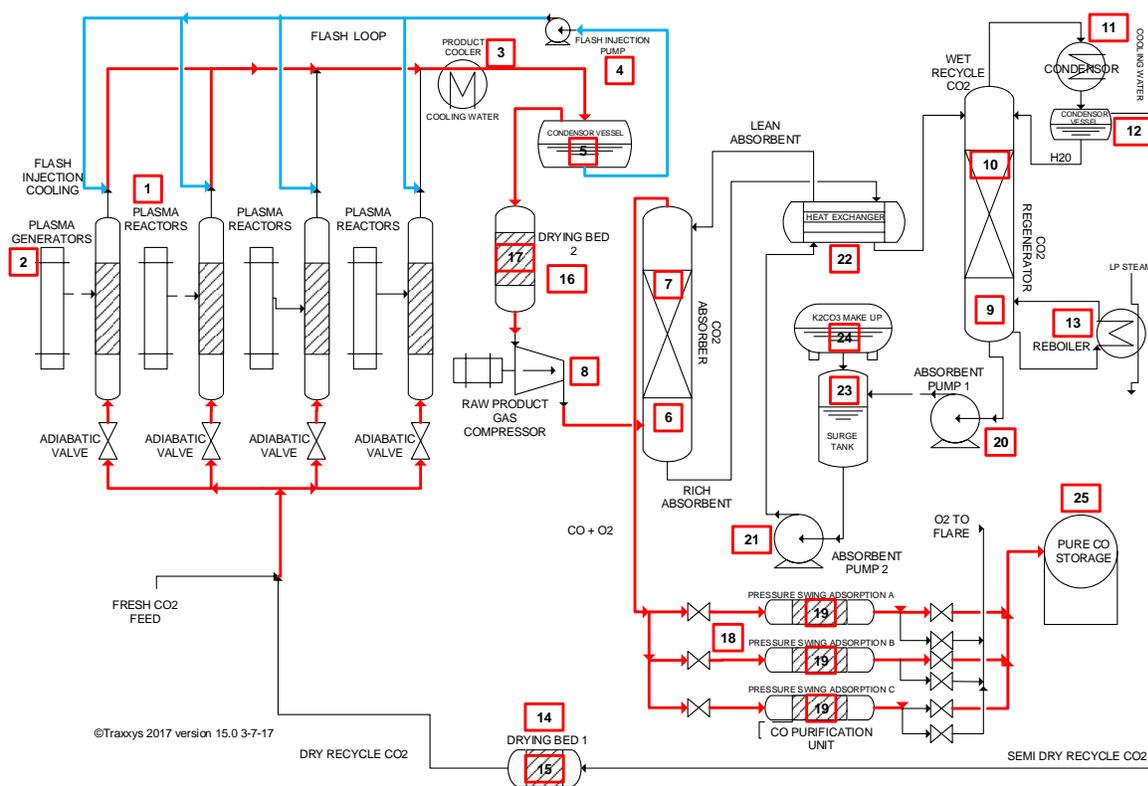


Figure 2: Block scheme for scaling up to a plasma plant that produces 20,000 ton/year pure CO. It is noted that the 4 depicted reactors represent a set of 264 parallel reactors to achieve the targeted production rate.

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<sub>2</sub> from the condenser vessel (14) of the regenerator (9) that is replenished with the fresh CO<sub>2</sub> 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 CO<sub>2</sub> 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<sub>2</sub>CO<sub>3</sub> in water at a pH > 7 enters the absorber in down flow. This countercurrent operation causes the acidic CO<sub>2</sub> gas to dissolve completely into the liquid

phase by chemically enhanced mass transfer:



The treated gas consists now of CO and O<sub>2</sub> and is sent directly to the PSA beds (19 A, B, and C). One bed adsorbs CO, yielding a contaminated O<sub>2</sub> 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<sub>2</sub> absorber (6), the unreacted CO<sub>2</sub> 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<sub>2</sub> regenerator (9) in down flow. At the bottom of this regenerator a low pressure (LP) 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 CO<sub>2</sub>. The CO<sub>2</sub> 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 CO<sub>2</sub> out of the liquid phase during the interfacial contact on the packed bed elements. A wet recycle CO<sub>2</sub> flow leaves the CO<sub>2</sub> 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 CO<sub>2</sub> regenerator (9). The semi-dry recycle CO<sub>2</sub> flow is fed to drying bed 1 (14) before combining with the fresh CO<sub>2</sub> 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 K<sub>2</sub>CO<sub>3</sub> solution is dosed from the make up tank (24) compensate for thermal K<sub>2</sub>CO<sub>3</sub> 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 CO<sub>2</sub> absorber (6) for the next absorption cycle.

## 6. CO manufacturing costs and sensitivity analysis

First aspect in the manufacturing costs analysis is the CAPEX (Capital Expenditures) 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/year 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/year 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. 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/year CO plant for base case performance.

		\$/ton CO
<b>Variable costs</b>		
Raw materials	CO <sub>2</sub>	31
	K <sub>2</sub> CO <sub>3</sub>	9
Miscellaneous materials	incl zeolite and silicagel	7
Utilities	electricity (0.0147 \$/MJ)	603
	Cooling and process water, LP steam	64
Total		<b>714</b>
<b>Fixed costs</b>		
Maintenance (incl materials)	5.5% of fixed capital	74
Operating labour & overhead	2 man/shift, 3 shifts/day	
	+ laboratory, supervision, plant overhead	28
Capital charges & overhead	including insurance, taxes, royalties	208
Total		<b>310</b>
<b>Sales expenses</b>		<b>204</b>
<b>Total production costs</b>		<b>1228</b>

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.

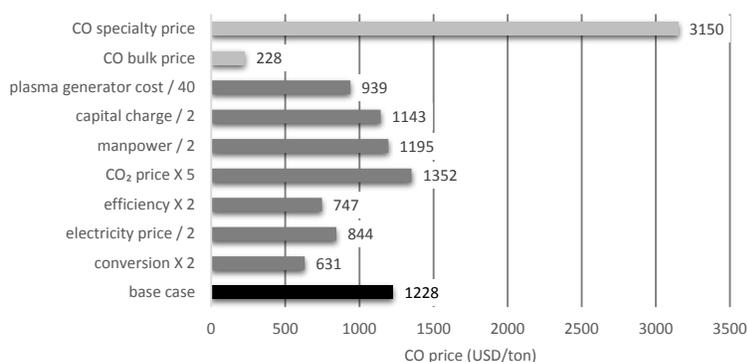


Figure 3: Sensitivity analysis for the main cost factors in the plasma CO price. As reference, also an estimate of the present CO bulk and specialty price are shown.

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, this gives a stored energy price that ranges between 0.22 (for double conversion) and 0.44 (for the base case) \$/kWh in CO. This price is to be compared with the input electricity price of 0.05 \$/kWh.

## 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<sub>2</sub> 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.

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