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# Microwave plasma emerging technologies for chemical processes

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## Abstract

Microwave plasma (MWP) technology is currently being used in application fields such as semiconductor and material processing, diamond film deposition and waste remediation. Specific advantages of the technology include the enablement of a high energy density source and a highly reactive medium, the operational flexibility, the fast response time to inlet variations and the low maintenance costs. These aspects make MWP a promising alternative technology to conventional thermal chemical reactors provided that certain technical and operational challenges related to scalability are overcome. Herein, an overview of state-of-the-art applications of MWP in chemical processing is presented (e.g. stripping of photo resist, UV-disinfection, waste gas treatment, plasma reforming, methane coupling to olefins, coal/biomass/waste pyrolysis/gasification and $CO_2$ conversion). In addition, two potential approaches to tackle scalability limitations are described, namely the development of a single unit microwave generator with high output power (> 100 kW), and the coupling of multiple microwave generators with a single reactor chamber. Finally, the fundamental and engineering challenges to enable profitable implementation of the MWP technology at large scale are discussed.

**Keywords**: microwave plasma, emerging technologies, industrial applications, roadmap

# 1. Introduction

A sustainable and green economy represents one of the major challenges of contemporary society. It involves mostly the reduction of waste generation, but also the optimization of raw material consumption in order to mitigate current alarming pollution problems and lower the energy requirements of industrial conversion processes. In this regard, the process intensification (PI) philosophy[1] has significantly improved such industrial conversion processes. By applying the PI principles,[2] various processing advances can be attained such as 1) higher energy efficiency, 2) lower raw material usage, 3) prevention of waste generation (improved product quality) and 4) safer process, as demonstrated in several industrial applications.[3-5]

For the chemical industry to progress towards a sustainable economy, novel waste-to-product approaches need to be developed to reduce the dependency on fossil fuels-based raw materials. Carbon Capture & Utilization (CCU) is an emerging concept, which utilizes waste (e.g. greenhouse gases) as chemical feedstock to produce valuable products.[6] In most cases however, the required energy input to transform waste into products tends to be rather high, making the re-utilization process unprofitable. Renewable energy sources, such as wind and solar power, are expected to have an increasing share in the future energy scene as a large fraction of the energy needed for chemical conversion processes can be obtained from these sources during peak electricity production periods. This falls within the so-called power-to-chemicals approach,[7] whereby greenhouse gases and/or water are converted into hydrocarbons by means of surplus electric power.

In the context of power-to-chemicals approach, a large variety of electricity-based chemical reactors, such as electrolyzers,[8] electrocatalytic reactors[9] and plasma-based reactors[10, 11] have been investigated. The first two reactor types require the use of a catalyst, which potentially introduces problems of thermal degradation and coking at high temperatures.[12] Concerning the use of electrolyzers, even though this technology has reached rather high voltage efficiencies (solid oxide electrolyzers, 80%),[13] the specific energy consumption compared to conventional hydrogen production routes (mainly steam reforming) is still relatively high. Plasma reactors represent a novel alternative technology due to certain processing benefits such as: fast process dynamics, process flexibility, no need for catalyst use in many processes, no need for (bulky and costly) gas-fired furnaces, low maintenance cost, and high quality products (low by-products formation). The performance of these three reactor types for the production of hydrogen was evaluated by Dincer et al. (2015).[13] From the cost and energy efficiency point-of-view, they concluded that the plasma-assisted reactor performs better compared to the other electricity-based reactors. In this work, we focus on microwave plasma (MWP)-assisted reactors, which appear to be one of the most promising plasma reactor types as discussed hereafter.

Plasma can be triggered and sustained by different energy sources. MWP in particular is a gas ionized by means of a high frequency (300 MHz – 300 GHz) electromagnetic field. The alternating electric field heats the electrons which provide energy mostly for ionization and excitation of neutral atoms and molecules creating and sustaining the discharge. The principal advantage of MWP over other discharge types is that it does not require electrodes, which must be placed inside the reactor leading to operational issues, such as regular maintenance (replacement) due to erosion caused by contaminants formation. MWP can also be operated in a wide pressure range (from $10^{-5}$ mbar – 1 bar). Furthermore, the power-to-plasma efficiency can reach up to 90%.[14] Concerning the reactor performance, the high frequencies at which MWP systems are operated produce a much larger fraction of electrons, i.e. higher electron densities, and higher electron temperature (energy) compared to other plasma sources. This results in high concentrations of active species rendering MWP an ideal highly reactive medium for chemical reactions. To date, most research has been carried out at laboratory-scale, while few successful industrial applications have been demonstrated. Some of the limitations that have hindered widespread implementation of MWP at industrial scale include the cost of equipment, challenges related to process scalability, controllability and stability as well as the cost of electric power. For further information on theoretical concepts related to MWP, the reader is referred to the literature.[14-19]

In this work, the state-of-the-art of MWP at laboratory stage, existing industrial chemical applications, current technical and operational limitations and an overview of the fundamental and engineering challenges for further development of the MWP technology are presented. Finally, some promising potential applications, which mainly concern high temperature processes, such as pyrolysis, gasification and reforming of organic waste, biomass and fossil fuels are discussed. Overall, this paper intends to set up a roadmap describing the main requirements and the next steps needed for the implementation of the MWP technology in the chemical manufacturing industry.

## 2. Microwave plasma technology: state-of-the-art

In this section, the necessary elements to operate MWP reactors are briefly described. Additionally, an overview of the laboratory state-of-the-art applications of MWP in chemical processing is given. Lastly, well-known industrial applications are discussed, showing the potential of the technology for commercial use.

### 2.1. Description of the main elements

In conventional chemical reactors, the design is characterized by process variables needing control during operation, such as temperature, pressure, concentrations of chemical species and throughput. With regard to MWP reactors, the waveguide components[20] are predefined and optimized for each particular operating frequency, whereas elements such as reactor sizing/shape/material, reactant inlet(s) (flow pattern) and cooling/control systems are design-related aspects that can be adjusted for optimization of the reactor performance. Table 1 and Figure 1 introduce the essential components of MWP systems. The component number 1 described in Table 1 (Microwave generator) is identified as the key element to scale up this type of reactors due to its limitation as to the maximum output microwave power. The reader is referred to the microwave generator section for further information.

**Table 1.** Description of the main elements enabling the operation of MWP reactors

| N° | Element | Function |
|---|---|---|
| 1 | Microwave generator<br>=<br>HV Power supply (switch mode) &<br>Microwave head | Generation of electromagnetic waves<br>Operating frequency 2.45 GHz: Maximum output power of 15 kW<br>Operating frequency 915 MHz: Maximum output power of 100 kW |
| 2 | Isolator | Protection of the magnetron from the reflected microwave field |
| 3 | Impedance tuner | Reduction of the reflected microwave power ensuring high energy transfer efficiency from the microwave generator to the plasma zone; manual or automatic operation |
| 4 | Reactor assembly | Conversion of raw materials into products<br>A plasma column is generated perpendicular to the incoming microwave field |
| 5 | Movable plunger | It positions the electromagnetic wave such that a local electric field maximum is located at the center of the plasma zone to maximize the microwave energy transfer from the generator to the plasma zone; manual or automatic operation |

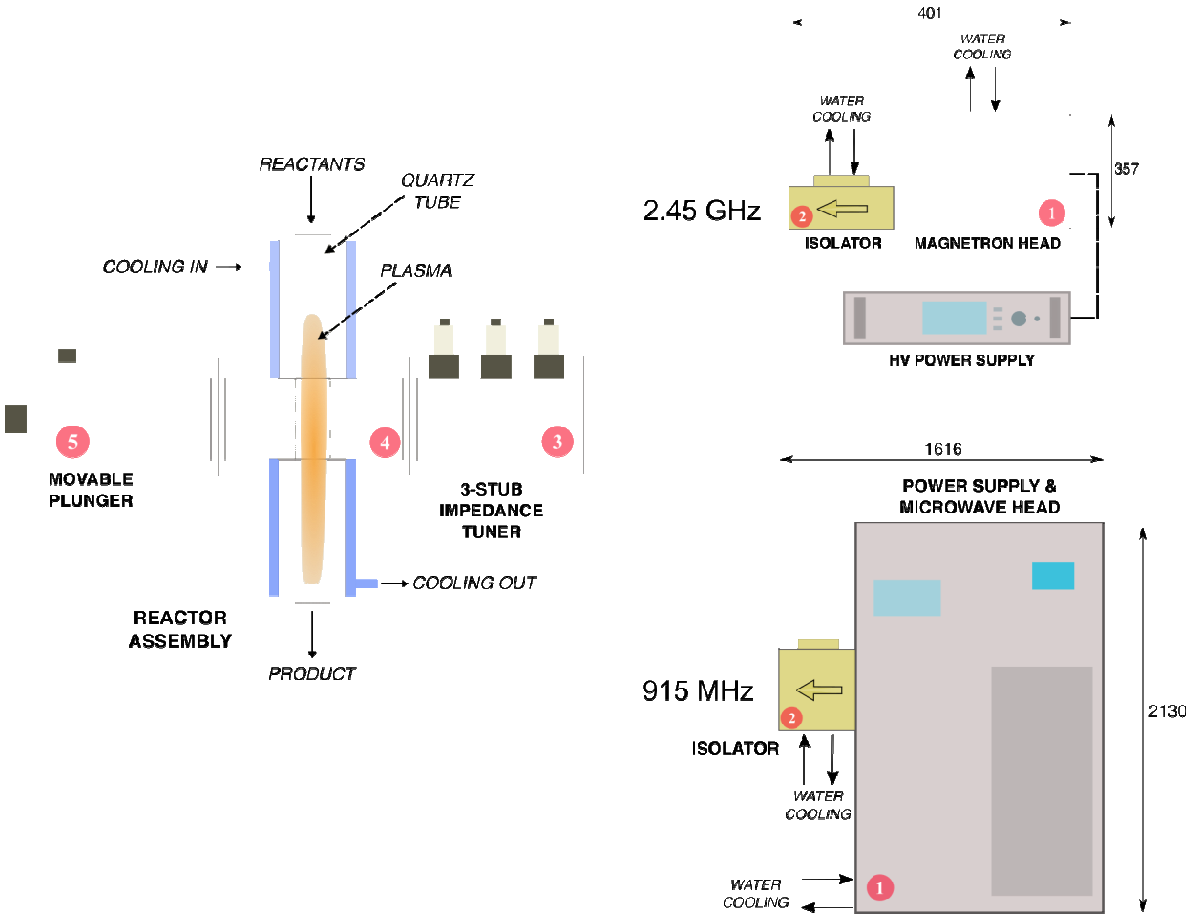


**Figure 1**. Sketch of the main elements needed to operate MWP reactors. Note that the two commercially available microwave generators for plasma applications (2.45 GHz - 15 kW and 915 MHz – 100 kW) are outlined including the relevant dimensions (mm); both generators consist of switch-mode HV power supplies. Circled numbers refer to the element numbers in Table 1; in this example, manually operated 3-stub tuner (3) and manually operated movable plunger (5).

## 2.2. State-of-the-art at laboratory stage

A remarkably broad range of chemical applications at laboratory-scale have been explored in different MWP systems with the exception of biomass gasification for syngas production, which has been investigated both at laboratory scale[21] and in medium-scale plants.[22, 23] Concerning chemical manufacturing applications, several processes are highlighted due to the large number of research studies (see Table 2), such as: plasma-assisted reforming, biomass gasification and pyrolysis, $H_2$ production, and $CO_2$ utilization. We should note that the MWP technology is also used for other applications, including: production of *carbon nanostructures* of high quality (nanotubes, graphene), production of *synthetic diamond* for gemstones and technical applications, *surface modification* for deposition of thin films to improve material properties, *water purification* (ozone/UV radiation), *photoresist stripping* for removal of polymeric photoresists in semiconductor manufacturing, and *medicine* (cancer treatment, sterilization of medical instruments and disinfection of living tissue).

Table 2 presents an overview of MWP-assisted processes for chemical applications. It is noticeable that the research focus has been on the production of synthesis gas or hydrogen. Herein, certain processes should be acknowledged due to the notably good performance shown in MWP reactors. As reported by Jasinski et al.,[24, 25] $H_2$ generation via plasma-assisted dry reforming of methane can be carried out at a specific energy consumption of ~3 kWh/m$^3$ $H_2$ and a $H_2$ generation cost ~2.3 \$/kg $H_2$ (assuming 0.06 \$/kWh). This value is close, within a factor 2, to the reported industrial cost of $H_2$ production (representative value: 1.5 \$/kg $H_2$)[26, 27] through the mature and highly integrated and optimized process of steam reforming of natural gas in high temperature furnaces. Another example is reported by Uhm et al. (2014),[22] in which the gasification of brown coal in a pilot-scale setup was studied, obtaining cold gas efficiency (CGE, calorific power of produced synthetic gas divided by the total input power to the system) values up to 84%, while conventional gasifiers, more specifically entrained flow gasifiers, have CGE values between 70-80%.[28] Additionally, one should take into account the evident gain in economy of scale and particularly the increase in the energy efficiency when microwave power above 1 kW is used to sustain the plasma chemical reactions, as displayed in Table 2.

**Table 2.** Summary of reported MWP processes for chemical applications.

| REACTANT MIXTURE | DESIRED PRODUCT | REACTOR TYPE | PRESSURE | POWER (kW) | FLOW RATE/ THROUGHPUT | CONVERSION | SELECTIVITY (%) | ENERGY EFFICIENCY | REF. |
|---|---|---|---|---|---|---|---|---|---|
| **PLASMA ASSISTED REFORMING** | | | | | | | | | |
| $CH_4 + H_2O_g$ | Syngas | 2.45 GHz | 1 bar | 5 (3-5) | 27 l/min $H_2O_g$ + 3-9 l/min $CH_4$ | 95% | 70 ($H_2$) & 19 (CO) | 300 l syngas/kWh | 29 |
| $CH_4 + CO_2$ | $H_2$ | 2.45 GHz | 1 bar | 4 | 6000 l/h $CH_4$ + 6000 l/h $CO_2$ | 1100 l/h $H_2$ | - | 350 l $H_2$/kWh | 25 |
| $C_2H_5OH + N_2$ | $H_2$ | 915 MHz | 1 bar | 5 | 2700-3900 l/h $N_2$<br>0.4-1.2 kg/h $C_2H_5OH$ | 1150 l/h $H_2$ | 100 ($H_2$) | 267 l $H_2$/kWh | 30 |
| $C_3H_7OH + CO_2$ | $H_2$ | 915 MHz | 1 bar | 5 | 2700 l/h $CO_2$<br>2.4 kg/h $C_3H_7OH$ | 1116 l/h $H_2$ | 37 ($H_2$) | 223 l $H_2$/kWh | 30 |
| $C_6H_{14} + H_2O_g$ + Ar | Syngas | 2.45 GHz | 1 bar | 2 | 34.6 mol/h $H_2O_g$<br>5 mol/h $C_6H_{14}$ | 36 mol/h $H_2$<br>14.4 mol/h CO | - | 0.24 kg syngas/kWh | 31 |
| $C_8H_{18} + H_2O_g$ + Ar | Syngas | 2.45 GHz | 1 bar | 2 | 34.6 mol/h $H_2O_g$<br>4.3 mol/h $C_8H_{18}$ | 21.6 mol/h $H_2$<br>10.8 mol/h CO | - | 0.17 kg syngas/kWh | 31 |
| $C_2H_6$ + Ar | $C_2H_4$ | 2.45 GHz | 20-73 mbar | 2 (0.1-0.8) | - | 95% | 50 ($C_2H_4$) | - | 32 |
| $C_5H_{12}$ + Ar | $C_2H_4$ | 2.45 GHz | 0.1 mbar | 2 (0.45) | 25 ml/min Ar + 7 ml/h $C_5H_{12}$ | 65% | 40 ($C_2H_4$) | 0.44 g $C_2H_4$/kWh | 33 |
| $C_6H_{14}$ + Ar | $C_2H_4$ | 2.45 GHz | 0.1 mbar | 2 (0.45) | 25 ml/min Ar + 7 ml/h $C_6H_{14}$ | 72% | 65 ($C_2H_4$) | 0.75 g $C_2H_4$/kWh | 33 |
| $C_7H_{16}$ + Ar | $C_2H_4$ | 2.45 GHz | 0.1 mbar | 2 (0.45) | 25 ml/min Ar + 7 ml/h $C_7H_{16}$ | 75% | 55 ($C_2H_4$) | 0.56 g $C_2H_4$/kWh | 33 |
| $C_8H_{18} + O_2$ + Ar | Syngas | 2.45 GHz | 1 bar | 0.10 | 0.2 ml/min $C_8H_{18}$ + 7 lpm Ar | 68.4 g/h syngas | - | 0.68 kg syngas/kWh | 34 |
| Gasoline + $O_2$ + Ar | Syngas | 2.45 GHz | 1 bar | 0.10 | 0.2 ml/min gasoline + 7 lpm Ar | 84.6 g/h syngas | - | 0.85 kg syngas/kWh | 34 |
| $CH_4 + O_2$ + Ar | Syngas | 2.45 GHz | 1 bar | 0.10 | 140 ml/min $CH_4$ + 7 l/min Ar | 46.8 g/h syngas | - | 0.47 kg syngas/kWh | 34 |
| $CH_4 + O_2$ | $CH_3OH$ | 2.45 GHz | 31 mbar | 0.02 | 30 ml/min $CH_4$ + 50 ml/min $O_2$ | 97% | 4.4 ($CH_3OH$) | 1.3 kg $CH_3OH$/kWh | 35 |
| **METHANE COUPLING TO OLEFINS** | | | | | | | | | |
| $CH_4$ | $C_2H_2$ | 2.45 GHz | 160 mbar | 0.4 | 500 ml/min | 94% | > 90 ($C_2H_2$) | 64 l $C_2H_2$/kWh | 36 |
| $CH_4$ | $C_2H_2$ | Pulsed 2.45 GHz | 15-65 mbar | 2 (0.07) | 150 ml/min | 94% | 71 ($C_2H_2$) | 85 l $C_2H_2$/kWh | 37 |
| **WASTE GAS TREATMENT** | | | | | | | | | |
| $SF_6 + N_2 + H_2O$ | | 2.45 GHz | 1 bar | 6 (5.4) | 80 l/min $N_2$ + 12 l/min ($H_2O + SF_6$) | 99.9% decomposition | | 1 $m^3$/kWh | 38 |
| CFC 12 + $H_2O_g$ | - | 2.45 GHz | 1 bar | 2 | 2 kg/h CFC 12 | 99.99% decomposition | - | 0.5 kg/kWh | 39 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| VOC ($CCl_4$) + Ar + He | - | 2.45 GHz | 1 bar | 1 | 1 l/min Ar + 5-12000 ppm $CCl_4$ | Reduction to ppb level | - | 3 kg/kWh | 40 |
| **PYROLYSIS/GASIFICATION** | | | | | | | | | |
| Brown Coal (Gasification) + $H_2O_g$ + air + $O_2$ | Syngas | 915 MHz (2) | 1 bar | 75 each (70) | 90 kg/h coal + 60 kg/h $H_2O_g$+ 320 l/min $N_2$ + 410 l/min $O_2$ | 99.8% CCE | 40 ($H_2$) & 32 (CO) | 84% CGE | 22 |
| Charcoal (Gasification) + $H_2O_g$ + air | Syngas | 2.45 GHz | 1 bar | 6 (5) | 1.26 kg/h charcoal +<br>1.1 kg/h $H_2O_g$ + 20 l/min air | 52% CCE | - | 43% CGE | 41 |
| Wood (Pyrolysis) + $N_2$ + Ar | Syngas | Plasma jet<br>2.45 GHz | 200 mbar | 2 (1) | 1 l/min $N_2$ + 1 l/min Ar plasma<br>10 g samples | 2 l/min syngas | - | - | 42 |
| Waste paper (Gasification) + air | Fuel gas | 2.45 GHz | 1 bar | 0.8 | 1-4 l/min air + 5 g sample | 3.3 $m^3$/kg paper | 7.7 ($H_2$) & 8.5 (CO) | 2.3 MJ/$m^3$ LHV | 43 |
| Rice straw (Pyrolysis) + $N_2$ | Syngas | 2.45 GHz | 1 bar | 2 (0.5) | 5 g sample + 50 ml/min $N_2$ | 80% mass reduction ratio | 55 ($H_2$) ; 17 ($CO_2$)<br>13 (CO) ; 10 ($CH_4$) | - | 44 |
| **$CO_2$ UTILIZATION** | | | | | | | | | |
| $CO_2$ and $H_2O_g$ | Syngas | Pulsed 915 MHz | 40 mbar | 1 | 3-6 l/min $CO_2$ and $H_2O_g$ | 0.72 mol/h CO<br>0.22 mol/h $H_2$ | - | 0.02 kg syngas/kWh | 45 |
| $CO_2$ | CO | 2.45 GHz | 10-250 mbar | 1 (0.6) | 5 l/min | 30% | - | 0.17 kg CO/kWh | 46 |
| $CO_2$ and $H_2$ | Syngas | 2.45 GHz | 20-50 mbar | 0.2 | 400 ml/min $CO_2$+$H_2$ | 85% | 100 ($CO_2 \rightarrow CO$) | 0.03 kg CO/kWh | 47 |
| **$H_2$ PRODUCTION** | | | | | | | | | |
| $CH_4$ | $H_2$ | 2.45 GHz | 1 bar | 6 (1-5) | 87.5 l/min $CH_4$ | 99.8% (0.87 kg $H_2$/h) | 100 ($H_2$) | 640 g $H_2$/kWh | 24 |
| $C_2H_2F_4$ | $H_2$ | 2.45 GHz | 1 bar | 6 (1-5) | 97 l/min $C_2H_2F_4$ | 84% (0.7 kg $H_2$/h) | 99.9 ($H_2$) | 670 g $H_2$/kWh | 24 |
| CO + $H_2O_g$ | $H_2$ | Reverse Vortex<br>2.45 GHz | 1 bar | 3 | 27 l/min $H_2O_g$ + 3 l/min CO | 85% (CO) | 36 ($H_2$) | 3.40 g $H_2$/kWh | 48 |
| $C_2H_5OH$/$CH_3OH$ + Ar + $H_2O_g$ | $H_2$ | 2.45 GHz | 1 bar | 0.2-0.7 | 2 l/min Ar + $CH_3OH$ + $H_2O_g$<br>0.5 l/min Ar + $C_2H_5OH$ + $H_2O_g$ | 100% ($CH_3OH$) | - | 0.41 g $H_2$/kWh | 49 |
| $CH_3OH$ + $N_2$ | $H_2$ | 2.45 GHz | 1 bar | 5 (1.4) | 12.4 l/min $N_2$ (5% $CH_3OH$) | 99% | 85 ($H_2$) | 2 g $H_2$/kWh | 50 |
| PFO (pyrolysis fuel oil) + Ar | $H_2$ | 2.45 GHz | 1 bar | 2 (0.85) | 5 l/min Ar | 446.3 ml/min $H_2$<br>27.4 ml/min $C_4$ | 92 ($H_2$) & 5 ($C_4$) | 2.8 g $H_2$/kWh | 51 |
| $CH_3OH$/$C_2H_5OH$/ $C_3H_7OH$ + Ar + $H_2O_g$ | $H_2$ | Tornado-type<br>2.45 GHz | 1 bar | 2 (0.45) | 1 l/min Ar + 9 ml/min ($CH_3OH$)<br>1 l/min Ar + 13.5 ml/min ($C_2H_5OH$)<br>1 l/min Ar + 8.5 ml/min ($C_3H_7OH$) | 0.10 g $H_2$/h<br>0.24 g $H_2$/h<br>0.18 g $H_2$/h | > 95 ($H_2$) | 0.24 g $H_2$/kWh<br>0.53 g $H_2$/kWh<br>0.45 g $H_2$/kWh | 52 |

## 2.3. Capital cost

The capital cost of conventional chemical reactors is mainly determined by the reactor dimensions (volume) and material of construction. In the case of MWP reactors, the main driver of the total capital investment is the microwave generator in combination with the waveguide components required to operate the plasma reactor. Figure 2 gives an estimation of the commercial price of MWP equipment (generator + components, see Table 1) as well as the commercial equipment cost per kW microwave power, as function of the total output power of the microwave generator. For the particular case of 100 kW, the equipment cost amounts to ~1400 €/kW microwave power. This value is calculated as the ratio between the MWP equipment price and the total output power of the generator (e.g. 1.4 $10^5$ €/100 kW). The prices given in Figure 2 include switch mode HV power supplies, which are required in the case of atmospheric pressure plasmas; the switch mode has low ripple and better control on the magnetron including the rise time or time needed for the magnetron to increase the power from 0 W to the requested power for plasma ignition. It is observed that the higher the output power of the microwave generator, the lower the equipment cost per kW microwave power as shown in Figure 2 (black line, square markers). Therefore, the development of single unit microwave sources with higher power (> 100 kW) should significantly reduce the high capital cost of MWP equipment.

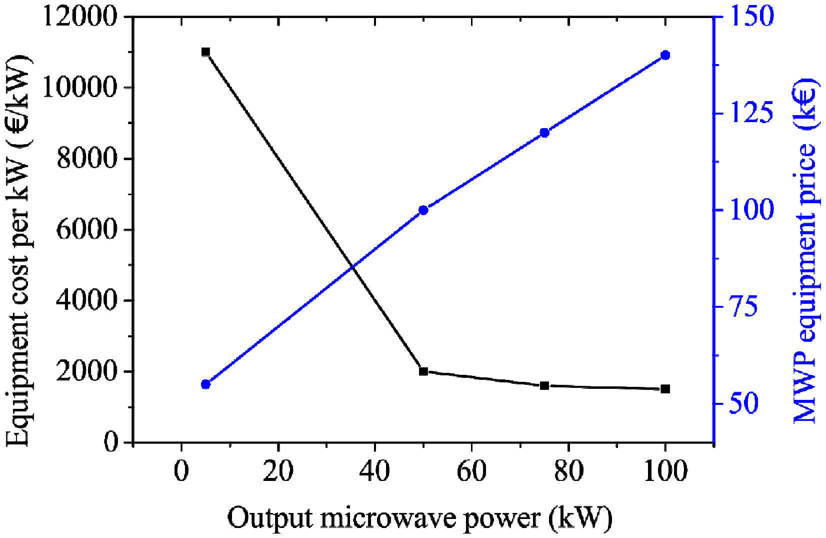


**Figure 2.** Commercial MWP equipment price (generator + components, see Table 1) and commercial equipment cost per kW microwave power (MWP equipment price (k€) divided by output microwave power (kW)) as function of the total output power of the microwave generator for equipment at 915 MHz frequency (microwave generator based on a switch-mode HV power supply).

## 2.3. Industrial applications of MWP technology

The applications of MWP at industrial-scale have been previously discussed in the literature.[16] In summary, the main industrial applications include: photoresist stripping in semiconductor manufacturing, deposition of barrier layers in PET bottles, high rate deposition process of quarts on polycarbonate windows, plasma photo curing of paintings applied to the automotive industry, UV disinfection for water treatment, waste gas treatment for decomposition of fluorine-based components such as $CF_4$, $C_2F_6$, $CHF_3$, and $SF_6$[38, 53] or ammonia, and plasma reforming to increase efficiency in wood gas engines. In the past few years, few advancements have been reported on the industrial application of this technology, although there are some novel processes that should be added to the existing list. Most of the future industrial applications of the MWP technology will be relevant to high temperature processes for chemical synthesis and (oxygenated) fuels conversion including pyrolysis, gasification and reforming of organic waste, biomass, and fossil fuels. Other application fields in which MWP will play a role are water and air purification, material synthesis (nano-particle production, diamonds, textiles) and biomedicine (cancer treatment, wound healing, disinfection).

Table 3 presents these applications together with a brief description of the main features of the process. Most of the future industrial applications of the MWP technology will be relevant to high temperature processes for chemical synthesis and (oxygenated) fuels conversion including pyrolysis, gasification and reforming of organic waste, biomass, and fossil fuels. Other application fields in which MWP will play a role are water and air purification, material synthesis (nano-particle production, diamonds, textiles) and biomedicine (cancer treatment, wound healing, disinfection).

**Table 3.** Summary of novel MWP processes for chemical applications.

| PROCESS/(COMPANY) | DESCRIPTION | MAIN FEATURES |
|---|---|---|
| BIOMASS GASIFICATION (Plasma2Energy)[23] | - Medium-scale plant for biomass gasification.<br>- It runs for four years.<br>- It exploited the concept of coupling multiple microwave generators to a single gasification chamber.<br>- The plant consumed only 20% of the energy generated. | ▪ Input microwave power = 30 kW (plasmatrons)<br>▪ Pressure (bar) = 1<br>▪ Annual Biomass Capacity = 3.3 kton<br>▪ Selectivity ($H_2$) = 50-52%<br>▪ Annual Production = 1830 $m^3$ ethanol & 253 $m^3$ diesel fuel<br>▪ Maintenance: 5 years<br>▪ Lifetime: 25 years |
| CARBON FIBER MANUFACTURING (RMX Technologies)[54] | - Low-pressure microwave plasma enhanced the oxidation and carbonization steps.<br>- Reduction in the residence time and the equipment size by 1/3.<br>- Energy requirements were reduced by 75% and manufacturing costs by 20% compared to conventional one. | ▪ Input MW power = 30 kW (915 MHz)<br>▪ Pressure (mbar) = 10<br>▪ Reactor size: Diameter = 0.05 m & Length = 4 m<br>▪ Energy efficiency = 17 kWh/kg carbon fiber |
| PECVD OF $Si_3N_4$ ON MULTI-CRYSTALLINE SILICON SOLAR CELLS[55] | - Deposition of silicon nitride anti-reflective layers on solar cell wafers by plasma enhanced carbon vapour deposition (PECVD). | ▪ Input microwave power = 2 x 4 kW (pulsed-type)<br>▪ Pressure (mbar) = 0.01-1<br>▪ Reactor size: Diameter = 0.02 m & Length = 1.5 m<br>▪ Production = 1500 solar cells wafers per hour |

| | | |
|---|---|---|
| TREATMENT OF CHRONIC WOUNDS (Adtec Europe SteriPlas)[56] | - Wound healing by reduction of microbial load and by modifying the wound microenvironment.<br>- Working gas is Argon, which ensures the reproducibility of generated active agents. | ▪ Input microwave power = 200 W<br>▪ Working gas = Argon, purity 99.95%<br>▪ Operating temp range = 10-30 °C |
| PRODUCTION OF SYNTHETIC DIAMOND MPECVD (ASTeX)[57] | - Synthetic diamond growth from the gas phase by microwave-plasma enhanced vapor chemical deposition (MPECVD).<br>- Synthesis diamonds are presented as a much affordable option over naturally mined diamonds. | ▪ Frequency = 915 MHz & Power = 90 kW<br>▪ Pressure (torr) = 180 & Gas temperature = 4000 K<br>▪ Working gas = $H_2$ + 1-5% $CH_4$<br>▪ Deposition rate = 1 g/h<br>▪ Annual production rate = 214300 carats (10 reactors)<br>▪ Diamond production cost = 14 $/carat |

## 3. State of development and outlook

### 3.1. Current status of the technology

In this section, the technical and operational limitations of the technology are discussed. The different possibilities to scaling up MWP technology are also addressed. Finally, the most relevant scientific and engineering challenges as for the implementation of this technology to commercial scale are presented in the form of a timeline.

#### *3.1.1. Microwave generator*

The largest single-unit continuous wave (CW) microwave generator, so-called magnetron, presents a limitation of maximum output power of 15 kW at a frequency of 2450 MHz and 100 kW at 915 MHz. There are magnetrons, operating at 15 kW max power, which are used for diamond synthesis at very low pressure; however, their performance seems to be quite poor and their lifetime rather short (few thousand hours range). In contrast, 15 kW generators work relatively well for laboratory applications, as those do not involve 24h operation. From an economic and regulatory point-of-view, there are two commercially preferable frequencies on the ISM bands, 915 MHz (L-band) and 2450 MHz (S-band)[54] that can be used for MWP reactors. The emissions at other frequencies can create electromagnetic interference and disrupt radio communications. To date, most of the work with MWP has been done at the standard microwave frequency of 2450 MHz.  Microwave generators at this frequency, which have been largely produced for decades (e.g. domestic microwave ovens), offer various benefits such as relatively high power capability, durability, low cost and compact size of MWP elements. In the case of the 915 MHz frequency, the waveguide components are characterized by larger sizes (about three times larger than those of one at 2450 MHz), which makes these microwave generators more costly compared to 2450 MHz generators. There are also devices operating at non-standard frequencies (20-250 GHz), known as travelling wave tubes or gyrotrons, with maximum output powers of 1-2 MW. These high power sources are mostly used in nuclear fusion and their evaluation is out of the scope of this paper.

### *3.1.2. Plasma ignition, stability and uniformity*

Plasma is ignited when the applied electric field strength overcomes the breakdown voltage of the working gas, which is called electric breakdown. Data for the breakdown voltage for different atomic and molecular gases as a function of the pressure and distance between two parallel electrodes, termed the Paschen curves, are well documented in the literature.[11] When low pressure MWP is considered, the required field strength to ignite and maintain the plasma is less demanding compared to MWP at atmospheric pressure where a rather high electron collision frequency is needed to energize the plasma. For large scale chemical applications, uniformity and stability become imperative in the production process, as it is highly important to ensure a constant and reproducible product composition. One of the major challenges for use of the MWP technology is its inherent instability, which has implications in reproducibility of the results. When operating MWP at atmospheric pressure and high power conditions, plasma stability depends mostly on the interplay between input microwave power and flow dynamics (working gas flow rate, feed gas composition, swirl flow). To obtain stable plasmas, it is important that the input power is adapted to the flow conditions. If the input power is excessive in relation to the gas flow, it can cause arcing and overheating of the quartz tube,[30] whereas if the power is too low, the degree of ionization along with gas bulk temperature will decrease resulting in plasma extinction. For high power equipment, a motorized sliding short circuit and automatic tuner can be used to compensate for variations of the reflected power, which represents a measure of plasma stability. However, operating at a minimum reflected power implies operation very close to or at unstable conditions that can lead to plasma loss or fluctuations (non-uniform).[58, 59] Another reason of instability is small fluctuations in the microwave frequency, which causes variations in the electron density, largely influencing the plasma frequency.[60] In this regard, there are a number of practical measures to improve plasma stability: 1) addition of a carrier/working gas; argon, helium, nitrogen, air and water are the most commonly used gases, 2) design of a novel reactor configuration such as “Vortex/Tornado-type”[48, 61] or multi-point microwave coupling[62], 3) combination of microwave and other fields (e.g. radio-frequency)[15] and 4) insulation of the reactor, which plays an important role in enhancing the stability by reducing heat losses.

### *3.1.3. Cooling of the plasma reactor*

MWP is characterized by high power densities, which enable MWP reactors to achieve energy efficiencies up to 90%. As a result, one of the major technical challenges is the cooling of the reactor due to the high values of power input per unit wall area (W/cm$^2$), which increases significantly the chance of reactor melting (quartz tube). Hence, MWP reactors require carefully designed cooling systems to ensure a continuous operation. The most common cooling techniques are forced-air/$N_2$ in combination with cooling water jacket-type[47] or, in more demanding cases, cooling oil, surrounding the plasma reactor. The area with the highest risk for reactor puncturing is the one found within the ignition plasma zone, i.e. where the waveguide crosses the quartz tube, which also presents the highest electric field strength. Frequently, MWP reactors are characterized by a one-sided incoming microwave field, meaning that the plasma is mostly energized on one side. This causes non-homogeneous plasma formation, which leads to hot spot formation.[62] When the power input per unit wall area becomes relatively high (> 40 W/cm$^2$),[14] a common measure of protection of the reactor wall is the use of high-speed tangential gas injection (swirl flow) to confine the plasma at the core of the reactor by creating a tornado/vortex gas motion, which isolates the reactor wall from the plasma column. Another alternative is the addition of an inert gas such as helium with high heat conductivity to increase the dissipation of heat generated in the plasma, thus reducing the possibility of reactor failure. Therefore, thermal management is one of the key engineering challenges to continuously operate this type of systems at large scale. Note that MWP reactors can be run under two different conditions: a) non-thermal/low pressure MWP and b) thermal/atmospheric pressure MWP. In the latter, the cooling requirements are rather demanding, as the temperature of the gas gets close to the temperature of the electrons – all species are close to thermal equilibrium – whereas in non-thermal MWP, the bulk gas remains rather cold (near room temperature) while having high kinetic electron temperature.

### *3.1.4. Reactor material*

As already stated, one of the main features provided by MWP is the high energy density, which also implies high temperatures inside the reactor. In this regard, the material of the reactor is a crucial aspect in MWP operation and must fulfill three requirements: 1) have high melting point to provide resistance to high temperature operation, 2) have thermal shock resistance and 3) be transparent to microwaves, i.e. it should not absorb or reflect microwaves. At lab-scale, the most commonly used material is quartz, which seems unsuitable for commercial applications due to its fragility. Therefore, other materials such as ceramics (alumina-based), aluminium oxynitride (melting point above 2000 $^{o}$C) or silicon carbide can be used to build large size MWP reactors. The latter has already been used in a plasma gasification unit.[63] Moreover, in the pilot-scale setup developed by Uhm et al. 2014,[22] alternative materials such as HACT180 (fire-resistance ceramic) and INCT120 (insulating-cement) were used to form the inner and outer layers of the MWP reactor respectively, showing great performance at temperatures up to 1800 $^{o}$C.

### *3.1.5. Process control and safety*

MWP-based processes show remarkably fast dynamics, in which most of the events take place in the micro/milli-second range. Such dynamics require demanding continuous process control tools that are capable of adjusting process parameters within a response time of milliseconds. Various control parameters are critical during MWP operation: 1) net input microwave power, 2) input gas flow rate, 3) operating pressure and 4) cooling flow rate.

The input power is the most important process variable, as it influences directly the absorbed energy by the plasma and consequently the temperature of the reactor. A practical way to control the forward power, while assuring reactor stability is by measuring the reactor wall temperature. This value is then compared to a setpoint that guarantees no reactor puncturing. The input power is then regulated based on the temperature difference between the readings and the setpoint.

The gas flow rate largely affects reactor stability as low flow rates can lead to severe increase in the specific energy input (SEI, $J/m^3$), i.e. the ratio between the input power and the inlet flow rate, causing rupture of the reactor. When the flow rates are excessive, plasma is extinguished due to the drop of SEI. The study of operating flow rate range should therefore be carefully assessed in MWP reactors.

Control of the operating pressure is particularly important when working with low-pressure MWP, as it influences both plasma ignition and sustenance. When pressure is increased, the number of collisions between electrons and other species also increases, implying that more input power is needed to sustain plasma.

Finally, as discussed, the cooling system (flow rate) requires a suitable design in which sufficient heat is removed from the plasma reactor to ensure proper function and stability of the system.

With respect to safety, the primary concern is related to exposure of operators and/or fuel to microwave radiation. Thus, the installation of microwave leak detectors is highly recommended when operating MWP equipment. In this regard, it is critical to assure good microwave shielding to eliminate any possibility of microwave radiation. If openings along the cavity are present, common practice is the installation of a metal mesh as an additional shield. Furthermore, considering the possible risk of reactor breaking, it is advisable to operate MWP reactors within a properly ventilated area to contain the hazard of a gas leakage.

### 3.2. Scalability

When evaluating the development of a new process, the production capacity represents the main design guideline, thus dictating the equipment requirements. Bulk chemicals are commonly produced on a very large scale, implying the need to operate at considerably high throughput and therefore demanding high energy input. As an example, a common methanol manufacturing plant[64] with a production rate of 100 kton/year and electricity usage of 550 kWh/ton is herein considered. The largest MWP unit developed so far was able to handle 3.3 kton biomass/year resulting in a production of 1.5 kton ethanol/year.[23] Hence, to meet the expected capacity for bulk chemical manufacturing, the current MWP reactors should be scaled up by a factor of 66 for this particular process, which is challenging.

Another pilot-scale MWP gasification unit was developed by Uhm et al. (2014).[22] In their work, two microwave generators of 75 kW output each were attached to the gasification chamber and enabled inlet flow rates of 2.2 ton coal/day with respective throughput of 1.9 ton syngas/day corresponding to a total calorific value of 0.5 $MW_{th}$. To date, the use of MWP reactors in bulk chemical manufacturing processes has been hampered mostly because the input microwave power required to sustain the plasma at rather high throughput cannot be directly delivered by the existing microwave generators. To our knowledge, there are two possibilities to address this technical limitation: 1) coupling multiple microwave generators to a single reactor chamber or 2) developing single unit microwave sources with > 100 kW output power at lower frequencies (e.g. 433 MHz).

The first approach has already been explored for a medium-scale gasification plant as shown in Sanchez A.L. (2010).[23] To increase the capacity, multiple 20 kW microwave plasmatrons were arranged around and along a single MWP gasification chamber. In a plasmatron, plasma is formed as an axial, cylindrical extension of the inner conductor of a coaxial line; microwave power is fed from a standard waveguide and a waveguide-to-coaxial transition carries out the wave mode conversion and impedance matching functions. A general advantage of these plasma sources is homogeneous plasma heating from all sides.[62, 65] A schematic representation is presented in Figure 3. When multiple microwave sources are to be combined, one should take into account the minimization of cross-coupling between generators, as this can cause a drastic reduction of the generator life and also non-uniformity of the energy delivered to the plasma. A more detailed description regarding design and application of multiple microwave generators is discussed in references [14, 62, 66]. As a final remark, the MWP gasification system reported in Sanchez A.L. (2010)[23] was designed to have maintenance every 5 years and a lifetime of 25 years, which is common practice in the chemical process industry.

The second alternative envisages the development of single unit microwave sources with > 100 kW output power. Within the microwave ISM frequencies for industrial processing, the frequency band 433.05 – 434.79 MHz (central frequency 433.92 MHz) appears to be the most interesting one for scale-up. Currently, there are no reported industrial applications operating at 433.96 MHz. However, according to magnetron manufacturers, CW magnetrons operated at this frequency can be designed to deliver much higher microwave power levels than the L-band (896 MHz, 915 MHz, 922 MHz and 929 MHz) magnetrons namely, between 0.5 and 1 MW. The design of high power 433.96 MHz equipment should consider the development not solely of the magnetron and the HV DC power supply, but also all the high power rated WR2100 waveguide components (isolators, impedance tuners etc.) required to run industrial applications.

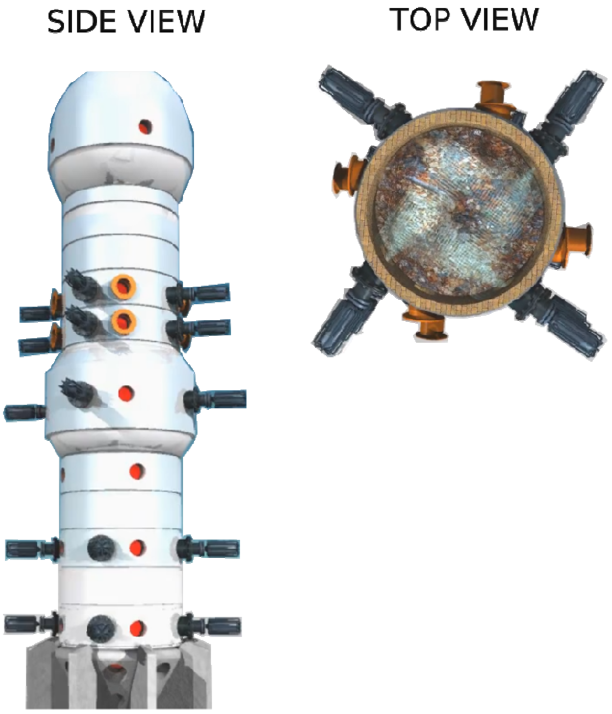
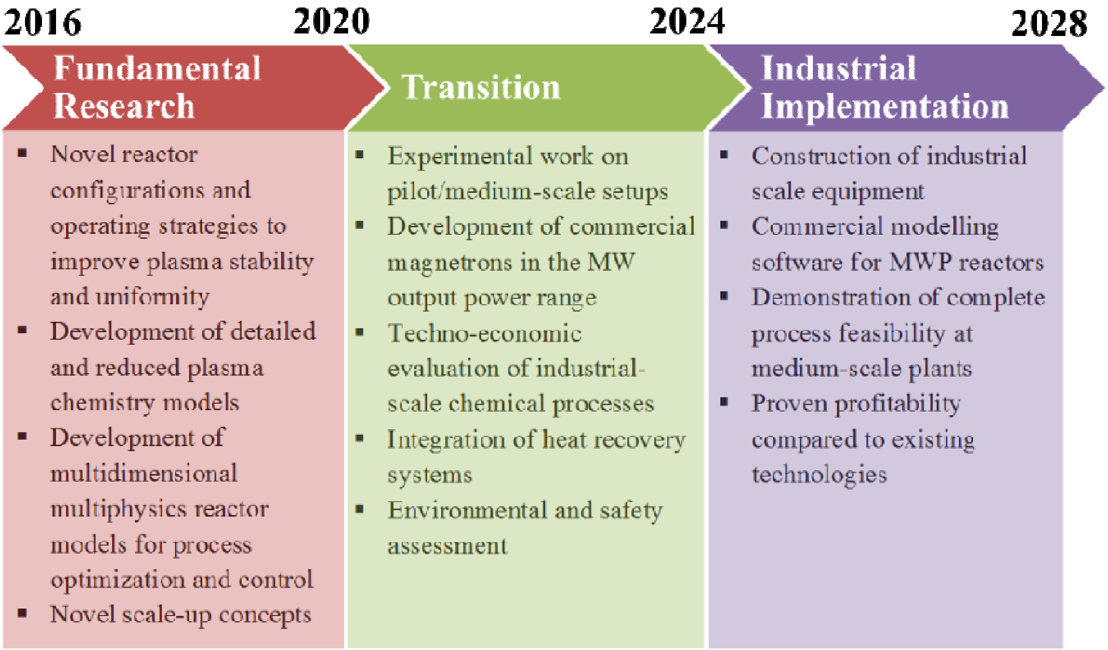


**Figure 3.** Schematic representation of multiple microwave generators attached to a single reactor.[23] Note that each of the black elements represents a 20 kW microwave plasmatron.

### 3.3. Potential of MWP for commercial chemical applications

At the current technological state of MWP, the concept of modularized production seems to be the most promising approach to respond to: (1) the decentralized electricity generation via renewable energy sources, and (2) the present volatile markets due to frequent fluctuations in factors such as demand, economic uncertainties, depletion of natural resources, demographic trends and oil and gas prices among others.[67] In this regard, the development of modular MWP units powered by locally generated renewable electricity for distributed manufacturing may, at least partially, change the current model of very large scale centralized industrial processing and also form an attractive strategy to overcome rapid changes in the market demand.[68] Therefore, the production of syngas, hydrogen, acetylene and localized waste treatment represent some of the opportunities that MWP technology can address at present.

As for bulk chemical manufacturing, the first steps to bring MWP technology to commercial scale have been taken, although some technical and operational challenges still need to be tackled before MWP can be extensively used in the chemical industry. Figure 4 presents in the form of a timeline, the main scientific and engineering challenges to be addressed. These challenges mainly concern: 1) development of higher than 100 kW microwave power sources and of effective plasma reactor designs that can be powered by multiple microwave generators to attain wide throughput range, 2) development of suitable reactor materials for MWP operation, 3) improvement of process reliability (controllability, stability and uniformity) and 4) development of chemical kinetic models that can be implemented into multidimensional multiphysics models for process design, optimization, and control.



**Fundamental Research**

- Novel reactor configurations and operating strategies to improve plasma stability and uniformity
- Development of detailed and reduced plasma chemistry models
- Development of multidimensional multiphysics reactor models for process optimization and control
- Novel scale-up concepts

**Transition**

- Experimental work on pilot/medium-scale setups
- Development of commercial magnetrons in the MW output power range
- Techno-economic evaluation of industrial-scale chemical processes
- Integration of heat recovery systems
- Environmental and safety assessment

**Industrial Implementation**

- Construction of industrial scale equipment
- Commercial modelling software for MWP reactors
- Demonstration of complete process feasibility at medium-scale plants
- Proven profitability compared to existing technologies

**Figure 4.** Timeline for the implementation of MWP technology in chemical manufacturing industry.

## 4. Conclusions

Microwave plasma (MWP) is one of the most promising enabling technologies for electricity-based reactors as regards the future partial electrification of the chemical industry. In this work, we have summarized the extensive research carried out on MWP at laboratory-scale combined with some successfully demonstrated industrial applications. Concerning chemical processing applications, high temperature processes, such as pyrolysis, gasification and reforming of organic waste, biomass and fossil fuels have the highest potential to benefit from MWP. However, it is imperative to perform research with medium-scale setups to quantitatively demonstrate the profitability, reliability and operational benefits of the technology, as already shown for biomass gasification. In parallel, work on development of a) single-unit microwave sources with >100 kW output power (0.5-1 MW), b) suitable reactor materials that can withstand harsh operating conditions and c) reaction kinetic models that can be implemented into multidimensional multiphysics reactor models appear to be key scientific and engineering challenges that need to be addressed to promote wider application of the technology to large scale operations.

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