Emerging Microwave-Plasma Technologies for Chemical Processes

Javier F. de la Fuente¹, Anton A. Kiss²-³, Marilena T. Radoiu⁴, Georgios D. Stefanidis⁵*

¹ Process & Energy Laboratory, Delft University of Technology, Leeghwaterstraat 39, 2628 CB, Delft, The Netherlands
³ Sustainable Process Technology Group, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE, Enschede, The Netherlands
⁴ Independent consultant
⁵ Chemical Engineering Department, Katholieke Universiteit Leuven, Celestijnenlaan 200f, 3001 Leuven (Heverlee), Belgium

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 CO₂ 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.

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. 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 products¹. 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 – that is, 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 approach², whereby greenhouse gases and/or water are converted into hydrocarbons by means of surplus electric power.

In this context, 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 byproducts formation). In this work, we focus on microwave plasma (MWP) assisted reactors, which appear to be one of the most promising plasma reactor types. The principal advantage of MWP over other discharges 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\(^3\). The high frequencies at which MWP systems are operated produce a large fraction of electrons, i.e. high electron densities, and high 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.

Here we present 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. 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. MWP technology: State-of-the-art

2.1. 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\(^4\) and in medium-scale plants\(^5,6\). Concerning chemical manufacturing applications, several processes are highlighted due to the large number of research studies (see Table 2 in Ref. [7]). These include plasma-assisted reforming, biomass gasification and pyrolysis, \(\text{H}_2\) production, and \(\text{CO}_2\) utilization. Figure 1 shows an atmospheric air microwave plasma at different values of net input power used for biomass gasification purposes at Delft University of Technology. Herein, certain processes should be acknowledged due to the notably good performance shown in MWP reactors. As reported by Jasinski et al.\(^8\), \(\text{H}_2\) generation via plasma-assisted dry reforming of methane can be carried out at a specific energy consumption of \(\sim 3\) kWh/m\(^3\) \(\text{H}_2\), and a \(\text{H}_2\) generation cost \(\sim 2.3\) $/kg \(\text{H}_2\) (assuming 0.06 $/kWh). This value is close, within a factor 2, to the reported industrial cost of \(\text{H}_2\) production (representative value: 1.5 $/kg \(\text{H}_2\))\(^9\) 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)\(^5\), in which the gasification of brown coal in a pilot-scale setup was studied, obtaining cold gas efficiency (CGE) values up to 84%, while conventional gasifiers\(^10\) have CGE values between 70-80%.

**Figure 1.** Atmospheric air microwave plasma at 2, 2.5 and 3 kW microwave power, from left to right.

2.2. Industrial applications of MWP technology

The applications of MWP at industrial-scale have been previously discussed in the literature\(^11\). 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 \(\text{CF}_4\), \(\text{C}_2\text{F}_6\), \(\text{CHF}_3\), and \(\text{SF}_6\)\(^12\) or ammonia, and plasma reforming to increase efficiency in wood gas engines. Table 1 presents the latest industrial applications of MWP together with a brief description of the main features of each 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 1. Summary of novel MWP processes for chemical applications.

<table>
<thead>
<tr>
<th>PROCESS (COMPANY)</th>
<th>DESCRIPTION</th>
<th>MAIN FEATURES</th>
</tr>
</thead>
</table>
| BIOMASS GASIFICATION (Plasma2Energy) | - Medium-scale plant for biomass gasification.  
- It run for four years.  
- It exploited the concept of coupling multiple microwave generators to a single gasification chamber.  
- The plant consumed only 20% of the energy generated. | ▪ Input microwave power = 30 kW (plasmatrons)  
▪ Pressure = 1 bar  
▪ Annual Biomass Capacity = 3.3 kton  
▪ Selectivity (H₂) = 50-52%  
▪ Annual Production = 1830 m³ ethanol & 253 m³ diesel fuel  
▪ Maintenance: 5 years  
▪ Lifetime: 25 years |
| CARBON FIBER MANUFACTURING (RMX Technologies) | - Low-pressure microwave plasma enhanced the oxidation and carbonization steps.  
- Reduction in the residence time and the equipment size by 1/3.  
- Energy requirements were reduced by 75% and manufacturing costs by 20% compared to conventional one. | ▪ Input MW power = 30 kW (915 MHz)  
▪ Pressure = 10 mbar  
▪ Reactor size:  
  Diameter = 0.05 m, Length = 4 m  
▪ Energy efficiency = 17 kWh/kg carbon fiber |
| PECVD OF Si₃N₄ ON MULTI-CRYSTALLINE SILICON SOLAR CELLS | - Deposition of silicon nitride anti-reflective layers on solar cell wafers by plasma enhanced carbon vapor deposition (PECVD). | ▪ Input microwave power = 2 x 4 kW (pulsed)  
▪ Pressure = 0.01-1 mbar  
▪ Reactor size:  
  Diameter = 0.02 m, Length = 1.5 m  
▪ Production = 1500 solar cells wafers per hour |
| TREATMENT OF CHRONIC WOUNDS (Adtec Europe SteriPlas) | - Wound healing by reduction of microbial load and by modifying the wound microenvironment.  
- Working gas is Argon, which ensures the reproducibility of generated active agents. | ▪ Input microwave power = 200 W  
▪ Working gas = Argon, purity 99.95%  
▪ Operating temp range = 10-30 ºC |
| PRODUCTION OF SYNTHETIC DIAMOND MPECVD (ASTeX) | - Synthetic diamond growth from the gas phase by microwave-plasma enhanced vapor chemical deposition (MPECVD).  
- Synthesis diamonds are presented as a much affordable option over naturally mined diamonds. | ▪ Frequency = 915 MHz, Power = 90 kW  
▪ Pressure = 180 torr  
▪ Gas temperature = 4000 K  
▪ Working gas = H₂ + 1-5% CH₄  
▪ Deposition rate = 1 g/h  
▪ Annual production rate = 214,300 carats (10 reactors)  
▪ Diamond production cost = 14 $/carat |
3. State of development and outlook

3.1. Current status of the technology

3.1.1. Microwave generator

The largest single-unit continuous wave (CW) microwave generator, namely magnetron, presents a limitation of maximum output power of 15 kW at a frequency of 2450 MHz and 100 kW at 915 MHz. 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) that can be used for MWP reactors. To date, most of the work with MWP has been done at the standard microwave frequency of 2450 MHz. 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.

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 breakdown17. 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. 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). Additionally, 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). 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” or multi-point microwave coupling, and (3) combination of microwave and other fields (e.g. radio-frequency).

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/cm²), 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/N₂ in combination with cooling water jacket-type18 surrounding the plasma reactor. When the power input per unit wall area becomes relatively high (> 40 W/cm²)3, 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.

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. 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 °C) or silicon carbide can be used to build large size MWP reactors. The latter has already been used in a plasma gasification unit19. Moreover, in the pilot-scale setup developed by Uhm et al.5, 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 °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. 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. The gas flow rate largely affects reactor stability as low flow rates can lead to severe increase in the specific energy input (SEI, J/m³), 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. Control of the operating pressure is particularly important when working with low-pressure MWP, as it influences both plasma ignition and sustenance.

With respect to safety, the primary concern is related to exposure of operators and/or fuel to microwave radiation. 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. A pilot-scale MWP gasification unit was developed by Uhm et al.(2014)⁵. 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 MWth. To our knowledge, there are two possibilities to address the high input microwave power required to sustain the plasma at rather high throughput: (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)⁶. To increase the capacity, multiple 20 kW microwave plasmatrons were arranged around and along a single MWP gasification chamber. A schematic representation is presented in Figure 2. As a final remark, the MWP gasification system reported in Sanchez A.L. (2010)⁶ was designed to have maintenance every 5 years and a lifetime of 25 years, which is common practice in the chemical process industry.

![Figure 2. Schematic representation of multiple microwave generators attached to a single reactor](image)

Note that each of the black elements represents a 20 kW microwave plasmatron.

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.

3.3. Potential for 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. 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. Therefore, the production of syngas, hydrogen, acetylene and localized waste treatment represent some of the opportunities that MWP technology can address at present.

Figure 3 presents in the form of a timeline the main scientific and engineering challenges to be addressed before MWP can be extensively used in the bulk chemical manufacturing industry. 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.

![Figure 3. Timeline for the implementation of MWP technology in chemical manufacturing industry.](image)

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 article, 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 (0.5-1.0 MW), (b) suitable reactor materials that can withstand harsh operating conditions, and (c) reaction kinetic models that can be implemented into multidimensional multi-physics 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.

For further reading:

About the Authors

Dr. Javier Fernandez de la Fuente will soon receive his Ph.D. at Delft University of Technology in the Netherlands on the application of microwave plasma technology to convert CO2 into high value chemicals. He completed his M.Sc. degree in Chemical Engineering at University of Valladolid (Spain) in 2012. He has broad experience as a R&D engineer, mostly focused on the production of liquid fuels through alternative technologies. He worked on projects such as the design of a pervaporation unit to separate butanol from acetone-butanol-ethanol (ABE) mixture as an alternative to distillation, and the start-up and optimization of an ammonia fiber expansion pilot plant to pre-treat wheat straw for the production of ethanol. Moreover, he explored a new approach to produce MCM-41 for ibuprofen encapsulation by ultrasound-assisted supercritical CO2 during his stage at Ruhr University of Technology in Germany.

For more information: https://www.linkedin.com/in/javierfdelafuente
E-mail: J.FernandezdelaFuente@tudelft.nl

Dr. Anton Alexandru (Tony) KISS is a senior project manager at AkzoNobel - Research, Development & Innovation, where he serves as an expert in fluid separation technologies, reactive-separation processes, process intensification, and integrated sustainable processes, as well as process modeling and simulation of industrial processes. He is also a part-time professor of separation technology at the University of Twente (Sustainable Process Technology) in the Netherlands. He has published several textbooks, book
chapters, patents, and more than 100 scientific articles. For his pioneering work and career achievements, he received in 2013 the Hoogewerff Jongerenprijs and the AkzoNobel Innovation Excellence Award. Kiss holds a PhD in chemistry and chemical engineering from the University of Amsterdam, and MS and BS degrees in chemical engineering from Babes-Bolyai University of Cluj-Napoca in Romania, and he was a post-doctoral research fellow at Delft University of Technology (TU Delft) and the University of Amsterdam. He is a member of AIChE, IChemE, Society of Chemical Industry (SCI), European Society of Mathematical Chemistry (ESMC), Process Systems Engineering – The Netherlands (PSE-NL), European Federation of Chemical Engineering (EFCE), and EFCE Working Party on Computer Aided Process Engineering (CAPE-WP).

For more information: [http://www.tonykiss.com](http://www.tonykiss.com)
E-mail: Tony.Kiss@akzonobel.com

---

**Dr. Marilena Radoiu**, Chartered Chemist (CChem) and Member of the Royal Society of Chemistry (MRSC), received her M.Sc. in Organic Technological Chemistry from the Polytechnic University of Bucharest in 1993 and her Ph.D. in Radiochemistry and Nuclear Chemistry from the same University in 1998. She has extensive work experience in different international academic and industrial environments. She has worked for 20 years in Romania, Canada, UK and France in the development of microwave-assisted technologies with applications to chemical synthesis, biomass extraction, plasma etc. Her work has included engineering and development of novel industrial and scientific standard and custom products, such as Zenith Etch and Sirius6000 - microwave plasma reactors for semiconductor gas cleaning, laboratory equipment such as MiniFlow 200, and Minilabotron 2000. Dr. Radoiu is also a member of several professional associations, including the Association for Microwave Power, Education and Research in Europe (AMPERE).

For more information: [https://www.linkedin.com/in/marilenaradoiu](https://www.linkedin.com/in/marilenaradoiu)
E-mail: marilena.radoiu@btinternet.com

---

**Prof. Georgios Stefanidis** (KU Leuven, Belgium) received his chemical engineering education from the National Technical University of Athens (M.Sc.) and University of Gent (Ph.D.). His research interests revolve around process intensification, alternative energy forms and transfer mechanisms (mainly microwaves and plasma), biomass gasification and pyrolysis, catalytic reforming and partial oxidation of hydrocarbons and oxygenated fuels and CO₂ utilization. He is co-author of more than 60 peer-review papers in the field of process intensification.

* Corresponding author, E-mail: [georgios.stefanidis@kuleuven.be](mailto:georgios.stefanidis@kuleuven.be)