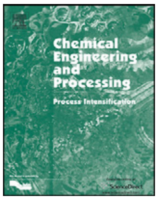
Chemical Engineering and Processing xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Chemical Engineering and Processing:
Process Intensification

journal homepage: www.elsevier.com/locate/cep



# Industrial applications of plasma, microwave and ultrasound techniques: Nitrogen-fixation and hydrogenation reactions

V. Hessel[a,*], G. Cravotto[b], P. Fitzpatrick[c], B.S. Patil[a], Jüergen Lang[d], Werner Bonrath[e]

[a] *Laboratory of Chemical Reactor Engineering/Micro Flow Chemistry and Process Technology, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[b] *Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, 10125 Torino, Italy*
[c] *C-Tech Innovation, Capenhurst Technology Park, Chester, Cheshire CH1 6EH, UK*
[d] *Innovation Management, Verfahrenstechnik & Engineering, Evonik Industries AG, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany*
[e] *DSM Nutritional Products Ltd., Research and Development, P.O. Box 2676, 4002 Basel, Switzerland*

ARTICLE INFO

*Article history:*
Received 20 December 2012
Accepted 1 February 2013
Available online xxx

*Keywords:*
Plasma
Plasma catalysis
Nitrogen fixation
Microwave
Hydrogenation
Ultrasound

ABSTRACT

The MAPSYN project (Microwave, Acoustic and Plasma assisted SYNtheses) aims at nitrogen-fixation reactions intensified by plasma catalysis and selective hydrogenations intensified by microwaves, possibly assisted by ultrasound. Energy efficiency is the key motif of the project and the call of the European Union behind (NMP.2012.3.0-1; highly efficient chemical syntheses using alternative energy forms). The material (catalysis) and process innovations given in the literature for the two demonstration examples (of the project) are reviewed and added by the project's own ones derived from the latest state of the art. From there still a gap to industrialization needs to be closed which needs innovation as well on the level of process control and plant operation, finally opening gates to new business models (distributed production and modular plant-numbering up instead of scale-up). Such systemic solution shall be developed under the supervision of energy and cost analysis as well as life-cycle analysis to ensure following a holistic approach. This demands for a new science management not focusing only on the key innovation, but as well as on other assisting enabling technologies needed and for the systemic vision with plant view and process control – all centered around industrial reaction equipment.

## 1. Introduction

In the last ten years considerable efforts in the industrialization of the microwave and plasma techniques were done, e.g. for (ore) drying and exhaust gas cleaning, respectively [1–4]. Yet, industrial applications in the field of chemistry remain isolated [1,3]. In the same time, energy costs have raised considerably, rendering conventionally heated processes more expensive. Also, micro process technologies and process intensification emerged which gave a considerable push to chemical processing [5–7]. In addition, the market and producing side changed. Many fine- and bulk-chemical processes are nowadays produced in China and other places in Asia.

This has led to a reconsideration of the use alternative energies for chemical industry on the side of the European Commission in its 7th Framework Program. A respective call under the umbrella of its Theme 4: NMP – Nanoscience, Nanotechnologies, Materials and New Production Technologies is entitled "Highly efficient chemical syntheses using alternative energy forms" (NMP.2012.3.0-1). The MAPSYN project (Microwave, Acoustic and Plasma assisted SYNtheses) was chosen here and is detailed at the end of the review paper. Two industrial applications are targeted – plasma driven nitrogen fixation reactions and microwave/ultrasound assisted selective hydrogenations. This bridges from bulk- to fine-chemical processes and comprises most of the current key technologies for alternative energies.

For the two applications of interest, the state of the art is reviewed first. A number of process and material (catalyst) innovations have been achieved over the years, yet in the plasma case over decades. Yet, this has mostly remained at the laboratory level, while advanced industrially proven reactor concepts have been developed for applications different from chemistry, such as exhaust-gas cleaning with plasma and (ore) drying with microwaves. A key enabler to further develop these innovations toward the needs of the MAPSYN project is seen in a plant innovation, i.e. to use modular, compact production platforms such as the Evotrainer which is detailed below. This shall serve, among others, the needs for industrial-suited process control, especially relevant for the energy side.

Beyond the missing last step in innovation focus is given on the interplay of the innovations. The three hierarchies of innovation (with respect to scale and complexity) – concerning materials,

---

* Corresponding author. Tel.: +31 0402472973.
*E-mail address:* v.hessel@tue.nl (V. Hessel).

0255-2701/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cep.2013.02.002

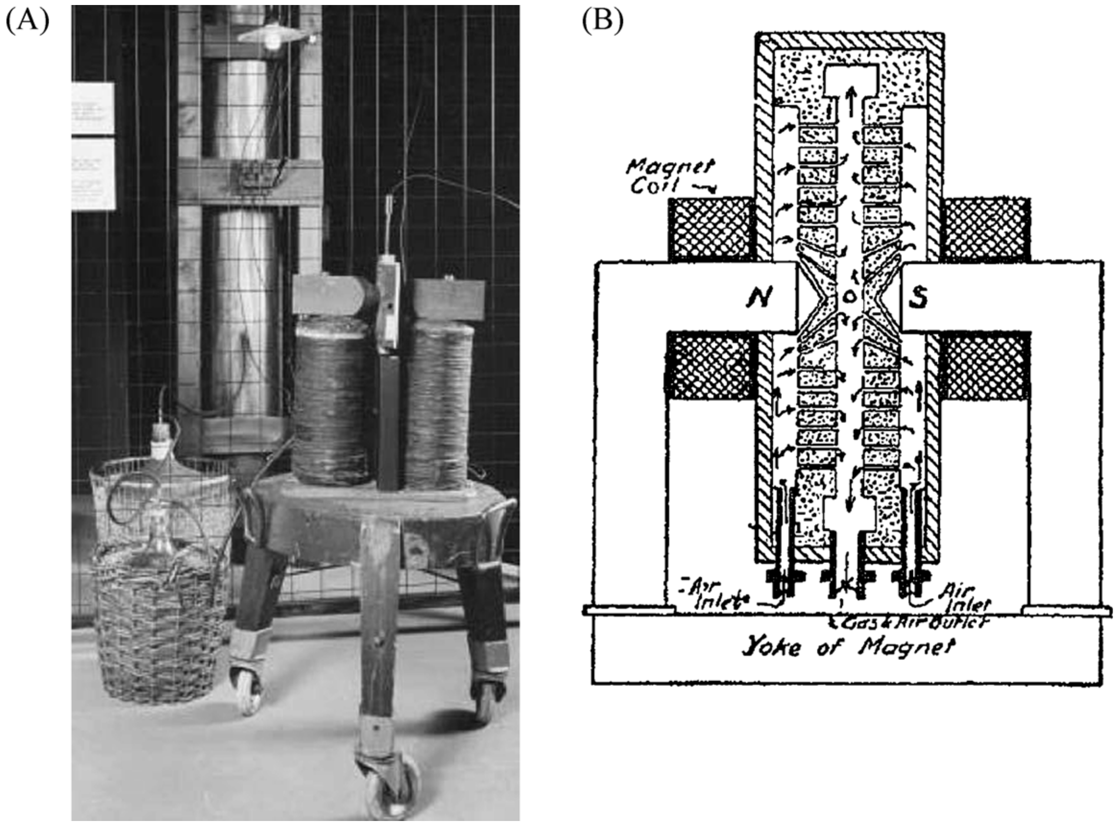


**Fig. 1.** (A) Birkeland's first experimental nitrogen-fixation set-up at the university. Nitric acid, converted from the nitric oxide generated in the plasma process, as final product of process was collected in glass container, whereas the furnace is mounted on top between two large electromagnets [21] (with kind permission of Springer). (B) Diagrammatic sketch of Birkeland and Eyde furnace [22] (with kind permission of Wiley-VCH).

processing and the plant environment – are not treated individually and step by step. Rather a systemic solution is to be developed which targets the full costs of the industrial process and includes a life-cycle assessment for the sustainability consequences. This includes the choice for the right demonstration applications from industry where energy management really dominates and provides a key for process intensification. The inclusion of micro process technologies and a miniaturization of the key equipment are believed to be assisting functions in the latter.

In the following, the state of the art in the two demonstration applications of the project will be each shortly reviewed and then the discussion will be closed with presenting the objective, key enabling technologies and proposed holistic innovation of the MAPSYN project.

## 2. Plasma processing applied to nitrogen-fixation reactions

### 2.1. Plasma background and early approaches

Plasma is the fourth state of the matter [8]. Plasma is generated by ionization, which takes place when sufficient amount of the electrical energy is supplied to a gas [8,9]. Highly excited atomic, molecular, ionic and radical species are generated in this way. The development of high frequency torches in 1948, of the DC arc torch [9] and of improved analysis techniques in the seventies led to better understanding of the kinetics and mechanism of plasma reactions, allowing a better connection between plasma process conditions and reaction products, therefore the number of studies in plasma chemistry increased significantly [9]. The first industrial nitrogen fixation reaction by using plasma reactor for nitric oxide synthesis was developed by Birkeland and Eyde in 1904 [10]. Their process components are shown in Figs. 1 and 2, which used arc plasma to produce nitrogen oxide from air, one of the nitrogen-fixation reactions of interest in this overview. The process had poor energy efficiency as compared to the classical Haber process with ammonia; hence it was abandoned from industry. With the rapid development in the understanding of plasma reaction kinetics due to advanced measurement techniques, a large number of publications on plasma nitrogen-fixation were given by number of research groups [11–20].

Fulcheri et al. proposed a new process for the fullerene process, where the carbon input rate can be independently controlled. Fig. 3A shows their AC plasma reactor used for the fullerene production from carbon powder [23]. Fig. 3B shows a hydrogen plasma reactor for coal pyrolysis operated under ultra-high temperature and with a residence time of milliseconds [24]. This reactor is multifunctional and stands for advanced, complex processing, i.e. it has upstream a mixing unit for solid–gas mixing (introducing fine coal particles) and then operates with a complex gas-particle flow to be quenched very shortly.

Acetylene and ethylene are examples of bulk chemical products that have been produced on industrial scale. These are made by cracking hydrocarbons using the Hüls, Hoechst-Hüls and DuPont electric arc processes [25]. A plant based on the use of Hüls electric arc process was in operation till 1993 with annual capacity of 120,000 t of acetylene and 50,000 t of ethylene in Germany. In the Hüls process, hydrocarbons (having a boiling point up to 200 °C) are cracked in a stabilized arc with internal temperature up to 20,000 °C, gas was passed through it for few milliseconds. The reaction products were quenched to 200 °C by water sprays. This process gave a yield of acetylene 1 t and ethylene 0.42 t per 1.8 t of hydrocarbon fed. This highly energy intensive process was abandoned in 1993 because of smaller market demands of

Please cite this article in press as: V. Hessel, et al., Industrial applications of plasma, microwave and ultrasound techniques: Nitrogen-fixation and hydrogenation reactions, Chem. Eng. Process. (2013), http://dx.doi.org/10.1016/j.cep.2013.02.002