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Energy, catalyst and reactor considerations for (near)-industrial plasma processing and learning for nitrogen-fixation reactions☆

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ABSTRACT

The MAPSYN project of the European Union (standing for *Microwave, Acoustic and Plasma SYNtheses*) aims at the utilization of plasma technology for nitrogen fixation reactions on an industrial scale and with industrial plasma reactor technology, developed and utilised commercially [1]. Key motif is enhanced energy efficiency to make an industrial plasma process viable for chemical industry. The corresponding enabling technologies – plasma catalysis, smart reactors (microreactors) and more – go beyond prior approaches. Continuing a first more project-based literature compilation, this overview focus on the two first enabling functions, plasma catalysis and smart reactor technology, which are reviewed for industrial and near-industrial plasma-based applications. It is thereby evident that notable promise is given for the nitrogen fixation as well and indeed this has been demonstrated also for nitrogen fixation; yet, initially and without the holistic system engineering dimension.

1. Plasma catalysis as enabling tool and energy efficiency – seen in the light of nitrogen fixation reactions

This review is written with the view on the coming utilization of plasma technology for nitrogen fixation reactions on an industrial scale using industrial plasma reactor technology, developed and utilised commercially, e.g. for the nitrogen fixations [2,3] or the synthesis of ultrapure silicon tetrachloride or germanium tetrachloride [4]. This is one of two exploitation pillars of the European MAPSYN project and details are shortly given in the following paragraph and the whole MAPSYN approach is actually given in another review paper [1].

The MAPSYN project (standing for *Microwave, Acoustic and Plasma SYNtheses*) aims at nitrogen-fixation reactions intensified by plasma catalysis and selective hydrogenations intensified by microwaves, possibly assisted by ultrasound [1]. 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). MAPSYN provides a new approach, besides for technological reasons as given above, also in terms of partnership and science management. While the key technology of the alternative energies comes more from the industrial partners at least when production is approached, the innovation of the academic partners is used for process and material innovation, detailed in [1]. The focus is thus not only on the alternative energies, but on the innovation level in hierarchy below (catalysis) and, more notably, above (yet not to be disclosed, since we plan to release that at a later stage after proof of principle).

We see plasma catalysis as an enabler for chemical intensification (in the way as defined in [5]) and the whole electric tuning system/process control around the plasma reactor as process-design intensification (again as defined in [5]). In this review, we aim to link that to the final process intensification objective which is “energy efficiency”, naturally at satisfying or improved product efficiency (conversion, selectivity, space-time yield, productivity, purity, costs, flexibility, time-to-market...). We see a lot of laboratory work been done, yet – also due to the complexity of the topic – with a number of open questions and not with satisfactory solutions so far to be transferred to an industrial process. This is, however, not at this point of development the focus of our reporting; rather we summarize existing literature at best practice.

With second priority, we like to combine that with “reactor configuration” as enabling tool; in particular, concerning different reactor configurations with respect to plasma catalysis, such

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as placing the catalyst in the plasma zone or thereafter (or even before). Thus, comparing multi-stage reactor operation with single-stage one and related generic options in reactor engineering.

As outlined also in detail in the MAPSYN related review paper [1], there is considerable evidence for the catalytic enabling function even for the nitrogen fixation reactions itself. For example, the use of a catalyst in a plasma reactor for the synthesis of nitric oxide has been investigated by number of researchers [6–8]. For a low-pressure reactor the yield of nitrogen fixation was 8% without catalyst, which was increased to 19% by use of WO_3 as a catalyst [7]. A significant increase in conversion for the hydrogen cyanide plasma synthesis was found in presence of a metallic grid; in the following order Mo > W > Ta > Fe > Cu [9]. These and other very promising findings have, however, not been industrialised and much of the industrial interest in commercial plasma-assisted nitrogen fixation seems to have slowed down or even stopped in the 70–80 s. Presumably, there has to be a reason for this and a missing gap which is needed to be closed such as process-design innovation. Yet, also a changing market with new needs ('Windows of Opportunity' [10], '50% Idea' [11]), new business models, new supply chains, and production entities ('Future Factories' [10]) might be game changing; in view of a restarted industrial interest in plasma technology for chemicals making.

In view of the latter and to have a larger scope and significance, the role of plasma catalysis (plus reactor configurations) and energy efficiency is outlined and detailed for industrial plasma applications – with focus on VOC/waste destruction and surface modification as major utilization of plasma processing – and, to our belief, one near-industrial application which is plasma-assisted fuel processing/decomposition. This goes along with MAPSYN's mission on industrial exploitation of the use of alternative energies for process-intensified industrial chemical production. It is clear that the latter is a difficult endeavour as good understanding of plasma catalysis is demanding and a development made from the beginning with industrial view is even more challenging. This poses considerable risk in the development so that a multi-partnership in a project as given is needed as approach.

2. Plasma applications with industrial potential/application – surface modification and VOCs treatment

Plasma technology has been implemented in various commercial applications, for niche applications, and here established as versatile tool for industrial process enhancement [12]. The advantages of plasma technology are mainly oriented towards the provision of high energy levels and temperatures by the generation of excited species in an electrical discharge. This facilitates processing under low temperature operating conditions and lower residence time compared to conventional methods. Apart from that, the utilization of electric energy eliminates the need of heat supply and gas pre-treatment, reducing by this way associated energy costs [13].

The well-known industrial application of cold plasma is the ozone production [14,15]. The capability of large ozone producing facilities can reach to several hundred kg/h with a power consumption of several megawatts, which decreased the ozone price less than 2 US$/kg. The main applications of ozone are in water treatment and in pulp bleaching, while other applications in organic synthesis like the ozonization of oleic acid and the production of hydrochinon, piperonal, certain hormones, antibiotics, vitamins, flavors, perfumes and fragrances [16].

Accordingly, the interest grows on plasma integration into energy-intensive industrial applications, such as the treatment of waste and toxic materials, as well as, material surface modification. In particular, the plasma decomposition of volatile organic compounds (VOCs), which constitute one of the most significant and hazardous air pollution source, has been thoroughly investigated. Frequently, plasma operation is combined with catalysis to yield a synergistic effect, as e.g. found for the VOCs and NO_x abatements, yielding higher energy efficiency and removal rates [17,18]. For NO_x removal, conversion is increased by 12–17% when incorporating titanium dioxide catalyst in the plasma reactor [18].

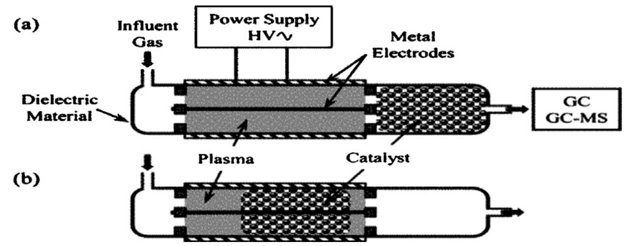

Fig. 1. Schematic setup of plasma reactor with: (a) the catalyst located after the discharge area and (b) the catalyst located within the discharge area.
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2.1. VOCs/toxic material destruction

2.1.1. Decomposition of VOCs as air pollutants

Oda has identified two major parameters that can improve energy efficiency of VOCs plasma treatment. The first parameter includes power supply features, such as applied frequency and voltage, and the configuration of the plasma reactor which constitutes one of the main factors determining the energy costs of the process [19]. The second parameter is the synergistic effect of plasma catalysis which triggers the reduction of energy consumption and increases the decomposition rates. An overview of the energy efficiency of plasma-catalysis in abating toxic materials is given in the following chapter with an intense focus placed on the role of different catalysts [18].

Harling et al. focused on the application of non-thermal plasma catalysis for the decomposition of VOCs such as toluene and benzene which are dangerous air pollutants present in indoor environments [20]. A two-stage non-thermal plasma catalytic reactor is compared for its efficiency of toluene and benzene destruction with both conventional catalysis and plasma techniques. At a temperature of 430 °C and using Ag/Al_2O_3 as catalyst, the non-thermal plasma catalysis yields full decomposition of toluene and 92% decomposition of benzene, whereas the conventional catalysis yields 89% and 70% decomposition, respectively. The temperature independence for the decomposition by non-thermal plasma catalysis is attributed to the high energy levels of plasma electrons which are capable to induce the catalyst activation without any supplementing heat source [20].

Than Quoc An et al. investigated the synergy of heterogeneous catalysis and non-thermal plasma in two different reactor configurations (Fig. 1) as a way to enhance the efficiency of VOCs removal [21]. The decomposition of toluene in a dielectric barrier discharge (DBD) non-thermal plasma reactor containing different integrated catalysts is compared with those of a separate non-thermal plasma and heterogeneous catalytic reactor [21]. The combination of non-thermal plasma and catalysis demonstrates a high efficiency in terms of the toluene removal, increasing up to 96% when using Au/Al_2O_3 and Nb_2O_5 as catalysts within the plasma discharge area, and 80% when using the catalysts in the post-discharge area. The toluene conversion is promoted at relatively high temperatures (over $T = 200$ °C). Without the effect of catalysis, the plasma reactor