SEVENTH FRAMEWORK
PROGRAMME

MAPSYN Summary Report

Project Reference: 309376

Funded Under: FP7-NMP [NMP 2012.3.0-1, Highly efficient chemical syntheses using alternative energy forms]

MAPSYN “Microwave, Ultrasonic and Plasma assisted Syntheses”

Project Participants

Number	Name	Short Name
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2	Technische Universiteit Eindhoven	TU/e
3	Evonik Industies AG	EI
4	Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e.V.	FRU
5	University of Hull Royal Charter	UH
6	DSM Nutritional Products Ltd	DSM
7	Coventry University	CU
8	Blacktrace Limited (formerly Syrris)	SYR
9	Universidad de Alicante	UA
10	Universita Degli Studi di Torino	TOR
13	Stichting Voor Fundamenteel Onderzoek der Materie-FOM	DIFFER

Executive Summary

The MAPSYN project “Microwave, Ultrasonic and Plasma assisted Synthesis’ aimed to demonstrate the suitability of alternative energy sources for chemical synthesis. This 42 month long project combined the expertise of 11 project partner organisations to develop novel process intensification (PI) methods to perform chemical processes of high industrial significance. Firstly, a plasma-assisted process was developed to provide a highly innovative new route for nitrogen fixation; an essential step in the production of fertilizers. Secondly, a continuous flow microwave process for semi-hydrogenation reactions was investigated. Semi-hydrogenation reactions are highly industrially relevant as they are key stages in the production of many fine chemicals; for example vitamins and aroma chemicals. Development of these novel processes required a multidisciplinary approach to bring together state-of-the-art expertise in flow chemistry, microreactors, catalysis and alternative energy sources (microwave, plasma and ultrasound).

For both of the core technology areas a fundamental MAPSYN objective was to demonstrate the scalability and industrial relevance of the approaches being developed. A key output of this work has therefore been the production of 2 ‘industrial demonstrator’ systems; one for plasma-assisted nitrogen fixation and the second for microwave semi-hydrogenations.

Numerous technology advances have been achieved across all MAPSYN research areas. A wide range of novel catalysts which combine high activity and selectivity with reduced toxicity (i.e. work has focused on lead-free, low Pd content catalysts) have been made and tested. Novel plasma reactors and microreactor systems for hydrogenations have been developed and refined to provide robust systems suitable for commercial exploitation.

Process modelling and analysis has provided valuable understanding in many areas. Simulations of 2-phase flow systems have helped to clarify the criteria which must be considered for development of a reactor with good mixing. LCA and economic studies of the 2 core processes (microwave hydrogenation and plasma nitrogen fixation) have clarified the influence of process parameters on economic and environmental impacts. Clear achievable performance scenarios have been identified which would deliver cost and environmental benefits for MAPSYN technologies.

In addition to technical objectives, the project has placed a strong emphasis on dissemination of project results and the broad promotion of the benefits which can be derived from adoption of novel PI approaches. Several PhD and undergraduate students have participated in the MAPSYN project, gaining a high level of knowledge in PI techniques and training for their careers as future researchers. This training focus of MAPSYN is also evident from activities such as PI Summer Schools which have been undertaken

Exploitation of project results is essential and key outputs include 2 patents on lead-free semi-hydrogenation catalysts and novel flow reactor modules which are already being sold commercially. The microwave hydrogenation and plasma nitrogen fixation demonstrator systems also represent key exploitable project outputs. These systems are currently undergoing extended testing by industrial project partners to benchmark performance and confirm commercial applicability.

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MAPSYN Project Context and Objectives

The MAPSYN project received funding under a FP7 call for projects focused on ‘Highly efficient chemical synthesis and using alternative energy forms’. This project has therefore focused on process intensification (PI) of chemical synthesis using novel energy sources.

A key objective of the MAPSYN project was to maintain and enhance the competitiveness of the European Chemical Industry through the development of more energy efficient, less polluting chemical processes for the production of essential bulk and fine chemicals. The EU is already world-leading in the development and utilisation of PI techniques. The MAPSYN project was focused on maintaining and enhancing this position by development of new PI applications.

There were two core technical areas within the project which each looked at a different field of chemical synthesis and different alternative energy forms. However, both areas were similarly focused on the demonstration of the enhanced efficiency which can be derived from the MAPSYN approach and in clearly demonstrating the scalability of the technologies developed. The use of continuous flow reactor systems and the development of these new reactors was also a core focus of the MAPSYN approach.

The two core areas within the MAPSYN project were as follows

- Use of microwave and ultrasound processes to carry out hydrogenation reactions of industrial significance.
- Use of novel plasma systems to carry out nitrogen fixation processes

The focus of the MAPSYN project is driven by the societal need for more efficient production of core chemicals. Process intensification achieved through flow processes is a key mechanism to enhance energy efficiency. The MAPSYN project therefore focused on 2 key processes of high industrial significance (hydrogenation and nitrogen fixation) in order to clearly demonstrate both the potential efficiency benefits and scalability of new approaches.

All the alternative energy forms utilised within MAPSYN, namely microwave, plasma and ultrasound, are electrical technologies and therefore present the opportunity for these novel processes to exploit the increasing availability of new ‘greener’ energy sources. A key focus of the nitrogen fixation work has been to investigate the potential for an alternative philosophy for nitrogen fixation processes. Use of plasma systems linked to renewable energy supplies (for example wind or solar installations) presents an opportunity for green, small-scale distributed production of fertilizer precursors.

Development of new processes in both technical areas has required a multidisciplinary approach with expertise from multiple partners to bring together several innovative aspects to provide a final solution. For example, the microwave hydrogenation process developed encompasses the development of novel catalysts, novel microreactors and an innovative microwave flow system in order to present a complete processing system. Moreover, the “Electrification of Chemistry” gives access to new business windows (technical term “Windows of Opportunity”), rather than “just” innovating existing business windows. The MAPSYN project targets a breakthrough innovation, which is very different in challenges and opportunities as compared to an incremental innovation. Among others, this involves the proactive creation of new business environments through intense contact with potential customers and interest platforms.”

The MAPSYN consortium included two industrial end user partners who ensured the industrial relevance and focus of work being carried out.

The project incorporated 5 technical work packages (WPs) each clearly structured to enable the project objectives to be achieved. A sub-set of project partners was involved in each WP in order to complete the specialised tasks within them. Each WP was led by a project beneficiary with extensive experience within the specific technical theme. This beneficiary assumed the responsibility of ensuring effective delivery of WP tasks. Earlier WPs (e.g. WP1 and 2) focused on conducting more fundamental research into the key project areas. WP3 then looked at development of the first complete flow systems for the MAPSYN processes. WP4 focused on process understanding and quantification of benefits (both environmental and economic) which could be derived from adopting MAPSYN processes. The final technical WP, WP5, relates to the production of up-scaled demonstrator systems and their testing for processes of industrial relevance.

Work Package 1; Novel MW-US and plasma assisted reaction development and physical modelling

The key objective of WP1 was to gain a fundamental understanding of the alternative energy systems (microwave, ultrasound and plasma) to be used within MAPSYN. Work involved preliminary consideration of the configuration of reactor systems and clear identification of gaps in knowledge. Extensive use of a range of modelling tools was involved. This included, for example, computational fluid dynamics (CFD) to gain an understanding of the influence of flow and turbulence in order to optimise reactions.

Work Package 2; Energy efficient engineered design of MW-US and CP assisted reactors and their flow processes

This WP incorporated the development and testing of the first laboratory systems for microwave hydrogenation and plasma nitrogen fixation. These α reactors provided the first small-scale systems to enable reactions to be trialled. Work also focused on the development of a range of microreactor systems and flow reactor modules.

Work Package 3; Exploration of selected alternative energy chemical syntheses and catalyst selection

This extensive WP covered several key areas of technology development. A central objective was development of novel catalysts systems for use in target processes and analysis of catalyst activity. A key objective for these catalysts was to show high activity and selectivity but also reduced environmental impact (for example many traditional catalysts incorporate toxic metals such as lead). Additional aims related to these novel catalysts included demonstrating catalyst reusability and developing methods to incorporate supported catalysts into microreactors.

Development of the first prototype systems (β systems) was an important target of WP3. This was achieved using learning from the original α systems built in WP2. These β prototypes were then trialled and their operation refined to enable final system upscaling to be achieved in WP5. The impact of ultrasound (US) on the designated target reactions was also intensively studied.

Work Package 4; Knowledge collection analysis and ‘toolkit’ development

The objective of this WP was to develop an understanding of the benefits that could be derived by exploitation of MAPSYN technologies; environmental, economic and energy. Work incorporated knowledge collection to identify knowledge gaps and key enabling potentials, life cycle assessment of both the MAPSYN hydrogenation and nitrogen fixation processes, economic analysis of both processes and an ASPEN-based energy analysis of the plasma nitrogen fixation process. The aim of these studies was to provide objective and comparative information to guide industrialisation of the processes developed.

Work Package 5; Demonstration; MW-US and CP reactors, industrial installation and testing

The key objective of this WP was to demonstrate the scalability of the two processes; microwave hydrogenation and plasma nitrogen fixation. Within this WP two up-scaled demonstrator systems (γ systems) were built based on the process understanding obtained through development and testing of the α and β systems. These demonstrator systems were then evaluated by carrying out reactions of industrial significance and data collected on system performance.

The final two MAPSYN WPs involved supporting activities rather than technical activities. WP6 ‘Dissemination and Exploitation’ was concerned with communicating the MAPSYN results to a broad audience; both technical and non-technical. Activities encompassed both a wide range of presentations and publications to the scientific community but also making project information available in a publicly accessible format. Courses on process intensification were also undertaken to assist with training future scientists in use of the techniques which are the focus of MAPSYN research. WP7 was concerned with overall Project Management.

MAPSYN Main S&T Results and Foreground

The MAPSYN project has delivered a high level of advancement in science and technology across a range of areas. Technology development within the project was divided into two separate focus areas.

1. Development of novel catalysts, microreactors and microwave systems for hydrogenations
2. Development of plasma assisted nitrogen fixation process

These two areas are discussed separately below although for both areas there are clear similarities between the areas of research. Both areas have involved:

- Development of novel catalysts
- Design and manufacture of new flow modules and flow reactors
- Exploitation of alternative energy sources (plasma, microwave and ultrasound) to enable energy efficient processing
- Upscaling of technology from laboratory scale to industrial demonstrator

1. Development of continuous flow microwave hydrogenation processes

The primary aim of the work in this section of the project was to develop a complete novel approach to carry out hydrogenation reactions in flow incorporating alternative energy sources; microwave and ultrasound. This work involved several concurrent research themes in order to enable development of a holistic highly innovative approach. These individual work themes are discussed below.

As work evolved, the consortium partners agreed that the final hydrogenation system would incorporate microwave as the primary energy source. By comparison to a dual-energy microwave and ultrasonic system this had the advantage of increased simplicity but also eliminated concerns about the impact of US on catalyst leaching. Ultrasound activities were therefore focused toward the use of US in catalyst synthesis and a broader research target to understand where US can add value in flow systems.

1.1 Novel Hydrogenation Catalysts

Development of new hydrogenation catalysts has been an area of significant focus within the MAPSYN project. Several partners, most notably UA, CU, UH and TOR have dedicated considerable effort to the synthesis of a wide range of novel catalysts for semi-hydrogenation processes. The focus of this work has been on synthesising catalysts which meet the following objectives:

- High activity; rapid hydrogenation reactions achieved
- High selectivity; reaction provides semihydrogenated product with minimal overhydrogenation
- Reduced content of toxic metals (e.g. lead)
- Reduced content of scarce metals (e.g. Palladium)

For much of the hydrogenation work within the project the semi-hydrogenation of MBY to MBE has been used as a test reaction. This reaction, which is shown in Figure 1, is a good test case to demonstrate the selectivity of novel catalysts as a range of side reactions are possible. Semi-hydrogenations of this type are also of significant industrial relevance due to their importance in the manufacture of a range of vitamins, carotenoids and aroma chemicals. The target within the MAPSYN project was to identify catalysts which could maximise the yield of MBE while minimising formation of any side-products.

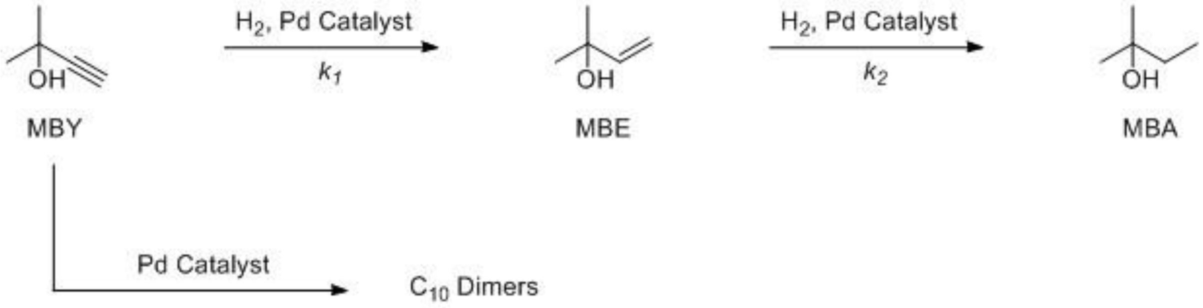


Figure 1: Reaction scheme of 2-methyl-3-butyn-2-ol hydrogenation and side reactions. MBY = 2-methyl-3-butyne-2-ol, MBE = 2-methyl-3-butene-2-ol, MBA = 2-methyl-3-butane-2-ol.

Ultrasound and Microwave Assisted catalyst synthesis

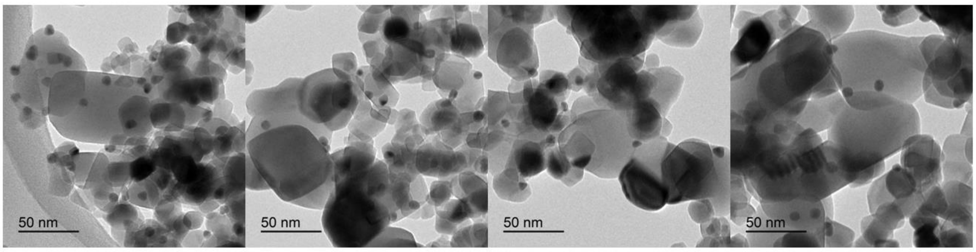
The use of both US and MW to synthesise lead-free palladium catalysts has been published within the MAPSYN project (ChemCatChem, 2015, 7, 952-959 Wu et al). The method, as developed by TOR, incorporates a one-pot method for catalyst preparation. Through US-assisted dispersion of palladium acetate in the presence of a surfactant/capping agent and a boehmite support highly active and selective catalysts are produced. These catalysts contain Pd nanoparticles and have a reduced number of pores larger than 4nm in the boehmite support. Extended trials of these catalysts for hydrogenation processes demonstrated their benefits. By comparison of the kinetic parameters for diphenyleneacetylene hydrogenation it is apparent that these catalysts have seven times the activity of the Lindlar catalysts. Selectivity to produce Z-stillbene was also high. Pd/boehmite catalysts can be prepared through US-assisted dispersion and microwave assisted reduction in water under hydrogen pressure without any surfactant.

Two patents have been filed on the novel lead free catalysts developed by TOR within the MAPSYN project. The applicability of these novel catalysts will be evaluated following completion of the MAPSYN project with a view to finding commercial applications within the fine chemical and pharmaceutical manufacturing sectors.

The use of Ultrasound for catalyst synthesis has also been widely investigated by CU. Their work showed that use of US can lead to the formation of more stable bimetallic catalysts when US at 20kHz is used for catalyst synthesis. Furthermore, the use of US was shown to have an impact on the Palladium (Pd) particle sizes formed within catalysts and formation of highly active Pd nanoparticles could be achieved. The size of nanoparticle formed was shown to be dependent on the US frequency used. However, selectivity with these nanparticulate catalysts materials was shown to be low.

The polyol method for the synthesis of hydrogenation catalysts

Several partners (UH, CU, UA) have employed the polyol method to prepare bimetallic catalysts based on palladium and supported on different oxides (Al_2O_3, TiO_2, ZnO, etc). Such a synthetic process can be enhanced by the simultaneous application of ultrasound as observed first by UA. Figure 2 shows TEM images of different PdM bimetallic particles supported on TiO_2 and prepared by the polyol+US approach.



Ni/Pd 1:1 Co/Pd 1:1 Mn/Pd 1:1 Zn/Pd 1:1

Figure 2. Bimetallic particles supported on TiO_2 and obtained by the polyol method with simultaneous application of ultrasound.

Catalyst immobilisation

TOR have developed novel processes for preparation of stable alumina bead supported palladium catalysts. These supported catalysts have then been evaluated as heterogeneous catalysts for semi-hydrogenation reactions in a range of reactor systems. These include within a commercially available microwave flow reactor (FlowSynth, Milestone) but also within the 3-phase reactor system developed by Syrris within the MAPSYN project.

Work by Fraunhofer ICT-IMM has also been undertaken to develop a novel method for coatings catalyst layers onto the catalytic plates present within the microwave-transparent FFMRs. This method was a modification on a previous approach used to coat metal surfaces which, within the MAPSYN project, was modified to be applicable to the non-metallic catalyst plate structures used for the microwave-transparent FFMR. These coating experiments were highly successful and provided stable and uniform catalyst surfaces which were shown to be extremely robust under prolonged operation.

Hull University Catalyst work

By alloying Pd with other metals, the electronic effects that influence the adsorption/desorption properties of different carbon-carbon multiple bonds or other functional groups, as well as geometric effects caused by dilution and/or ordering of the Pd atoms at the surface can be altered. This can have a crucial effect on the activity and selectivity of a catalytic reaction that takes place on the metal surface. It is therefore important to understand the nature and composition of this active component in heterogeneous catalysts.

The incorporation of a second metal to form bimetallic nanoparticles can result in a variety of materials such as random or ordered nanoalloys, core-shell or intermetallic nanoparticles, or simply incorporated as surface adatoms. The resulting active compound in the catalytic material is however, often poorly understood, as is the case in the Lindlar catalyst, in which the exact composition continues to be a subject of debate even after well over half a century of use.

UH prepared a range of Pd – containing nanoalloy materials, and focussed on the resulting materials which best perform as catalysts; the systems Pd-In and Pd-Sn. Pure phase alloys or intermetallic compounds containing Pd-In or Pd-Sn using variations of a simple polyol method, varying the metal precursor ratios, the polyol used, and hence the temperature at which the materials are prepared. A combination of PXRD and elemental analysis (ICP) was used to identify the phases present.

Finally, successful pure-phase compounds were re-prepared as nanoparticles in the presence of a metal-oxide support. The resulting catalyst materials were tested in the semi-hydrogenation of 2-methyl-3-buyn-2-ol (MBY) and their activity and selectivity for production of 2-methyl-3-butene-2-ol (MBE) was assessed. The results were compared to the performance of the monometallic Pd/TiO_2 and Lindlar catalyst.

A number of alloys and intermetallic compounds in pure-phase form have been prepared for the first time. These include some novel compounds that cannot be prepared by traditional, high-temperature melting techniques. Many of these materials exhibit superior selectivity towards MBE compared to their pure Pd counterparts and some of the catalysts match or outperform Lindlar catalyst with comparable, if not superior activity.

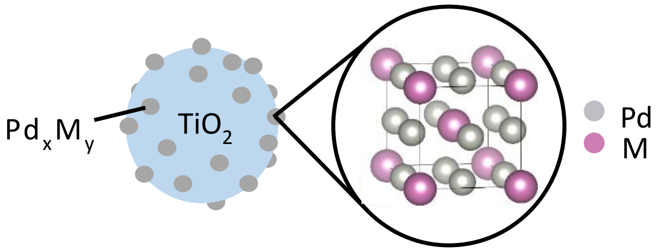


Figure 3: Representative structure of intermetallic catalyst system.

1.2 Ultrasound promoted hydrogenations

Coventry University investigated the use of US to carry out the selective hydrogenation of MBY using the Lindlar catalyst. This work has been published (Paniwnyk et al, Ultrasonics Sonochemistry, 2015, Vol 26, 445-451) and compared conventional stirring with sonication at different frequencies of 40, 380 and 850 kHz. Under conventional stirring, the reaction rates were limited by intrinsic kinetics, while in the case of sonication, the reaction rates were 50-90% slower. However, the apparent reaction rates were found to be significantly frequency dependent with the highest rate observed at 40 kHz. The studies showed that sonication led to the frequency-dependent fracturing of polycrystalline support particles with the highest impact caused by 40 kHz sonication, while monocrystals were undamaged. In contrast, the leaching of Pd/Pb particles did not depend on the frequency, which suggests that sonication removed only loosely-bound catalyst particles. Further investigation showed that, with the Lindlar catalyst, leaching of Pd appears a significant side effect of performing these hydrogenations with US. This was attributed to the cleaning ability of US and microjet formation. It does however have negative implications for the suitability of US for use to promote hydrogenation reactions. Use of ultrasound for carrying out hydrogenation reactions was discontinued after this clear evidence of leaching was observed.

The degassing nature of ultrasound has also been shown to not be beneficial for performing hydrogenation reactions as it reduces the concentration of hydrogen in solution and therefore its availability for reaction.

1.3 Use of Ultrasound in flow systems

Several partners within MAPSYN (UA, CU, TOR) have devoted efforts to investigate the potential advantages that power ultrasound, applied to microreactor technology, can provide. As a first step, the efficient acoustic design of sono-microreactors have been addressed by UA researchers as a requisite to attain the maximum capabilities of these devices. For instance, Figure 4 shows how this modeling can predict the homogeneity of the acoustic field in a stacked microreactor.

In addition from the insights obtained via simulation, UA researchers have found experimentally that ultrasound can be applied to miniaturized bed reactors to induce partial bed fluidization, thus reducing channeling phenomena. Besides, low-power ultrasound can be also applied to capillary tubing to avoid the formation of clogs or even locally unclog the channels.

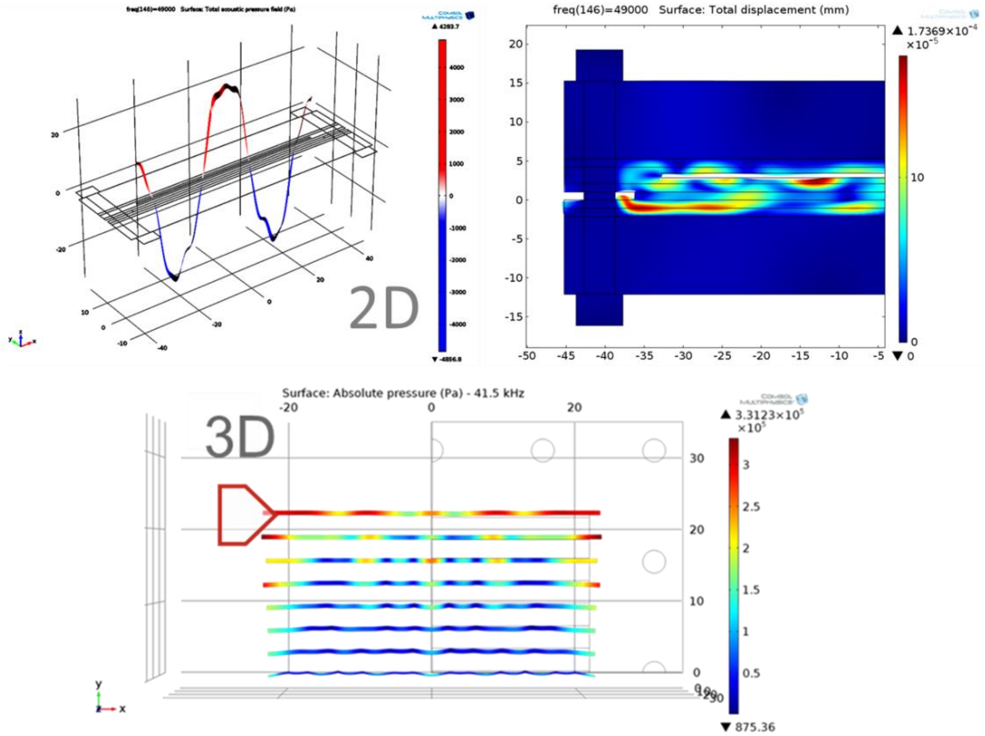


Figure 4. Calculated acoustic pressure within the reaction channels and displacements for a Teflon stacked microreactor (2D model). The bottom figure corresponds to the calculated acoustic pressure within the reaction channels when using a 3D model.

1.4 Novel Microreactor systems

Several project partners within the MAPSYN project had a pre-established high level of expertise in microreactors and flow modules for PI applications. Through the MAPSYN project they have been able to develop additional products for new applications.

Microwave transparent FFMRs

A Falling Film Micro Reactor (FFMR) is a highly efficient device for contacting gasses and liquids and for performing reactions between these phases. The liquid is distributed into open channels of small width and flows downwards due to gravity. In this way, thin films of thicknesses in the range of 0.1 mm are formed which enable efficient gas-liquid mass transfer. In case of coating the channel walls with a catalyst, this provides also good access to its solid surface. Since the development of the first FFMR for lab scale experimentation about 15 years ago by the former Institut für Mikrotechnik Mainz (IMM), it has found numerous worldwide uptakes for the investigation of gas-liquid reactions, without and with wall coated catalysts.

Within MAPSYN, Fraunhofer ICT-IMM developed a laboratory FFMR which can be used under microwave irradiation for heterogeneously catalysed gas-liquid reactions, for example hydrogenations. The well-proven wash coating technique for metal surfaces was transferred to glass ceramics, enabling wall coating of the microchannels with novel catalysts developed by the universities of Turin and Hull. The pilot scale was achieved by equalling-up, i.e. increasing the number of microchannels, and smart dimensioning, i.e. increasing also the channel length which allowed for longer residence times. The pilot scale reactor (see picture) was destined to be operated within the large multi-mode microwave cavity of the demonstration plant developed by C-Tech Innovation.

For this purpose, based on the FFMR family which were made of stainless steel, the design was adapted to the needs of the intended application within the microwave cavity and to the materials which were identified to be sufficient microwave transparent, chemically resistant and coatable with catalyst. On the laboratory scale, versions with different housing and reaction plate materials were manufactured. As compromise between microwave transparency, chemical resistance and material and manufacturing costs, a mechanically treatable glass ceramic was used, both for the reaction plate and the housing. Without major modifications, the housing could also be made from polypropylene if less harsh operating conditions (temperature, pressure) allow for it. As materials of choice on pilot scale, glass ceramic was used for the microstructured, catalyst coated reaction plate and polypropylene for the housing. Preliminary tests under microwave irradiation revealed the importance of the installed cooling system comprising the whole length of the reaction plate on its backside and an additional sump cooling to avoid local overheating of the collected liquid due to microwave irradiation. For safety reasons, the cooling system was realised as a closed system which avoids the potential transfer of hydrogen in case of a breakage of the glass ceramic plate.

Controlling the flow rate of the discharge pump according to the liquid level in the sump is necessary for the automatic operation of the FFMR. The liquid level should be maintained within its optimal range to prevent hydrogen from entering the liquid outlet lines with negative operational and safety consequences. For this purpose, a special fibre optic sensor for detecting the liquid level in the sump of the FFMR was developed and realised. The related evaluation unit outside of the microwave cavity converts the optical information into electrical signals and connects the level sensor with the distributed control system.

In its last version, the pilot scale FFMR was successfully operated for several weeks at the industrial site of DSM and several partial hydrogenation reactions were carried out.

Novel Flow Modules

Project Partner Syrris are a technologically innovative SME who focus on selling modular flow chemistry equipment. Within the MAPSYN project they developed several new flow modules to sell as additional components to their existing product range.

New flow modules developed within the project included

- **Three phase Reactor**: Reactor suitable for 3 phases (liquid, solid and gas) that can be microwave heated or conventionally heated. This module has potential applications for the flow hydrogenations of interest to the MAPSYN project.
- **Conventional Heating Module**: Heats the 3 Phase Reactor up to 150°C. Provides a control to assess the benefits of microwave heating versus "classic" heating
- **Active Cooling Module**: Compact cooler to enable active cooling after or during a microwave process. No cooling fluid is required and enables cooling down to -100°C.
- **Flow Electrochemistry Module**: MAPSYN is all about "Highly efficient syntheses using alternative energy forms". Electrochemistry enables unique activation of chemical reactions.

Photos of 3 of these new module systems are shown below in Figure 5.

Figure 5: 3-phase reactor, active cooling module and flow electrochemistry module.

Additional modules were also investigated within the project; specifically a microwave heated module and a gas introduction module. These modules are continuing to be developed following completion of the MAPSYN project.

Within the project, the 3-phase reactor was evaluated as a system for carrying out hydrogenations using immobilised versions of some of the novel catalysts developed within MAPSYN. This work showed that high conversion and selectivity could be achieved with a system of this type.

By the end of the MAPSYN project the active cooling and electrochemistry modules were already part of Syrris commercial product range and numerous of these new modules have been sold.

1.5 Novel Microwave systems

Use of microwave heating as a mechanism for organic synthesis is increasingly well known within the scientific literature. A range of advantages have been seen for microwave chemistry which include

- **Significant increases in yields and selectivity**; for example a dihydropyrimidine synthesis has been performed by C-Tech with a 2-fold increase in yield compared to conventional heating
- **Reduced reaction times** C-Tech have performed Suzuki reactions where reaction time has been reduced from 2h to 1min.
- **Reduced energy use;** up to 90% reductions seen for some reactions.

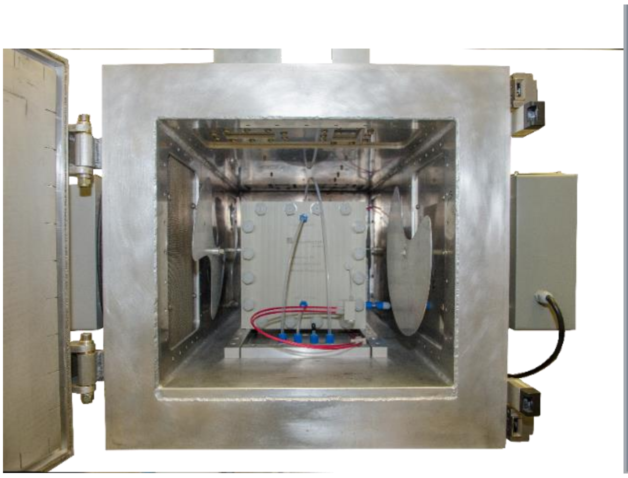
A small range of companies, including MAPSYN partner C-Tech, sell microwave flow reactors which are suitable for up-scaled chemical synthesis. For example, C-Techs standard system offers a throughput of up to 1L/min. Systems of this type represent a greener approach to performing chemical synthesis. This is due to both the lower energy consumption (up to 90% reduction) which can be achieved but also the reduced chemical inventory that is needed for a flow process.

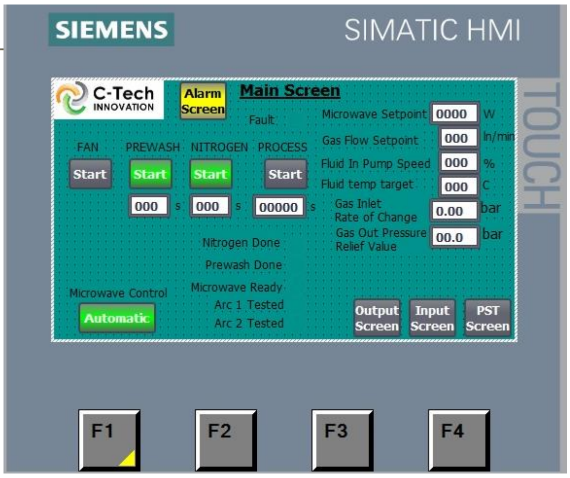
Catalytic microwave process have also been reported within the chemical literature and there is evidence that interaction of metallic catalysts with the microwave field offers very significant yield enhancements. This is attributed to the generation of catalyst ‘hot spots’ through the selective heating of these metallic components to temperatures considerably higher than the bulk reaction medium.

This suite of demonstrated benefits was a key driver for the MAPSYN project to extend the scope of microwave processing to encompass continuous hydrogenations.

A key output of the MAPSYN project has been the development of an up-scaled microwave demonstrator system. To the best of our knowledge this system represents the first application of a microwave flow reactor to carry out hydrogenations. This demonstrator comprises a microwave flow system, a novel microwave-transparent microreactor, and innovative MAPSYN catalysts. The novel FFMR microreactors used in this system have been discussed in detail in the previous section.

C-Tech Innovation were responsible for development of the microwave system which was a key component of the flow reactor. This reactor is shown in Figure 6 and comprised a variety of mechanisms to help provide a uniform microwave field within the cavity and therefore enable uniform heating to be achieved. This system is also highly tunable which enables it to be used effectively with relatively small ‘microwave loads’. Effective system tuning is essential to enable optimisation of process efficiency and reduce the quantity of microwave power which is reflected back to the generator rather than absorbed to heat the product. The MAPSYN system provided good one pass heating of the reaction mixture with <10% reflected microwave power.





PREWASH 000 s
NITROGEN 000 s
PROCESS 00000 s
Microwave Setpoint 0000 W
Gas Flow Setpoint 000 ln/min
Fluid In Pump Speed 000 %
Fluid temp target 000 C
Gas Inlet Rate of Change 0.00 bar
Gas Out Pressure Relief Value 00.0 bar

Figure 6: *Microwave Cavity for hydrogenations in flow and HMI control screen.*

A significant innovative aspect of the MAPSYN microwave system was the innovative control system developed to operate the process. The control program, written specifically for the MAPSYN process, combines control of multiple aspects of process operation as well as providing a user-friendly operator interface. Some of the challenging aspects of developing this systems included:

- **Safety**: Essential safety criteria include processes to minimise the risk of hydrogen leaks exceeding the hydrogen LEL (lower explosion limit) and immediate system shut-down if leaks are detected.
- **2-phase flow control:** Accurate control of the flow rates of both the liquid reaction medium and the gaseous hydrogen is essential for good process control.
- **Temperature and pressure control:** Achieving temperature control within a microwave system presents its own unique challenges as standard thermocouples cannot be used within a microwave field. The MAPSYN demonstrator incorporates a system for temperature monitoring and control where the microwave power level is automatically adjusted to achieve a target temperature. Accurate measurement and control of hydrogen pressure within the system is also essential both to ensure that safe limits are not exceeded but also to provide optimal processing conditions.

1.6 Industrial Demonstrator Testing

Extended commissioning of the complete system, comprising both FRU's novel FFMR and C-Tech's microwave flow system, was required to ensure that the system operated both robustly and safely. As a result of this work, robust operational parameters were identified and the system was then sent to end-user partner DSM for extended industrial trials.

The extended trials at DSM carried out hydrogenation reactions for a prolonged period of time under a variety of conditions. This work had a variety of aims including

- To demonstrate system robustness and suitability for use in hydrogenation reactions
- To benchmark the conversion and selectivity achievable for selective hydrogenation reactions
- To understand the impact of variation of parameters such as temperature, pressure and flow rate on the conversion and selectivity seen.
- To gain initial data on catalyst longevity based on prolonged usage of a catalytic plate.

A suite of highly interesting results on the system have been obtained which provide a clear view of the performance and benefits which could be expected from a system of this type. These results are subject to a high level of confidentially and therefore cannot be disclosed within this report. However, the following highly positive findings on system operation can be communicated.

- Significantly, the demonstrator system has been shown to operate robustly over a period of approximately 3 months with no operational issues.
- Initial results on catalyst longevity are highly promising and indicate that the immobilised catalyst can be used for an extended period without replacement.

Systems of this type, or based on this approach, are anticipated to find numerous applications within the speciality and fine chemical industries following project completion for carrying out a range of hydrogenations.

1.7 Modelling of microreactor systems

As an alternative to the FFMR, Blacktrace (formerly Syrris) together with UA suggested that a miniaturized Packed Bed Reactor (mPBR) could be used in conjunction with ultrasound (US) or microwave (MW) irradiation. This type of reactor allows for adjustable flow rates and residence times in continuous two-phase flow synthesis, using the catalyst material attached to a fixed bed inside a tube. The catalyst material can be coated on alumina beads or on any other support material. More importantly, the catalyst can be easily replaced when needed, reducing significantly operation costs and making these reactors highly versatile. By using a small particle size in the bed (0.1 mm of diameter), the two-phase flow is exposed to an increased surface reactive area, which reduces reaction times. However, significant pressure drop may arise from the small channel dimensions and particle diameter.

Miniaturized packed bed reactors, also known as high throughput reactors, which are extensively used both in academia and in the industry for carrying out hydrogenations, have been studied within MAPSYN to get a better understanding allowing us to work on scale-up concepts as well as to introduce alternative energy sources (such a power ultrasound or microwaves).

Several partners of MAPSYN have worked on this type of devices (Blacktrace, TOR, UA). In particular, work within MAPSYN has demonstrated that state-of-art simulation tools can be now applied to miniaturized packed bed reactors reproducing wall- and gas-channeling phenomena common at this scale, which constitute main limitations of this technology. There is a significant lack of understanding of these non-idealities. As opposed to the large scale packed bed reactors —known also as trickle bed reactors— at this scale capillarity, wettability and surface tension determine their complex fluid dynamics. UA has validated these phenomena at the pore-scale level and provided insight by means of a physicochemical model solved by computational methods (finite element method). In addition, a less computationally expensive model was developed in order to deal with gas-channeling on a larger scale (meso-scale) without the need of defining and solving the complex geometry of the bed. The two-level modeling addressed within MAPSYN is illustrated in Figure 7. This shows the modeling framework proposed by UA researchers where both pore-scale and averaged meso-scale are used to simulate packed bed reactors with small particle size (0.1 mm diameter). Pore-scale (left) reproduces the unwanted gas-channeling phenomena, while meso-scale (right) is able to capture preferential channels and the effect of the inlet/outlet, wall and diameter of the reactor. The modeling framework can be used for proper design of miniaturized bed reactors.

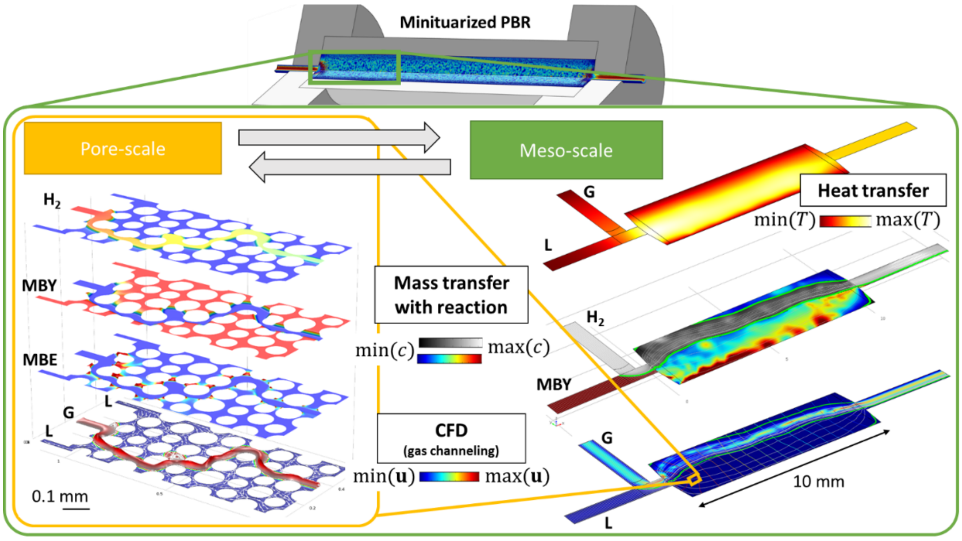


Figure 7. *Modeling of miniaturized packed bed reactor*

Importantly, the modeling framework proposed by the UA may allow chemical engineers to study pressure drop, mass transfer coefficients, the appearance of hot spots and the influence of the inlet or outlet configuration for this type of miniaturized reactor. The information and insights provided by these simulations are expected to be useful for a proper design of miniaturized packed bed reactors, including the possibility of scaling them up.

1.8 Process Analysis for hydrogenation process

In order to gain a detailed understanding of the potential benefits of a MAPSYN microwave hydrogenation process a detailed life cycle analysis (LCA) and economic assessment were performed. This work focused on comparing the economic and environmental performance of a MAPSYN process compared to standard batch technology for semi-hydrogenation processes. A scenario approach was adopted in order to understand the sensitivity of economic and environmental impacts to variation in key process parameters; for example energy use or catalyst reusability.

This work, which was led by C-Tech, reached the following main conclusions:

Environmental Performance

- A microwave MAPSYN process has potential to deliver considerable reduction in the Global Warming Potential (GWP) impact associated with energy use by comparison to a batch process. Based on an assumed optimized MAPSYN process; reductions of up to 50% in this impact due to energy use could be envisaged.
- The use of lead free catalysts with low palladium content has potential to reduce the Abiotic Depletion Potential (ADP) impact associated with catalyst use. The reductions achievable are highly dependent on catalyst longevity which has not yet been fully quantified. However, based on catalyst lifetimes already proven within the MAPSYN reactor, a benefit in this impact by comparison to a batch process is already seen. By extrapolating catalyst performance data it was possible to quantify the benefits which would be seen for a stated catalyst lifetime. This indicates that 50% reductions in ADP impact associated with catalyst use should be achievable at a realistic level of catalyst longevity.

Economic performance

- By contrast to a batch reactor system, a MAPSYN flow reactor is relatively complex. Consequently, the anticipated CAPEX of a MAPSYN system is noticeably higher than that of a batch reactor. Relative levels of technology commercialization also influence this figure. A competitive market exists for supply of batch system components, thereby keeping system costings low. By contrast, many components within the proposed MAPSYN system are more bespoke and therefore command a relatively high price. Future commercialization of microwave components and flow reactors would be expected to reduce MAPSYN costs in the longer term.
- The reduced energy usage and high catalyst reuse anticipated for an optimized MAPSYN process show that significant benefits in variable OPEX could be achievable by comparison to

a batch system. However, the system CAPEX has an impact on OPEX fixed costs and therefore on total OPEX which reduces the impact of this improvement.

For both environmental and economic studies it was apparent that starting material impact is significant. Starting material represents a high proportion of total GWP, total ADP and variable OPEX. Within the studies carried out, the test reaction used was a semi-hydrogenation process which is highly optimized in a batch process; both high conversion and selectivity is obtained. Moving to a MAPSYN process therefore has minimal scope to enhance yield and thereby reduce the use of starting material and its associated environmental and cost impacts. This is, however, unlikely to be true for all processes. There are numerous examples in the literature where use of a microwave process has been shown to considerably enhance yield and selectivity in organic synthesis. In processes of this type a MAPSYN system would be expected to show considerable economic and environmental benefits based on a reduced requirement for raw materials. Furthermore, examples of where a microwave process can proceed under considerably milder conditions than a conventionally heated system are also well known. Reactions of this type could offer a MAPSYN process considerable gains in terms of reduced energy use, as well as potentially removing the need to operate in high pressure systems.

The key conclusion from this process analysis work is therefore that the benefits obtained will be highly dependent on the specific chemical transformation being performed. Where a MAPSYN process enables higher yields or selectivities to be achieved, or enables conversion under significantly milder conditions, considerable environmental and OPEX benefits would be anticipated.

2 Development of Plasma-Assisted Nitrogen Fixation Process

Nitrogen is the most basic element responsible for the growth of living creatures on earth, being an important constituent of amino acids it is essential for life on earth. However, this abundant element of atmosphere is hardly accessible to most living beings, because of the extremely stable N-N triple bond, which demands unusually high activation energy barrier. To become accessible, nitrogen must be chemically bonded to oxygen or hydrogen through the process of nitrogen fixation. The chemical nitrogen fixation process is one of the most important chemical processes and artificially fixes nitrogen with hydrogen through the Haber-Bosch process producing ammonia. This process sustains 40 % of today's population and its role will only grow along with the rapidly growing global population. However, the Haber-Bosch process, developed at the beginning of the 20th century, is notoriously energy-inefficient. It consumes almost 2 % of world's total energy production and emits 300 million metric tons of CO_2. Modern technological and ecological standards require a considerable reduction in its environmental footprint and an increase in its energy efficiency. Nevertheless, the modern Haber-Bosch process has almost reached its theoretical limits on energy efficiency, so further improvements require a thorough search for a totally different approach.

Among several alternatives, electricity-driven plasma processes are considered to be very attractive candidates for the Haber-Bosch replacement. The idea arises from the thermodynamically non-equilibrium nature of non-thermal plasma (NTP), where electrons have a temperature of thousands of degrees, while the bulk gas is close to room temperature. As a result, highly reactive species are formed, enabling NTPs to conduct thermodynamically unfavourable reactions at low temperatures. It is striking to note that nitrogen fixation *via* NTP, has a theoretical energy consumption 3 times lower than the Haber-Bosch process, offering a possibility of a fossil-free nitrogen fixation using renewable electricity with a fraction of the current energy costs. Compared to the high-pressure Haber-Bosch process, plasma nitrogen fixation offers an opportunity for atmospheric pressure and ambient temperature reactions with substantially improved plant safety, decreased operational and capital costs. It will, however, add new (electrical) equipment to the process such as transformers and electrical power supply system which are needed for plasma generation.

The plasma processes are more attractive on a smaller scale such as a container or modular plant. The concept of de-centralized production of chemicals is gradually gaining an acceptance in chemical industry, and hence, opens new doors for containerized plasma nitrogen fixation process. This development would benefit remote and stranded areas in enabling them to produce their own fertilizer and fuels, using only renewable energy sources such as solar or wind.

2.1 Novel plasma reactor development

Optimal energy efficiencies are achieved in plasma dissociation of feedstock molecules if vibrational excitation is maximized. This requires minimization of gas heating, which is the essence of the cold plasma approach within MAPSYN. The plasmatron par excellence for producing cold plasma at atmospheric pressure is the gliding arc. For that reason, the gliding arc approach has been followed from the beginning of the MAPSYN project. Dielectric Barrier Discharge (DBD) has been investigated as alternative plasma source, this technology approach focused on screening of different catalysts for synergetic coupling of plasma with catalyst – understanding fundamentals.

The electrical parameters of the gliding arc reactor, such as frequency, pulse width, and amplitude were investigated. Increase in frequency, pulse width and amplitude results in increased specific energy input and NOx concentration whereas discharge behaviour of arc changes drastic – this has been documented first time with high speed photo camera.

Small-scale investigations accelerate transfer from laboratory to pilot plant and to real production. A container-based process is usually designed to be a continuous process, not least due to the smaller volume of the required devices. For chemists, this is a paradigm shift, since a laboratory or pilot scale production process is usually developed as discontinuously operated process. A complete chemical plant in an extremely small space! How does that work for a plasma process? Finding an answer to this question has been one of the objectives of Evonik experts, in cooperation with other nitrogen-fixation partners. For early bird evaluation of process design, lab research results were used for preparation of C&I charts of the pilot stage including or effecting e.g. first safety analysis.

Microwave Plasma development

In the research phase of the plasma activated nitrogen fixation part of MAPSYN, predominantly carried out at TUe, emphasis was on gliding arc and dielectric barrier discharges. Performance of these reactors was benchmarked and interfacing with catalysts for further enhancing nitrogen fixation was explored. DIFFER has contributed to the research phase by adding microwave plasma based conversion to this palette. The rationale behind broadening to microwave plasma was based on high energy efficiency performance reported in literature and proven concepts to scale to input power levels of 100 kW. Proof-of-principle experiments were carried out with traces of oxygen (up to 2%, in view of safety precautions) in nitrogen. Diagnostic coverage towards conversion, selectivity and efficiency was by means of mass spectrometry and Fourier Transform Infrared spectroscopy. These experiments confirmed the potential of microwave plasma in these respects. Incorporation of catalysts in the reactor afterglow was not extensively tested due to delayed availability of catalysts in combination with the relocation of the DIFFER laboratories to a new building in Eindhoven.

Choice of Plasma Reactor for system demonstrator

A decision to use a microwave plasma reactor approach in the demonstration phase was taken on basis of the following considerations:

- Gliding arc discharges are the approach par excellence for achieving strongly non-equilibrium plasma conditions that are favourable to drive chemical reactions efficiently. However, scaling up in power is impeded by transition to equilibrium arc discharging and no concepts have been proven within or outside the present project to circumvent this limitation;
- DBD based nitrogen fixation research within MAPSYN had not proven that the desired energy efficiencies would become within reach at a demonstration level;
- Microwave equipment could be made available by DIFFER to base a demonstration reactor upon.

2.2 Nitrogen fixation results from laboratory test systems

In the MAPSYN project, 2 different non-thermal plasma reactors were investigated in TU/es laboratories for nitrogen fixing reactions. The two nitrogen fixing reactions investigated in this project are;

1. Nitric oxide synthesis:

$$N_2 + O_2 \xleftrightarrow{\text{Plasma catalysis}} 2NO \qquad \Delta H = 90\,\frac{kJ}{mol} \approx 1eV$$

2. Ammonia synthesis:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \qquad \Delta H = -46.27\,\frac{kJ}{mol}$$

These two chemicals can be synthesized by using renewable electrical energy to produce plasma, which then activates the abundantly available reactant gases (such as water and air), as shown in Figure 8.

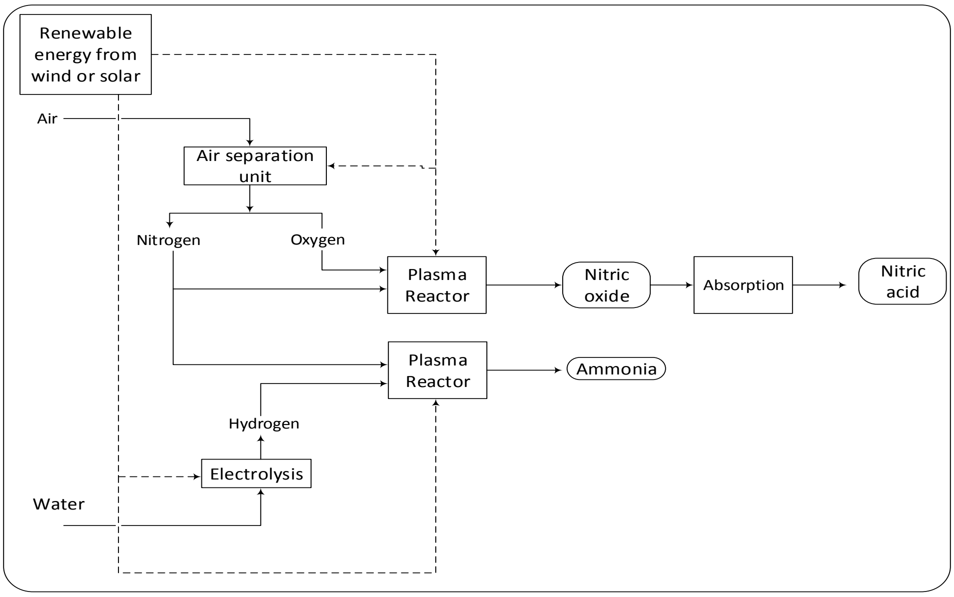


Figure 8: *Concept of chemical production from renewable sources and using plasma as an alternative energy source.*

Summary of the Experimental Results

The results obtained for lab scale experiments at TU/e on plasma assisted nitrogen fixation reactions are summarized below;

- The electrical parameters of the gliding arc reactor, such as frequency, pulse width, and amplitude were investigated. Increase in frequency, pulse width and amplitude results in increased specific energy input and NOx concentration.
- The production of NOx from air, air + oxygen, and N_2-O_2(a nitrogen and oxygen mix) at atmospheric pressure and low temperature was investigated by employing pulsed powered milli-scale gliding arc non-thermal plasma reactor, which is considered as “PROTOTYPE α-2”. The effect of various feed options and O_2 %, feed flowrates, argon addition and feed preheating are investigated for NOx production and specific energy input. Air was found to produce slightly lower amount of NOx than the N_2-O_2 mixture and it also consumed lower power. Addition of oxygen to air enhanced the production of NOx to some extent. The feed ratio (N_2/O_2) of 1-1.5 was found to be the optimum for higher NOx production in GA. The lower flowrates found to produce highest concentration of NOx, owing to their higher

residence times. Lower flowrates tend to produce NO_2 and higher flowrates preferentially produced NO. Addition of argon to the feed stream and preheating of the feed resulted in negative effects on the NOx production. The highest concentration of NOx produced was 1.3 vol% for 0.5 L/min and lowest energy consumption of 1.1 MJ/mol was achieved for 0.7 L/min. Milli-scale gliding arc reactor gave an energy efficiency of 8.6 %, consuming 9 kWh/kg of NOx.

- Direct synthesis of NOx from N_2 and O_2 was studied by packing different catalyst support particles in a dielectric barrier discharge (DBD) reactor. The types of support materials and particle sizes both showed significant influences on the concentration of NOx. Key factors included different surface areas, dielectric constants and particles shapes. The γ-Al2O3 with smallest particles size of 250-160 µm gave the highest concentration of NOx and the lowest specific energy consumption among all the tested materials and particle sizes. The NOx concentration of 5700 ppm was reached for the highest residence time of 0.4 sec investigated and the N2/O2 feed ratio of 1 was found to be the most optimum for NOx production. In order to intensify the NOx production in plasma, a series of metal oxide catalysts supported on γ-Al_2O_3 were tested in a packed DBD reactor. The 5 % WO3/Al2O3 catalyst increased the NOx concentration further by about 10 % compared to that of γ-Al2O3, while oxidation catalysts such as Co_3O_4 and PbO provided a minor (~5 %) improvement. This data suggests that oxygen activation plays a minor role in plasma catalytic nitrogen fixation under the studied conditions with the main role ascribed to the generation of microdischarges on sharp edges of large-surface area plasma catalysts. However, when the loading of active metal oxides was increased to 10%, catalyst's activity was evident for NO selectivity. Since a well-known active oxidation catalyst 10% Co_3O_4/Al_2O_3, provided enough active oxygen species for oxidation of NO into NO_2, giving considerable increase in NO_2 concentration compared to 5 % loading. All the results of this study are summarized in Figure 9.

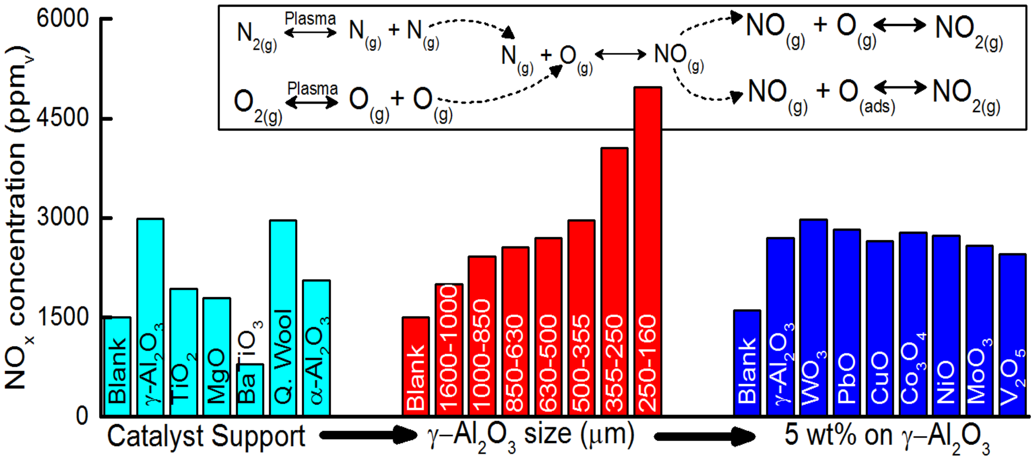
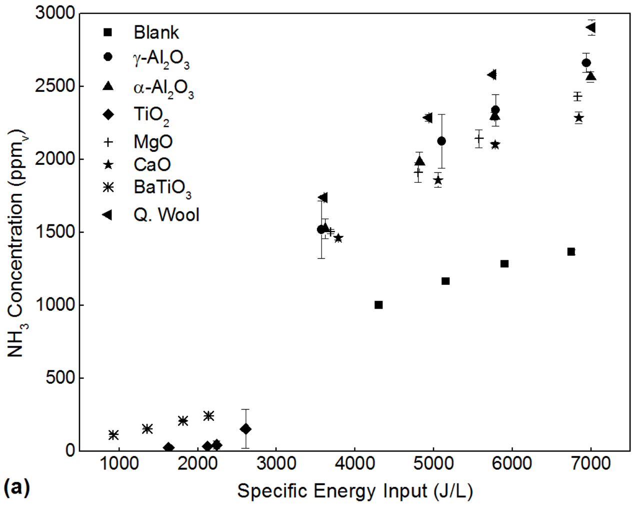
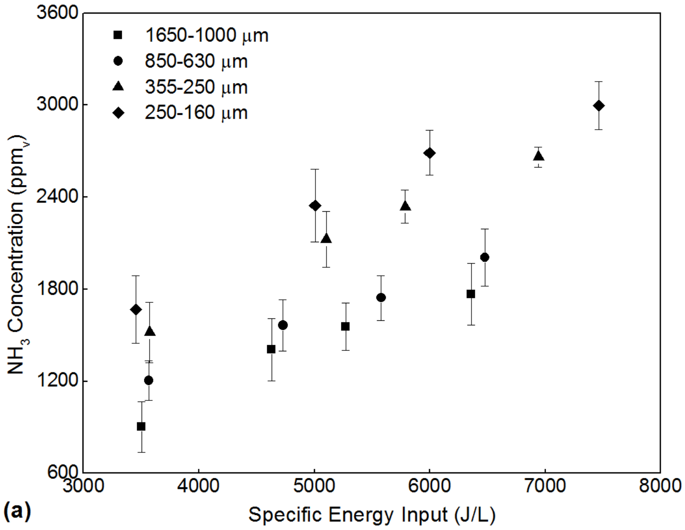


Figure 9. *Performance of various catalyst supports, particle sizes and active metal oxide catalysts for NOx production.*

- Plasma assisted ammonia synthesis in a packed Dielectric Barrier Discharge (DBD) reactor at atmospheric pressure is presented, which considerably enhances the NH_3 formation. The commonly used catalyst supports, γ-Al_2O_3, α-Al_2O_3, TiO_2, MgO, CaO, quartz wool, and $BaTiO_3$, have been thoroughly investigated for the synergetic effect by packing them in the discharge zone of the DBD reactor. All the support materials have substantial effect on the ammonia production. The quartz wool followed by γ-Al_2O_3 produce the highest amount of ammonia, 2900 and 2700 PPM respectively, due to their ability to generate intense filamentary microdischarges. The size of support particles also has a pronounced influence on the synergy between support and the plasma. The particles with average diameter of 200 μm yielded 64% higher concentration of NH_3 than the 1300 μm diameter particles, seemingly because of its amplified electric field strength from upsurge in particle-particle contact points and higher curvatures at sharp edges. The process parameters such as feed flow ratio (N_2/H_2), flow rate and % argon dilution have also been investigated. A feed flow ratio of greater than 2 gives higher concentrations of NH_3 with improved energy efficiency than the stoichiometric feed ratio of 0.33. The feed flowrate have a negligible influence, however specific energy input per unit volume shows greater impact on the ammonia production. Dilution with 2-5% of argon is optimum, which yielded on an average 2% improvement in the concentration and energy efficiency. Figure 10 shows the effect of the catalyst support material and particle size on ammonia production.



(a)



(a)

Figure 10. *Effect of various catalyst supports and particle size on ammonia synthesis.*

2.3 Development of plasma nitrogen fixation demonstrator system

A major objective of the work on plasma-assisted nitrogen fixation was to confirm the scalability of this technology through the construction of an industrial demonstrator system. The containerised 'Ecotrainer' pilot plant built by EI to fulfil this objective is shown in Figure 11.

Figure 11: *Plasma nitrogen fixation demonstrator*

The Ecotrainer concept: How the time from product idea to final production process can significantly be reduced is shown in the following. The core of the idea is to centralize the development process in one infrastructure. With this, knowledge about the process as well as all know how around the process generated (e.g. safety issues) were cumulated at one place. These circumstances make it possible to avoid interface problems. Figure 12 shows in sketches the main steps of bringing a new product idea to market:

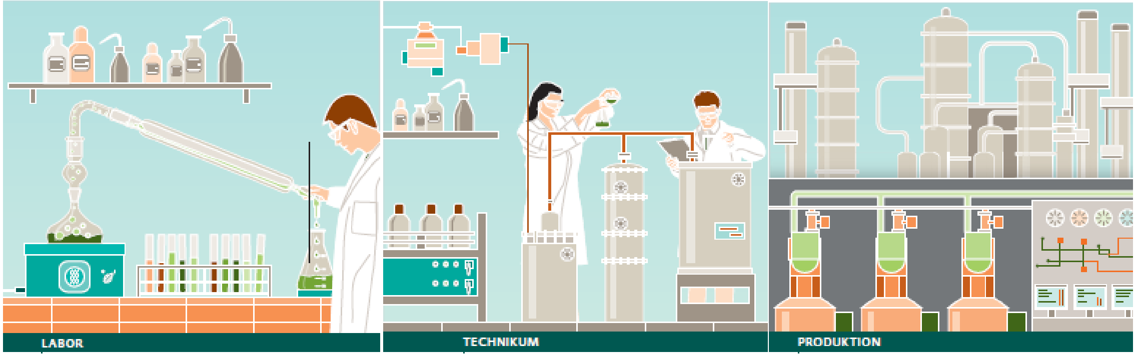


Figure 12 *The main steps of bringing a new product idea to market: from lab to production.*

Now, all these steps can be carried out in the EcoTrainer environment. The EcoTrainer is the mobile small-scale production facilities from Evonik. Behind the catchy name is a concept that could thoroughly transform the fertilizer production from central to a decentralized way.

Within previous FP7 project PolyCat, the EcoTrainer 4G was developed and first used at the site of Fraunhofer ICT-IMM for pharmaceutical production. After this, the results were disseminated. An analysis of hidden bugs from PolyCat project followed by de-montage of process modules in EcoTrainer. , This “lesson-learned-phase” covered a continuous improvement mode about module installation. Meanwhile the EcoTrainer was transported back to Evonik Hanau site, where the new plasma synthesis process for the production of NOx (N_2O_4) were integrated. With this, the first re-use of EcoTrainer plant could be demonstrated successfully with start of operation in June of 2016 – which is beside the plasma technology results one of the important outcomes of the MAPSYN project for Evonik.

In line with the proposed approach for new products, Evonik plans to develop and test the process under real-life conditions in an EcoTrainer environment and develop it to full maturity there. One elegant advantage of the EcoTrainer concept is to work with the same kind of equipment and processes as those found in industrial scale facilities. Even the process control system is further developed and can described with the pre-configuration functionalities as a new standard. This makes the potential jump to a large-scale facility later much easier, faster, and more secure. The machine operators could be trained directly on the real-life systems so that they can learn as effectively and early as possible.

The EcoTrainer significantly cuts planning costs because all required infrastructure has been thoroughly planned and is ready for installation. The facility is divided into four areas: the process room, where the pilot process takes place; the airlock through which the process room is entered when the system is in operation; the control room, which houses the process control technology; and the logistics room for objects such as exhaust treating unit including scrubber. Basic equipment includes a process control system that is used to the system’s operation from the control room. In the EcoTrainer also an extended process control station was implanted prototypic. The ventilation and air conditioning systems are installed in the ceiling powered by an external module. The exhaust air is regulated by the exhaust air management system module located in the logistic room for evaluation. Partition walls can generally be set up in the EcoTrainer to create safety zones that protect against explosion risks. The outer envelope has e.g. an F30 fire-resistance rating and hermetically seals the container. Depending on needs, the system were fitted with sensors that detect specific air-borne substances like NO, NO_2 and Hydrocarbons as well. A sprinkler system was installed to deal with hazardous NOx gases – potentially emitted. The EcoTrainer were supplied with 1 Megawatt electricity power, compressed air, Nitrogen and auxiliary materials from outside. The interfaces for the supply systems are hidden behind a rollup shutter in one of the long sides of the container.

Regardless of the process, modularization and standardization plays a key role in small-scale plants. A module comprises of a particular plant area or component with certain technical requirements. As a rule, modules are standardized and prefabricated structural elements or component groups that accelerate the planning and construction of a plant and reduce the costs of operation. Small-scale design and modularization are mutually beneficial. A module may always be less than optimal because of the compromises one frequently makes between requirements, but it can be available fast and at a reasonable price – e.g. exhaust treatment module or preconfigured and preinstalled process control module.

In the demonstration phase, DIFFER designed the microwave power infrastructure to be installed in the Evonik Ecotrainer at Hanau. This involved waveguides, a newly purchased tuner and plunger system. Furthermore, DIFFER has supplied the conceptual designs for the flow reactor and its coupling to the microwave source. These conceptual designs were based on the in house research grade reactors that are used for CO_2 reduction and CH_4 activation. On that basis, Fraunhofer ICT-IMM designed and provided the demo-scale microwave plasma reactor. In the last phase of the project, DIFFER has been assisting in installing and commissioning the equipment at the Evonik site.

2.4 Nitrogen Fixation Process Analysis Activities

A considerable focus of activities within the nitrogen fixation team has been carrying out a range of activities to obtain an in-depth understanding of the process and its potential benefits in terms of both environmental and economic parameters. This work has focused on identifying scenarios where adoption of a plasma-assisted nitrogen fixation process would be expected to represent a viable economic and environmental approach.

These activities are summarised below

An ex-ante process design of the plasma-assisted nitric acid synthesis has been realized and simulated in ASPEN Plus software for a production capacity of 10 TPD. The effect of different process design parameters- NO yield, plasma power consumption, recycle of the tail gas and the total energy recovery of the plasma reactor input power with the form of steam production- on the environmental footprint of the plasma process incorporating renewable energy sources has been evaluated in “a cradle to gate” Life Cycle Assessment (LCA) study and compared against the conventional process. The environmental assessment has been implemented based on eight impact factors -Acidification Potential-average European (AP), Global Warming Potential in 100 years (GWP), Eutrophication Potential-average European (EP), Human Toxicity Potential in 100 years (HTP), Marine Aquatic Ecotoxicity Potential in 100 years (MAETP), Photochemical Oxidant Creation Potential (POCP), Ozone Depleting Potential in 10 years (ODP) and Cumulative Energy Demand (CED): As shown in Figure 13, the incorporation of wind and hydro energy demonstrates an improvement in the GWP profile of the plasma process- for 6% NO yield and 7.77 kWh/kg NO power consumption-over the conventional by a percentage of 15% and 23%, correspondingly. Additionally, as depicted in Figure 14 the tail gas recycle and energy recovery scenarios for the plasma process powered by solar energy demonstrate lower GWP values as to the conventional by 19% and 142%, respectively. With respect to the remaining environmental impact categories, the energy recovery case seems to outperform both all other plasma-process scenarios and the conventional process.

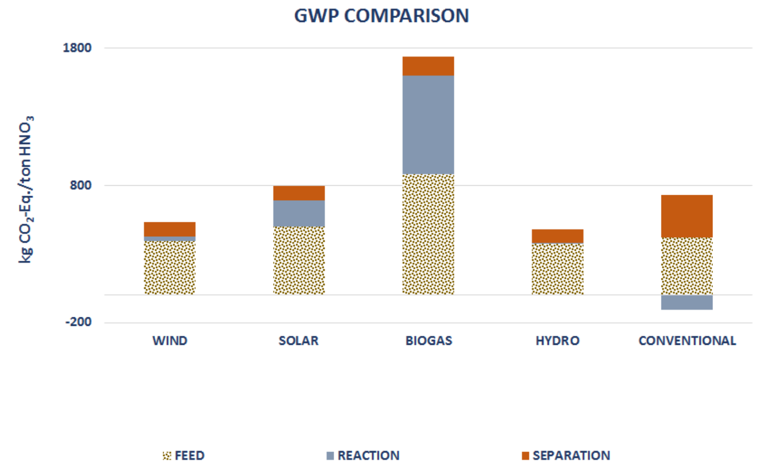


Figure 13. *Comparison of the Global Warming Potential of conventional and plasma-assisted process powered by different energy sources (feed, reaction and separation refers to mass and energy exchanges involved in the upsteam, reactor and downstream activities, respectively)*

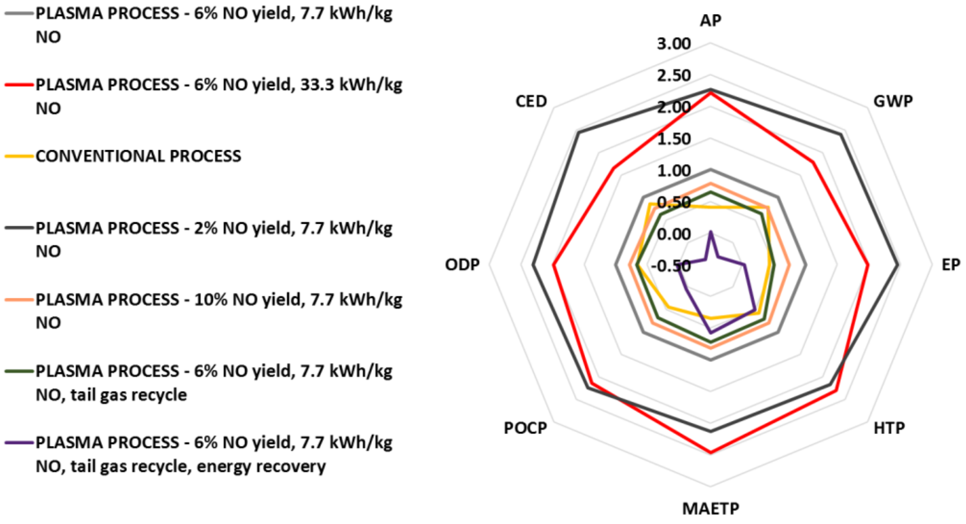


Figure 14. *LCIA comparison of the examined plasma-assisted process scenarios incorporating solar power and the conventional process*

In order to further evaluate the long-term sustainability of the plasma nitric acid synthesis based on the best environmentally performing process design scenario, an eco-efficiency analysis consolidated on the BASF methodology has been conducted and assessed against the conventional process for 280 and 10 TPD. More precisely, the impact of 20%, 40% and 60% energy recovery of the plasma reactor input power – 7.7 kWh/kg NO – with the form of steam production on the eco-profile of the plasma process powered by wind energy and incorporating the recycle of the tail gas has been examined. As it can be deduced from Figure 15, the application of the energy recovery scheme seems to improve considerably the overall eco-efficiency of the plasma-assisted process for 6% NO yield. This is mainly attributed to the lower environmental and operating costs incurred by the steam production. With respect to the large-scale conventional process, although plasma process demonstrates lower environmental impact, it still underperforms due to its higher life- cycle costs, denoting higher production cost. However, the different energy recovery scenarios, when compared with the conventional process at the same production capacity, exhibit either a marginal or a markedly better eco-efficiency profile, as being located to the top right corner of the plot. Upon these facts, plasma process seems to demonstrate promising industrial potential. At this point it is important to mention that the selection of a case study for decentralized production-like the "Africa" case study described below- and the consideration of the entire supply chain costs are likely to yield a better eco-efficiency profile for the plasma process even against the conventional process at large scale.

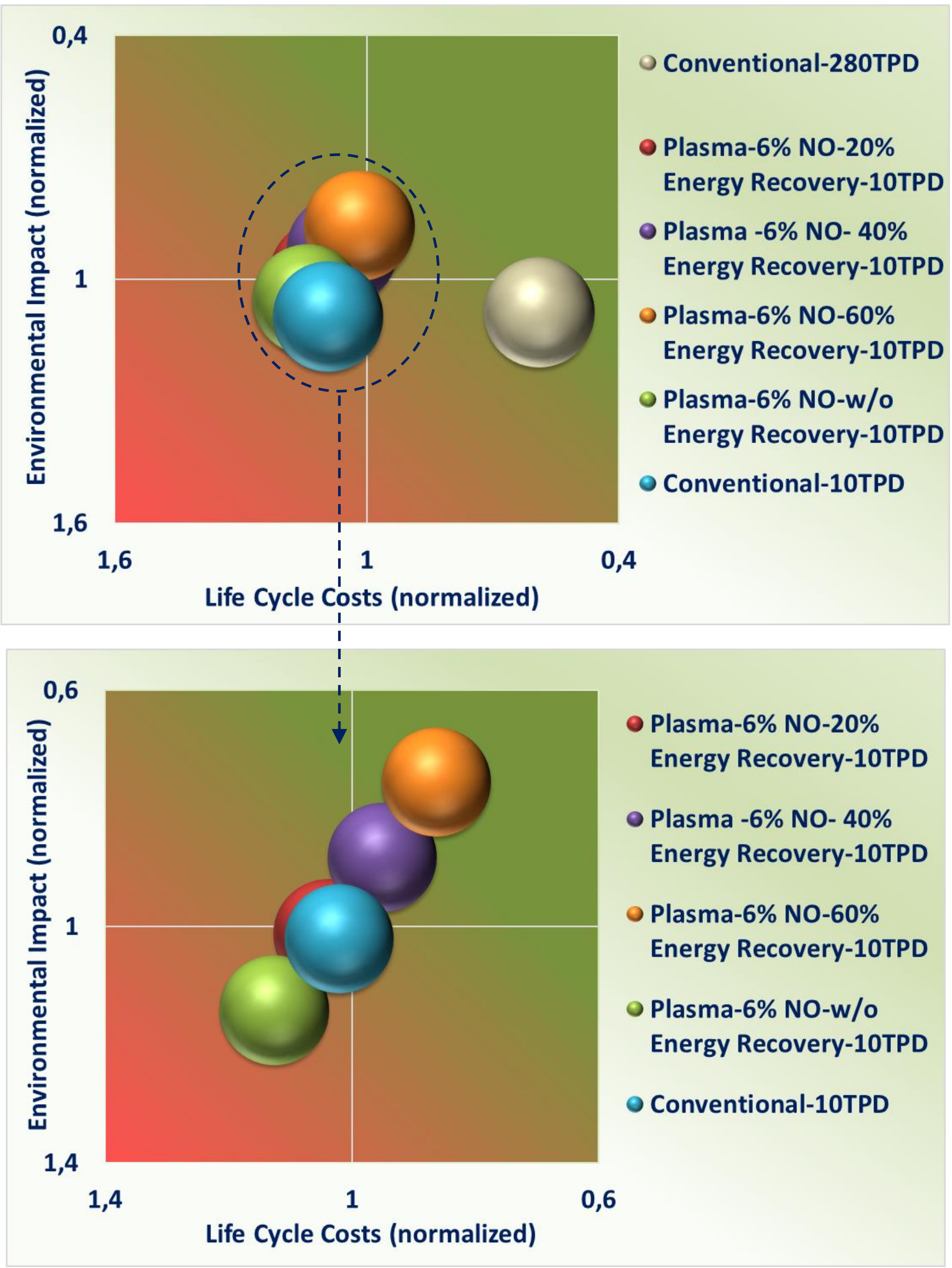


Figure 15. Eco-efficiency portfolio of 1 ton HNO_3 (60% w.w.) produced by the plasma process - 6% NO yield for different energy recovery scenarios- and the conventional process

As it can be deduced from Figures 16 and 17, a preliminary economic assessment of a plasma-assisted nitric acid plant of a production capacity of 3,400 TPY (6% NO yield and 7.7 kWh/kg NO) reveals a capital expenditure mainly dominated by the cost of the plasma reactor and an operating expenditure highly dependent on the energy consumption. The profile of the OPEX of the plasma process is actually opposite to that of the large conventional nitric acid plants which is merely material oriented by an approximate percentage of 60%. This fact provides a competitive advantage to the plasma process with respect to its long-term sustainability provided that overall energy efficiency is kept to high level.

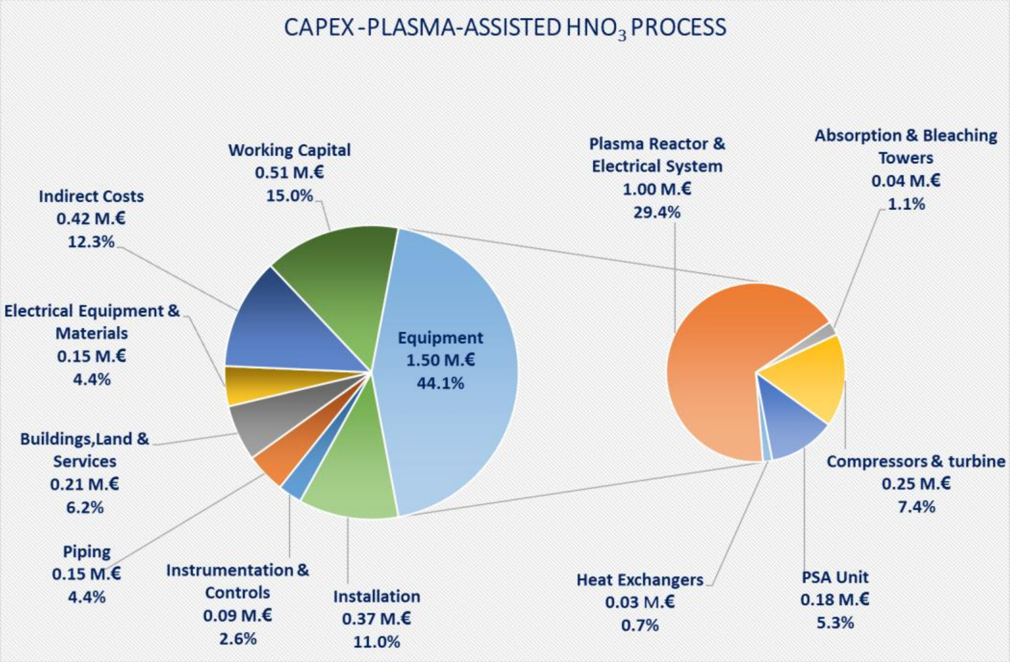


Figure 16. CAPEX of plasma-nitric acid process powered by wind energy (Capacity of 3,400 TPY).

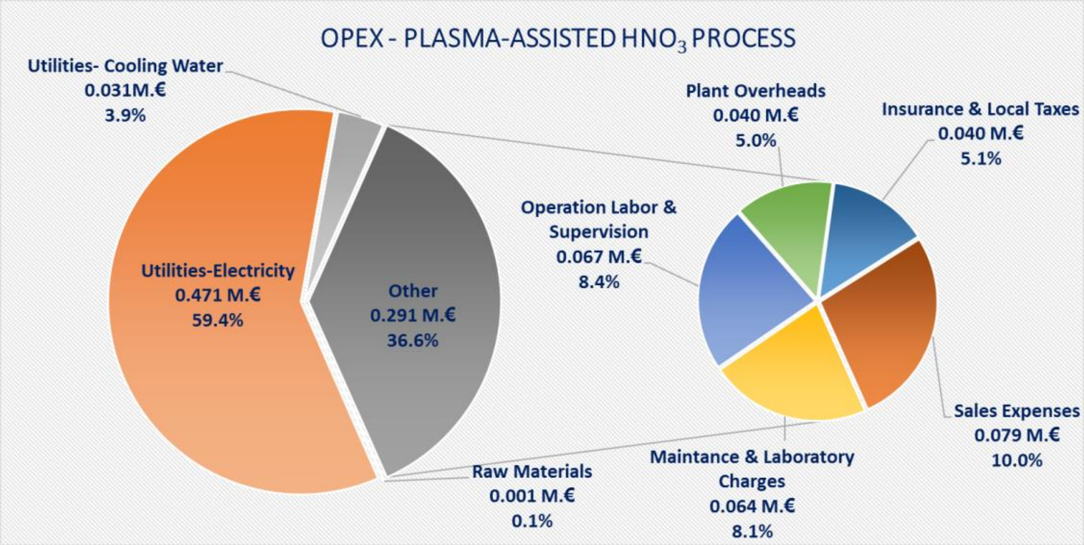


Figure 17. OPEX of plasma-nitric acid process powered by wind energy (Capacity of 3,400 TPY)

MAPSYN Potential Impact

1. Socio-economic impacts

A key objective of MAPSYN is to enhance the competitiveness of the European chemical industry through the exploitation of new flow chemistry processes and techniques. Process Intensification (PI) technology is becoming a great strength for the European chemical industry and projects such as MAPSYN help to reinforce and enhance this position. The outputs of MAPSYN will help Europe to be the most dynamic and knowledge-based economy in the world. These outputs include potential commercialisation of novel catalysts as well as development of innovative flow chemistry processes at both the industrial and laboratory scale. The broad societal consequence will be enhanced wealth generation and the creation of jobs in a high-skilled sector.

Adoption of MAPSYN technologies has potential to move towards an ‘electrification of chemistry’ where electrical energy is used with high efficiency to perform chemical reactions. This approach is well-integrated with the current exponential development of renewable energy sources thereby providing the potential for future chemical processes to exploit the availability of green energy sources for production of essential bulk and fine chemicals. The potential business model suggested for the plasma nitrogen fixation process is a more distributed production on a smaller scale. This localised nitrogen fixation, utilising local renewable energy assets, could provide a far greener approach to produce the fertilizers required by agriculture and also minimise the negative societal implications of transport from large-scale fertilizer production sites. Since the plasma-based N-fixation valorization plans are in the best sense breakthrough innovations, the respective strategic marketing challenges need to be considered. A proactive approaching of customers with intense communication and mastering to their special needs is required. Consequently, the creation of a Windows of Opportunity (i.e. a vital business case of the customer) is part of the delivery service; at least, for the customers of first generation. Thereafter, the innovation will slowly turn from breakthrough to incremental.

The work developed within the project is already generating economic value for the project partners including for the projects’ technology-focused SMEs. For example partner Syrris is already deriving commercial value through the sale of flow modules developed within the MAPSYN project. The Industrial end-users partners have had the opportunity to trial up-scaled reactor systems using the MAPSYN technologies and can now make informed decisions and de-risk future investment in PI technologies. The opportunity for project partners to grow their businesses based on the exploitation of project results serves to safeguard existing jobs and create new ones in technology areas which have been identified as high priority by the EC.

2. Societal impacts

A key achievement of the MAPSYN project has been to bring together researchers and organisations from across Europe to compile a consortium with a powerful multi- and, where needed, interdisciplinary capability. The success of the project is due to this approach and the skill set of all partners has been enhanced by the constructive and proactive collaborative approach. Technologies developed within the project could not have been achieved without the collaborative format. The societal benefits of these technologies are expected to be broad ranging, including enhanced competitiveness of industrial partners, enhanced research capabilities of academic organisations and training of a future generation of researchers.

Success of the project can be judged by the high contribution made to the scientific literature and scientific knowledge-base which has been achieved by the project. A lasting legacy of the cross-sector collaboration is that the MAPSYN project placed the requirements of industry at the heart of the project. This ensured that development of advanced research skills was focused on tackling real-world problems to accelerate development of innovative sustainable technologies.

The MAPSYN project has performed a valuable function for training future generations of researchers in PI techniques. Numerous students, including 6 PhD students whose thesis work has been focused on MAPSYN, have been employed by the project and have gained valuable expertise in the development and applications of novel MAPSYN technologies. These young researchers have benefitted from collaboration and mentoring from industrial partners, had the opportunity to present their work at major prestigious international conferences and expand their skill set through exposure to the wide range of technology disciplines involved within MAPSYN. A much wider pool of future scientists has been engaged through dissemination activities, most notably the summer schools in Process Intensification methods which were a key project deliverable. These young scientists, trained by the MAPSYN project, will be ambassadors for process intensification technologies and form an extended legacy of the MAPSYN project.

In addition to this, the plasma-based N-fixation valorization plans might also have social impact. In some regions of the world fertilizers are poorly accessible. For example, Uganda uses 3 kg / ha, while Netherlands' average is 250 kg / ha. The Uganda case is typical for Africa, which actually has quite good conditions and enough good-quality farming land for cereal harvesting in its central part. Too high import taxes and transport costs raise the actual price for fertilizers to 2- or 3-times that in Europe. The establishment of small-capacity distributed container plants with plasma reactor technology could provide a local source of fertilizers which flexibly reacts do the local needs and seasonal changes. In this way, the plasma-based MAPSYN technology has potential to help in one of the most urgent issues of mankind, the poverty and hunger in the under-developed regions of the world.

3. Environmental impacts

Detailed LCA studies have been carried out on the two main technology areas within the MAPSYN project; plasma assisted nitrogen fixation and microwave hydrogenation.

The study of the microwave hydrogenation process highlights potential benefits which may be derived from replacing traditional batch hydrogenation reactions with MAPSYN flow processes. A key potential benefit is the potential for reduced energy consumption of the process. Although final figures on optimised process efficiency are not yet available it is anticipated that an optimised MAPSYN process has potential to offer up to 50% reductions in the Global Warming Potential associated with process energy use. Furthermore, the replacement of traditional hydrogenation catalysts with novel MAPSYN catalysts could deliver environmental benefits. Use of lead-free catalysts removes use of a highly toxic metal. Additionally the reduced Palladium content of catalysts has significant implications with respect to resource depletion. Palladium is a scarce and expensive metal and reductions in its use offer both environmental and economic benefits for hydrogenation processes.

The LCA work carried out on the plasma-assisted nitrogen fixation process highlights that this approach has considerable potential to deliver environmental benefits by comparison to existing processes. These benefits are highly dependent on 2 key factors; the yield of NO which is obtained and the extent of energy recovery which is achieved. However, the analysis shows that, at realistic levels for these factors, considerable environmental benefits would be achieved. These benefits are seen for all 8 of the environmental impacts considered by this study. The targeted route for exploitation of this technology is through 'distributed production' of NOx as a precursor for fertilizers. By linking these small-scale plants to renewal energy assets, for example wind farms, a green energy alternative to the conventional high-energy fertilizer synthesis can be envisaged. The reductions in, for example transport costs, which are envisaged from this localised manufacture also delivers environmental and economic benefits.

4. The main dissemination activities

The MAPSYN project has undertaken a wide range of dissemination activities. These include the following major activities to disseminate the results to the scientific community:

- 11 peer reviewed scientific papers
- 30 oral presentations at scientific conferences
- 13 posters at scientific conferences
- 8 articles in the popular press

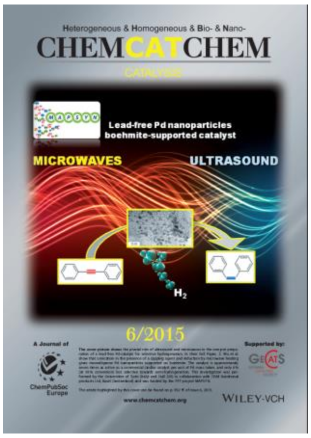
These activities have encompassed the full multidisciplinary aspects of the project and have included activities relating to all main technical areas. For example dissemination covers novel catalysts, novel microreactors, novel plasma and microwave systems, the use of ultrasound for catalyst formation and catalytic processes and modelling of flow in 3-phase microreactors.

Some of the more prominent dissemination activities are highlighted below

EPIC/ECCE 2015 MAPSYN project participated in a joint 1-day session with the ALTEREGO project at the EPIC/ECCE 2015 conference. This internationally renowned conference on flow chemistry and process intensification provided an excellent forum for partners to present the exciting results generated within the MAPSYN project.

Processes-Special Issue on Design and Engineering of Microreactor and Smart-Scaled Flow Processes **(Editor: V.Hessel)** This is, to our best knowledge, the first compilation on advanced process design research & development based on process intensification. Among this is a MAPSYN review paper giving a conceptual approach towards the industrial process design of small-scale plasma-assisted nitric acid and ammonia plants with respect to energy and environmental perspectives. The whole Special Issue was chosen by the publishing house to be printed as book.

Cover Article for ChemCatChem A paper jointly prepared by DSM and Turin University featured on the cover of the prestigious journal ChemCatChem in Mar 2015. This paper entitled 'Ultrasound and Microwave-Assisted Preparation of Lead-Free Palladium Catalysts: Effect on the Kinetics of Diphenylacetylene Semi-hydrogenation' presented some of the MAPSYN projects most exciting work on the development of highly active novel hydrogenation catalysts.



Heterogeneous & Homogeneous & Bio- & Nano-

CHEMCATCHEM

Lead-free Pd nanoparticles boehmite-supported catalyst

6/2015

WILEY-VCH

Figure 18; Cover Article of ChemCatChem highlighting novel MAPSYN catalysts

In addition to the high number of activities focused on dissemination to the scientific community, dissemination activities have addressed the following

- Publicly accessible presentations of results for a non-scientific audience
- Presentation of results to Brussels policy makers
- Training in process intensification techniques

Publicly accessible dissemination

Partners have compiled information on all technical areas which is presented on the MAPSYN website in a readily accessible format. This provides a highly accessible repository of non-confidential information on PI techniques and the core technologies (microwave, ultrasound, plasma, microreactors and catalysis) which were the focus of MAPSYN. The website also includes project newsletters which are presented in a non-technical format, thereby making project results accessible to a broad and non-technical audience. Throughout the projects partners have disseminated information on key project aims and objectives as well as important results through their own websites.

Training courses

As part of the MAPSYN project TOR has held 2 summer schools focused on training students in chemical process methods for process intensification (PI) engineering. These courses play an essential role in educating future generations of scientists and engineers in the techniques involved in the rapidly evolving area of PI. They also provide a forum for the benefits of these techniques to be more broadly appreciated; ensuring that future generations of researchers will exploit these technologies as core tools within their work. These two events, one at Turin in 2013 and the other at Krakov 2015, each involved a week long schedule incorporating both lectures and practical laboratory sessions. A total of 90 young researchers participated in these events.

Presentation to Brussels stakeholders

Representatives from several members of the MAPSYN consortium (C-Tech, DSM and Eindhoven University) participated in an industrial workshop in Brussels on 2 March 2016 to promote the use new energy technologies in chemical synthesis and manufacturing. The goal was to present the exciting recent results obtained in the project to Brussels policy makers and encourage their further implementation.

The MAPSYN project joined together with two related project consortia who also received funding under the same EU call. The InnoREX project (http://www.innorex.eu/) has developed a novel reactor concept for metal-free polymerization using laser, ultrasound and microwaves. The Alterego project (http://www.alterego-project.eu/CMS/) has used ultrasound, microwave and plasma technologies for the synthesis of pharmaceuticals, green fuels and bulk chemicals.

Overview; Microwave hydrogenation

- Target test reaction; semi-hydrogenation of acetylenic alcohols
  - Challenging targets for conversion and selectivity
  - Process of high industrial relevance (e.g. synthesis of vitamins and aroma compounds)
- Evaluate different types of microreactor; packed beds, falling film microreactors (FFMR)
  - Challenge to achieve good contact between 3 phases of hydrogenation reaction; rapid reaction
  - Suitability for use in a microwave system; requires novel systems
- Develop microwave flow prototype
  - Focus on rapid, efficient and controllable heating of reaction media; one-pass through microreactor.
  - Process control and automation; Innovative, integrated system to control gas and liquid flows, MW and key process parameters (e.g. T and P).
  - Demonstrate process benefits; yields, energy efficiency, speed of conversion

Figure 19*; Dr Rachel James presents an overview of microwave hydrogenation technology*

At the end of the workshop, all the participants agreed in the potential of these new “enabling technologies” and committed to further promote their implementation in chemical production.

5. Exploitable results

Exploitable results within the MAPSYN project cover all areas of technology developed within this 3 ½ year long project.

Novel Hydrogenation Catalysts

Development of novel catalysts was a key focus of work for several of the MAPSYN project partners. Work explored the development of various novel types of catalysts incorporating a range of synthetic techniques; for example the use of ultrasound and microwave for catalyst synthesis. Catalysts prepared were then intensively evaluated to understand their abilities to promote hydrogenation reactions. Key criteria for the catalysts developed were high activity, high selectivity and high reusability. A key objective of the MAPSYN hydrogenation work was to synthesise new catalysts which could present viable alternatives to current catalysts for industrial hydrogenation processes. The Lindlar catalyst, for example, is the catalyst of choice for many industrial selective hydrogenation processes. Developed in the 1950s, this catalyst has many areas where improvement is needed. Most significantly it contains both palladium and lead metals and is only useable in batch mode. Within the MAPSYN project the target has been to develop catalysts which offer numerous benefits over the Lindlar catalyst. Target benefits include environmental benefits (lead free and reduced palladium content), suitability for use in continuous flow systems and enhanced activity and selectivity.

Catalysts developed within the MAPSYN project show considerable potential to provide viable industrial alternatives to the Lindlar catalysts. High activity and selectivity has been observed with lead-free catalysts with low palladium content. These catalysts have also been shown to be suitable for use in continuous flow systems and to have a high level of reuseability.

Two patents have been filed to protect the novel catalysts developed within this project (jointly owned by DSM and TOR).

Work with these catalysts is ongoing to provide a comprehensive evaluation of their properties for a range of hydrogenation processes of industrial relevance. It is considered highly likely that, following conclusion of the MAPSYN project, commercial applications of these novel catalysts will be confirmed.

Flow Reactor systems

Within the MAPSYN project several types of novel flow reactor system have been developed. Some of these new systems are subject to a high level of confidentiality so only a high-level overview is presented here.

Flow modules MAPSYN Partner Blacktrace (a UK SME) is an industry leader in the sale of modular flow reactor systems for chemical synthesis. Within the MAPSYN project they have developed several new modules some of which are already available commercially. Most notably the 'Active Cooling' and 'Flow Electrochemistry' modules have already generated considerable commercial interest during the lifetime of the MAPSYN project. Blacktrace estimate that they have already sold a total of >15 of these units. This equates to a total sales value of ≈€100k; but is associated with probably five times this value in terms of system orders. They anticipate considerable sales growth in upcoming years. Other modules which have been developed within the MAPSYN project are also in the process of being commercialised; for example the 'Gas Introduction Module' is currently available to be manufactured on request.

Throughout the MAPSYN project Blacktrace have actively promoted their modules at 'hands-on' flow chemistry workshops around the world as well as is newsletters, through website and marketing campaigns.

Microwave Transparent FFMR MAPSYN partner Fraunhofer have developed novel Falling Film Microreactors (FFMR) as a key output of the project. Building on their existing expertise in this area, Fraunhofer have revised their design of stainless steel FFMRs to make a version suitable for use in a microwave system. This novel system is manufactured using a microwave transparent housing which enables microwaves to penetrate the FFMR and selective heat the reaction medium contained within. Two sizes of microwave FFMR have been developed within MAPSYN; an initial small scale system and an up-scaled prototype which has been incorporated into the industrial demonstrator system. Fraunhofer have developed several new and highly innovative aspects of this FFMR design. For example, the inclusion of an optic level sensor within the FFMR sump enables monitoring of liquid levels within a microwave field.

The novel FFMR systems developed within this project have potential applications within the Speciality Chemical and API production industries.

Novel Plasma Reactors During the course of the MAPSYN project a range of plasma technologies and reactor systems have been used. For example work has encompassed the use of dielectric barrier discharge (DBD), Glide-Arc and Microwave Plasma systems. Eindhoven University (TU/e) have a plasma system suitable for carrying out nitrogen fixation reactions in both DBD and Glide-Arc reactors (including novel Glide-Arc reactors developed within MAPSYN). The final nitrogen fixation demonstrator system has involved a joint development between partners TU/e, Evonik, DIFFER and Fraunhofer. This system incorporates a specifically developed up-scaled microwave plasma reactor which incorporates the facility for heat recovery.

Trials of both the Plasma Industrial Demonstrator at Evonik and the laboratory plasma system at TU/e will continue after completion of the MAPSYN project. It is anticipated that, by optimising process conditions, a new nitrogen fixation technology which can compete commercially with existing processes may be identified.

Microwave Hydrogenation Process

The development of a continuous flow microwave hydrogenation demonstrator has been a focus of work within the MAPSYN project. A key output has been the microwave system developed by C-Tech Innovation which incorporates both the novel FFMRs developed by Fraunhofer and immobilised MAPSYN catalysts. This system has been used to demonstrate microwave heated hydrogenation reactions. To the best of our knowledge the MAPSYN project represents the first use of microwave systems to carry out continuous hydrogenation processes. This achievement was not a trivial undertaking. The prototype had to incorporate the following key aspects:

- Uniform microwave heating
- Controlled flow rates and pressures of liquid and gas through the FFMR
- Monitoring and control of key process parameters; e.g. temperature and pressure
- A high level of safety functionality to enable safe operation with hydrogen gas

A key innovative aspect of the system developed was therefore the control methodology and bespoke control software which was developed.

Following completion of the MAPSYN project it is anticipated that trials of the microwave demonstrator system to benchmark its performance for industrial hydrogenations will continue. This may identify commercial opportunities for the use of this system for production of specific fine or speciality chemicals.

Figure 20*; Microwave flow system*

More broadly, this system (as shown in Figure 20) will have a high value as a continuous microwave demonstrator system capable of clarifying the benefits of adopting continuous flow microwave technology for a range of synthetic applications. The software developed for process control also has potential to be exploited by C-Tech Innovation to improve the functionality of their standard microwave flow reactors.

Plasma assisted Nitrogen-Fixation process

The containerised plasma nitrogen fixation system has been developed to provide an up-scaled demonstrator of the potential for a plasma-assisted nitrogen fixation process. This prototype incorporates the novel microwave plasma reactor discussed above within a complete system. Key challenges for development of this system include the requirement to include effective exhaust treatment to avoid emission of toxic gases (e.g. NOx) to the environment. Installation of the complete system also required considerable development of the PCS (programming, safety, control). At project completion this system was complete and operational with an extended program of evaluation planned. It is anticipated that this work will demonstrate both the technical and economic viability of this system leading to identification of clear commercial applications.

Ultrasound Processes

The use of ultrasound (US) was investigated for a range of purposes within the MAPSYN project. The use for synthesis of hydrogenation catalysts was broadly explored by several partners; notably Universities of Alicante, Coventry and Turin.

Use of US for performing hydrogenation reactions was also investigated. At the start of the project it was envisaged that use of ultrasound may assist with dispersion of catalysts and reducing blocking in flow systems. Work during the project showed that US was not beneficial to hydrogenation reactions due to its degassing nature. US can also lead to leaching of metals from some catalysts. Although an extensive study of the impact of US on all catalysts of interest within the MAPSYN was not carried out, it was decided to not progress with use of US within the flow reactor systems being developed due to concerns about leaching of metals. However, investigation of flow through designs for inclusion of US within capillary systems have been carried out as concurrent activities within the project.

Understanding 2-phase flow in microreactors

Project partner University of Alicante has carried out considerable work to understand 2-phase flow in microreactors. Based on providing an improved understanding of hydrogenation systems this work has looked at hydrogen and liquid reaction mixture flow within millipacked bed systems at both the micro and meso scale. This work has highlighted the issues of ‘hydrogen channelling’ and provided a good level of understanding of the flow configuration and effectiveness of mixing which would be expected for liquids and gases in a system of this type. This work has been validated by comparison to experimental data and shown to provide a robust model of this type of system.