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De Rondon 1
5612 AP Eindhoven
Postbus 6235
5600 HE Eindhovenwww.tno.nlT +31 88 866 50 00
F +31 88 866 88 19

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Auteur(s)	Dr. ir. Jan Harm Urbanus, Ir. Peter Wolfs
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1 VP Sustainable Chemical Industry

1.1 Summary

In 2016 the VP Sustainable Chemical Industry achieved important results, both in terms of Roadmap and direction as well as knowledge development in the two subprograms Green Chemistry and Smart Materials. TNO actively collaborates with industry and academia through three Public Private Partnerships: Brightlands Materials Center (BMC), Biorizon and VoltaChem.

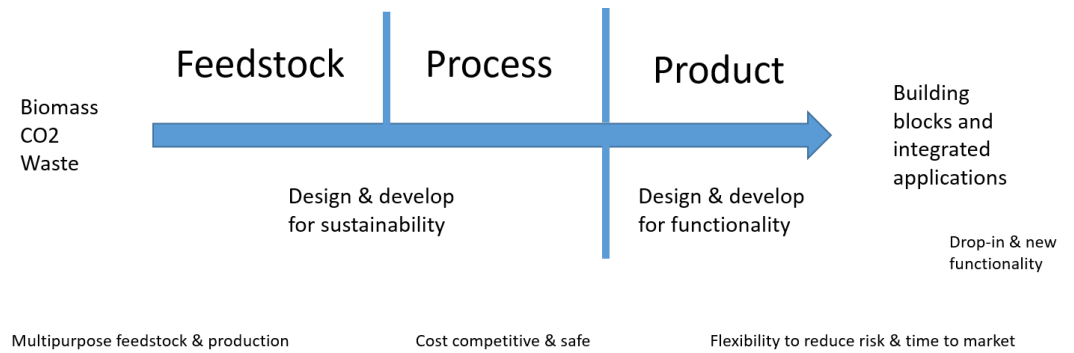
Main results for BMC are a clear definition of the program line Sustainable Buildings, the scale up and operation of pilot infrastructure for synthesis of nanoparticles within Co-Pilot project and the start of the Enef project to develop thermochromic coatings.

The most important results for Biorizon are 1) the accession of ECN to the existing partnership between TNO and VITO, 2) the improved embedding of Biorizon in the Biobased Delta, 3) the collaboration with InSciTe and 4) the results obtained in the projects Waste2Aromatics, SCELIO-4B and BIO-HArT that altogether enable the scale up from laboratory experimentation to pre-pilot skids with which samples can be prepared and important techno-economic features can be evaluated.

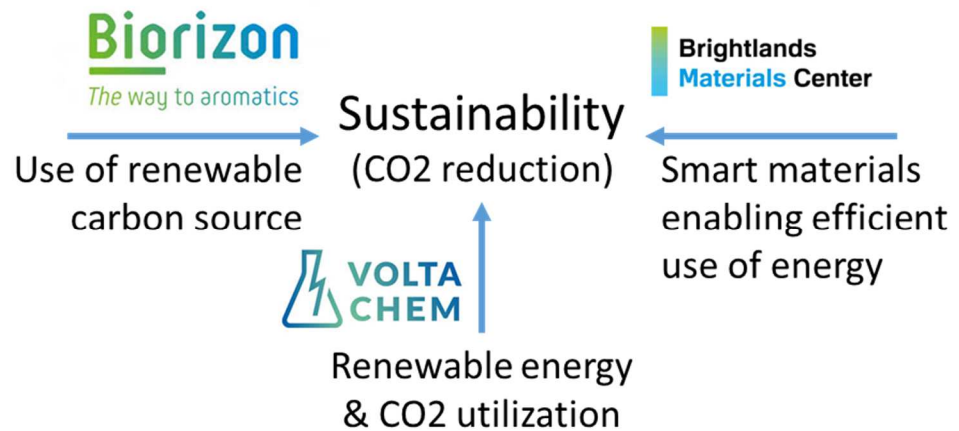
This year, VoltaChem successfully turned research into attractive results. Starting with the TTI Transitie Chemie budget, TNO and ECN accomplished to initiate a multi-year program, with concrete projects in which various companies from the chemical, energy and equipment supply sector are involved. Innovative concepts have been developed with potential to compete in challenging arena's (e.g. ammonia, hydrogen peroxide, hydrogen, heat, selective oxidations). Ultimately, continuation of VoltaChem activities is guaranteed through collaborations with industry and academia in several projects.

1.2 Short description

This report describes the results achieved in the second year (2016) of the TNO program for the chemical industry for the period 2015-2018. The ambition and related objectives of this TNO program are described in TNO report 0100173227 (Speurwerkprogramma 2015-2018 Theme Sustainable Chemical Industry), specifics for 2016 can be found in TNO report 0100289197 (Sustainable Chemical Industry program – Annual plan 2016). In short, the ambition of TNO is to contribute to a sustainable chemical industry that enables a sustainable society. To accomplish this, TNO designs and develops materials and chemicals of which intrinsic properties offer a benefit for an improved sustainability (& functionality) in the use phase and are wherever possible sustainably produced from renewable or recyclable materials like biomass, CO₂ or waste (see scheme below).



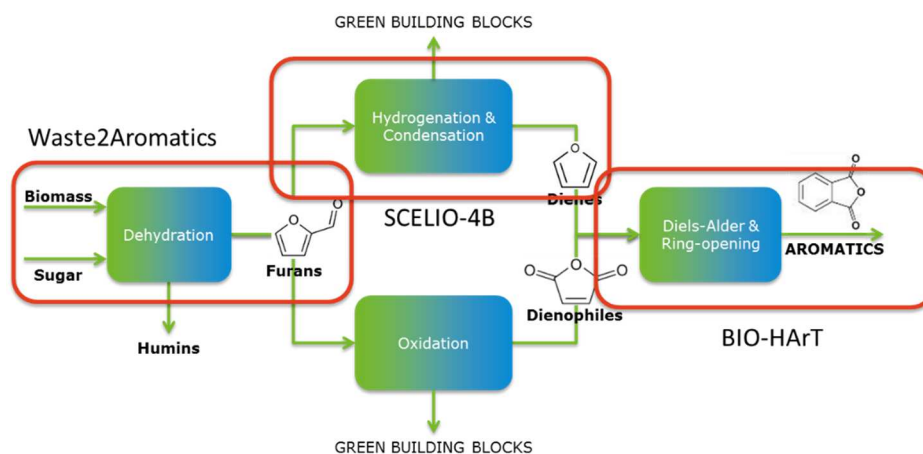
The TNO report 0100289197 describes that the TNO activities, which support the ambition, are clustered in three subprograms: “advanced materials with the right functionality” (AMRF), “advanced materials from renewable sources” (AMRS) and “modular and flexible production technology” (MFPT). However, during 2016, through discussions with industry, TKI Chemie and other stakeholders, the TNO program for Topsector Chemie became more focused, resulting in two subprograms: Smart Materials and Green Chemistry. The impact of TNO’s activities should ultimately lead to implementation on a commercial scale by the industry. Scaling up of the technologies is essential and will be done together with the industry through Public Private Partnerships (PPPs). The TNO activities in the two subprograms are consolidated in three different PPPs: Biorizon and VoltaChem for Green Chemistry and Brightlands Materials Center (BMC) for Smart Materials. The picture below shows their relation to the overall ambition of a sustainable chemical industry.



1.3 Highlights

1.3.1 Green Chemistry – Biorizon

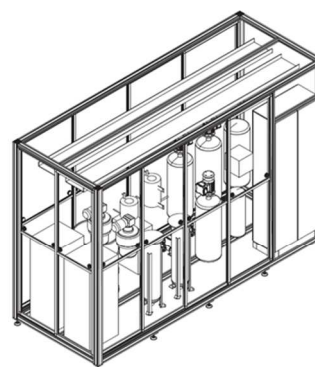
In 2016 three large projects were granted: Waste2Aromatics (TKI Chemie), SCelio-4B (OP-Zuid) and BIO-HArT (Interreg Vlaanderen-Nederland). The picture below shows the connection between these projects and the TNO focus in Biorizon (program line “Sugars-to-Aromatics”).



The overarching goal of these projects is to scale up technology for the conversion of waste biomass into aromatic compounds. Within SCELIO-4B a biphasic reactor has been constructed for the conversion of heterogeneous waste (manure, diapers, sewage sludge & SSO) into furanic intermediates. Within Waste2Aromatics, Proof of Principle has been demonstrated for new feedstocks (e.g. manure) and the initial scale up has been prepared. In BIO-HaT, focused on the conversion of furanic intermediates into the desired aromatic chemicals, several Proof of Principles have been developed. In addition, the design and construction of a reactor for Diels-Alder chemistry started. Finally, the first bio-aromatics samples (100-300 grams) have been distributed and (partially) analysed by our industrial partners (e.g. Covestro, Beckers, Klueber) with promising results.



Biphasic reactor for conversion of waste into furans (kg/hr)



Diels-Alder reactor for production of bio-aromatics (kg/hr)

The triple helix collaboration with the Province of Noord-Brabant resulted in a plan for accelerating Biorizon. ECN has become partner in Biorizon and ties with InSciTe have been strengthened.

1.3.2 Green Chemistry – VoltaChem

Just before Christmas '14 the collaboration between ECN and TNO on "Electrification of the industry" was initiated. During 2015, this collaboration was launched as VoltaChem during an event with 'Topsector Chemie'. This collaboration is crucial with regard to the symbiosis of the energy and chemicals sector in the future. The TTI Transitie Chemie has allowed for the start of VoltaChem

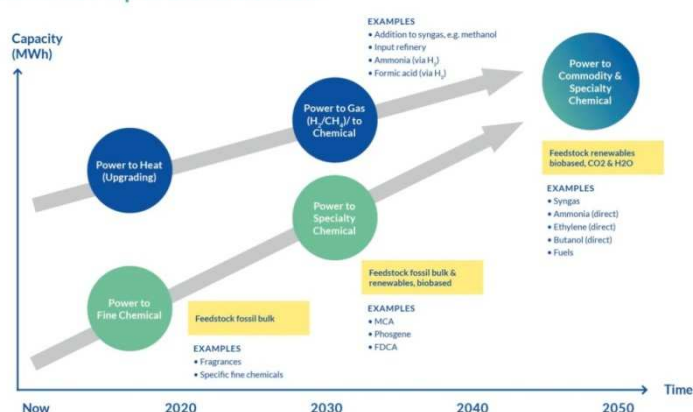
(<http://www.voltachem.com/>), which targets the use of green electricity as energy source in the chemical industry.

Below, results for the four areas of VoltaChem (community, power to heat, power to hydrogen and power to chemicals) are described. The activities of TNO are aligned with the research done in the early research program, topic Energy Storage and Conversion, Electron to Chemicals (ref. "Annual plan 2015 – TNO ERP 2015").

COMMUNITY

The activities within the community, where ECN and TNO are working closely together, bring together stakeholders from relevant sectors (chemicals, energy, equipment industry and service providers) in an exclusive forum. A multi-year high-level Roadmap for implementation of electrification and decarbonization in the industry and society as a whole is developed and maintained (see figure below).

High level Road Map of Electrification



Specific high-level non-technical projects that are needed for implementation of the Roadmap were carried out such as technology-, innovation-, and business scouting, value web analysis for electrification technologies & markets, development of hit-lists for industrial electrification options, development of frameworks for infrastructure integration, development of electrification scenario's and policy and organizing workshops and events. In 2016 the Whitepaper "Empowering the Chemical Industry – opportunities for electrification" has been released (<http://www.voltachem.com/whitepaper>), where promising opportunities are offered to significantly reduce the CO₂ footprint of the industry by using electrification.

External parties can join the community with an in-cash or in-kind contribution. In 2016, the community consisted of the following partners and associates: Magneto, OCI Nitrogen, STEDIN, FME, Energy Valley, InnovatieLink, Topsector Chemie, ENGIE, Vattenfall-NUON, MAGNETO, Arkema, DOW, University of Twente, Perstorp, Technip, Coval Energy, Hydron Energy, Proton Ventures, Saudi Aramco, Sasol, TNO, ECN (see website for up-to-date list).

Other parties with relationship to the VoltaChem program e.g. by working together in projects with VoltaChem members, are DIFFER, Solliance Eindhoven, JRC, ISPT, Deltalinqs, TU Eindhoven, TU Delft, Akzo Nobel, Hydrogenics, Siemens and Innovation Quarter. In 2016 the project E-Match: hit-list for Electrification has been carried out, Matching Processes with Electrification Technologies, led by ECN with a strong contribution from TNO and together with Arkema, Akzo Nobel, OCI Nitrogen, Stedin and DOW. The project has resulted in identification of 11 electrification options at the 4 industrial partners. With the results of these

electrifications scans an estimate was made of the total potential for Power2Chemicals and P2Heat for the Dutch industry.

POWER TO HEAT (P2H)

Power to Heat means the use of renewable electricity (e.g. wind, solar and hydro) as source to upgrade heat and steam. This involves the development of high temperature compression heat pumps, a combination with heat and cold storage, and the development of alternative concepts for heat generation & upgrading, e.g. electrical heating, steam compression & multifunctional heat pumps. Work within this topic is done at ECN.

In 2016, high temperature heat pump refrigerant options have been evaluated. The idea was to extend the working range of a compression heat pump to 180°C using other working media. It was concluded that electrically driven heat pump leads to energy and cost savings at today's price levels of energy. Two options have been identified, which have to be experimentally validated. First indication is that a business case is within reach.

A technical and economic feasibility study of a flexible thermoacoustic system was performed. The system can operate as a heat pump for different operation temperatures and temperature lifts or as a heat engine and can be driven by heat or electricity depending on availability and the price. The operation of the system as heat pump and as engine is simulated in the thermoacoustic computer code DeltaEC. The simulation results show that the same system can operate as a heat pump for different temperatures and temperature lifts without any impact on performance. The same system can also operate as an efficient engine. The study shows that a flexible thermoacoustic system can be designed to operate in different applications. This will lower the cost and improve the efficiency and flexibility of the industry. A CHP system with heat storage was modelled as flexibilisation option for the industry. The study shows that a flex-CHP system is technically feasible, however the business case is challenging.



POWER TO HYDROGEN (P2H₂)

The main objective of this topic is the use of renewable electricity as energy source for direct chemical transformations via hydrogen, where in P2H₂ the focus is on efficient hydrogen production and the use of hydrogen to create bulk chemicals (e.g. ammonia). Work within this topic is executed by ECN.

Within the ELECTRE project, ECN is focused on life time testing of electrolyser components. In 2016, the facility for testing single cell electrolysers has been designed and construction had commenced. First evaluation of electrolysers has identified three key degradation mechanisms: corrosion of the anode current collector, degradation of the membrane due to gas cross-over and catalyst dissolution. Accelerated stress testing (AST) protocols are being developed to

understand degradation. For this, ECN joined an EU working group to connect to the key European players in the field.

Within the Power to Ammonia project (P2A), ECN has been investigating different routes for using sustainable hydrogen in the production of ammonia for the cases of Nuon (carbon free fuel) and Stedin (energy storage), leading to an R&D Roadmap for technologies with high potential for Power to Ammonia production. Four different P2A systems, designed to use PEM, battolyser, Solid Oxide Electrolytic Cell (SOEC) and Solid State Ammonia Synthesis (SSAS), have been evaluated for deployment in the year 2023 and 2030. The cost of ammonia was evaluated in the year 2023 and 2030 with varying levels of fuel prices and renewable penetration. It is found that the cost of ammonia in the year 2023 and 2030 is always higher for the electrochemical than for the SMR. However, in the year 2030 with high renewable penetration, this trend is reversed. Only the SOEC and battolyser are able to achieve lower costs than the SMR. These can be attributed to the high efficiency of the SOEC and the additional revenue generated by the battolyser by acting also as a battery.

POWER TO CHEMICALS (P2C)

The main objective of this topic is to use renewable electricity as energy source for conversion of raw materials to chemicals and fuels, where P2C is focused on the electrochemical conversion of renewable raw materials as feedstock for chemical production. Feedstocks are e.g. biobased feedstock, biogas (CH₄), H₂O, O₂, N₂ and CO₂. Work within this topic is done at TNO.

In 2016, the focus of TNO was on system development for demonstration of continuous operation of electrochemical oxidation, including processing and purification. As a showcase, the oxidation of HMF to FDCA was selected. FDCA is a potential building block for renewable plastics. User requirements for the demonstrator have been established. Then, laboratory experiments have been carried out to determine the operating window of the electrolyser and the downstream processing equipment. With this information the specifications of both the electrolyser module and the processing/separation module have been drafted and some variants of process designs were made. This research has led to new ideas on the purification of FDCA which are commercially attractive. Therefore, a patent application has been submitted.

Subsequently the equipment has been procured and a bench scale setup has been build, integrated and commissioned (see picture below). The method has been experimentally proven and optimized and a maximum separation yield of ~80% has been achieved when the electrolysis selectivity is ~90 % and with 10wt% HMF concentration in the feed.



In addition, research has been done on the use of in-situ produced hydrogen peroxide to oxidize HMF on the cathode. At this moment, the reaction at the cathode leads to the formation of hydrogen. The generic idea was to develop a system whereby instead of cathodic formation of hydrogen, hydrogen peroxide (H_2O_2) is produced. This H_2O_2 can react with molecules such as TEMPO, which can also oxidize HMF. This new method for oxidation ("paired electrosynthesis") will lead to a significant improvement in efficiency due to the formation of FDCA at the cathode and anode simultaneously. It was proven that this approach can indeed work more efficiently. A patent search, to analyse if the idea could be protected, revealed that it was already patented very recently by a US University. Contacts have been established with a commercial party that is interested in licensing and further development of this approach into an industrial scale system.

In 2016, within the ERP E2C project, a novel concept for the production of H_2O_2 (hydrogen peroxide) based on oxygen and water has been developed. This concept has been validated. Based on the initial results, a Proof of Concept system has been made. This system was capable of producing in a continuous manner up to 100 gram of H_2O_2 per liter for many days. To become competitive, the energy consumption needs to be reduced. Several approaches have been identified for this. Furthermore, the principle used is also applicable for commercially interesting peracids (e.g. peracetic acid).

1.3.3 *Smart Materials – BMC*

Brightlands Materials Center (BMC) is a research and development center in the field of polymeric materials, established March 2015. Brightlands Materials Center performs programmatic research, from molecule to application, driven by the industrial and societal challenges of tomorrow. Brightlands Materials Center is a collaboration between the Province of Limburg and TNO. For TNO it is one of its Joint Innovation Centers.

The overall ambition of Brightlands Materials Center (BMC) is to come to new application technologies in selected application areas, relevant for the industry and supporting solutions for the Grand Societal Challenges. BMC connects leading universities to its programs, securing state of the art knowledge to support its innovative activities. It connects science to entrepreneurship by inviting innovative

SMEs to work alongside its R&D to implement findings into practical and commercial products. BMC invites companies large and small to collaborate in shared programs to shorten time to new technologies. BMC develops its own programs and related knowledge and builds an infrastructure available for industry and supporting its programs.

BMC has selected the following program lines:

- Materials for Additive Manufacturing (AM)
- Sustainable Buildings (SB) (formerly opto-electronic (OE))
- Materials for Lightweight Automotive (LA)

In 2016 the VP Sustainable Chemical Industry invested in the development of knowledge for the Sustainable Buildings program line. Within that program line the window of the future is one of the key applications. The 'window of the future' should not only be able to perform as the current product of glass manufacturers (highly transparent, heat insulating and 'low-E' coated), but should ideally be optimized for energy-efficiency in both warm and cold weather. An important result of 2016 was the sharp definition of the following key research questions:

- How would an optimized window perform?
- What energy performance can be achieved without negatively influencing the insulating properties and the transparency of glass?

The solution that BMC aims to offer lies in the promise of nano- and micro-structures (composites) and their interaction with light (i.e. particle size versus wavelength of light). More detailed research questions lay in the area of integration of features of nano/micro-structures in the product. Ultimately, this product includes active and autonomously adaptive materials that can control light and heat flows through building skin materials. Four important research questions have been identified and are cornerstones of the roadmap:

1. What is the relationship between chemical composition, nano/micro-structure and optical functionalities?
2. How to scale-up the production of nanoparticles (with a focus on those that can be exploited as functional additives for high performance optical composites)?
3. How can we control the distribution of nanoparticles in the composite matrix?
4. What is the performance of such composite materials in functional devices?

In 2016 results were obtained in the project Co-Pilot and Enef.

Co-Pilot is an European (H2020) project. It is focused on realizing piloting infrastructure for the manufacturing of nanoparticles and nanocomposite materials.

- TNO developed and implemented analytical instruments (DLS and UNPS) to monitor the production process of nanoparticles online using the new infrastructure at 2L and 15L (see picture below). Transfer of technology up to 100L scale has been initiated at the premises of project partner Fraunhofer.



- Furthermore, TNO implemented and validated an innovative centrifuge module to address the adequate and automated downstream processing of the nanoparticle dispersions. Also a process safety analysis was performed to assess the safety of the working with the centrifuge during the nanoparticle processing. Adaptations of machine were done and procedures were made, based on the outcome to optimize working safety.
- The TNO pilot line was tested with the four selected industrial nanocomposite types.
- First formulations were transferred to other partners for processing into final composite products through various polymer processing techniques, like an extruder with aqueous nano-dispersion addition possibilities). These partners performed their first tests.
- TNO started the preparations of turning the infrastructure of TNO and that of partner Fraunhofer ISC into an European open access infrastructure for SMEs interested in the production of high quality (multi-)functional nanocomposites on a pilot scale.
- TNO made plans for the exploitation of the pilot infrastructure beyond the project. Business- and exploitation plan developed. Other communications performed to make the Co-Pilot infrastructure known to the outside world and identify potential future clients. We identified more than 60 organizations (mostly SME) that have serious interest in using the infrastructure on a commercial basis. Discussions with several of these organizations are ongoing.

Enef is an European (Interreg-EFRO) project and also part of the BMC program Sustainable Buildings. The project started on September 1st, 2016 and will run for three years. The project aims to develop thermochromic nanocomposite coatings for glass windows. The energy-efficiency of buildings can be improved significantly with an adaptive window of the future: a window that is functionalized with a coating to optimally interact with visible and infrared light thus leading to a lower indoor energy need for keeping comfortable indoor climate (see Figure below).

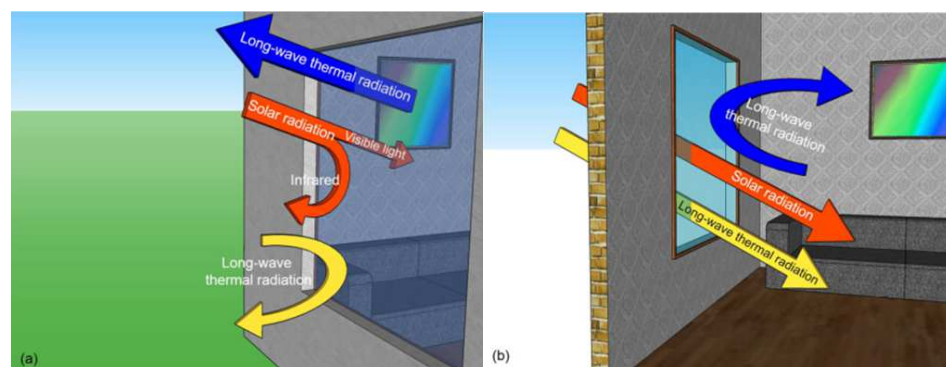


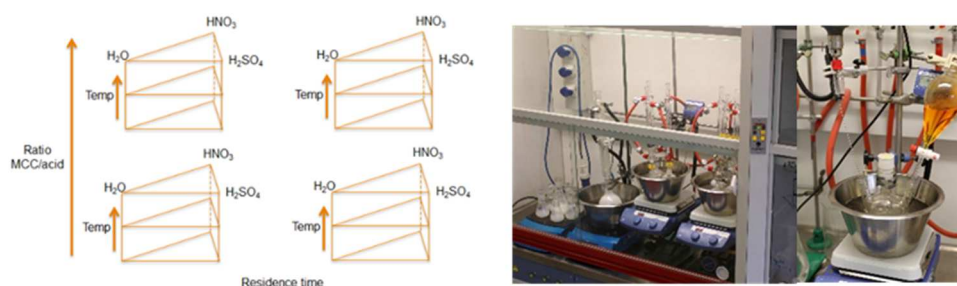
Figure. The energy flow regulating adaptive window of the future: a window that is functionalized to optimally interact with visible and infrared light thus leading to a lower indoor energy need for keeping comfortable indoor climate. Figure taken from Long, L. & Ye, H. How to be smart and energy efficient: A general discussion on thermochromic windows. Sci. Rep. 4, 6427; DOI:10.1038/srep06427 (2014).

1.3.4 Supporting activities

The H2020 SPIRE CSA-project “INSPIRE” (Towards growth for business by flexible processing in customer-driven value chain) started in Q4-2016 and aims for elaborating a few promising business models with regards to flexibility. Flexibility is

regarded as an important possibility to revive the competitiveness of the European industry. In this project, TNO partners with PNO, ITIA-CNR and ZLC. In the first months a selection of promising case studies was made. For TNO, the case studies “Waste2Aromatics”, “Polymer Building Blocks”, “Remote Chemical Production” and “Functional Molecular Production” are key.

The TKI Toeslag project “Continuous Nitrations” aims at developing continuous nitration processes that can nitrate complex molecules at small-scale, enhancing product control, reducing safety risk and reducing the footprint of the process. In 2016 the focus was on use case 1, which concerns the development of a continuous production setup for the production of MCNC (Micro Crystalline Nitro Cellulose). From multiple reaction pathways the mixed acid process was selected, with a potential future replacement by the Phosphoric Acid process. A DoE was developed and executed to determine the sweet spot for continuous nitration and to evaluate the relations between reaction performance and the reaction mix, temperature and reaction duration. The DoE approach and DoE experiment setup are given below.



At the end of 2016 all preparatory research work before moving into a continuous setup was completed and the building of the continuous setup was started in preparation of synthesis trials. Additionally the in-line quality control of the process is challenging and various routes have been being explored for the direct or indirect determination of the nitration depth and yield.

1.4 Dynamics

In 2015 the TNO activities, which support the ambition, were clustered in three subprograms: “advanced materials with the right functionality” (AMRF), “advanced materials from renewable sources” (AMRS) and “modular and flexible production technology” (MFPT). However, during 2016, through discussions with industry, TKI Chemie and other stakeholders, the TNO program for Topsector Chemie became more focused, resulting in two subprograms: Smart Materials and Green Chemistry. The former subprogram AMRF is continued in the subprogram Smart Materials, while AMRS is continued in Green Chemistry. The activities of MFPT concerning ‘electrification of the chemical industry’ are continued in the subprogram Green Chemistry. A selection of the other TNO activities on MFPT is continued in a supportive role to the two subprograms.

Within Smart Materials/BM two program lines are in place, “Sustainable Buildings” and “Lightweight Automotive”. New projects have been initiated within these lines.

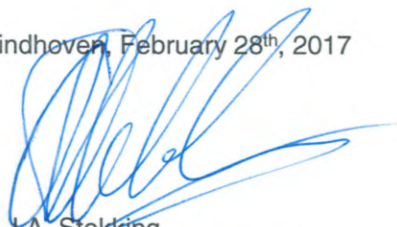
Within Green Chemistry/VoltaChem several projects have started to follow-up on the TTI transitieplan budget of 2015 & 2016.

Within Green Chemistry/Biorizon three projects were established with great involvement of waste & chemical industry. In 2016, ECN became partner in Biorizon. Acceleration of Biorizon through program financing from Province of Noord-Brabant is ongoing.

2 Signature

Eindhoven, February 28th, 2017

TNO

A handwritten signature in blue ink, consisting of several loops and a long horizontal stroke extending to the right.

A.J.A. Stokking
Managing Director Industry