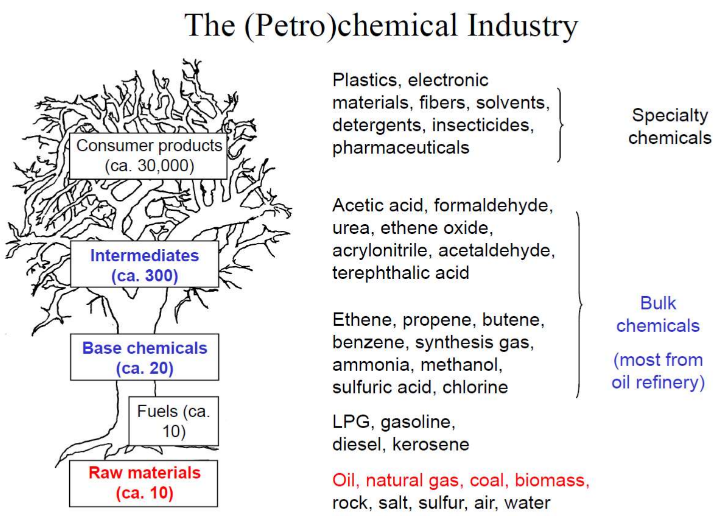
8. Green H2 and Electrons for Intermediates and Speciality Chemicals

Part 8.1.: Green Hydrogen

Introduction

A shift from the use of fossil-based fuels to green hydrogen and electricity provides tremendous additional challenges and opportunities for development of the new chemistry of the future. Speciality chemicals and intermediates derived from base (petro-)chemicals comprise a major part of the chemical-, materials-, agro- and pharmaceutical industries (see the chemistry tree, Figure 1) and, due to the enormous waste formation and energy consumption associated with the production of these chemical building blocks, major steps are needed to make these conversion processes sustainable. Here, green hydrogen, renewable feedstock and direct use of green electrons and development of novel chemical transformations, will allow a concerted approach to tackle these major energy, feedstock and waste issues with a major industrial and societal impact on a large part of our chemical industries, thereby greenifying the Dutch chemical infrastructure.



The focus in this subprogram is on the next stages in the production of chemicals, the so-called intermediates and specialty chemicals using green hydrogen (Chapter 8.1). The next sub-chapter (Chapter 8.2) will focus on the stage beyond that, using the green electrons directly in the chemical processes, thereby providing ambitious routes towards a circular economy. The increasing availability of green hydrogen through the development of large-scale electrolyzer facilities in the Netherlands and abroad, plus the growing availability of renewable feedstock (like biomass and municipal waste) allow the development of new, integrated chemical conversion platforms. These platforms are “double green”: using green hydrogen and green (i.e. renewable) feedstock.

Catalytic hydrogenation is an alternative to current cracking processes in the petrochemical industries. This is particularly important for biomass as a basis for high value chemistry, e.g. deoxygenation of carbohydrates, depolymerization of complex biomass streams, such as lignins, and upgrading the intermediates thereof. To use biobased raw materials for high-quality building blocks requires real breakthroughs in realising new mild catalytic processes; even splitting a simple C-O-C bond in lignin (or sugar / cellulose) is already a major challenge, and the chain of useful building blocks for chemistry usually starts with that. The envisaged program will take these initial efforts as a starting point and develop new catalyst and reactor technologies to create new interfaces between biorefineries, oleochemicals refineries, and/or wastewater treatments and validate these new technologies in relevant industrial environments. These transformation processes are not in direct competition with the electrochemical production of hydrogen from water as the goal is to produce another product than oxygen in water splitting; for example, to remove oxygen atoms from oxygenated hydrocarbons. Examples include the production of additives, cosmetics and cleaning agents, lubricants, coatings and paints, which contain fats, fatty acids, amines, organic acids and alcohols, as well as a large variety of intermediates and monomers for plastics and other materials. The size of the materials and oleochemicals industries is relatively large, also in the Netherlands, and is strongly coupled to

agricultural activities. In the manufacturing processes, chemistry plays an important role, including isomerization, esterification, amination as well as hydrogenation reactions.
Furthermore, there is a global trend in which waste streams are regarded as resources for the production of new materials and chemicals. This also holds for e.g. waste water from households and industrial activities. Especially the latter provides (new) streams of high-value (oxidized) organic compounds, which require further upgrading using hydrogen technology. Carbohydrates (e.g., cellulose, starch, dextran and chitin) are versatile starting materials for materials applications, but part of the oxygen needs to be removed. If this can be done by reduction with hydrogen, thereby producing water as waste, this would be a major (and essential) step forward, in which hydrogen use is essential.

EU and global perspective

The prospects of a sustainable and circular economy requires that intermediates and speciality chemicals are made by waste-free chemical transformations and from renewable instead of fossil resources. Well-known examples are the production of vanillin and polyglycerol, which can be produced starting from crude oil, but also directly from e.g. wood and agricultural residues. In addition, traditional chemical conversions including numerous functionalizations have to be replaced by sustainable ones based on e.g. catalytic hydrogenation and CH functionalization. In other words, this global trend towards the use of renewable derived products and additives and more direct catalytic transformations may positively contribute to the lowering of the CO_2 footprint, the decrease of the use of fossil resources, reduction of energy consumption and waste. Whereas worldwide, a lot of attention is currently going into the development of conversion technologies for the activation of small molecules, including methane, CO_2 and N_2, there are also emerging developments with a focus on more complex molecules with increased functionalities and economic value.

Scoping

The envisaged program aims to realize the above-mentioned goals along several lines of action some of which are identified here.

First of all, the large amounts of green hydrogen can be directly used in processes which are currently employing fossil-derived hydrogen. Examples include the hydrogenation of fats and fatty acids to selectively convert carboxylic acid moieties to linear alcohols and/or remove double bonds from organics to increase their stability, for e.g. food and cosmetics applications (e.g., Croda in Gouda), or the hydrogenation of sugars to e.g. ethylene glycol, a base chemical for the production of polyester textiles and (biobased) plastics (e.g, the Avantium pilot plant in Delfzijl).

Secondly, hydrogen can be used for the production of biobased monomers and intermediates. There are many challenges to develop a real green chemistry with efficient catalytic reduction processes such as sugar conversion to diols and diacids, furans and furan-derived aromatics, N-containing building blocks from, for example chitin. Green polymers are also in the spotlight (e.g., using biobased monomers for polymers like caprolactam). In the Netherlands, there is much high-level expertise available, because of earlier large public-private partnerships, like B-Basic and CatchBio.

Third, the catalytic use of hydrogen for deoxygenation to convert biobased feedstock into valuable building blocks and monomers. Here the key challenge is to remove hydroxyl groups from carbohydrates to aliphatics, furans or phenols to valuable aromatics. Similar catalytic hydrogen-based deoxygenations coupled to C-C bond formation and functionalization offers tremendous opportunities for speciality chemicals production.

Urgency

The Dutch and European ambitions on CO_2 mitigation require a concerted action through which the materials and speciality chemicals industry makes a further transition to become independent of fossil resources and use more sustainable conversions. The use of green hydrogen as chemical reagent will make it possible to develop a new science and technology basis. The large scale production of electricity and hydrogen in the Netherlands offers an excellent opportunity for the large and established agricultural industry in the north of the country to be involved e.g. companies CoSun, Avebe, FrieslandCampina, but also for medium-sized companies like Syncom-Merkachem and Polyvation, and start-ups like Carbexplore or establish new start-up companies.

Part 8.2.: Green Electrons

Introduction

The abundant availability of green electrons urges us to aim for an even more ambitious goal: to use green electrons directly to perform organics electrosynthesis and electrocatalysis. Electrochemical hydrogen production, based on renewable (green) energy sources means that other parts of the chemical industry will also need to be 'electrified' to accommodate the development of numerous novel redox-chemistry based transformations. The electrification of future chemical manufacturing will require a paradigm shift in current chemical synthesis, catalysis and chemical engineering. For instance, we will have to (re-)invent and implement electrochemical synthesis, design novel electrochemical- and photo-redox catalysts, learn how to perform redox-based functionalization/polymerization, etc., and electrochemical conversion of biobased feedstock into speciality chemicals. Direct use of CO_2 (and other small molecules) via electrocatalytic processes is another option, as has been discussed in Chapter 6. Other directions include electrocatalytic recycling of plastics/materials and novel electrochemical and engineering towards photoredox reactors e.g. flow photo-, electro-, chemical facilities. Together with new electrode materials, electrolyzers and membranes, this will lay the foundation for the green and electrical energy-based chemistry of the future. Electrosynthesis offers unique possibilities for the fine-chemical industry, such as late stage functionalisation, improving energy efficiencies, enabling complex skeletal rearrangements or driving otherwise thermodynamically 'uphill' reactions. This work package aims to develop new chemistry for intermediates and specialities for the future, making use of green electrons, with the aim to align with large-scale facilities for sustainable hydrogen production and the availability of cheap electrical energy sources.

EU and global perspective

The world's response to the global climate change will foster a paradigm change from fossil to renewable energy in all areas of our society. The production and direct use of hydrogen in chemical conversions to produce higher value products is highly desirable but requires hydrogen production from water electrolysis. Furthermore, the production of oxygen as a by-product from water electrolysis, whilst a useful alternative to capture from air, is in general a wasteful use of oxidizing equivalents. However, the scale of demand for hydrogen cannot be matched by the demand for the corresponding product of oxidation and hence need the use of redox chemistry (electrochemical oxidations and reductions) in a holistic sense. It is essential that a wide range of reactions are available to build the redox-based chemical transformations of the future. The state of the art of oxidation and reduction in chemical conversions is to use high-energy carriers, such as hydrogen, azides, diazo compounds and peroxides. The next stage is to bypass these reactions and to use electrons directly or with catalytic mediators as a basis for modern scalable chemical conversions. Most electrochemical reactions are easily scaled up and have a great potential in industrial applications.

Scoping

Society is in urgent need of scientists that can develop synthetic routes based on the knowledge of stoichiometric chemistry, computational chemistry, catalytic approaches and precision tuned electrochemical methods to design better and cleaner production processes along the value added chain as described in the EU Action Plan for the Circular Economy of the future. The overall aim of this work package is to improve the sustainability and energy efficiency of speciality and fine chemical

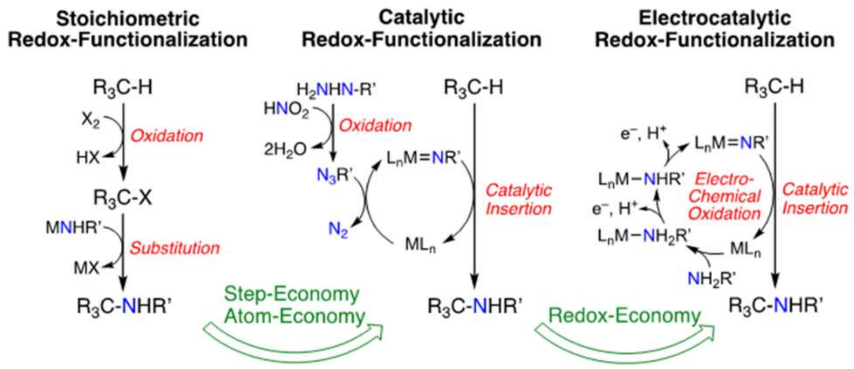
synthetic routes by developing electrochemical transformations in which the use of high-energy reactants for the functionalisation of unreactive groups is avoided.
This work package aims in particular at improving the *redox economy*[29] of chemical syntheses and the competitiveness of chemical industries employing these more environmentally friendly methods. This can be achieved with state-of-the art electrosynthetic approaches, by combining catalysis with electrochemistry. As such, it couples selectivity to energy efficiency. Many catalytic approaches can be combined with electrosynthesis, e.g. hydrogenation reactions, carbon-carbon and carbon-element bond formation, or complex skeletal rearrangements, which provide powerful methods to improve the selectivity of challenging transformations, including stereoselectivity as required for advanced pharmaceuticals. It is evident that there is not a single strategy for the implementation of redox economic synthesis through the combination of synthesis, catalysis and electrochemistry. The electrification of the chemical industry has many aspects; the national research capacity in electrochemistry has to build through a national concerted effort. The following research and technical development topics all carry the potential to establish the Netherlands as a world player in the electrification of the chemical industry:

1. Catalytic oxidation. A major part of the chemical industry depends on selective oxidation processes with alcohols, phenols, epoxides, etc. as prominent products. These oxygenated products find widespread applications, ranging from detergents and plasticizers to coatings and drug intermediates. The challenge is to develop electrochemical methodology for direct selective oxidation (direct use of redox process) or generates the essential oxidizing agents for a range of catalytic oxidations processes.

2. Deoxygenation of biomass. One of the key challenges to build future chemical processes and products on biomass-derived materials, especially towards specialty and fine chemicals, is selective deoxygenation. In particular, arene C-O bonds are extremely hard to cleave while e.g. selective deoxygenation of C-O moieties in carbohydrates pose another major challenge. Mild and selective C-O bond cleavage via sustainable redox based processes will have to be developed urgently to bring forward the promises of biobased chemical products.

3. Catalytic C-C bond formation. The aim is to develop electrochemical coupling procedures. Catalytic C-C bond formation is the structure building class of transformations par excellence for chemistry, polymers and organic materials. Direct redox catalytic processes need to be developed to replace key steps in current base and fine chemical manufacturing.

4. Reactive intermediates for catalytic C-N bond formation.



Energy-balanced, redox-economic electrocatalytic C-H bond amination

[29] "Redox economy refers to the endeavours to reduce the number of non-strategic (...) or corrective oxidation and reduction steps in synthesis, not only because these steps lower the overall efficiency of a synthesis, but also since many redox reactions are difficult to scale up in industrial settings and are frequently the source of noxious by-products and environmental problems" (Baran & Hoffmann, 2009. *Angew. Chem. Int. Ed.*, 48, 2854).

Many stoichiometric and catalytic processes rely on the use of high-energy redox agents, which are in fact “over-oxidized” or “over-reduced”. Production of these redox agents is associated with substantial waste formation, serious safety issues and unwanted energy losses. For example, the atom economy of catalytic nitrene transfer reactions, which have advanced as a powerful method for the amination of unactivated C–H bonds, is already much improved over ‘traditional’ stoichiometric amination reactions, but still relies on “over-oxidation” of the nitrogen source.
The nitrene transfer reactions in the figure are merely an illustrative example of the many possibilities offered by combining electrosynthesis and catalysis towards sustainable redox economy.

5. Functionalization, polymerization and recycling. A major part of contemporary chemical synthesis is based on hydrocarbon functionalization including, halogenation (followed by substitution), oxidation, and olefin- or arene- conversions. Green direct halogen free functionalization producing less (or no) waste using electrochemical conversions is highly warranted. Polymerization and co-polymerization are among the main areas of chemistry and form the basis of an enormous variety of materials ranging from packaging and household products to automotive and aircraft building materials. The aim is to replace existing procedures with redox catalytic protocols for selective oligo- and polymerization. A major challenge is depolymerization to recycle polymer waste into monomers. Here electrolytic cleavage and catalytic hydrogenation need to be developed as future basic technologies.

6. Materials, cells and reactors for electrochemistry and electrochemical engineering. Emerging (photo)electrochemical applications put strong requirements on materials, e.g. for electrodes, membranes, porous separators and gas-diffusion materials, in terms of controlled mass transport, reduction of crossover, conversion rates and integration of different materials. This research area aims to improve cell and stack design for particular application areas through increasing our understanding of the processes that take place at cell level. Electrochemistry under industrial conditions, system integration and system engineering are the next steps towards industrial application. It is still unclear which aspects of existing plants would benefit from electrification, and how to integrate individual electrochemical processes with classical catalysis steps. Taking these system level aspects into consideration, guidelines should be developed to accelerate engineering of electrochemical systems that go beyond catalyst/material optimization.

Urgency

Society is in urgent need of new synthetic routes with reduced energy consumption are that are much less polluting. In principle, this is possible by coupling electrochemistry with synthesis and catalysis. However, developing such methodology requires new fundamental research with input of well-trained chemists, with fundamental knowledge of stoichiometric chemistry, computational chemistry, catalysis, precision tuned electrochemical methods and chemical engineering. With these skills, they will be able to design better and cleaner production processes along the value-added chain as described in the EU Action Plan for the Circular Economy of the future. As such, the fundamental research in this work package will contribute to improving the sustainability and energy efficiency of future synthetic routes by developing new catalytic reactions for desirable transformations which avoid the use of high-energy reactants for the functionalisation of unreactive groups. Furthermore, since it is expected that electrification is the way forward for the chemical industry, there is a worldwide surge in the interest in electrochemistry. Other countries, Germany and Switzerland, have already committed to huge investments in this area, unleashing a “war on talent”. The Netherlands is in a good position to develop its talent base, because of existing public-private partnerships, like ARC CBBC, Brightsite, ISPT and the ECCM platform.

Work package 6: Green H2 and Electrons for Intermediates and Speciality Chemicals

Work package number	**6.1**
Work package title	Green hydrogen and green feedstock for specialty chemicals
Participants (private & public)	RUG, UvA, UU, TUD, RU, VU, WUR, TU/e, UL, TNO, DSM, AkzoNobel, Nouryon, BASF, Dow, Avantium …

Objectives

This work package aims to manage: The direct use of renewable H_2 and biobased feeds for

A. Development of stable and poison-resistant catalyst materials to convert food and agricultural products and intermediates derived thereof into fully renewable products, in all kinds of hydrogenation processes, replacing methane-derived H_2.

B. Demonstration of novel process technology through integration of efficient hydrogenation catalysis and biomass (pre-)treatment technologies to convert food and agricultural products into renewable intermediates and monomers for a.o. food ingredients, specialty chemicals and pharmaceuticals.

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Description and deliverables

Task 6.1.A. Direct use of renewable H_2 and biobased feedstock for all kinds of hydrogenation processes, replacing methane-derived H_2.

Activities:

In order to convert agricultural products into fully renewable products:

1. Development of more stable and poison-resistant catalysts
2. More efficient reactor technologies, with a strong emphasis on hydrogenation catalysis.

Input/tasks needed to complete activities above:

1. Development of non-noble metal hydrogenation catalysts, which are sufficiently robust and poisons-resistant.
2. Development of multifunctional catalysts, which are capable to combine renewable hydrogen and agricultural streams into products with high added value, but combining e.g. hydrogenation and isomerization catalysis.
3. Development of new reactor systems and catalyst-reactor combinations, which are capable to convert renewable H_2 and food and agricultural streams in a wide portfolio of products.

Deliverables:

1. New non-noble metal hydrogenation catalysts.
2. New multifunctional catalysts.
3. New catalyst-reactor combinations for the efficient use of H_2 for the direct conversion of food and agricultural streams.

Task 6.1.B. Direct use of renewable H_2 and biobased feeds for the production of biobased chemicals.

Activities:

1. Demonstration of integrated catalytic reactor concepts, which are capable to convert renewable H_2 and food, agricultural products and intermediates derived thereof in a wide portfolio of green chemicals
2. Production capabilities for renewable chemical platforms, which allow the evaluation of replacement potential in end-user application at kg-scale
3. Development of green processing technologies using milder conditions, green (or no) solvents, earth-abundant/metal-free catalysts and biocatalysts.
4. Development of advanced enzyme-engineering techniques for the development of novel and efficiënt tailor-made catalysts.

Input/tasks needed to complete activities above:

1. Implementation of novel strategies combining hydrogenation technologies and food and agricultural feedstock conversions into novel product streams supported by technoeconomic analysis and life-cycle assessment
2. .

Deliverables:

1. New catalyst-reactor concept combinations for the efficient use of H_2 in the direct conversion of renewable or circular feed streams into sustainable chemicals.

2. One or more small-scale pilot-scale facilities for the synthesis of high-value products for the food, polymer, lubricants, solvent and/or cosmetics industries

3.

Work package number	**6.2**
Work package title	Green electrons for specialty chemicals

Participants (private & public)	RUG, UvA, UU, TUD, RU, VU, WUR, TU/e, UL, TNO, DSM, AkzoNobel, Nouryon, BASF, Dow, Avantium …

Objectives

This work package aims to deliver future plug-in technology for fine chemical industries to align with ongoing developments to 'electrify' chemical synthesis and to use green and sustainable energy and H_2 sources:

- Combining electrosynthesis with catalysis.
- Direct use of green electrons/holes in catalytic organic synthesis, in a redox-economic manner.
- Enabling 'uphill' reactions.
- Preventing the use of 'over-oxidized' or 'over-reduced' reagents in fine chemical transformations.
- Enabling the use of green hydrogen for hydrogenation and other reduction reactions in fine chemical transformations.
- Development of novel electrosynthetic methods for late stage functionalisation.
- Energy storage in molecules.

Description and deliverables

Task 6.2.A: Research and development activities paramount to the electrification of the chemical industry involving complex molecules.

Activities:

1. Catalytic oxidation.
2. Deoxygenation of biomass.
3. Catalytic C-C bond formation.
4. Reactive intermediates for catalytic C-N bond formation.
5. Functionalization, polymerization and recycling.
6. Materials, cells and reactors for electrochemistry and electrochemical engineering.

Input/tasks needed to complete activities above:

1. Catalytic Oxidation:
   a. Direct selective oxygenation of alkanes using electrochemical conversion, C-H activation
   b. Hydroxylation of aromatics to phenols using electro-or photo-redox catalytic transformations.
   c. Catalytic epoxidation either via direct electrocatalytic methods or using electrochemical generated benign oxidants (like H_2O_2 from O_2 reduction in novel electrolysis processes)
   d. Electrocatalytic (hetero-) arene coupling for advanced (electro-optical) materials.
2. Deoxygenation of biomass:
   a. Selective deoxygenation of multi oxygenated materials like carbohydrates to valuable intermediates and synthons.
   b. Electrocatalytic methods for deoxygenation phenols and phenol ether especially for lignin upconversion.
   c. Decarboxylation/deamination -coupling procedures for biomass conversion.
3. Catalytic C-C bond formation
   a. Direct electrochemical coupling of alkanes and alkenes. Oligomerization reactions for instance towards higher olefins or isomerization of branched alkanes (fuel additives).
   b. Functionalization of aromatics, replacement Friedel Crafts alkylation/acylation, arene coupling.
   c. Reductive carbonylation and carboxylation reactions.
   d. Electrocatalytic alternatives for carbonyl alkylation, condensations via single electron redox transformations.
4. Reactive intermediates for catalytic C-N bond formation.
   a. Precise adjustment of redox potentials, reducing overpotentials.
   b. Efficient electrochemical generation of high-energy intermediates.
   c. Preventing the use of 'over-oxidized' or 'over-reduced' reagents in fine chemical transformations.
   d. Direct use of green electrons/holes in catalytic organic synthesis, in a redox-economic manner.
5. Functionalization, polymerization and recycling.
   a. Electrocatalytic or photoredox catalysis based selective C-H activation methods.
   b. Arene hydroxylation, carboxylation and amination (avoiding non-benign nitration).
   c. Direct amide bond formation from alcohols and amines via electrochemical methods.
   d. Developing electrocatalytic methods for monomer synthesis i.e. acrylates, acids, alcohols, olefins (dehydrogenation).
   e. Replacing polymerization procedures /catalysts (i.e. peroxides) by direct redox based protocols).
   f. Electrolysis procedures for bond cleavage/depolymerization.
   g. Catalytic hydrogenation procedures/electrolysis for depolymerization biomass-based materials in particular lignin to high valuable aromatics.
6. Materials, cells and reactors for electrochemistry and electrochemical engineering:
   a. Highly active, selective and stable electrode materials (small and large scale).
   b. New approaches for material selection (i.e. circular), characterization and integration (i.e., membrane electrode assemblies).
   c. Scalable fabrication of advanced micro-/nanostructured thin films and multi-layer 3D architectures for electrochemical applications.
   d. Ion-exchange membranes resistant to extreme conditions (e.g. acidic or alkaline environment, high temp/pressure).
   e. Monovalent selective ion exchange membranes.

f. Ionomers, porous separators and gas-diffusion materials for electrochemical applications.
g. Design and characterisation of cells and stacks (membrane electrode assemblies, 3D electrodes, gas diffusion electrodes, bipolar plates).
h. Modelling of mass, heat and current transport and gas-liquid flows in electrochemical cells and stacks (using e.g. computational fluid dynamics, Maxwell-Stefan, Nernst-Planck).
i. Experimental characterisation of cells using electrochemical techniques, high speed cameras, X-ray, mass spectroscopy, etc.
j. Circular design and characterisation of electrochemical cells that can operate at high temperature, pressure and current density, taking into account material limitations.
k. Bringing materials from lab to industry: (accelerated) testing at industrial conditions (strong electrolytes, increased temperatures and pressures) and in situ and ex situ characterisation of these materials.
l. Role of electrolysis in a future power system based on renewable energy (i.e. which steps in an overall conversion would benefit from electrification).
m. Device/system (circular) design and development.

Deliverables:

Improved overall efficiencies and reduced energy waste in organic synthesis.
New routes for organic synthesis starting from renewable energy and resources, including biomass and municipal waste
Greenification of production processes of food ingredients, pharmaceuticals and specialty chemicals.

Overall budget in MEUR

- 6.1. Estimated budget: 10.0
- 6.2. Estimated budget: 10.0

Total estimated budget: 20 MEUR