

PROJECT FINAL REPORT

PUBLIC SUMMARY



CyclicCO₂R
Fine chemicals from CO₂

**Production of Cyclic Carbonates from CO₂
using renewable Feedstocks**

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Executive summary

The CyclicCO₂R project, *Production of Cyclic Carbonates from CO₂ using renewable Feedstocks*, was a four year project that ended at the end of 2016. The project focused on the development of a continuous process which produced cyclic carbonates from CO₂ and renewable feedstocks. Two main routes were investigated throughout the project, namely the direct combination of CO₂ with diols to form the corresponding cyclic carbonate and an indirect route, where the diol was first epoxidized and then combined with CO₂ to form the cyclic carbonate. The main scientific activities were catalyst development, process development, and process scale up, while dissemination and assessment of alternative routes (through e.g. electrochemistry) were important parallel activities.

The activities around catalyst development were focussed mostly on the indirect route and successfully combined experimental work with detailed molecular modelling, resulting in a greater understanding of the reaction mechanism and next generation catalysts with improved activity. Research into catalyst immobilisation showed the potential to greatly increase the specific catalyst loading should the process be developed further. For the direct route, a high-throughput screening exercise identified a number of promising catalysts and more detailed studies gave new insights into the reaction mechanism.

The process development work took a structured approach of funnelling reactor designs, identifying downstream processing operations, building and operating a laboratory scale reactor, modelling the full process, and finally scaling up the process to a mini-pilot plant scale. Due to a change in project focus about half way through the project, the process was redesigned and caused a setback in the project progress. Polymerisation issues within the reactor were also observed after the focus change and required substantial effort to circumvent. This led to less time to operate the mini-plant and complete a full testing campaign, but the process was still fully demonstrated for one week with successful production of the target compound.

In parallel to the main thermochemical routes for producing cyclic carbonates from CO₂, the potential to produce cyclic carbonates, or feedstocks to be converted into cyclic carbonates, from CO₂ and water was also investigated. Advances were made using electro- and photochemistry, especially in the production of ethylene, and the work is continuing through other projects at the involved partners.

Although the process is at this time not planned to be further upscaled and commercialised, the results have been disseminated through several conference presentations and 12 accepted publications (with more still expected to come). Several scientific advances were made that are applicable to a range of processes involving the utilisation of CO₂. In addition, this project showed the importance of the cooperation between catalyst developers and process engineers in realising a feasible process based on new chemistry. This and other lessons learned will be shared in a future publication and will be an important impact of the project.

1 Description of project context and objectives

Project context

Carbon capture and storage (CCS) has been demonstrated by the European Union to be a key area of innovation. Implementation of initiatives, such as the CCS Demonstration Project Network, show that it is crucial to realize widespread commercial applications of carbon-reduction technologies in order to meet the ambitious targets, set forth by the Europe 2020 strategy. While the Emissions Trading Scheme (ETS) boosts the economics of CCS,¹ CO₂ utilisation technologies have the potential to significantly advance the EU towards meeting its goals while capitalizing on Europe's leadership in developing green technologies and production methods. By utilising CO₂ directly from industrial flue gases and off-gases, the cost for CO₂ capture could be dramatically reduced by 30 – 60 €/ton CO₂, about 82% of the total cost for a CCS chain. The other main drivers for the development of CO₂ utilisation technologies, closely connected to the priorities for achieving sustainable growth in Europe 2020, were:

- The realization of a shift towards a resource-efficient, low-carbon economy, which is accomplished by both reducing CO₂ emissions and reducing the resource intensity of what is used and consumed²;
- The need to maintain the competitiveness of European industry by supporting businesses, especially SME's, through the transition to a low-carbon economy. By covering every part of the chain—from raw materials supply to offered services—jobs will be created and the Gross Domestic Product will be increased across Europe;
- The necessity to secure the supply of energy and feedstocks by decreasing the dependency on imported fossil fuels, which subjects the businesses and consumers of the EU to costly price fluctuations and regional political instabilities.

Each of these points was strongly addressed in CyclicCO₂R. The industrial CO₂ emissions of Europe could be reduced by the development of a process with a high energy efficiency and net uptake of CO₂. SME's were highly involved, which makes key knowledge developed within the EU accessible to the project and increased the impact of the project results through dissemination to the EU market. Finally, renewable, bio-based materials readily available in the EU could be utilised, especially those mostly present as waste streams. In this way, otherwise discarded materials could be valorised and contribute to the EU economy.

Cyclic carbonates have been produced based on CO₂ for many years^{3,4}, whereby the corresponding epoxides, derived from non-sustainable crude oil, are produced in an energy intensive process and used as energy-rich reactants. Cyclic carbonates are important materials with a large number of applications. They are used as electrolytes in lithium ion batteries, coatings, chemical intermediates, polar solvents, and additives to cosmetics/personal care products and detergents.^{5,6,7} Varying their structure renders cyclic carbonates as very versatile in their (potential) applications. By developing the process envisioned in CyclicCO₂R, it could be possible for the EU to establish a leading position in energy efficient processes, starting with that for cyclic carbonates, which reduce the dependency on fossil fuels and utilise CO₂ as a feedstock in driving the market

¹ http://ec.europa.eu/energy/coal/sustainable_coal/ccs_project_network_en.htm, accessed 6-3-2012.

² http://ec.europa.eu/europe2020/priorities/sustainable-growth/index_en.htm, accessed 6-3-2012.

³ W. J. Peppel; *Ind. Eng. Chem.*; **1958**; 50; 767–770

⁴ P. P. McClellan, Jefferson Chemical Company; US2873282; **1959**

⁵ B. Schäffner et al.; *Chem. Rev.*; **2010**; 110; 4554-4581

⁶ W. Clegg et al.; *Tetrahedron: Asymmetry*; **2010**; 21; 1262–1271

⁷ M. North et al., *Tetrahedron Let.*; **2009**; 50; 4452 – 4454

for CO₂ capture technologies. Connection with the bio-based economy through the use of bio-glycerol further increased the impact that could be achieved on the economics, environment, and society of the EU. Glycerol is a readily available renewable raw material that potentially could be transformed into cyclic carbonates in a few steps, giving a boost to the energy efficiency and ensuring its sustainability.

The current general view of CO₂ is as a polluting gas, because of its contribution to climate change. However, the development of CO₂ utilisation technologies gives the opportunity to show that CO₂ is not only a gas to be prevented, but that it can form a contribution to the closure of the anthropogenic carbon cycle and can be a valuable raw material for sustainable production processes. CyclicCO₂R aimed to be at the forefront of this transition, both in providing technologies to the European industrial sector and creatively disseminating results in an accessible way to the general public.

Project objectives

The overall objective of the project, Production of Cyclic Carbonates from CO₂ using Renewable Feedstocks (CyclicCO₂R), was the development of a continuous process that converted CO₂ and bio-based renewables into high value-added products in a sustainable manner and that was competitive with conventional fossil-based processes. A highly efficient integrated process was envisioned that would remove the dependency on fossil fuels and increase the energy efficiency such that it created a reduction in CO₂ emissions. These aims were to be achieved by focusing on the use of bio-based materials and waste CO₂ from several sources (power plants, cement factories, chemical plants, etc.). As an inexpensive waste product from bio-diesel production, glycerol was to be the main raw material, along with CO₂, ensuring cost effectiveness and, thereby, a maximum commercial potential. With the potential to use CO₂ directly from flue gas streams, the cost and energy requirements of carbon capture could have the potential to be reduced such that, through realization of the process by industrial end-users, CyclicCO₂R would decrease industrial CO₂ emissions while driving the implementation of the entire carbon capture and utilisation chain.

The basis of CyclicCO₂R was the creation of a new continuous and highly efficient process which produced industrially relevant cyclic carbonates, especially those based on glycerol derivatives. The overall concept, based on bio-based renewables, is depicted in the schematic of Figure 1.1. The consortium behind CyclicCO₂R wanted to kick-start the implementation of CO₂ utilisation technologies by converting CO₂ into a high value-added product, thus providing a showcase that inspired industry to further develop technologies utilising CO₂ as a sustainable raw material and valorising CO₂ in such a way that drove the market for CO₂ capture and utilisation.

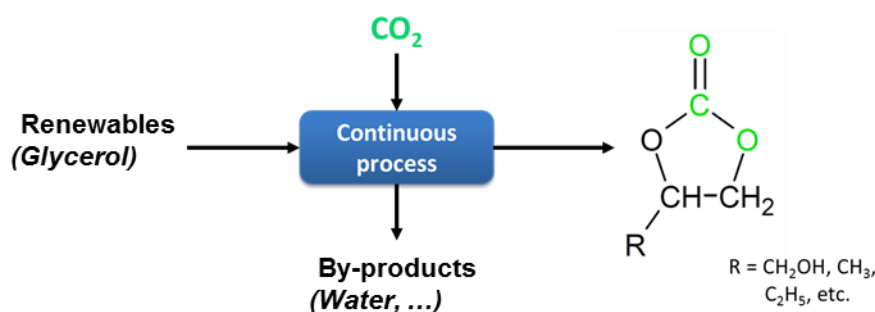


Figure 1.1 Black box schematic of the envisioned process

The consortium behind CyclicCO₂R wanted to kick-start the implementation of CO₂ utilisation. This ambition was captured in the high-level aim of CyclicCO₂R: **Development of a showcase continuous process combining CO₂ and renewables in a manner competitive with fossil fuel-based processes while reducing the stress on the environment.**

The CyclicCO₂R consortium, consisting of an industrial end user committed to the technology, SMEs pioneering in sustainable CO₂ utilisation processes, the leading academic groups in the field of CO₂-based catalysis, and two of the largest RTO's in Europe, set out to reach this high level objective by:

- Positioning the project on producing valuable chemicals of industrial interest, thereby valorising CO₂ and renewable raw materials;
- Developing active and robust catalytic systems that were cost-effective and environmentally acceptable with the potential to be used directly with industrial flue gas streams, eliminating the need for expensive capture plants;
- Demonstrating a continuous process which efficiently converted CO₂ into a value-added chemical and could be extended to other industrially important products, thus increasing the overall impact;
- Investigating the feasibility of alternative technologies that could produce intermediates of the reaction directly from CO₂ and water, giving the project access to state-of-the-art results in photo- and electrocatalytic technologies and working to secure the supply of raw materials;
- Analysing the entire chain from sustainably produced feedstocks and CO₂ to end-products in order to ensure CO₂ emissions reduction, product market potential, and the development of an implementation plan.

The project was divided into three parts: catalyst development combining high throughput screening with optimisation of state-of-the-art catalysts utilising advanced molecular modelling; integrated process development to ensure high efficiency with *in-situ* product separation and catalyst recovery in order to achieve the maximum product yield; and demonstration of the technology to be a showcase in proving the potential of CO₂ as a chemical feedstock and accelerating the implementation of CO₂ chemistry within the European chemicals industry.

The biggest challenge in incorporating CO₂ into (fine) chemicals was its high thermodynamic stability. Energy, in some form, had to be added to CO₂ in order to activate it to a level at which it can take part in a reaction. With the production of this energy, CO₂ was usually generated. This made the net use of CO₂ as a raw material inherently coupled with the efficiency of the process, the increase of which was a main focus of CyclicCO₂R. A key advantage of bio-based sources over fossil-based sources was the degree of oxygenation of the starting materials. A bio-based material starts out more activated than a fossil-based material. Fossil-based materials would always require some selective oxidation—a difficult and energy-intensive process—prior to their use as chemicals. The result was less energy input required for the reaction with CO₂. Furthermore, in recent years new catalytic systems and reactor concepts had been developed that had the potential to continue to reduce the energy that goes into the process.^{8,9}

One path to a sustainable process was to produce the epoxide in a renewable manner, for example directly from bio-ethanol.^{10,11} However, more advantageous was the use of glycerol, as it was a readily available

⁸ J. Melendez et al., *Eur. J. Inorg. Chem.*; **2007**; 21; 3322 – 3326

⁹ A. Berkessel et al., *Organic Letters* ; **2006** ; 20 ; 4401-4404

¹⁰ M.J. Lippits et al.; *Catalysis Today*; **2010**; 154; 127-132

¹¹ US2011137096

renewable raw material that was cheap and usually regarded as a waste product. This was directly related to the goal of CyclicCO₂R to develop a sustainable, continuous process for the production of cyclic carbonates from CO₂ and renewables as raw materials. The CO₂ resulting from the production of the energy used in the process should have been less than the CO₂ utilised as a raw material in the process.

The positioning of this project was based on investigating three different routes. The first route, the *direct route*, was the direct synthesis of glycerol carbonate from glycerol and was envisioned to be the primary reaction that would be developed. It also had a lower technology readiness level (TRL). The second route, the *indirect route*, was the route for the production of glycerol carbonate (and other cyclic carbonates) through the corresponding epoxides and was further developed than the first route, as it is connected to then current processes. At a specified point in the project, the indirect route with a specific functionalised target product (based on glycerol derivatives) was identified as having the most promise in achieving the objectives outlined above and was chosen to be developed further to the demonstration scale. The third route, the *alternative technologies route*, involved the synthesis of the required materials directly from CO₂ and water, utilising alternative CO₂-neutral energy sources, and was investigated in parallel to the other two routes.

Direct route: Glycerol, and related diols, were reacted with CO₂ using an innovative catalyst to create the corresponding cyclic carbonate. Glycerol was a green renewable feedstock that was readily available as a by-product from biodiesel production. Challenges were in the equilibrium limitation, side reactions, by-product (water) removal and process conditions. While technologies existed for the conversion of glycerol into valuable products, the combination with CO₂ utilisation and energy efficiency had not yet been accomplished and were key aspects.

Indirect route: An alternative route for the production of glycerol carbonate from glycerol was through first forming the allyl alcohol¹², epoxidizing the allyl alcohol to glycidol¹³, and then performing a cycloaddition of CO₂ to form glycerol carbonate. The focus of this work was on the cyclo-addition of CO₂ to glycidol, the epoxide of glycerol, and other epoxides derived from glycerol to form the corresponding cyclic carbonates. The challenges were envisioned to be in making the process continuous and more efficient through mild reaction conditions.

Alternative technologies route: Also explored in this project was the use of CO₂ in combination with water as raw materials in the production of intermediates (alkenes, epoxides) for cyclic carbonates. Literature references showed that this was, in principle, possible with photo- and/or electrochemistry. There were large challenges to be overcome; however, the successful development of such a process could dramatically increase the net CO₂ uptake of the overall process. The exploration was aimed at evaluating the future feasibility of these processes to increase the CO₂ uptake.

¹² W. Bühler et al.; *J. Supercritical Fluids*; **2002**; 22; 37–53

¹³ G. Hutchings. et al.; *Catalysis Letters*; **1996**, 39, 83-90

2 Description of the main S&T results/foregrounds

SP 1: Synthesis of cyclic carbonates from diols and CO₂ (direct route)

The main objective of sub-project 1 was to develop highly efficient catalytic systems for the direct route, which are active in a continuous process transforming diols (e.g. glycerol) with CO₂ into cyclic carbonates (e.g. glycerol carbonate). This sub-project was divided into three different work packages. The progress that was made in each WP is explained in more detail below. The main partners within SP 1 were: the University of York, SINTEF, RWTH Aachen University, and FeyeCon.

WP 1.1: Catalytic system selection and development

This WP was split into three consecutive tasks which progressed from identifying and reproducing the benchmark, realizing catalysts that performed better than the benchmark, and finally optimizing those catalysts based on the knowledge gained throughout the project.

Task 1.1.1: Establishment and understanding of the benchmark reaction

The goal of this activity was the establishment of the groundwork for the subsequent high throughput screening of catalysts for the direct route to glycerol carbonate, including determination of a benchmark and an analytical procedure for determination of improved performance vs. the benchmark. The primary catalysts that were studied were those based on di-*n*-butyl tin centers, which were chosen based on data available in literature. It was possible to reproduce results reported in the literature with a maximum yield of 1.4 mol% glycerol carbonate using a version of the standard di-*n*-butyl tin-based catalysts. These yields were obtained after overnight reactions at 180 °C and 50 bar CO₂, or at 120 °C and 35 bar CO₂ in the presence of a large excess of methanol.

Due to difficulties in establishing a robust analytical procedure for the glycerol/glycerol carbonate reaction mixture (primarily due to the high viscosity of glycerol), the carboxylation of propylene glycol to propylene carbonate was chosen as a surrogate reaction for the carboxylation of glycerol, for which both reliable GC HeadSpace analyses and an active benchmark catalyst system existed. A robust analytical procedure was also already in place at the task's lead partner, SINTEF, from earlier projects. Therefore, the high throughput catalyst screening studies were completed for this surrogate reaction under the assumption that catalysts, which are active for propylene glycol carboxylation, would also be active for glycerol carboxylation. This assumption will be tested in continuing work.

Task 1.1.2: Catalyst discovery studies in the high-throughput reactor

More than 125 different catalysts were screened using the high-throughput screening process based on propylene glycol carboxylation. Several hits with improved performance were discovered and these were selected for performance verification in large-scale reactors with glycerol and CO₂. These improved catalysts were faster and gave ca. 50 % higher product yields than the benchmark system. In general, Zn salts outperformed other transition metal salts. The currently best catalyst was zinc triflate Zn(OTf)₂ and this was taken further with mechanistic studies. The kinetic profiles of these new catalyst systems showed some unexpected behaviours and were further studied.

Task 1.1.3 Mechanistic investigations

The reaction profiles of the benchmark catalyst zinc acetate (Zn(OAc)₂) + *para*-chlorobenzenesulfonic acid (*p*-CIBSA) and the improved catalyst zinc trifluoromethylsulfonate (Zn(OTf)₂) were investigated by removal of

reaction samples directly from the reaction vessel and subsequent analysis by ^1H NMR spectroscopy. The changes in the amounts of the propylene carbonate (PC) product and the by-products arising from the chemical trapping of water by added acetonitrile for both systems are shown in Figure 2.1.

The initial formation of the by-products for the $\text{Zn}(\text{OAc})_2/p\text{-CIBSA}$ system was attributed to the formation of acetic acid (HOAc) by the $p\text{-CIBSA}$, which then reacts quickly with the propylene glycol. The formation of PC is comparatively relatively slow. At the same time, the reaction with $\text{Zn}(\text{OTf})_2$ is much faster, particularly between 1 to 3 hours reaction time. During this time, the formation of PC and the by-products are essentially concurrent, which is what might be expected for a reaction producing equivalent stoichiometric amounts of PC and water. After about 3 hours of reaction, the formation of PC slows, but remains increasing, while the amount of by-product stays more or less constant.

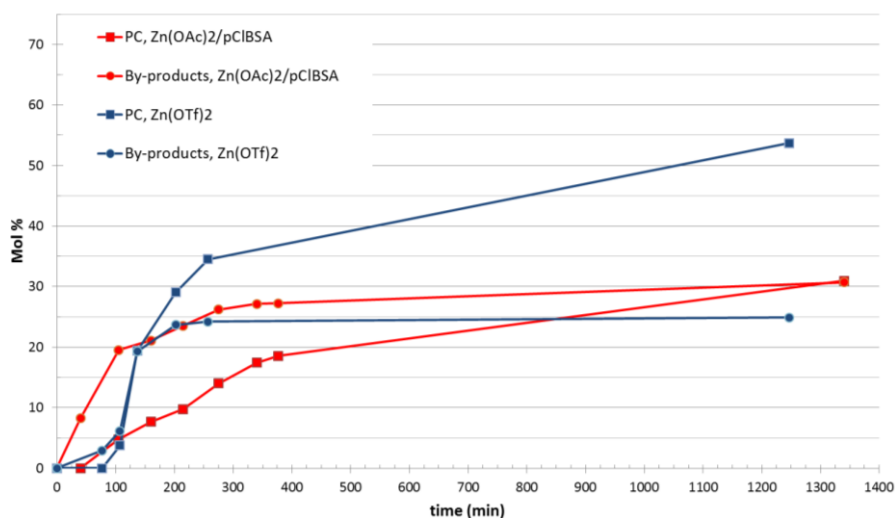


Figure 2.1 Time vs. yield profiles of propylene carbonate and by-products with $\text{Zn}(\text{OAc})_2/p\text{CIBSA}$ and $\text{Zn}(\text{OTf})_2$ as catalysts.

The same trend was also observed for the $\text{Zn}(\text{OAc})_2/p\text{-CIBSA}$ system, but to a lesser extent. This observation was inconsistent with the concomitant formation of PC and water (by-products). It has been shown that the by-products do not react with CO_2 to give PC. Data suggested that a redistribution/transesterification reaction is also taking place, as illustrated in Figure 2.2, particularly at long reaction times. This secondary reaction would increase the propylene glycol concentration while not affecting the observed amount of by-products. If this is confirmed, it suggests that high reaction rates for PC formation could be achieved as long as enough propylene glycol was available.

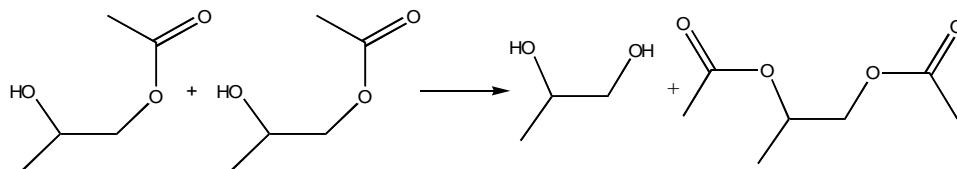


Figure 2.2 Hypothesized redistribution/transesterification reaction.

Samples removed periodically during the reaction of propylene glycol (PG) and CO_2 with $\text{Zn}(\text{OTf})_2$ as catalyst have been analyzed by ^1H and ^{19}F NMR spectroscopy. While the signals were all suggestive of potential

intermediates in the reaction, it was not possible to determine with any certainty the exact nature of the intermediates. Numerous attempts to synthesize potential model complexes with various Zn salts and PG failed to provide any tangible species that could shed light on the nature of the reaction pathway, or that could serve as pre-catalysts for the reaction.

WP 1.2: Theoretical studies on cyclic carbonate synthesis from diols

RWTH was the lead partner in WP1.2, which was split into three tasks; however, only two of the tasks were completed due to the shift in project focus to the indirect route. The results of this WP mostly fed back into WP1.1.

Task 1.2.1: Choice of model and method for the molecular modelling

The modelling work concentrated on the establishment of the methodology for a meaningful study on the catalysis in the direct route. The model package used electronic structure calculations within the framework of density functional theory (DFT). Experimentally, it was found that zinc-compounds combined with Brønsted acids could catalyse carbonate formation from propylene glycol and CO₂. To validate the applicability of the methodology, zinc-based catalysts were modelled, for which crystallographic data was available. Excellent agreement was found with calculated and experimentally measured bond lengths and angles.

Task 1.2.2: Modelling of commercially viable homogeneous catalysts, which are active for cyclic carbonate formation from diols and CO₂

In the direct route, the hydrolysis of acetonitrile was used as water trap. The hydrolysis could be catalysed as well and was therefore studied. The modelling of the unassisted, un-catalysed hydrolysis of acetonitrile showed comparable results with previous calculations. This was reassuring for the applied methodology and revealed the importance of the participation of an alcohol in the reaction mechanism. Based on the results of this and previous modelling, a change in reaction mechanism was expected along with a substantial reduction in activation energies for the hydrolysis of acetonitrile and acetamide in the presence of alcohols, such as propylene glycol.

The isolation and characterisation of zinc-based catalysts in the condensation reaction of glycerol and CO₂ was eventually performed by partners within the CyclicCO₂R project. The group of Michael North succeeded to obtain X-Ray structures of some zinc-based catalysts, which were used as a basis for the computer models. With these models, the interaction with acetonitrile could be studied.

A full modelling on the catalysis of the condensation reaction of glycerol and CO₂ in combination with the hydrolysis of acetonitrile, as intended before, was not possible. It was decided within the project to focus all efforts on the indirect route, the formation of cyclic carbonates via epoxides and CO₂. Thus, this task was not pursued further.

Task 1.2.3: Iterative procedure starts upon discovering new lead structures

This task was no longer a part of the work plan given the shift in focus to the indirect route.

WP 1.3: Catalyst immobilisation

WP1.3 aimed at the immobilisation of the homogeneous catalysts identified in WP1.1 either *via* covalent bonding to a solid support or using the supported ionic liquid phase (SILP) strategy or a biphasic system. As the SILP technology was found to not be suitable for the direct route to glycerol carbonate, other reactor concepts were investigated in task 1.3.2, as described below.

Task 1.3.1: Immobilization of homogeneous catalysts via covalent bonding to supports

Investigation into 16 different Lewis acid catalysts and 7 different Brønsted acid co-catalysts at the University of York, along with SINTEF's high throughput screening of 81 different metal salts, showed anhydrous zinc triflate to be one of the most active catalysts towards the synthesis of propylene carbonate from propylene glycol. Optimisation of the reaction parameters—temperature, CO₂ pressure, catalyst loading and reaction time—resulted in a synthetic procedure able to achieve very good conversions of 42% propylene carbonate, using lower temperatures and pressures than previously reported in the literature.

With the project directed towards green and sustainable chemistry, a heterogeneous version of the zinc triflate catalyst was developed. Initially, a number of physisorbed catalysts were prepared through an ion exchange method using well-known inorganic and organic supports: pillared montmorillonite clay, sulphated zirconia, zeolite Y and styrene divinylbenzene polymer resin exchanged with Zn²⁺. However, the activity of these catalysts was very poor, with the Zn-clay, sulphated zirconia and zeolite Y giving 0% conversion and polymer resin giving 2% after 24 hours. As such, investigation into a more robust method of immobilisation was performed—complexing zinc to ligands which had been chemisorbed on to an inorganic support. A reaction screening using 12 different nitrogen containing ligands along with the zinc triflate catalyst was performed and showed that most of the ligands investigated had a similar effect, achieving conversions of 26–30% to propylene carbonate. One of the ligands gave 0% conversion due to presence of a ketone functional group, which gave some insight into the mechanism of the synthesis.

In order to understand more about the interaction between the ligands and zinc triflate, three samples were crystallised for X-Ray Diffraction analysis (XRD). Ligands 2,2'-bipyridine, 1,10-phenanthroline and methylenebis(3,5-dimethylpyrazole) were chosen due to the good conversions achieved in the previous ligand screen. The resulting structures can be seen in Figure 2.3 below, with only [Zn(3,5-Me₂-bis-pyrazylmethyl)₂(OTf)](OTf) not previously reported.

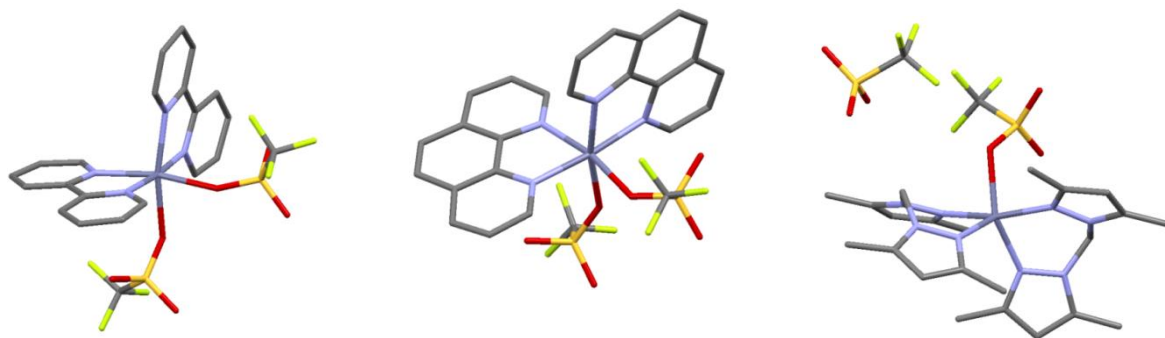


Figure 2.3 XRD crystal structures of organo-zinc complexes: from left to right, Zn(bipy)₂(OTf)₂, Zn(phen)₂(OTf)₂ and [Zn(3,5-Me₂-bis-pyrazylmethyl)₂(OTf)](OTf)

All three organo-zinc complexes were active catalysts giving conversions of 30%, 32% and 39% to propylene carbonate, respectively. Of the various ligands investigated for immobilising zinc triflate onto a silica support, imination of a dipyrazyl ketone ligand was chosen as the preferred method due to the reliability and relative simplicity of the procedure. Initially, commercially available silica was modified by tethering the ligand via an amine pendant, followed by immobilisation of zinc triflate. However, this method gave low loadings of zinc bound to the support, resulting in the heterogeneous catalyst being inactive. To overcome this, a series of high loading hexagonal mesoporous silicas (HMS) were synthesised, allowing incorporation of the tethering species during formation of the silica support. A smaller ligand was chosen for immobilisation in order to minimise

diffusion issues into and out of the support and steric interference. This method allowed for a much higher loading of ligand, and subsequently zinc triflate, to be immobilised on the synthesised HMS material; around 1.4 mmol of zinc triflate per gram of HMS. As such, these second generation heterogeneous catalysts gave good conversions of between 18 – 26% to propylene carbonate.

Task 1.3.2: Supported Ionic Liquid Phase (SILP) Catalysis and biphasic catalytic testing

The synthesis of glycerol carbonate from glycerol and carbon dioxide using K_2CO_3 as the catalyst and acetonitrile as a chemical water trap was investigated in detail. Again, as the SILP process was found to be unsuitable for this system, other reaction configurations were investigated.

Although $Zn(OTf)_2$ was proven to be an active catalyst for the synthesis of propylene carbonate from propylene glycol and CO_2 using acetonitrile as a chemical water trap, a very low yield of only 3% was obtained in the carboxylation of glycerol to glycerol carbonate. Thus, building upon the results of Huang *et al.*, several inorganic and organic bases were investigated for the synthesis of glycerol carbonate. With K_2CO_3 as an inexpensive Brønsted basic catalyst, an isolated yield of up to 18% glycerol carbonate could be obtained in batch reactions. Also, since water is formed as a by-product of the reaction, the water sensitivity of the reaction system was studied. Up to 5 mol% of water (with respect to glycerol) was tolerated without a decrease in glycerol carbonate yield.

The reaction network was investigated and several side products were identified that resulted from the reaction of acetonitrile's hydration products (acetamide and acetic acid) and glycerol. The main side products were glycerol monoacetates. With higher reaction temperatures and longer reaction times, the amount of side products increased as glycerol carbonate was esterified and nitrogen compounds, like oxazolidinones, were formed. The amount of these side and consecutive products critically depends on the reaction conditions and, thus, the yield of glycerol carbonate. The reaction progress was qualitatively monitored by *in-situ* IR spectroscopy. The key result was the observation that the peak area of the glycerol carbonate signal first increased, reaching a maximum, and then decreased, clearly indicating an optimum reaction time for maximizing the yield. This was confirmed by a series of batch experiments where the reactions were stopped at various reaction times. Through a better understanding of the reaction network and a consequent adjustment of the reaction conditions suggested by the reaction monitoring, this study allowed for maximization of the yield of glycerol carbonate to 18%, which was a significant improvement over the state of the art where yields of 6.9% were reported at the beginning of the project.

The removal of water through a non-reactive system would largely avoid the formation of side-products. To this aim, the use of a bubble column reactor operating semi-continuously was investigated. By purging the reaction mixture with CO_2 , the formed water was continuously stripped out by the CO_2 flow and a glycerol carbonate yield of up to 6% could be obtained.

SP 2: Synthesis of cyclic carbonates from epoxides and CO_2 (indirect route)

The main objective of SP2 was to develop highly efficient catalytic systems for the indirect route, transforming epoxides (including those derived from glycerol through known chemistry) with CO_2 into cyclic carbonates. The focus of the indirect route changed during the course of the project to the production of highly functionalized cyclic carbonates, while also being chosen as the main focus for the project. This sub-project was divided into three different work packages, with the status of each WP explained in more detail below. The main partners within SP2 were the University of York, SINTEF, and RWTH Aachen University.

WP 2.1: Catalytic system selection and development

This WP was led by the University of York and was originally divided into two tasks. The second task was removed from the work plan with the change in project focus to more functionalized cyclic carbonates.

Task 2.1.1: Development of commercially viable homogeneous catalysts for cyclic carbonate synthesis from epoxides and CO₂ at ambient conditions

The bimetallic aluminium salen catalysts used since the beginning of the project (brought in as background knowledge from the University of York) were also shown to be active for the conversion of the more functionalized cyclic carbonates investigated later in the project after the shift in project focus. Thus, work focussed in this task on identifying new catalyst structures with even higher activities.

Two salphen-based homogeneous catalysts were synthesised and their catalytic activity for the synthesis of cyclic carbonates from epoxides and CO₂ have been tested and showed remarkable activity. Using 1.5 mol% of either catalyst, in the presence of tetrabutylammonium bromide (TBAB) at 25 °C and 1 bar CO₂ pressure, a range of terminal epoxides were transformed into their corresponding cyclic carbonates. Overall, good to excellent yields were achieved for all substrates using both catalysts. Highly functionalized cyclic carbonates were synthesised from the corresponding epoxides with an 83% yield at 50 °C and 50 bar CO₂ pressure. A greater than 99% conversion was achieved when 2.5 mol% catalyst was used at 100 °C and 50 bar CO₂ pressure

A series of internal epoxides were also examined as substrates in order to further expand the substrate scope. As internal epoxides are considered to be more challenging substrates for cyclic carbonate synthesis, the reactions were carried out using 1.5 mol% of the most active catalyst and TBAB at 50 °C and 10 bar CO₂ pressure under solvent free conditions for 24 hours. Under these conditions, the corresponding cyclic carbonates were isolated in good to excellent yields in almost every case.

WP 2.2: Theoretical studies on cyclic carbonate synthesis

RWTH was the lead partner in WP2.2, which was split into three tasks. The results of this WP mostly fed back to WP2.1.

Task 2.2.1: Choice of model and method for the molecular modelling

The modelling work concentrated on the establishment of the methodology for a meaningful study on the catalysis in the indirect route. An oxygen-bridged bis aluminium salen complex, $[\{Al(salen)\}_2(\mu-O)]$, was modelled for which crystallographic data was available and found good agreement with calculated and experimentally measured bond lengths and angles. A comparison with experimental thermodynamic data was carried out and found good agreement.

Task 2.2.2: Modelling of commercially viable homogeneous catalysts, which are active for cyclic carbonate formation from epoxides and CO₂ at ambient conditions

The catalytic cycle published before the start of the project for pre-existing catalyst **1**, shown in Figure 2.4, was shown to be not possible in the absence of Bu₄NBr. In order to understand the mechanism better and perhaps design a catalyst that would be active without the need for a co-catalyst, DFT calculations were performed and indicated that the formation of carbonate complex **3** would occur ($DG^\ddagger = 58 \text{ kJ mol}^{-1}$ and $DG^0 = 6 \text{ kJ mol}^{-1}$). Complex **3** was subsequently detected experimentally when complex **1** was treated with CO₂ at 50 bar pressure by m/z, IR and ¹H NMR and shown to be catalytically active. DFT calculations also indicated that complex **1** is not Lewis acidic, but that complex **3** is a Lewis acid and will coordinate to epoxides.

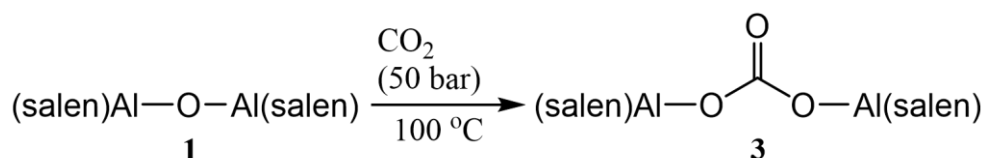


Figure 2.4 Catalyst structures investigated in the modelling work.

Based on the DFT results and investigations of several possible configurations of the ligands and their interactions with the epoxide, the following reaction mechanism was proposed and has since been published in M. North, *et al. ChemSusChem* **2016**, *9*, 791–794.

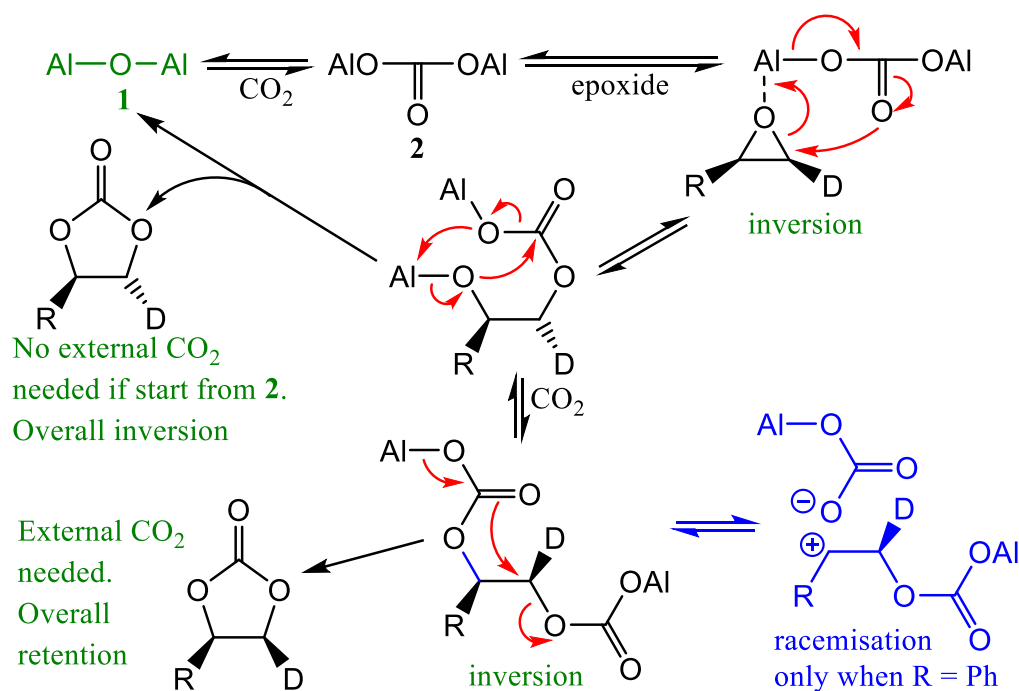


Figure 2.5 Proposed catalytic reaction mechanism based on the DFT modelling

Task 2.2.3: Iterative procedure starts upon discovering new lead structures

The experimental and theoretical work from the first three years of the project were used to iterate new classes of catalysts for the synthesis of cyclic carbonates from epoxides and carbon dioxide. The first iteration was the synthesis of complexes **1** and **2** as shown in Scheme 1 (Figure 2.6). These complexes were designed to include:

- i) Tertiary amines to facilitate CO_2 interactions.
- ii) A salphen rather than salen backbone to increase stability.
- iii) Two different metals to allow the Lewis acidity to be varied.

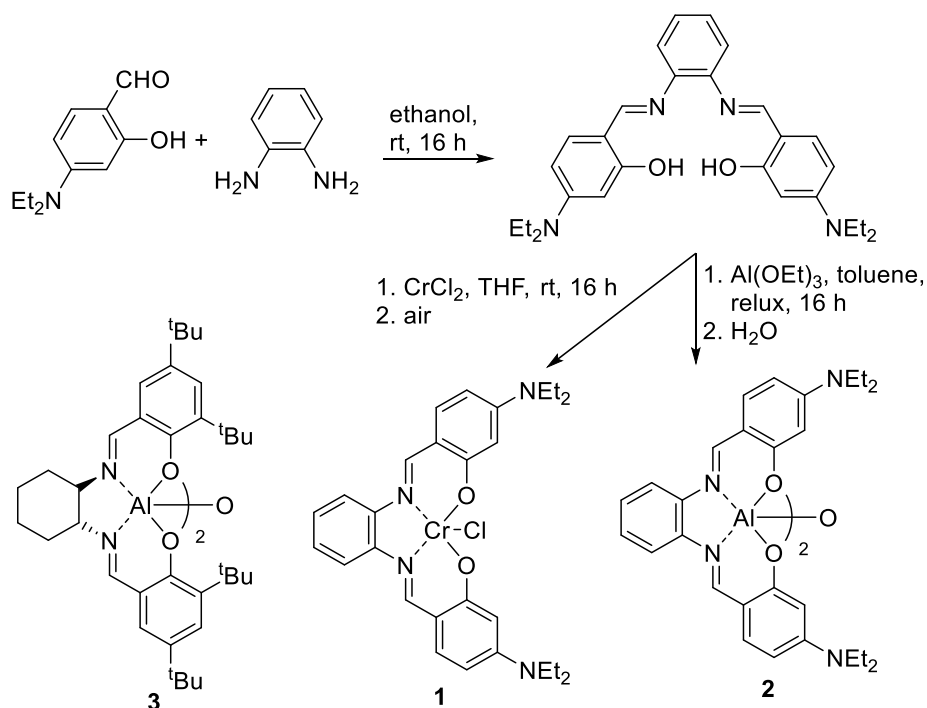


Figure 2.6 Scheme 1: Synthesis of chromium complex 1 and aluminium complex 2

Complexes **1** and **2** were both found to be active catalysts for cyclic carbonate synthesis in the presence of a co-catalyst (8 investigated with tetrabutylammonium bromide being optimal).

We were delighted to find that complex **2** was more active than the lead complex **3** (on which the theoretical studies were based) for the addition of carbon dioxide to terminal epoxides. This allowed the catalyst and co-catalyst loading to be reduced from 2.5 mol% for complex **3** to 1.5 mol% for complex **2**. In contrast, complex **1** was more active for internal epoxides, and allowed these substrates to be used under relatively mild reaction conditions. We attribute the difference between complexes **1** and **2** to complex **2** being electronically more active, but quite sterically hindered due to its dimeric nature. Therefore, it is the best catalyst for unhindered terminal epoxides whilst for internal epoxides where steric effects are more important, the less hindered chromium complex gives higher activity. In the future we will be looking for theoretical studies to confirm this hypothesis and then allow further iterations based on complexes **1** and **2** resulting in the development of even more active catalysts.

WP 2.3: Catalyst immobilisation

WP2.3 was split into two tasks, the immobilisation of the bimetallic aluminium-based catalyst firstly via covalent bonding to a solid support and secondly via the supported ionic liquid phase concept or a biphasic system. As the SILP technology was found to not be suitable for the target compound in the project, no further work was pursued for task 2.3.2.

Task 2.3.1: Immobilization of homogeneous catalysts via covalent bonding to supports

Work in this area concentrated on increasing the catalyst loading by use of well-defined mesoporous silicas. Thus, four different mesoporous silicas were prepared by literature methods and used as supports to prepare silica-supported catalysts. Each silica supported catalyst was then tested with eleven terminal epoxides with differing sizes and hydrophobicities. The best results were obtained with catalysts supported on silicas which

had large enough pores to allow the catalyst to be immobilised within the pores and still leave room for the substrate and product to diffuse in and out.

SP 3: Process development

The main objective of SP3 was to design a reactor and process concept proving the production of cyclic carbonates, which was sustainable and had a reduced CO₂ footprint relative to the benchmark reaction. The focus of the sub-project in the last year of the project was on optimization of the reactor design and troubleshooting to improve the final design for the mini-plant of SPs 4 and 5. The main partners within SP3 were: TNO, FEY, and CRI.

WP 3.1: Reactor design

This WP was divided into four tasks. These tasks required extensive input from SP's 1 and 2 and fed input directly into the following WPs of SP3 to result in a complete process design.

Task 3.1.1: Funnelling of reactor designs

The purpose of this task was to define the type of reactor and the mode of operation to be employed for the synthesis of the target cyclic carbonate. The design of a reactor for both the direct and indirect routes offered several engineering challenges, such as operation with two phase boundaries, catalyst recovery, and *in-situ* product and by-product (*i.e.* water) removal. In addition, the reactor was required to be continuous in order to be industrially applicable.

The reactor concepts were chosen based on a funnelling process, which began by defining key criteria and weighting factors. Criteria were divided between fundamental criteria, such as mass transfer and pressure range, and applied criteria, such as maintenance requirements and commercial availability. Using knowledge within the consortium on the phase behaviours of the reaction mixture, a long list of known reactor concepts with potential to be applicable for the reaction was made for both routes. The final concepts were chosen for each route based on a ranking against these criteria, completed with input from each of the WP partners. The best choices of reactor concepts to take forward were a trickle bed flow reactor for the direct route and a fixed bed reactor with heat recovery for the indirect route. As the project focus was on the indirect route, only the fixed bed reactor was built and tested.

Task 3.1.2: Reactor prototypes construction and testing

Direct route

For the direct route, water removal was of utmost importance. The examined methods were as follows:

Membrane Separation through pervaporation

Two examined configurations, *i.e.* a standard vacuum pervaporation and a sweep gas (CO₂) configuration, provided a proof of concept of dehydrating glycerol. The results indicated that the removal of water could be done at 130 °C. As per the manufacturer's specifications, the membranes could withstand temperatures up to 150 °C. The choice of the operating temperature for the membrane depends on the process concept in combination with the reactor. Moreover, transmembrane pressures up to 6 bar were tested, within the manufacturer's limit of up to 10 bar. In the end, it was not possible to selectively remove water from the reaction mixture using the pervaporation membranes tested as the membranes were permeable by CO₂. This meant that the membrane unit could not be integrated with the reactor unit. As the project focus changed to the indirect route, further research was not completed on this topic

Use of adsorbent for water removal

Zeolites were used as dehydrating agents in this method for water removal. The experiments were performed in two different modes: batch and fixed-bed reactors. The amount of water expected to be in the reaction mixture is about 0.4 wt.%. Although equilibrium tests indicated that it was possible to achieve 0.2 wt.% water using the employed zeolites even at temperatures of 65°C, none of the experiments in the fixed bed were able to achieve the same. Along with resistance to intra-particle diffusion, external mass transfer limitations in the surrounding film were expected to hamper the overall adsorption of water. To build this into a viable process, the continuous removal of water with CO₂ method would require further investigation, but this was not done within the project.

Selective extraction using CO₂ for water removal

Mixtures of glycerol-water and glycerol carbonate-water were subjected to CO₂ extraction to examine the possibility to remove water counter currently in a trickle bed reactor. In the trickle bed reactor, the glycerol was added from the top of the bed and CO₂ was added from the bottom. The CO₂ extracted the water and left at the top of the reactor, enabling continuous production of glycerol carbonate. At high temperatures, i.e. 100-150 °C, selective extraction of water was achieved, reducing the water content down to 1.2-1.5 % and 0.15 % of glycerol-water and glycerol carbonate-water mixtures, respectively. As the project focus changed to the indirect route, this technique was not further investigated.

General reactor design

A trickle flow reactor with a counter-current flow and continuous removal of water during the reaction was determined to be the best choice of reactor for the direct route; however, immobilized catalysts were necessary for the study of the reactor and process development in WP3. Such a catalyst had only been developed for the indirect route for the conversion of epoxides to the corresponding cyclic carbonates. As the indirect route was chosen as the focus of the project, further work on the direct route did not continue.

Indirect route

The best reactor system for the developed immobilized catalyst for indirect production of cyclic carbonates was a basic fixed bed reactor. The apparent challenge was the catalytic activity under the operating conditions, as well as some polymerization in the product stream, which had to be inhibited; this could be accomplished by limiting the time that the reactants and products were exposed to heat and/or by adding polymerization inhibitors. These issues were investigated further in the following tasks.

Task 3.1.3: Investigation of chemical reactions and phase behaviours

A series of experiments were performed in the fixed bed reactor for the indirect route while varying the temperature, pressure, residence time, reactant ratio, and reused vs. fresh catalyst. The key results was that increasing the residence time increased the conversion to products until a point when polymerisation occurred and blocked the reactor. In order to circumvent further blockage of the catalyst bed and further investigate the effect of the residence time on the reactivity, experiments were conducted at an intermediate residence times before blockage was expected to occur. The catalyst was rinsed after each reaction and the recovered solution contained 100% product (no reactants) with a residence time of 60 minutes.

In the same experiment, when the reactor was opened, a dough-like substance was found on top of the catalyst bed, as shown in Figure 2.7. In order to avoid this formation, p-Benzoquinone (p-BQ), which is known for its radical scavenging function, was used as an inhibitor for polymerisation. Firstly, tests were performed to study the effect of the inhibitor on the epoxide only under various conditions. For instance, the presence of

water, air, nitrogen and catalyst were tested at different concentrations and temperatures up to 80 °C. ¹H NMR and LCMS analyses confirmed no change in the chemical structure of the epoxide in the presence of the inhibitor. Therefore, experiments were conducted with 0.6 wt.% p-BQ added to the epoxide. Indeed, all of the experiments with the inhibitor added showed no blockages and high yields of product. The design basis was selected to be 80 °C and 80 bar, which gave a good ratio of reactants, pressure drop, and solution viscosity, facilitating the wetting of the bed and penetration of the reactants into the catalyst pores.



Figure 2.7 Dough-like catalyst right after opening the reactor when no inhibitor was used due to the product residue in the catalyst bed

Task 3.1.4: Reactor modelling

In order to gain an in-depth understanding of the reactions, which aids in reactor design and scale-up, reactor models have been written and implemented for both routes, based on the reactor concepts from task 3.1.1. The reactions of the two routes consisted of multiple phases with multiple components of varying physio-chemical properties, making it a complex system to model requiring significant resources. Thus, relatively simple models were devised for the trickle bed and fixed bed reactors (TBR and FBR, respectively) to obtain the necessary information with reasonable accuracy. The TBR model was made using a first principles approach *i.e.* obtaining mass balances of the three phases (gas, liquid, and solid). The FBR was a type of a plug flow reactor, which was available as a unit operation in the software ASPEN Plus. Thus, ASPEN Plus v8.0 was chosen to model the FBR as several built-in functionalities, such as extensive thermodynamic databases, heat transfer calculations, pressure drop calculations, *etc.*, could readily be used. The results were used to guide the reactor design for the indirect route, but not further pursued given a decision to focus on modelling the process as a whole for further work in SP3 and as input for the calculations in SP6.

WP 3.2: Peripheral equipment

Task 3.2.1: Funnelling of unit operations concepts

The use of nanofiltration (NF) membranes was investigated for catalyst recovery. The main challenge in organic solvent nanofiltration was finding suitable materials which were robust against harsh acidic and basic environments, swelling and leaching, and were selective. Polymeric materials offered a wide variety of tuneable properties which might be used for this application. The liquid permeated through the NF membrane and was collected in a vessel which was on a weighing scale, so that the flux over a period of time could be calculated. The setup included a recirculation of the feed stream and could mimic a co-flow or cross-flow configuration. Several sampling ports allowed for frequent sampling.

Various membranes from the manufacturer SolSep B.V. and from Evonik were used. The obtained results indicated up to 90.4 wt% catalyst recovery in the retentate stream. Further investigations would be needed to be performed in order to increase catalyst recovery to make the process viable. Furthermore, recovery of the co-catalyst TBAB was not possible. As the catalyst was successfully immobilized with high enough activity, this system was not developed further for the mini-plant.

Task 3.2.2: Determination of optimal equipment

Although full conversion was achieved in the experiments, for the mini-plant a yield of 75% was assumed to have some contingency for process variations. However, the typical purity level for any commercial product is at least 95% or more, depending on the application. Therefore, it was prudent to develop separation methods to obtain high purity product from the reaction mixture. It was known that the product was not stable enough for using distillation as a separation technique. Therefore, a suitable alternative for separation was required. Crystallisation as separation method was investigated. Differential Scanning Calorimeter (DSC) measurements were performed to measure the phase transition temperatures for pure reactant and product and their mixtures.

In view of the constructed phase diagram, it was impossible to obtain product crystals from the reaction mixture. It would be possible to solidify the complete mixture and then only melt the product. Filtering off the solids would leave the product as a liquid. However, this could then still be a little contaminated with other compounds. So multiple solidification- melting cycles would be necessary to obtain the pure product. This process would probably not be economically feasible.

A simulated moving bed (SMB), an advanced adsorption technology, could be used to separate the reactant from the product. Specifically, we proposed to use supercritical CO₂ as a desorbent. Two product streams would be generated: an extract stream, in which the produced would be produced diluted in supercritical CO₂; and a raffinate stream, in which the reactant would be recovered diluted in supercritical CO₂. The reactant/CO₂ mixture could be recycled to the reactor. By releasing the pressure, CO₂ could be flashed out from the extract, leading to high purity product. Due to time limitations, this method was not tested experimentally.

WP 3.3: Process modelling and laboratory testing

Task 3.3.1: Process modelling

Several process modelling activities were performed. Process modelling was done using Aspen Plus, with input of additional components database as necessary. These results were used for techno-economic evaluation and carbon footprint estimation in WP6. Firstly, process modelling of the benchmark case of production of glycerol carbonate was performed, for which two different processes of producing Dimethyl carbonate (DMC) using oxidative carbonylation were considered. Subsequently, the so-called direct route of using glycerol and CO₂ was considered. The direct route using acetonitrile as a sacrificial molecule to react with water in order to shift the equilibrium (also referred to as chemical water trap), was simulated. Additionally, the direct route using a physical water trap, i.e. a membrane pervaporation unit was simulated. Finally, the production of the functionalised target product through the indirect route was considered with multiple reaction steps starting from glycerol to the functionalized cyclic carbonate. Since no data was available for of the process, a process model was formulated in order to obtain the mass and energy balances for the process.

Task 3.3.2: Construction and operation of laboratory scale process

Catalyst bed construction

For good flow distribution, it was beneficial to have the same carrier material as used for the catalyst, silica or glass beads, on both sides of the catalyst bed with increasing particle size. The dead volume in the reactor was also minimised, for instance using a Teflon or steel 'rod' to fill the unused space in the reactor. The catalyst bed itself was held in place using a fine mesh.

Duration test

The purpose of the duration test was to investigate the occurrence of plugging of the reactor by side reactions and catalyst deactivation. This was of interest for performing the reaction at larger scale, i.e. in the pilot mini-plant reactor. Plugging of the pilot reactor would be catastrophic as it would likely render the catalyst useless due to the recovery and reactivation issues.

The duration test was performed for 7 days at reaction conditions of 50°C and 50 bar in the laboratory fixed bed reactor. While polymerisation did not occur, catalyst deactivation did occur. It was determined that leaching of the co-catalyst species from the catalyst particles occurred, indicating that the co-catalyst would need to be fed to the reactor with the reaction mixture in the mini-plant.

SP 4: Optimization of process for scale-up

The main objective of SP4 was to complete the research tasks needed to scale up the process for demonstration in the mini-plant and further development. This sub-project was divided into 3 different work packages. Task 4.1.1 was removed from the description of work following the change in project focus. The main partners within SP4 were: CRI, UOY, and SINTEF.

WP 4.1: Catalyst optimization and production

Task 4.1.2: Production for process development

Due to the timescales involved, this task was combined with production for process development and all work is reported within Task 4.1.3.

Task 4.1.3: Production for process demonstration

The procedure to produce the catalyst was repeated in multiple batches in order to produce the quantity of material required to satisfy the requirements of process development and process demonstration. The final catalyst materials were isolated as orange powders in yields of 13.5 – 14.0 g per batch. Each batch of heterogeneous catalyst was analysed by ICP-MS to determine the degree of metal center loading. Subsequently, testing the catalyst in the solvent-less reaction of styrene oxide and carbon dioxide to styrene carbonate confirmed that each batch was catalytically active. The separate batches were divided into two sealed vials, with each vial containing 6.5 – 7.0 g of catalyst (Figure 2.8). In total, 310 g of heterogeneous catalyst was prepared during the period September 2015 to July 2016.



Figure 2.8 250 g of heterogeneous catalyst prepared for use in pilot plant studies.

WP 4.2: Mini-plant design

Task 4.2.1: Reactor design

A reactor design was agreed upon, using a 1000 mm long tubular reactor with an internal diameter of 36 mm. The reactor was designed to be operated at 80°C and 80 bar pressure and was equipped with heaters controlled by internal thermocouples. With scaling up from the laboratory scale reactor, it was expected that 250 g of undiluted catalyst would be required with a bead height of 300 mm. The product production rate was expected to be 80 g/hour.

Task 4.2.2: Mini-plant design

The automated mini-plant was designed to be able to produce cyclic carbonates from epoxides and CO₂ in a continuous process. A user requirements document guided the design to ensure it complied with the project objectives and met the expectations of the industrial partners. During the final design phase, a what-if analysis was performed in order to minimize hazards and risks regarding the operation of the system. Recommendations during the what-if analysis were used for the final design of the plant.

The mini-plant was designed in such a way that the experience from operating the mini-plant could be used to improve the basic design and operation of the continuous process on a larger scale. The scale selected was four orders of magnitude smaller than an expected commercial production volume of the target product, which was given to be 5 kton per year or 600 kg/h.

SP 5: Process demonstration

The main objective of this sub-project was to demonstrate the technical feasibility and potential for producing renewable cyclic carbonates in a continuous process while validating the catalysts and process units at a mini-plant level to a degree that was acceptable to the end-users in the consortium. This sub-project was divided into 3 different work packages. The main partners within SP5 were: TNO, CRI, and FEY.

WP 5.1 Construction of the mini-plant

Task 5.1.1 Mini-plant construction

The mini-plant for the production of cyclic carbonates was constructed in accordance to the specifications determined in SPs 3 and 4. The system was partially integrated into current installation in the CRI laboratory. Most system components were connected via ¼" stainless steel tubing with Swagelok fittings, withstanding the 100 bar pressure requirements. The CO₂ and reactants were pressurized on the supply side and on the reactor side the flow of CO₂ was regulated and the two streams combined and mixed. The mixture entered the reactor and was heated to the reaction temperature and converted to the target cyclic carbonate via the heterogeneous catalyst. After the reactor, the pressure of the mixture was dropped, the liquid collected and any remaining CO₂ vented.

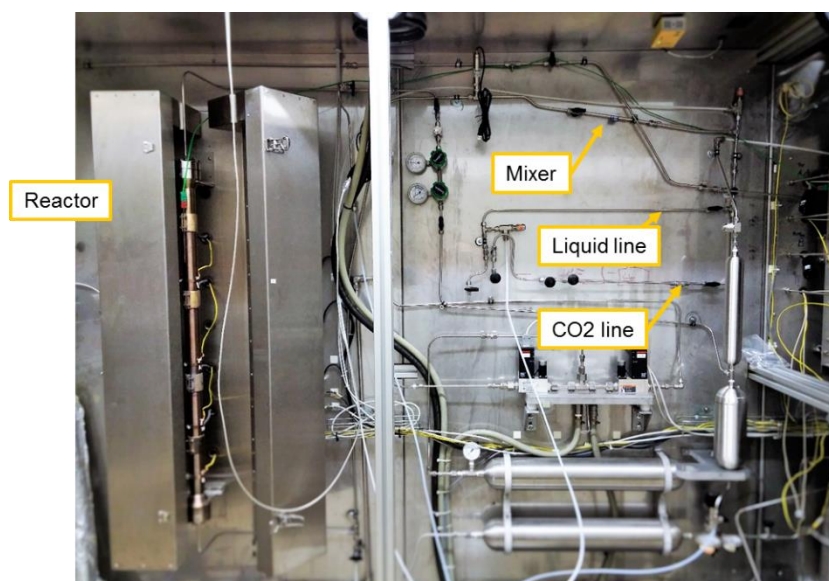


Figure 2.9 Reaction side of the mini-plant

Task 5.1.2 Mini-plant commissioning

Each system part was initially tested individually prior to final assembly in order to grasp strengths and weaknesses of each equipment part. Following that, the system as a whole was tested rigorously according to the procedure agreed upon by the consortium partners, yielding the mini-plant acceptance test report.

The first actual use of the system was when 25 g (10% loading) of catalyst were tested in order to increase the likelihood of success of the full scale test. A memo was created that described the test and the results from it. In short, all the equipment functioned as expected. The conversion of the epoxide to the cyclic carbonate started out at an acceptable level for the catalyst loading, but the conversion dropped down to virtually nothing in less than a day. It was hypothesised that this could be due to the loss of bromide co-catalyst from the catalyst matrix.

It was established that the polymerization inhibitor p-benzoquinone (p-Bq) could act as a bromide indicator, colouring the bromide containing reactant, indicating the loss of the bromide co-catalyst from the heterogeneous catalyst. Therefore, it was proposed to use a proven co-catalyst, tetrabutylammonium bromide (TBAB), to facilitate the reaction in the 250 g catalyst test to counter the loss of bromide.

WP 5.2 Pilot plant testing of catalytic activity and mapping of process parameters

Following the change in project focus and what was ultimately achieved in terms of the overall development in the project, the activities performed for the mini-plant were much more research oriented rather than the demonstration that was originally foreseen. Therefore, the work in SP4 was more extensive and the work in SP5 was less than originally planned, as described below.

Task 5.2.1 Catalyst testing and process optimization

The loading of catalyst and operation of the mini-plant was performed in accordance to the standard operating procedures (SOP). 250 g of catalyst powder were loaded into the reactor, diluted with a varying portion of fine mesh SiO₂ sand. The reactants were >99% pure CO₂ and 97% pure epoxide mixed with 0.6% TBAB, in order to combat the reaction decrease due to loss of bromide. Initially, plans were done to use the polymerisation inhibitor as well as the TBAB; however, during testing it was discovered that the inhibitor was not compatible with the TBAB. The plant ran continuously for 7 days with a short stop due to a clogged filter. An extra day was added in order to test the system activity with a doubled concentration of TBAB.



Figure 2.10 Flasks containing the accumulated product from the 250 g run

The flow into the system remained stable throughout the test period, except for when the particle filter after the reactor got blocked and the flow was stopped during the repair. The liquid collection only happened intermediately and therefore quite a lot of variance was observed, also dependent on the gas/liquid equilibrium throughout the entire system. The temperature in the reactor was kept stable at 80°C ± 1°C for the entire run. It proved somewhat more difficult to keep the pressure of the system stable. The pressure was controlled by a pair of spring loaded back pressure regulators. Initially, the pressure remained above 80 bar pressure and within a few bar gap with short bursts of pressure dropping below the set pressure.

Using the above mentioned operating parameters, the mini-plant produced the target cyclic carbonate at a starting concentration of approximately 90%, decreasing to approximately 70% over the span of 7 days. No attempt was made to identify possible by-products. These result indicated that a purification step would be required unless the quality could be improved by increasing the retention time or increasing the CO₂ concentration and pressure.

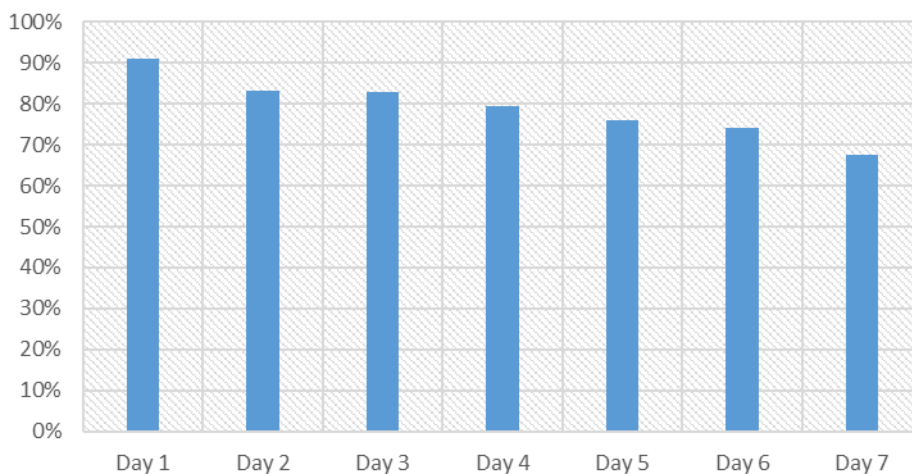


Figure 2.11 Cyclic carbonate concentration in the product according to HPLC analysis during the mini-plant testing

In order to characterize the performance of the catalyst, two derived numbers were calculated for the mini-plant and the catalysts conversion. The reaction rate for the system was calculated based on the rate of product collected and the cyclic carbonate concentration of the product divided by the amount of catalyst. The turnover frequency was calculated in a similar way, except for using the molarity of the catalyst. Results showed that the reaction rate started at around 1.1 mmol/g*h and gradually dropped to around 0.7 mmol/g*h.

Due to time limitations and more focus on R&D activities, the other tasks in this work package were not completed.

SP 6: Environmental and techno-economic assessment

The main objective of SP6 was to complete an environmental and techno-economic assessment for the full process, thereby verifying the CO₂-savings potential for various strategies at key moments in the project and assisting in the choices between final process design and the direct vs. indirect routes. In order to meet this objective, the following activities were completed:

- Perform estimations of the CO₂ emissions with increasing level of detail based on ASPEN® simulations. One of the focus points was the CO₂ use per unit product combined with an estimation of the cost of production per unit product;
- Provide market information to help with further decisions.

The main partners within SP6 were: EVO and TNO

WP 6.1: Bench mark processes

The purpose of this task was to estimate the CO₂ emissions for the benchmark process for the production of glycerol carbonate (GC) and provide a starting point that the project developments must beat. The estimations were thus crucial for the development of the direct route and indirect route during the project. The results of the benchmark process allowed for the correct comparison of results of the project progress with the existing benchmark. Afterwards, the environmental benefit could be quantified and suggestions (*e.g.* required catalyst activities, reaction conditions and downstream design (energy consumption)) could be defined.

For the first benchmark process, a two-step synthesis of GC was considered with dimethyl carbonate (DMC) as the key intermediate. Two different pathways for the synthesis of DMC were compared in a sensitivity analysis. A third route, phosgenation, was excluded from the analysis due to the intensive use of halides. It turned out that the Mitsubishi process *via* propylene carbonate was not environmentally-competitive to the oxidative carbonylation of methanol. Therefore, the latter process was used for the synthesis of DMC.

Furthermore, it was shown that GC production *via* trans-esterification was dependent on the plant oil used to produce the glycerol. In the simulated cases, the incorporation of CO₂ during the growth phase was calculated separately. By including biogenic CO₂ uptake, the carbon footprint of GC was calculated to be 1.7 kg CO₂/kg GC when glycerol was derived from palm oil. If the glycerol was derived from rapeseed, the carbon footprint lowered to 0.4 kg CO₂/kg GC.

Through the benchmark calculation, it was shown that the largest share of CO₂ emissions was due to the production of DMC. Replacing the use of DMC by direct use of CO₂ could be the major factor in improving environmental performance of the overall process.

WP 6.2: Direct route towards glycerol carbonate and propylene carbonate as an intermediate for dimethyl carbonate

The global warming potential (GWP) of the direct route was estimated for a conversion of 50 % at 145 °C and 5.2 MPa. As the carbon footprint of the direct conversion of glycerol with CO₂ is dependent upon the plant oil used to produce glycerol, two scenarios with different raw material sources were considered: glycerol derived from i) palm oil and ii) rapeseed oil. Based on the results of SP 1 and SP 3, an ASPEN® simulation of the targeted process was performed. However, the process for the direct route remained very theoretical, as only limited data were available and many assumptions had to be made, e.g. the separation steps were not defined in detail.

The carbon footprint of GC from palm oil was 1.0 kg CO₂ / kg GC and resulted in a GWP of –0.2 kg CO₂ / kg GC when considering the biogenic carbon of glycerol. The largest share of CO₂ emissions and reduction potential was allocated to the used raw materials, whereas the utilities only negligibly contributed to the GWP. Direct carbonation of glycerol from rapeseed oil resulted in a total carbon footprint of 1.5 kg CO₂ / kg GC or 0.4 kg CO₂ / kg GC when including biogenic carbon allocation. Compared to the benchmark process, a two-step synthesis of GC from dimethyl carbonate (DMC) and glycerol, the carbon footprint of the direct carbonation of glycerol was significantly reduced for both raw material scenarios. By using palm oil derived glycerol, the direct conversion with CO₂ even enabled a net CO₂ uptake and clearly showed the high CO₂ saving potential of this route. However, the chemical conversion was difficult as the catalytic realization was very challenging. Due to the main focus on the indirect route, no further activities were completed for the carbon footprint estimation of the direct route.

WP 6.3: Indirect route towards glycerol carbonate and functionalised derivatives

As the use of bio-based raw materials was targeted in the CyclicCO₂R project, the global warming potential was not only calculated for reaction step of the CO₂ insertion into the epoxide, but also the used raw materials starting from glycerol were taken into account. Furthermore, with the change of the target product, the benchmark product and/or process needed to be modified accordingly. The target product was a completely new product to the market, which was currently not available on industrial scale. Therefore, the comparison with a benchmark production process was not applicable. In a first approximation, the new product was compared to fossil-based similar product which would have similar applications. However, due to the novelty

of the product, the use phase was also considered in the carbon footprint estimation in a first draft (cradle-to-grave analysis).

First, the production process was defined as a three-step process from glycerol to the target cyclic carbonate. The first and third process steps were modelled with Aspen® based on available reports for the commercial process or current experimental results with an assumed yield of 98 % at 100 °C and 0.5 MPa. The second process step was purchased as an open dataset from Thinkstep, in which the calculated GWP was included. For the base case scenario, glycerol derived from palm oil was assumed as the raw material biomass. In a sensitivity analysis, the GWP for the process with glycerol from rapeseed oil (scenario B) or with a conversion yield of 65 % (scenario C) as the lower limit for an economically feasible process were evaluated as well.

The global warming potential (GWP) of the base case scenario was estimated with 5.9 kg CO₂ / kg product. The raw materials had the largest share in CO₂ emissions, whereas the processing only made up a small contribution. By including the use of CO₂ in the process and the biogenic carbon allocation, the carbon footprint of the product from glycerol was reduced to 5.1 kg CO₂ / kg product. Compared to the fossil based benchmark with its accounted CO₂ emissions of 8.3 kg CO₂ / kg product, the indirect route also showed a high CO₂ saving potential, if the use phase of the product was not taken into account. Due to different functionalities of the target product and benchmark, the molecules needed different reaction partners and conditions in the final application. A detailed review of suitable application areas was therefore needed. While not being able to report details here, it was found that depending on the application, the indirect route process was a significant improvement or slightly worse than the application-based benchmarks in terms of GWP. The results showed the importance of including the application phase in the carbon footprint estimation for new products.

In the sensitivity analysis, the carbon footprint of GCMA from rapeseed derived glycerol (scenario B) was estimated to be 5.3 kg kg CO₂ / kg product, including CO₂ uptake in the process and biogenic carbon allocation. For scenario C, an assumed yield of 65 % in the final product production step also resulted in similar CO₂ emissions with 5.2 kg CO₂ / kg product. Although the CO₂ emissions of the utilities were increased due to recycling of unconverted substrates, this contribution to the GWP was quite small in comparison to the share of the main raw materials.

These results implied that a more detailed review of suitable application areas needs to be done to clearly show CO₂ saving potentials in the final markets. Therefore, application tests with the target product would be needed to specify the process conditions and performance within the use phase, for which higher produced amounts of product were needed. This detailed analysis of the final application areas was addressed in WP 6.5.

WP 6.4 Preliminary market evaluation

The economics of the indirect route were evaluated for the new target molecule. At the time of the project, the product was supplied by very few companies, like Specific Polymers, with no information on production capacities and sales. In general, prices were reported from approximately 4.5 to 10 € / kg, depending on the application area and final product. As the final application area was unknown, the lowest achievable price by considering various existing products in the addressed application areas was used as benchmark price (worst case). By using the given economics and the framework settings from the earlier analysis in the project for glycerol carbonate, a feasible economic situation could be shown: the overall product expenses, including also

a roughly estimated ROI share, were estimated to be 4.0 € / kg, which needed to be achieved as the minimum price on the market.

Finally, it has to be stressed that all scenarios discussed were calculated in a bottom-up cost scenario according to known studies and processes based on PEP reports and internal estimations / discussions. Therefore, the final values for the process as well as the achievable sales price could differ significantly from the project calculations.

WP 6.5 Final environmental and techno-economic life cycle assessment with implementation plan

The economics for the modified target product following the change in project focus were reassessed based on estimations resulting from recent experimental work and preliminary data from the pilot-plant studies. In deviation from previous assumptions, and based on the ASPEN simulation performed by TNO for the carbonation step, the estimated CAPEX was 10.2 m. € for 75 % conversion and using SS 316L as the material of construction. Most of the CAPEX (> 75 %) was incurred from the separation steps, i.e. compressors and distillation column. It could be assumed that this was the worst case scenario for the separation step and would need to be replaced in the final process since extensive distillation was not feasible in industrial scale for the sensitive product. However, the CAPEX was still within or even below the value assumed in the preliminary cost estimate and alternative separation methods, such as crystallization, could further reduce the investment costs. Furthermore, the major change compared to previous calculations was the adjusted product yield of 75 %, resulting in significantly increased raw material costs. By using the given economics and framework settings the product was estimated with overall expenses of 4.7 € / kg, which should be achieved as minimum value on the market. While still within the price range of the benchmark class of products (4.5 to 10 € / kg), the estimated minimum market value exceeded both the previous economically feasible estimation (4.0 € / kg) and the lowest expected benchmark price (4.5 € / kg), thus rendering the process not competitive with the chosen benchmark. However, the considered benchmark price was at the lower limit of the expected price range and by assuming a higher price of the benchmark with e.g. 6 € / kg, the process would become viable. The increase of overall expenses in the calculation was mainly driven by raw material costs due to a reduced conversion rate (75 % vs. 98 %).

The techno-economic assessment suggested, in principle, economic viability for the investigated product and process, but was based on a mere bottom-up cost scenario according to known studies and processes based on PEP reports and internal estimations and discussions. Therefore, a detailed market analysis with a top-down value-based estimation would be essential for a potential product launch and the present cost analysis could only serve as a first indicator and a comparison with existing benchmarks. A market price derived from of a top-down value-based assessment translates into reliable maximum overall expenses and thus into specific areas of optimization or adaptation for scale-up to commercial scale synthesis. Furthermore, since crucial experimental results from continuous operation in the mini-plant were absent at the time of the techno-economic analysis, no final conclusion with respect to project results on technology implementation could be drawn. An evaluation of the process regarding full-scale implementation to a commercial product would require a validation of the catalyst and process units at small scale, since validated and reliable data will be crucial for further process scale-up.

SP 7: Alternative technologies

The main objective of SP7 was to explore the use of electro- and photochemical technologies in generating the raw materials needed for the production of cyclic carbonates from only CO₂ and water. By achieving this

objective, it would be possible that both the direct and indirect routes could become independent of fossil fuels and the net CO₂ uptake could be significantly increased. This work package was also ideally suited to keep track of all of the developments outside of the project that could have an impact on the technologies being developed. This sub-project was divided into four different work packages. The main partners within SP7 were UT and TNO.

WP 7.1: Photocatalytic synthesis of compounds containing a C=C double bond from CO₂

One of the key reactions in achieving efficient CO₂ conversion, either in electrocatalytic reactors or photocatalytic reactors, is the oxidation of water to produce oxygen. Not only does the oxidation of water require a significant thermodynamic potential, the so-called over-potential to overcome kinetic barriers is also significant. Water oxidation catalysts have been reported to be able to reduce this over-potential to a significant degree, but the metal (oxides) usually applied are rare and expensive, such as IrO_x and RuO_x. Recently, (oxides of) more earth-abundant elements have been found to have significant water oxidation activity, in particular when supported in, or on silica based mesoporous materials. Co-based structures (Co₃O₄/SBA-15, Co(II)/SBA-15, etc.) have been reported to be particularly effective. Co-TUD-1 catalysts were synthesized according to common procedures, and were found effective in the oxidation of water. Synthesis parameters were varied, to achieve the best possible distribution of Co in the matrix, and the structure-activity correlation was investigated with detailed electron microscopy studies to further analyze the structure of the obtained materials, and correlate this to activity. In addition, the stability of the catalysts was also checked by recycling and centrifugation procedures. The Co/TUD-1 catalyst showed quite good stability, and could be used for several cycles without significant performance decrease. This result was different to results reported for other silica matrices and suggested, together with the other results, that the TUD-1 matrix was very favorable to the obtained Co-based water oxidation catalysts as compared to other mesoporous silica materials.

WP 7.2: Electrocatalytic synthesis of compounds containing a C=C double bond from CO₂

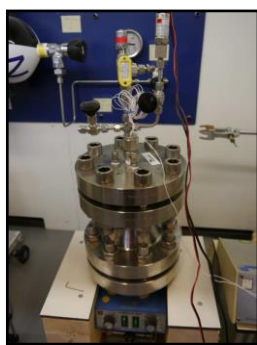


Figure 2.12 High pressure electro-chemical reactor at TNO

Significant progress was achieved in the electrochemical conversion of C=C to epoxides. It was decided to focus on this chemistry at UT, which was very relevant for other activities in the project, and include practical work for analysing the effect of process conditions on electrocatalytic efficacy. In particular, the nature of the electrolyte (*e.g.* ionic liquids) and effect of catalytically active molecular catalysts and/or nanostructures (*e.g.* nanopillars) was investigated.

Parallel to this, an internship project was completed at TNO looking at the electrochemical production of ethylene using a copper catalyst and a potassium carbonate electrolyte with the system shown in Figure 2.12. Several parameters were varied, such as temperature, electrolyte volume, type and size of catalyst, and distance between the electrodes. During the internship, only hydrogen was produced, however, continuing work looked at the effects of voltage, higher temperatures, and elevated pressures (up to 150 bars were possible).

WP 7.3: Epoxide synthesis

The work in this WP continued from the work of WP 7.1. By combining the photo-reactor concepts of TNO and UT, a new design of the previous reactor was made. This design combined the advantages of the monolithic reactor at UT, the high pressure and temperature features of TNO's design, and the use of thin glass rods instead of optical fibers (also TNO). A schematic of the design is given in Figure 2.13.

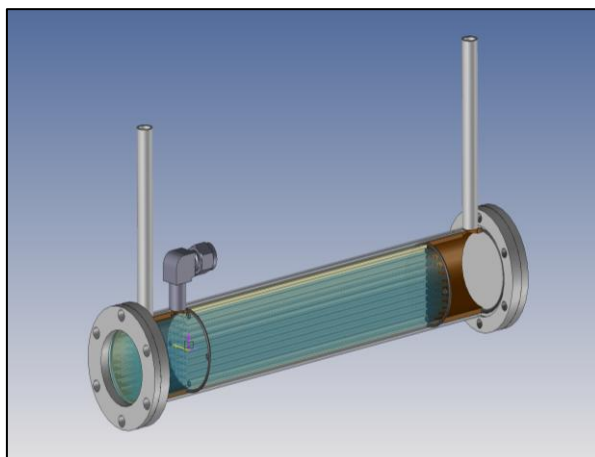


Figure 2.13 New design for photo-reactor for internal illumination of the channels of a monolith.

As can be seen from Figure 2.13, thin, coated glass rods (1 mm thickness) were inserted through the channels of a monolith. On the left hand side, an optical window is present to guide the light coming from the external light source of choice through the glass rods. The glass rods could be coated with the catalyst of choice and were kept in place inside the channels of the monolith using O-rings. Tests of light propagation were initiated at UT and a high power LED light source to induce sufficient reaction was ordered. Due to constraints in resources, a full experimental campaign could not be completed.

WP 7.4: State-of-the-art monitoring and synergy

Part of SP7 was dedicated to keep track of the state-of-the-art in the production of cyclic carbonates from carbon dioxide in general and specifically glycerol carbonate. Due to the change of focus halfway through the project, also the state-of-the-art in the production of the new target compound was focused on. It was found that in terms of direct synthesis of carbonates (SP1), only a handful of articles were published every year. This coincided with the experiences encountered during the CyclicCO₂R project, as this was route was seen as the more complicated one. Results on the indirect synthesis route (SP2), however, were reported more frequently in literature, roughly 100 articles per year. For SP7, the alternative feedstock work package, roughly 30 useful articles were published per year.

The produced roadmap showed that significant progress was made during the four project years and that the pilot plant was nearly up and running near the end of the project. The stability of the catalyst remained a point of attention, a point that was perceived to make or break the developed technology.

3 Potential impact, main dissemination activities and exploitation of results

Potential impact

The results of CyclicCO₂R in relation to the expected impacts from the original call text and the foreseen impacts at the start of the project are summarised in Table 3.1.

Table 3.1: Expected and foreseen impacts vs. project results

Expected Impact	CyclicCO ₂ R foreseen impact	Relevant project results
New industrial routes for using CO ₂	<ul style="list-style-type: none"> By combining elements that are proven in principle, a new process will be developed that enables the production of cyclic carbonates from renewables and CO₂. Advances in molecular modelling of raw material and catalyst interactions will aid the use of complex and heterogeneous catalysts in CO₂ application in general. The developed processes will showcase the increase in understanding of the application of CO₂ efficiently in process equipment, easing the use of CO₂ in different fields. 	<ul style="list-style-type: none"> A new process combining CO₂ and epoxides to produce cyclic carbonates was developed up to a mini-plant scale. The understanding of the reaction between CO₂ and epoxides and the catalytic mechanism was greatly improved through experimental work and molecular modelling. The need for catalyst developers and process engineers to work collaboratively throughout the development process was shown to be essential in realizing new industrial routes.
Commercial viability of the new process	<ul style="list-style-type: none"> Continuous comparison against the benchmark will ensure the development stays relevant to industry. The Environmental and Techno-economic Analysis work package will be headed by the end-user, which will ensure economic feasibility and provide an important result to be communicated to stakeholders. Developments will be applicable to other fields. Prime examples will be the use of the developed catalyst improvements and novel processes in the bulk production of ethylene and propylene carbonates. 	<ul style="list-style-type: none"> An extensive analysis of the techno-economic aspects of the developed process was completed and showed that there was a possibility for the product to be commercially viable based on comparison to benchmark products. Due to remaining technical issues at the end of the project, a more concrete conclusion could not be made as to the expected final costs of a commercial process. The new class of highly active catalysts are applicable to the production of a wide range of cyclic carbonates and could be central in several commercial processes based on CO₂.
Reduction of overall greenhouse gas emissions deriving from industrial processes in Europe	<ul style="list-style-type: none"> The developed process will focus on energy-efficient processing so that the reduction will be maximised. The connection with raw materials from renewable origin will increase the independence from fossil fuels and will increase the reduction in greenhouse gas emissions. The different aspects of the process will be knowhow applicable to other processes, increasing the impact beyond the direct project objectives. 	<ul style="list-style-type: none"> The analysis of the global warming potential (GWP) showed the importance of considering the application phase in comparing a new product based on CO₂ to a fossil-based benchmark. For some applications, a significant reduction in GWP could be realized, when taking into account the biogenic carbon uptake from bio-based feedstocks. For other applications, the GWP was about the same or even slightly worse than the benchmark.

Socio-economic impact

The most important impact from the process developed in CyclicCO₂R was opening up new possibilities for the industrial use of CO₂. Cyclic carbonates are fine chemicals in their own right and can replace organic solvents, but can also act as platform chemicals for the production of polymers and as raw materials for speciality chemicals and pharmaceuticals. The process that was developed was specifically aimed at increased efficiency and use of renewable feedstocks in order to prepare for the transition from a fossil-based to a renewable (bio)-based chemical industry. The results showed the potential of CO₂ as a raw material and have the potential to help in initiating an increased use of CO₂ as a raw material in the production of other fine chemicals, bulk chemicals and eventually fuels, where the impact from CO₂ consumption in their production would be large. For example, with the current process to produce the most widely used cyclic carbonate, ethylene carbonate, 0.86 tonne of carbon dioxide per 1 tonne of ethylene oxide is produced.¹⁴ Included in this number is the fact that roughly 20-25% of the ethylene feedstock is converted to carbon dioxide directly in the direct oxidation process.¹⁵ Just eliminating this complete oxidation route (from ethylene to carbon dioxide and water) in the process would already save a substantial amount of carbon dioxide produced annually, considering the fact that roughly 20 million tonnes of ethylene oxide are produced per annum.¹⁶

Cyclic carbonates, including glycerol carbonate and other derivatives of glycerol, have a large number of applications. They are used as electrolytes in lithium ion batteries, coatings, as chemical intermediates, as non-toxic polar solvents, and as additives to cosmetics/personal care products and detergents.^{17,18,19} A competitive price for the target compound will open up various possibilities to use the compound as a fine chemical in the late stage synthesis of speciality chemicals. One highlighted possibility is the use of the product for coating resins. Current coating resins are based on the use of methyl methacrylate as chemical. The world market for this segment in the use of methacrylates was predicted to increase from 581 kt in 2008 (value of 0.83 Bill. €) to 682 kt in 2013. In total, the European market had a size of 120 kt in 2008. To compete with established coating resins, new competitive routes for renewable products are required. Other further applications have yet to be determined if the process is developed further. However, the target product has a high boiling point, low toxicity, and low environmental footprint. This makes the compound suitable for applications in consumer care products as well as in bio-based lubricants. Cyclic carbonates, however, rarely sold directly as products to consumers and will primarily be used as intermediates in the production of other products.

The process developed in CyclicCO₂R has the potential, with further development, to aid in the valorisation of glycerol, which is overproduced as a by-product from biodiesel production (biodiesel production in 2010 in Europe was estimated at 9.5 million metric tonnes²⁰; glycerol production is roughly 100 kg/tonne biodiesel). Due to mandates in the European and other countries worldwide, the source of glycerol from biodiesel will expand in the future. During the last decade, the availability of glycerol increased dramatically²¹, as shown in Figure 3.1. The overproduction of glycerol has also caused the prices to drop, from historically 1.3-2.0 \$/kg to about 0.11 \$/kg in 2006^{22,23}. The low price of glycerol has caused an increasing problem for the producers since

¹⁴ J.Garcia Moretz-Sohn Monteiro, O. Queiroz Fernandes Araujo, J.Luiz de Medeiros, *Clean Techn. Environ. Policy*, 11 (2009), p. 459.

¹⁵ Kirk-Othmer Encyclopedia of Chemical Technology.(4 ed.). New York: John Wiley & Sons. 1994.

¹⁶ SRI Consulting, WP Report Ethylene oxide, 2009.

¹⁷ J.H. Clements et al.; *Ind. Eng. Chem. Res.*; **2003**; 42; 663-674

¹⁸ W. Clegg et al.; *Tetrahedron: Asymmetry*; **2010**; 21; 1262-1271

¹⁹ C. Beattie et al.; *Molecules*; **2011**; 16; 3420-3432

²⁰ European biodiesel board; <http://www.ebb-eu.org/stats.php>

²¹ Frost & Sullivan **2008**.

²² D.T. Johnson; *Environmental Progress*; **2007**, 26; 4, 338-348

²³ M. Pagliaro; *Angew. Chem. Int. Ed.*; **2007**; 46; 4434-4440

the selling price does not even cover the costs for transportation of the crude material to the buyer. Furthermore, the glycerol from biodiesel production is generally of low quality, containing water and catalyst residues as impurities (a typical sample contains 85 wt% glycerol, 10 wt% water and 5 wt% residues (mainly salts²⁴). Due to the lower purity and low costs, most glycerol is simply burned to cover some of the energy demand of the biodiesel production. In contrast to this, glycerol which is actually used is of very high purity (pharmaceutical grade). This quality is only available for 5-10% of the overall glycerol supply and is achieved by energy-intensive purification with various washing steps and subsequent film evaporation. Therefore, pure glycerol is sold at a much higher price (about 600 \$/t).²⁵

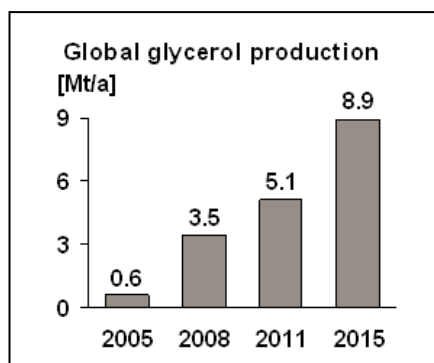


Figure 3.1 Global glycerol production between 2005 – 2015.

The current oversupply of glycerol has two effects: (1) glycerol is available at low-cost, and (2) the use of glycerol will help balance the effects of the transition to renewables. In recent years, several research activities were initiated to improve the current glycerol situation by accessing chemicals *via* new routes from glycerol. One example from Solvay, with a glycerol-to-epichlorohydrin (Epicerol) factory in Thailand.²⁶ It produces 100,000 tonnes epichlorohydrin from glycerol. A similar process was developed by Dow Chemicals and was applied in a new factory in China.²⁷ Furthermore, Arkema has developed a new route towards acrylic acid from glycerol, which was developed in parallel by Nippon Shokubai.²⁸

The process developed in CyclicCO₂R has the potential to utilize various glycerol-based epoxides, produced via epichlorohydrin, to produce cyclic carbonates, while consuming CO₂, and thus expanding the market for glycerol. Given the moderate market volumes of the cyclic carbonates, one could imagine decentralised solutions connected with biodiesel plants which utilise the waste glycerol and produce the desired cyclic carbonates. Furthermore, the direct route did show potential to be further developed, just not within the timeframe of the project. This could present another solution for the production of cyclic carbonates with the possibility of using impure glycerol, although this was not investigated in the project. Therefore, the production of value-added intermediates, like glycerol carbonates, in smaller quantities, and with the process designed to be energy efficient with producing the small quantities, could give a way to use the small glycerol streams of a biodiesel plant more efficiently, making the process interesting for stakeholders on both sides of the glycerol value chain.

²⁴ Periodic report – GLYFINERY, <http://cordis.europa.eu/>, visited 04 November 2011

²⁵ Glycerol spot price from ICIS Feb. 2012.

²⁶ Press Release Solvay: http://www.solvay.com/EN/NewsPress/20120228_epichlorohydrin.aspx

²⁷ Press Release Dow Chemicals: <http://www.dow.com/germany/standort/stade/produkt/hightech.htm>.

²⁸ SRI PEP Report 2011.

Besides aiding the transition from a fossil-based industry to a renewable (bio)-based industry, the process has the potential to also assist in the efforts to implement carbon capture chains, including carbon utilisation. For the immediate reduction of greenhouse gas emissions, carbon capture is an important technology with new technologies being demonstrated throughout Europe.^{29,30} One of the challenges, both technologically and socially, in implementation is finding acceptable storage locations, especially with the societal concerns about the safety of storage of carbon dioxide having become a difficult barrier, as illustrated by various resistance actions.^{31,32} Public involvement and good communication will overcome these challenges.³³ Showing that CO₂ can be used as a valued raw material will help in improving its perception by the public and will allow for an acceleration of carbon capture and utilisation implementation.

Next to the relevance for large industrial companies, CyclicCO₂R has contributed to strengthening the position of European SME's. In their communication COM(2008) 394 final *"Think Small First: A Small Business Act for Europe"*, the Commission stated that our capacity to build on the growth and innovation potential of small- and medium-sized enterprises (SMEs) will be decisive for the future prosperity of the EU. In a globally changing landscape characterised by continuous structural changes and enhanced competitive pressures, the role of SMEs in our society has become even more important as providers of employment opportunities and key players for the well-being of local and regional communities. This is stressed specifically in the EUROPE 2020 strategy, which states:

"The EU needs an industrial policy that will support businesses – especially small businesses – as they respond to globalisation, the economic crisis and the shift to a low-carbon economy, by:

- *supporting entrepreneurship – to make European business fitter and more competitive*
- *covering every part of the increasingly international value chain – from access to raw materials to after-sales service"*

Vibrant SMEs will make Europe more robust to stand up against the uncertainty thrown up in the globalised world of today. This project had a large SME input and enabled FeyeCon and CRI (both SMEs) to broaden their knowledge base and increase their experimental and innovative capabilities through the construction and operation of the laboratory and mini-plant processes, which can be extended beyond the project to further applications based on CO₂. The types of reactors, in which gas, fluid and solid are contacted together in combination with by-product removal and product separation will become increasingly important as processes become more intensified. Process intensification is of specific value in reducing energy consumption, waste production and reducing the carbon footprint of (chemical) industry.³⁴

Through the participation in this consortium, the SMEs collaborated with prime RTOs and academic partners in the field of CO₂ utilisation within Europe, while also being directly connected with key industrial stakeholder, Evonik. This enhanced the transfer of knowhow, thus strengthening the collaborative backbone of the European industry. Furthermore, one of the partners within the consortium was the joint director of the CO₂Chem network, ensuring connection to the CO₂ utilisation community within Europe. These aspects all ensured that the project was directed towards achieving the EUROPE 2020 objectives:

²⁹ Overview of the CCS project Network; 10 May 2011; Network dissemination event; CCS network press release.

³⁰ http://en.wikipedia.org/wiki/Carbon_capture_and_storage; accessed 28 October 2011.

³¹ http://www.expatica.com/nl/news/local_news/CO2-storage-meets-resistance-in-Barendrecht_50221.html; accessed 28 Oct 2011.

³² <http://www.spiegel.de/international/germany/0,1518,710573,00.html>; accessed 28 October 2011.

³³ Review of the Public Participation Practices for CCS and non-CCS projects in Europe; Institute for European Environmental Policy; January 2010.

³⁴ <http://www.energietransitie.nl/publicaties/report-european-roadmap-for-process-intensification-0>

- *Harnessing EU-scale networks to give our businesses (especially small manufacturing firms) an additional competitive advantage*
- *Improving the business environment, in particular for SMEs*

Finally, the work that was performed in this project helped in maintaining advanced technology and experimental facilities, such as the catalyst screening facilities at SINTEF. It increased the understanding of catalyst structure and modelling, as well as the relation between the model and the actual catalyst performance. The developed catalysts and process are examples of high added-value materials and processes that have the potential to create high quality jobs within Europe. The implementation of the process would require knowledgeable personnel in both operation and maintenance, further strengthening the knowledge-based job pool in Europe.

Wider societal implications

The re-use of CO₂ is connected to the greenhouse gas challenge. The World Economic Forum has estimated that, in the coming 10 years, 500 billion US\$ are required to put the world on the trajectory that will stabilize greenhouse gas emissions, with carbon capture and utilisation having been identified as being a key enabler.

The strategy paper “EUROPE 2020 – Smart, Sustainable and Inclusive Growth” shows the commitment of the European Union to enhance a more resource efficient, greener and more competitive economy. The utilisation of CO₂ should be an integral part of this strategy. One of the targets of 2020 is the reduction of greenhouse gases by 20% (even 30%) in comparison to 1990. This ambitious goal requires investing in short-term practical applications and long-term breakthrough solutions. Effective utilisation connects the use of CO₂ through energy efficient processes with the renewable fuel and chemicals markets. The potential is huge. Markets and Markets (M&M) estimated that the renewable chemicals market would grow from €30 billion in 2010 to €52 billion in 2015, which would mean a growth of 11% each year. Sustainability in EUROPE 2020 means, amongst other things, a more competitive, low-carbon economy and new green technologies capitalizing on the leadership of the EU in this field. While the chemicals market will not have a large enough impact on overall CO₂ emissions, the high value products will be used to develop technologies that will eventually lead to the production of bulk chemicals and fuels from CO₂, which will have the dramatic impact necessary to achieve the Europe 2020 goals.

CyclicCO₂R supported this strategy as it used state-of-the-art knowledge to create a showcase sustainable process to incorporate CO₂ in high-value added materials. The target compound was a fine chemical with a promising outlook. With the use of the new process for the production of cyclic carbonates, CO₂ could account for a maximum of 35% by weight of the products. With a current production of 200,000 tonnes of cyclic carbonates per year, the CO₂ incorporation into chemicals could be 70,000 tonnes per year. The creation of new industrial routes to cyclic carbonates would, therefore, in itself have limited impact (total GHG CO₂-equivalent emissions from European industry in 2009 were 321 million tonnes³⁵). This accounts for 7% of the total emissions, with the bulk producers of greenhouse gases being energy production and agriculture and the fine chemical industry directly accounting for less than 0.4% of the greenhouse gas production. The use of cyclic carbonates as replacements for organic solvents could increase the reduction of CO₂ emissions dramatically beyond that possible only for fine chemicals, while also having environmental benefits due to the lower toxicity of most cyclic carbonates. Still, as organic solvents fall into the bulk chemicals category, the impact of greenhouse gas emissions in the fine chemicals sector will therefore always be limited.

³⁵ Annual European Union greenhouse gas inventory 1990-2009 and inventory report 2011, EEA Technical report | 2/2011

The successful application of CO₂ in the efficient production of fine chemicals will pave the way for viewing CO₂ from a different perspective. CO₂ will be viewed as a viable feedstock on which to partly base the industrial production of (fine) chemicals, while acting as a showcase for eventual production of bulk chemicals and fuels from CO₂. In addition, the use of CO₂ will form a strong synergy with the available state-of-the-art knowledge on carbon capture within Europe to create an overall solution to the mitigation of the effects of greenhouse gases in the atmosphere.

Main dissemination and exploitation of results

Dissemination activities

The main objective of the project dissemination activities was to promote CyclicCO₂R and its results as widely and effectively as possible to all relevant stakeholders. All partners were involved in the dissemination sub-project while TNO was the lead partner. The dissemination focus progressed throughout the project in the following manner:

- Period 1: Focus on promoting the project to gain interest and dissemination of first scientific results
- Period 2: Focus on disseminating scientific results through conference presentations and publications
- Period 3: Focus on sharing technical results, networking with stakeholders, and expanding the impact of the project through activities applicable for the general public.

Visibility of the project was ensured through the maintenance of an external website (www.cyclicco2r.eu) with general information on the project and partners, news items, regular updates on future and past events in relation with the project, and publications that could be made available to the general public. The website was found on a regular basis throughout its online existence, with a noticeable spike in traffic after the release of the app CO₂Go (described below).

Towards the scientific community

The first method to broadening awareness of the results in the scientific community was presenting the project at relevant conferences, congresses, workshops and meetings. Throughout the project, 47 oral presentations, posters, and invited lectures were given based on results obtained through the project. The project had a strong showing at each of the International Conferences on Carbon Dioxide Utilisation that took place during the project duration (three in total: Washington, D.C., Singapore, and Sheffield), including the organisation of a networking event at the last conference in Sheffield, UK.

Results were also published that were open for dissemination towards the scientific community. As results were achieved, these were evaluated in view of what would be the optimal manner of dissemination. Intellectual property rights were ensured by following a pre-publication process in which all consortium partners could object in case they felt something should not be published. The IPR regulations were explained and elucidated in several training courses throughout the duration of the project. The list of publications that resulted from the project, 12 in total, is given in Table 3.2. It is possible that up to 8 more publications will become available after the end of the project.

Table 3.2 Publications resulting from the CyclicCO₂R project

#	D.O.I.	Title	Author(s)	Journal	Volume	Date
1	10.1002/chem.201404117	Development of a Halide-Free Aluminium-Based Catalyst for the	J. A. Castro-Osma, M. North, X. Wu	Chemistry - A European Journal	Vol. 20/ Issue 46	07/10/2015

Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide						
2	10.1002/chem.201500790	Synthesis of Cyclic Carbonates Catalysed by Aluminium Heteroscorpionate Complexes	J. Martínez, J. A. Castro-Osma, A. Earlam, C. Alonso-Moreno, A. Otero, A. Lara-Sánchez, M. North, A. Rodríguez-Diéguez	Chemistry - A European Journal	Vol. 21/ Issue 27	26/06/2015
3	10.1002/chem.201504305	Synthesis of Cyclic Carbonates Catalysed by Chromium and Aluminium Salphen Complexes	J.A. Castro-Osma, M. North, X. Wu	Chemistry - A European Journal	Vol. 22/ Issue 6	01/02/2016
4	10.1039/c5fd00061k	New catalysts for carboxylation of propylene glycol to propylene carbonate via high-throughput screening	J.A. Castro-Osma, J.W. Comerford, R.H. Heyn, M. North, E. Tangstad	Faraday Discussions	Vol. 183	01/01/2015
5	10.1002/cssc.201501664	Unprecedented Carbonato Intermediates in Cyclic Carbonate Synthesis Catalysed by Bimetallic Aluminium(Salphen) Complexes	J.A. Castro-Osma, M. North, W.K. Offermans, W. Leitner, T.E. Müller	ChemSus Chem	Vol. 9/ Issue 8	21/04/2016
6	10.1039/C4GC01719F	Sustainable metal-based catalysts for the synthesis of cyclic carbonates containing five-membered rings	J.W. Comerford, I.D.V. Ingram, M. North, X. Wu	Green Chemistry	Vol. 17/ Issue 4	01/01/2015
7	10.1039/C5CC90511G	Highlights from the Faraday Discussion on Carbon Dioxide Utilisation, Sheffield, UK, September 2015	J.A. Castro-Osma, J.R. Dodson, I.D.V. Ingram, M. Moss, M. North, E. Alessandra Quadrelli, L. Quintana-Gómez, D.G. Reed, P. Styring, A. Villa-Zaragoza	Chemical Comm.	Vol. 52/ Issue 2	01/01/2016
8	10.3390/sym8010004	Synthesis of Chiral Cyclic Carbonates via Kinetic Resolution of Racemic Epoxides and Carbon Dioxide	X. Wu, J. Castro-Osma, M. North	Symmetry	Vol. 8/ Issue 1	01/01/2016
9	10.1039/C6CY00134C	Homogeneous and silica-supported zinc complexes for the synthesis of propylene carbonate from propane-1,2-diol and carbon dioxide	J.W. Comerford, S.J. Hart, M. North, A.C. Whitwood	Catalysis Science and Technology	Vol. 6/ Issue 13	01/01/2016
10	10.1021/acscatal.6b01386	Cr(salophen) Complex Catalyzed Cyclic Carbonate Synthesis at Ambient Temperature And Pressure	J.A. Castro-Osma, K.J. Lamb, M. North	ACS Catalysis	Vol. 6/ Issue 8	05/08/2016
11	10.1002/cssc.201601131	A Bimetallic Aluminium(Salphen) Complex for the Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide	X. Wu, M. North	ChemSus Chem	Vol. 10/ Issue 1	10/01/2017
12	10.2174/2213346101666140604215627	Synthesis of Cyclic Carbonates from Polyols and Carbon Dioxide, Urea or Carbon Monoxide	J. Castro-Osma, M. North	Current Green Chemistry	Vol. 1/ Issue 3	04/06/2014

Another responsibility of the project was broadening awareness of the challenges and opportunities the required reduction in greenhouse gases represents. In particular, the future generations will be affected by the accompanying climatic changes due to the greenhouse effect. Several students received their continuing training through the project, as listed in the table below.

Table 3.3: Students and PhD's partly educated within the project

WP	Subject	Gender	Lead beneficiary	Type
7	Photocatalytic reactor testing	M	TNO	Internship
7	Electrocatalytic reactor testing	F	TNO	Internship
7	Photocatalytic and electrocatalytic catalyst exploration and testing	M	TNO	Masters
3	Production of glycerol carbonate (IR) using a packed bed type reactor + Separation GC/water with CO ₂	M	FEY	Internship
1	Synthesis of catalytic intermediates/resting states/dead catalysts	F	SINTEF	Internship
2	Zhang Guo	M	UOY	Masters

New media & interactive tools towards the general public

Following discussions within the consortium, it was decided to develop an app for use on iOS and Android tablets in order to disseminate not only the results of CyclicCO₂R, but also the benefits of CO₂ utilization in general. The app was developed to inform and educate a broad audience, from the general public to policy makers to the scientific community. This was accomplished by having several depth levels which give increasingly more detailed explanations about the technologies and rationale behind recycling of CO₂.

The impact of the app will only be realized when it is widely used. With this in mind, a simple gaming aspect was introduced that allows the user to determine how much of several products can be made from a given source of CO₂. Aspects such as the type of energy that is used to make the products, i.e. from different energy grids or from renewables, and other co-reactants that are needed, i.e. hydrogen and how that hydrogen is produced, were included that allow the user to play with different scenarios. Together with a basic economic calculation, the user "wins" when he can find a scenario that is positive for the environment while still being feasible.

The app "CO₂GO" was completed and officially launched at COP 22 in Marrakech, November, 2016 and is available only on tablets and the Web. It was developed in conjunction with Katy Armstrong of the CO₂Chem Network at the University of Sheffield, UK, since Katy had already much of the background data on electricity mixes and CO₂ footprints of different energy sources.

The app presents eight different products that can be made from CO₂. Four of these products are "chemicals" (acrylic acid, plastics, polyurethanes and formic acid), while the other four are "fuels" (diesel, aviation fuel, methane and methanol). As a basis of the calculations, all products are made from CO₂, H₂ and electricity. The electricity is used both to generate the H₂ and to drive the reaction. The electricity sources are the grid mixes for six different European countries, wind energy and solar energy. If the player chooses renewable energy sources, the number of wind turbines and solar panels are indicated.

Links:

<https://itunes.apple.com/us/app/co2go/id1151795919?mt=8>

<https://play.google.com/store/apps/details?id=com.nomtek.sintef>

<http://co2go.cyclicco2r.eu/>

Next to this, a movie was produced to give the motivation for the project and highlight the issues surrounding reducing CO₂ emissions and CO₂ utilization in general. This task was led by FEY with input from TNO. The movie is available on YouTube at <https://www.youtube.com/watch?v=p0xyfupEPzs>.

Exploitation of results

The exploitation of the results around the specific process developed in the project will be very limited. This is due to a restructuring at the main end-user partner which resulted in there no longer being a focus on the utilisation of CO₂ as a feedstock. At this time, there are no plans to develop the process further.

On the other hand, the sub-results will be exploited in different ways with each of the partners. The SME's, FeyeCon and CRI, have strengthened their frontrunner positions in CO₂ utilisation technologies and expanded their portfolios into the area of chemicals production. The challenges of the work gave focus to the development of a very energy efficient process, automatically leading to flow chemistry and process intensification, both important topics for today's chemicals sectors.

The research institutes, SINTEF and TNO, have increased their existing knowledge in the fields of catalysis and process intensification, respectively. The work has strengthened their positions in the CO₂ utilisation knowledge domain and is expected to result in numerous follow-up research projects, also broader than CO₂ utilisation. Their knowledge base has been increased in CO₂ technologies, a field whose future developments will be of increasing importance, while training employees in this field will strengthen the knowledge-intensive job market.

The universities of York, RWTH Aachen, and Twente have strengthened their positions in catalysis, specifically CO₂ catalysis, while at the same time valorising the knowledge they already had in this area. The project enabled them to educate ambitious researchers in the field of CO₂ utilisation and catalysis (modelling), thereby ensuring future developments in high value-added catalyst materials. The several conference presentations and publications from the academic partners have greatly increased their visibility and are expected to result in at least two follow-up projects in the near future for each institute.

4 Project public website and relevant contact details

The project website provides background information on the project and partners, along with publicly available presentations and other media. The website can be found at <http://www.cyclicco2r.eu/>.

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