Electrochemical COnversion of CARBohydrates (ECOCARB)

Ted Slaghek, Johan Timmermans, Roel Bisselink (WFBR), Dhruva Marathe, Erwin Giling, and Saskia Bubberman (TNO), Harry Raaymakers (COSUN), Erik Hagberg (ADM), and Roel Bosschaerts (ECOVER).

PUBLIC

WAGENINGEN
UNIVERSITY & RESEARCH

Electrochemical **CO**nversion of **CARB**ohydrates (ECOCARB)

Authors Ted Slaghek, Johan Timmermans, Roel Bisselink (WFBR), Dhruva Marathe, Erwin Giling, and Saskia Bubberman (TNO), Harry Raaymakers (COSUN), Erik Hagberg (ADM), and Roel Bosschaerts (ECOVER).

Wageningen Food & Biobased Research
Wageningen, January 2024

Public

Report 2492
DOI: 10.18174/639790

WFBR Project number: 6220119900
Version: Final
Reviewer: Jacco van Haveren
Approved by: Chris Claesen
Carried out by: Wageningen Food & Biobased Research
This report is: Public

The research that is documented in this report was conducted in an objective way by researchers who act impartial with respect to the client(s) and sponsor(s). This report can be downloaded for free at https://doi.org/10.18174/639790 or at www.wur.eu/wfbr (under publications).

"Het project is uitgevoerd met subsidie van het Ministerie van Economische Zaken en Klimaat en het Ministerie van Landbouw, Natuur en Voedselkwaliteit, Nationale regelingen EZK- en LNV-subsidies, Topsector Energie uitgevoerd door Rijksdienst voor Ondernemend Nederland."

PO box 17, 6700 AA Wageningen, The Netherlands, T + 31 (0)317 48 00 84, E info.wfbr@wur.nl, www.wur.eu/wfbr.

Contents

1 Summary and aim of the project

Electrochemistry is an ideal tool for converting carbohydrates to a broad range of products. It is characterized by high energy efficiency, high selectivity, ambient conditions, and the potential to utilize green electricity directly. Combined with the biobased original of the feedstock, this can allow significant reduction of the carbon footprint. This project will develop and demonstrate, together with the industry, a novel electrochemistry based methodology for the production of alternatives for polyacrylates, which have a broad range of uses (e.g. as detergents). Replacing the currently used polyacrylates by electrochemically produced bio-based alternatives will both benefit the reduction of CO_2 and reduce waste production. Furthermore, the electrochemical process will produce hydrogen at the counter electrode. This hydrogen will be used for the reduction of bio-based feedstock such as fructose to mannitol, resulting in a total usage of the electrochemical process – again increasing energy efficiency. Therefore this project will design and develop such an electrochemical process using bio-based feedstock (soluble [poly] saccharides such as sucrose and inulin). Also this project will develop a benign granular starch oxidation process using milder conditions than currently used, aiming at lower carbohydrate loss whilst simultaneously reducing drying energy use.

The project was executed with the following partners in alphabetical order: ADM, COSUN. ECOVER and TNO together with WFBR. ADM delivered the starch compounds, COSUN delivered the sucrose and inulin and performed tests on calcium sequestering efficacy, Unfortunately ECOVER was not able to do the washing trials within the project, TNO took care of the scale up of the electrochemistry and WFBR developed the electrochemistry on lab scale.

2 Samenvatting in het Nederlands

2.1 Introductie

Elektrochemie is een ideale manier om koolhydraten (in dit project is gebruik gemaakt van oplosbaar zetmeel [granulair zetmeel gaf te veel problemen in de huidige opstelling], inuline en sucrose) te kunnen modificeren en verschillende producten te kunnen produceren. De modificatie van koolhydraten gebeurt veelal bij kamer temperatuur, met hoge efficiëntie van groene stroom en waar mogelijk bij hoe selectiviteit. Deze combinatie kan ervoor zorgen dat de 'carbon footprint' van producten, die op deze manier worden geproduceerd, significant omlaag kan worden gebracht. Het ECOCARB project laat zien dat het mogelijk is om samen met industriële partners alternatieven voor polyacrylaten te synthetiseren (oxidatie met 4-acetamido TEMPO als intermediair) via elektrochemie die de potentie hebben een breed palet aan toepassingen (o.a. wasmiddelen) kunnen hebben. Naast het verlagen van de 'carbon footprint' zorgt deze manier van produceren ook de vorming van afvalstromen. Het gebruik van elektrochemie, waarbij een anode en een kathode nodig is om een stroom te kunnen laten lopen door het systeem, geeft de optie dat tegelijkertijd aan de niet werk electrode (in het geval van ECOCARB de kathode) ook een modificatie kan plaats vinden. In ECOCARB is dit waterstof maar het kan ook een andere modificatie zijn, bijvoorbeeld een reductie (aan de anode vindt de oxidatie plaats). In dit project is onderzocht of aan de kathode de reductie van fructose mogelijk is naar mannitol en sorbitol. Hiermee wordt de efficiëntie van het elektrochemische proces verhoogd.

The is project is samen de volgende partners in alfabetische volgorde uitgevoerd: ADM, COSUN, ECOVER en TNO. ADM heeft de oplosbare zetmelen geleverd, COSUN de inuline en sucrose, ECOVER zou was experimenten uitvoeren en TNO heeft de opschaling van het lab proces uitgevoerd.

2.2 Resultaten en conclusies

2.2.1 Resultaten

In dit project zijn zetmeel, inuline en sucrose gebruikt voor de elektrochemische oxidatie met 4-acetamido-TEMPO als intermediair. Het project is begonnen door op lab schaal de condities, waaronder de oxidatie van de koolhydraten maximaal kan verlopen met een minimum aan nevenreacties, te onderzoeken. De eerste stap is door middel van cyclische voltammetry deze condities te bepalen. Vervolgens zijn deze condities toegepast op oplosbaar zetmeel en inuline. Gebleken is dat met een kleine verandering van reactietemperatuur een nagenoeg volledige omzetting van oplosbaar zetmeel en inuline mogelijk is.
Deze lab condities zijn vervolgens als basis genomen voor de opschalingsexperimenten die bij TNO zijn uitgevoerd. Gebleken is dat de lab condities goed zijn te vertalen richting de opschaling. TNO geeft gebruik gemaakt van een 100 cm^2 anode gemaakt van carbon felt (dit een koolstof elektrode met een groot oppervlak). Uiteindelijk is het TNO gelukt om monsters te produceren van de drie gekozen koolhydraten voor eerste testen als calcium inhibitoren. Helaas laten de testen zien de geoxideerde koolhydraten niet dezelfde hoeveelheid calcium kunnen invangen als vergelijkbare producten die op de markt zijn.
Ook is in project onderzocht of aan de kathode het mogelijk is om fructose te reduceren tot mannitol en sorbitol. Na een uitgebreid literatuur zijn een tweetal mogelijke elektrode materialen naar voren gekomen, namelijk lood en indium. Beide metalen zijn getest en gebleken is dat de selectiviteit tussen mannitol en sorbitol niet aanwezig is en date de opbrengsten van de gereduceerde producten niet hoog was.

2.2.2 Conclusies

De conclusies van dit project zijn:

- Het is mogelijk om 4-ac-TEMPO te activeren met behulp van elektrochemie.
- Carbon felt als anode materiaal werkt goed als het gaat om 4-ac-TEMPO te activeren.
- De oxidatie van koolhydraten met behulp van de ontwikkelde elektrochemie is mogelijk zolang er gebruik gemaakt kan worden koolhydraten, die goed oplosbaar zijn in water en geen hoge viscositeit opbouwen tijdens het oxidatieproces. Daarom is het gebruik van langketenig zetmeel geen optie.
- De gebruikte koolhydraten (sucrose, inuline en goed oplosbaar zetmeel) kunnen tot bijna 100% worden geoxideerd.
- De verkregen geoxideerde koolhydraten hebben geen goede calcium bindende eigenschappen.
- Het is mogelijk om fructose te reduceren aan de kathode tot sorbitol en mannitol.
- Zowel lood als indium lijken te voldoen als electrode materiaal voor de reductie van fructose.
- De reductie van fructose moet geoptimaliseerd worden.

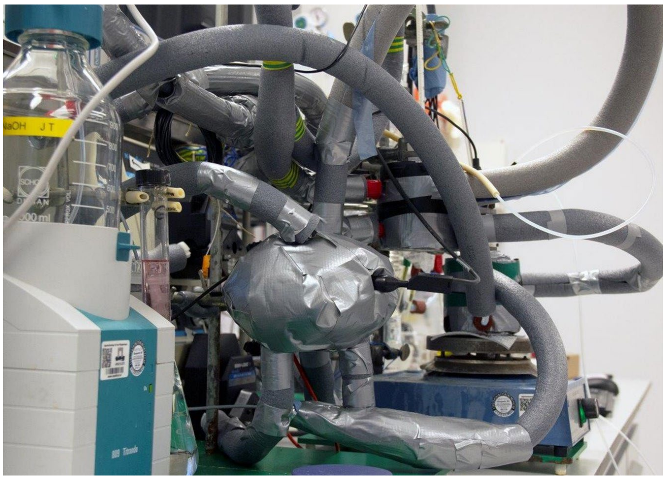
3 Results obtained, conclusions, hurdles taken and future prospects

3.1 Results obtained

The project was divided onto 4 work packages as indicated below aiming at the oxidation of starch, sucrose and inulin and the reduction of fructose. The oxidation chemistry was focused on the use of TEMPO mediation. This specific type of oxidation targets the primary hydroxyl groups in carbohydrates. TEMPO is usually activated by another oxidant such as sodium hypochlorite. This project will use instead of sodium hypochlorite electrochemistry for the activation of TEMPO which subsequently will oxidize the primary hydroxyl groups present in the carbohydrates.

WP	Short Description	Category: IO of EO	Performers	Result	Timing
1	Builder from oxidised polysaccharides	**EO**	**WFBR**, ADM, Cosun, Ecover, TNO	Development of electro-chemical oxidation process which is ready for upscaling	M1 – M24
2	Builder: Sucrose oxidation	**EO**	**TNO**, Cosun, WFBR, Ecover	Electrochemical process developed	M1 – M24
3	Fructose reduction to mannitol	**EO**	**WFBR**, Cosun, ADM, TNO	Electrochemical process developed	M1 – M24
4	Dissemination	**IO**	**WFBR**, TNO, Cosun, ADM, Ecover	Clear view on dissemination strategy	M20 – M24

The project started with the lab scale experiments and a specific set up was designed to follow the progress of the oxidation as shown in the picture below. The design included pH and temperature control. At specific intervals aliquots were taken for analysis by LC-MS for monitoring the progress of the oxidation.



Lab scale set up of the electrochemical oxidation.

The lab scale experiments started with circular voltammetry experiments in order to determine the optimal conditions for the activation of TEMPO in the presence of carbohydrates. The results of the cyclic voltammetry experiments showed that the optimum conditions for performing the electrochemical oxidation using TEMPO were at pH 9 with a potential between 0.5 and 0.6 V and keeping the temperature around 10°C. Once these conditions were determined the next step was to perform the actual oxidation chemistry on the chosen carbohydrates for each of the chosen carbohydrates, sucrose, inulin and readily soluble starch. In the end all these carbohydrates could be oxidized to near completion.

Once the lab scale experiments were finished, obtaining satisfactory results, such as a high degree of oxidation, after optimization of the reaction conditions. The optimized reaction conditions were transferred to TNO for up-scaling the electrochemical conversion process. A picture of equipment used at TNO is given below.

Scale up facility at TNO

At TNO the research started by validating experimental results generated on lab scale. In the end an electrolyser having 100 cm^2 electrodes of carbon felt were used for the electrochemical oxidation and products were generated for application testing.

The isolated products from the upscaling experiments were tested on the application as builder and anti-scale inhibition. Results show that builder properties did not reach the results which are achieved with current additives used in detergent formulations. Also in scale inhibitions the products obtained did not reach the desired threshold.

Concerning the fructose reduction after a thorough search in literature lab scale experiments were conducted using indium and lead electrodes. Unfortunately these experiment these did not reveal a high turnover to sorbitol and mannitol and also there was no preference for one over the other.

3.2 Conclusions

The conclusions of this project are:

- It is feasible to activate 4-ac-amio TEMPO using electrochemical conditions.
- Carbon felt as the anode works well in the activation of 4-ac-amido-TEMPO.
- The oxidation of carbohydrates using the developed electrochemical system is feasible as long as the carbohydrates are soluble in water and do not build up viscosity. Therefore long chain starches such as pre-gelled starch and granular starch are less suitable.
- The carbohydrates used in this research (sucrose, inulin and readily soluble starch) can be oxidized to near completion.
- The oxidized carbohydrates do not perform well as calcium sequestering agents or as calcium inhibition additives.
- It is feasible to electrochemically reduce fructose at the cathode into sorbitol and mannitol.
- Both lead and indium seem to be good electrodes for the reduction of fructose.
- Optimisation is necessary in order to increase the yield of sorbitol and mannitol.

3.3 Hurdles that had to be taken

During the course of the project different hurdles had to be addressed. They will be discussed separately.

3.3.1 The use of granular and high molecular weight soluble starch

In the beginning the project was aimed at granular and high molecular weight starches. During the experiment on lab scale with the equipment used the increase in viscosity and the granular form of starch were clogging the system. Therefore we abandoned this route and focused on readily soluble starches for the oxidation.

3.3.2 Larger batches

Unfortunately the scale up experiments did not reach the amount of product that is needed for washing tests. There it was decided that via a conventional route oxidized starch would be produced benefitting the washing trials. Unfortunately within the time frame of the project ECOVER was not able to perform these washing trials.

3.3.3 Downstream processing

In end quite some effort has to be performed in obtaining pure compounds. Especially desalting after the electrochemical oxidation was an issue which was resolved in the end.

3.3.4 Future perspective

The project has clearly shown that it is feasible to modify carbohydrates using electrochemistry. This opens the possibility for other routes to convent carbohydrates into valuable compounds. At this moment several options are under discussion

3.4 Contribution to the program

This project has contributes to MMIP 6 section 2, aim of the project is to close production chains, and use of bio-based raw material. By using electrochemistry for the production of products the project also showed that the use of renewable electricity is feasible for the modification of carbohydrates and therefore contributes to MMIP 8. As such the ECOCARB project addressed both the TKI Energy & Industry program lines 2 (Electrification of processes) and program line 3 (Circular raw materials, processes and products). Electrification is addressed by the development of a successful electrochemical conversion technology both on lab scale and already achieved a first scale up. Starting from a natural circular feedstock (biomass, and more specifically sugars), fully circular products have been produced for the envisaged applications.

3.5 Spin-off within and outside

At the moment the status of the technology spin-offs are not a topic at the moment. The companies involved are currently evaluating the results and deciding how to progress with the results obtained.

3.6 Publications

At the moment the current status of the project does not allow for publications describing in detail the results of this project. In the near future a non-scientific publication is fore seen that will be published on the websites of TNO and WFBR.

3.7 Report request and contact person

If there is the desire to obtain a copy of this report than an email should be sent to: ted.slaghek@wur.nl.

To explore the potential of nature to improve the quality of life

Wageningen Food & Biobased Research
Bornse Weilanden 9
6708 WG Wageningen
The Netherlands
E info.wfbr@wur.nl
wur.nl/wfbr

Report 2492

The mission of Wageningen University & Research is “To explore the potential of nature to improve the quality of life”. Under the banner Wageningen University & Research, Wageningen University and the specialised research institutes of the Wageningen Research Foundation have joined forces in contributing to finding solutions to important questions in the domain of healthy food and living environment. With its roughly 30 branches, 7,600 employees (6,700 fte) and 13,100 students and over 150,000 participants to WUR’s Life Long Learning, Wageningen University & Research is one of the leading organisations in its domain. The unique Wageningen approach lies in its integrated approach to issues and the collaboration between different disciplines.