Format rapportage projectinformatie PPS-en TKI BBE

Datum versie: 7 december 2020

Uit projectplan (svp zoveel mogelijk invullen)

1. Projectinformatie

1.1 Organisatie/financiering *(keuze maken)*	TKI BBE/WR-PPS/overig
1.2 Projectnummer	**BBE-1705**
1.3 Project titel	**EC2Fuels**
1.4 Projectleider	**G. Mul – G.Mul@utwente.nl**
1.5 Startdatum (*dd-mm-jjjj)*	**1-10-2017**
1.6 Einddatum (*dd-mm-jjjj)*	**31-12-2020**

2. Projectomschrijving

2.1 Samenvatting *Geef een korte samenvatting van wat het project inhoudt en beoogt. Het gaat om een publiek beschikbare samenvatting (doel, bijdrage aan de missie, op te leveren resultaten in termen van kennis voor doelgroep x en de partners in het project).*

'EC2Fuel' has investigated the feasibility of sustainable, electrochemical conversion of liquid biomass derived products ('bioliquids') into fuel intermediates or precursors. Reactions include the decarboxylation of acids and C-C-bond formation with concomitant evolution of CO_2 (the socalled electrochemical *Kolbe* reaction), and cathodic, H^+ and e^- induced, hydrogenation of ketones to alcohols. These reactions are an alternative for unsatisfactory catalytic hydrogenation technology, and essential for the exploitation as transportation fuels of bio-oil resources by the industrial partner BTG.

Research activities have focused on Pt (for *Kolbe*) and Cu (for hydrogenation) catalysts. In laboratory electrochemical cells, the effect of the composition of the electrolyte, including pH and (a combination of) substrates, has been evaluated, aiming to generate data for the future development of redox flow cells at mild operating conditions and modest scales, while allowing a flexible and easy integration with renewable electricity.

A laboratory scale cell was constructed for *Kolbe* electrolysis of acetic acid, in which Pt electrodes were found quite feasible in batch operation, but only at a pH ~4.

A laboratory scale cell was also constructed for aldehyde hydrogenation, in which butanal and croton aldehyde were evaluated *Kolbe* electrolysis of acetic acid, in which Pt electrodes were found quite feasible in batch operation, but only at a pH ~4.

2.2 Doel van het project *Wat gaat het project bijdragen aan de doelen van de KIA?*

The chemical industry in the Netherlands needs to decrease its environmental footprint, in particular by lowering emission of CO_2, associated with the use of fossil resources for the production of fuels and chemicals. In this project technology has been evaluated which might contribute to these goals.

2.3 Motivatie *Licht toe waarom dit project passend en nodig is voor de KIA*

Utilization of Biomass and renewable electricity are means to decrease the environmental footprint of the chemical industry. However, pyrolysis oil, produced from wood, does not have the desired composition to be easily converted in a clean, environmentally benign fuel. In particular the oxygen levels of the oil are too high to allow socalled cracking in an oil refinery. An essential step in the conversion and stabilization of biomass related (pyrolysis) oils is the selective functionalisation of oxygen containing molecules. The required hydrogenation reactions are currently deployed in reactors operated at elevated temperatures, applying hydrogen at high pressures (approx. 200 bar) in the presence of heterogeneous catalysts. Unfortunately, often these catalysts suffer from deactivation, limiting practical application. Interestingly, one other possibility to stabilize and convert biomass related pyrolysis oils, is by electrochemical techniques.

2.4 Resultaat *Zo SMART mogelijke beschrijving van de beoogde resultaten van het project. Het gaat om zowel de inhoudelijke resultaten (in relatie tot vraag 2.2) als resultaten zoals bijeenkomsten en rapporten. Geef zoveel mogelijk ook de planning per jaar.*

The proposal was aiming at the following results:

Table A. The State of the Art and advances beyond for prototype and process development in EC2Fuel

	Existing	**EC2Fuel**	**TRL** 2017/2019	**Outcome EC2Fuel**
Feed	model components; CO_2, levulinic acid, acetone, ..	Technical feed such as pyrolysis liquids	*2 / 4*	Fundamental understanding
Electrochemistry				
(single cell) reactor	model components, batch, small scale	prototype, testing	*3 / 4*	Understanding Catalysts, Electrode and Membrane (CEM) assembly
Continuous reactors	N/A	prototype (24/7)	*2 / 4*	Reactor system bench scale
Catalysts, Electrodes, membrane	screening done on 'standard' precious metals, oxides, ..	dedicated catalysts for oxidation / reduction	*2 / 4*	Parts for prototype testing

Several of these results have been achieved as indicated in the following.

Model component testing for fundamental understanding

Kolbe electrochemistry of acetic acid.

Various electrode materials have been screened for performance, but the majority of electrode materials were instable (such as graphite, carbon based electrodes), or produced excessive quantities of O_2, such as Ni electrodes (in situ transformed into NiO/NiOOH). Another alternative material material showing promising initial results is Boron Doped Diamond, but again instability was observed, and therefore the study mainly focused on Pt as anode, of which the surface is likely oxidized (PtO) during electro-oxidation of acetic acid.
All measurements were carried out in a single compartment (100 ml) three electrode glass cell equipped with a platinum foil (0.025mm thick, 99.9% pure, Alfa Aesar) working electrode (1 cm^2 geometric area), a platinized titanium mesh (Magneto Special Anodes B.V.) counter electrode (4 cm^2 geometric area) and an Ag/AgCl (3M NaCl, ProSense) reference electrode, connected to a Biologic VMP3 Potentiostat. Gaseous products were analysed by gas chromatography (GC, Interscience CompactGC, the Netherlands). Light gases (H_2, O_2, CO_2) were detected with a ShinCarbon micropacked column (ST 80/100 2m, 0.53mm at 90°C) connected to a thermal conductivity detector (TCD) at 110°C. Hydrocarbons (C1-C4) were detected on a Rt Q BOND PLOT

(0.32mm ID, 10µm, 15m, at 60°C) column connected to a flame ionization detector (FID) at 150°C. Gaseous products were collected using a He (5.5) purge at a constant flow rate of 30 mL/min. External calibration was performed individually for the possible products. The cell and GC analysis was successfully evaluated and the GC calibrated (Batch, small scale reactor indicated in the Table).

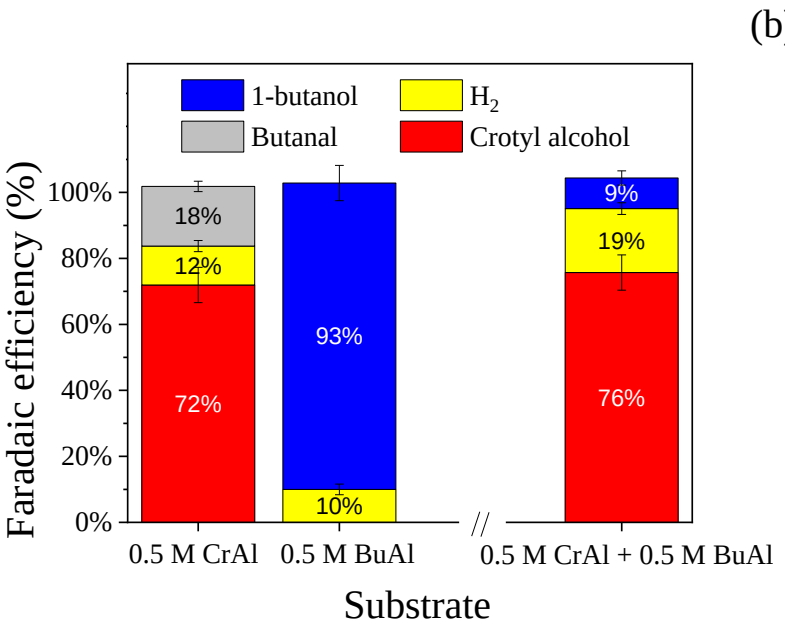
Using this equipment, we have shown that the electrochemical conversion of acids is feasible with high selectivity (preventing the excessive formation of oxygen) using Pt electrodes (Deliverable D2). A detailed investigation on the electrolyte pH for Kolbe electrolysis of acetic acid was performed. At mildly acidic pH, the high concentration of free carboxylate ions, and the low solubility of carbon dioxide in the electrolyte, resulted in high (>95%) and stable ethane production. At low pH, the selectivity to ethane was low, because of excessive formation of O_2. Furthermore, at strongly alkaline conditions (pH 9 and 12), deoxygenation was less effective, since a shift from ethane to the formation of methanol was observed, likely associated with the dissolution of CO_2 and formation of (bi)carbonate. It can thus be concluded that the selectivity during Kolbe electrolysis of acetic acid towards deoxygenation and formation of ethane is favored at a pH of ~4.

Hydrogenation of butanal and croton aldehyde

An H-type electrochemical cell was used to conduct all experiments at room temperature (25 ± 1 ^{o}C) and atmospheric pressure (1 bar) using a Bio-logic VMP-9 workstation. Fresh cathode, membrane and electrolytes were used for each new experiment to avoid cross-contamination. The cathodic compartment housed the working electrode (copper foil with a geometric area of 0.75 cm^2) and the reference electrode (Ag/AgCl, 3.5 M KCl), and was filled with 50 mL of a solution containing a known concentration of BuAl or CrAl mixed with 0.5 M potassium acetate buffer (0.45 M KAc and 0.05 M HAc, pH 5.5) as supporting electrolyte and stirred at 500 rpm with the use of a magnetic stir bar. The anodic compartment housed the counter electrode (platinum mesh) and was filled with 50 mL of 0.5 M of either H_2SO_4, $NaClO_4.H_2O$ or NaOH, depending on the experiment. Both compartments were separated by a Nafion 117 membrane pre-activated in solutions of H_2O_2 (30 wt%) and H_2SO_4 (1 M) for 30 minutes at 60 ^{o}C, followed by rinsing with H_2O to remove excess of acid. The catholyte was bubbled with 10 sccm of Helium (99.999%, Linde) for 15 minutes previous to each measurement. Butanal (BuAL) and crotonaldehyde (CrAl) were selected as model molecules for the electrochemical hydrogenation of aldehydes. Gas products were continuously collected from the catholyte headspace and directed inline to a gas chromatograph (CompactGC 4.0, Interscience) containing both FID and TCD detectors for identification of hydrocarbons (i.e. butane, butene) and H_2, respectively. Liquid products (i.e. crotyl alcohol, butanal, 1-butanol) were hourly analyzed in a GC Agilent 7810A, after catholyte sampling (0.5 mL) and pH measurement (pH meter MODEL).

To evaluate the reactivity of aldehydes, also *in situ* surface analysis was performed. All spectro-electrochemical experiments were performed in a homemade three-electrode setup, containing a polycrystalline copper foil, a platinum mesh and a Ag/AgCl electrode (3 M NaCl, BASi) as working, counter and reference electrode, respectively.

Copper electrodes were found to be quite feasible for the selective hydrogenation of aldehydes. Butanal was found to adsorb perpendicularly to the copper surface through bidentate binding, favoring 1-butanol formation under high surface coverage conditions with a remarkable selectivity of 93% at -0.8 V vs RHE (-15 mA.cm^{-2}) relative to the formation of Hydrogen. This is shown in the figure below (middle column, in 0.5 M Butanal). The Copper surface is also effective for the electro-hydrogenation of Croton aldehyde (left Column) showing 90% selectivity (Faradaic Efficiency) towards the hydrogenation products in comparison to Hydrogen. Of the 90%, 72% efficiency towards the reduction of the aldehyde functionality is observed (yielding crotyl alcohol), while only 12% selectivity towards hydrogenation of the C=C double bond of the molecule is observed, yielding butanal.



The Cu electrode was substrate specific in mixtures of butanal and croton aldehyde. The specificity towards croton aldehyde is very high (compare the product distribution in the left with the right column). In the presence of croton aldehyde butanal is hardly converted, and only 9% 1-butanol is formed. Raman spectroscopy demonstrates this is likely due to a very strong adsorption of crotonaldehyde on the Cu surface through the C=C bond, preventing adsorption of butanal. Our work shines light on the importance of the chemical nature of bio-oil components and their interaction with electrode surfaces and their effect on adsorption geometries and product selectivity. In particular if the oil would contain (even small amounts) compounds containing C=C bonds, these would limit the conversion of butanal-like molecules without conjugated systems.

Jaarrapportage (svp ook laatste jaar invullen)

3. Status project

3.1 Status project *(keuze maken)*	Project has been finished
3.2 Toelichting incl. voorziene wijzigingen t.o.v. het oorspronkelijke werkplan	• Due to the complexity of the analysis of 'real' pyrolysis oil, these compositions have not yet been evaluated in electrochemical upgrading • So far, the electrochemistry has been evaluated in batch operation. While preliminary data have been obtained for flow reactors (prototype testing), further research is necessary to derive valuable scientific data from these experiments.

4. Behaalde resultaten

4.1 Korte beschrijving van de inhoudelijke resultaten en hun bijdrage aan de KIA (zoals beschreven in 2.2)
4.2 Deliverables (bijeenkomsten en andere output, die niet benoemd wordt in 4.3 en 4.4)
4.3 Communicatie (lijsten)
4.3.1 Wetenschappelijke artikelen en hun doi (*Digital Object Identifiers)*
4.3.2 Rapporten/artikelen in vakbladen
4.3.3 Overige communicatie-uitingen (inleidingen/posters/radio-tv/social media/workshops/beurzen)
4.4 Overige resultaten: technieken, apparaten, methodes
4.5 Projectwebsite: geef het adres van de projectwebsite (indien beschikbaar)

Eindrapportage

5. TRL bij afsluiting van een project

Technology Readiness Level (TRL) van de technologie bij afsluiting van het project. Er zijn twee indicatoren die verschillen in detailniveau. Vul zo mogelijk het detailniveau in. Als dat niet mogelijk is, vul dan de hoofdcategorie in.

5.1 Hoofdcategorie *(keuze maken)*	Fundamental Reasearch
5.2 Detailcategorie bij start van het project *(in cijfers, nummer van de betreffende categorie, zie bijlage voor toelichting)*	Aim was to have a working demonstration of the Kolbe electrolysis in he laboratory, which has been achieved at TRL 3/4
5.3 Detailcategorie bij afsluiting van het project	TRL 3/4

6 Status project bij afronding

Status project *(keuze maken)*	1. Het project is afgerond conform de oorspronkelijk scope. Alle mijlpalen zijn behaald.

7 Output over het hele project

		aantal
7.1	**Aantal gerealiseerde wetenschappelijke publicaties** *gepubliceerde artikelen in peer-reviewed journals*	-
7.1 lijst	Zie lijst onder 4.3.1 voeg evt. artikelen uit eerdere jaren toe (incl. doi)	-
7.2	**Aantal verwachte wetenschappelijke publicaties**	2
7.2 lijst	Electrochemical hydrogenation of butanal and crotonaldehyde on copper surfaces, *Liniker de Sousa[1], Robbie Venderbosch[2], Guido Mul[1]** *(1) Photocatalytic Synthesis Group, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.* (2) *Biomass Technology Group BV, Josink Esweg 34, 7545 PN Enschede, The Netherlands.* --- Study on the effect of electrolyte pH during Kolbe electrolysis of acetic acid on Pt using real-time monitored product selectivity *Margot Olde Nordkamp[1], Bastian Mei[1], Robbie Venderbosch[2], Guido Mul*[1]* *(1) Photocatalytic Synthesis Group, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.* (2) *Biomass Technology Group BV, Josink Esweg 34, 7545 PN Enschede, The Netherlands.*	
7.3	**Aantal gerealiseerde niet-wetenschappelijke publicaties**	-
7.3 lijst	Zie lijst onder 4.3.2 voeg evt. publicaties uit eerdere jaren toe	-
7.4	**Aantal aangevraagde patenten**	-
7.4 lijst	Geef van elk patent de doi, wanneer beschikbaar	-
7.5	**Aantal verleende licenties**	-
7.5 lijst		
7.6	**Aantal prototypes**	-
7.6 lijst		
7.7	**Aantal demonstrators**	2
7.7 lijst		
7.8	**Aantal spin-offs/ spin-outs**	-

7.8 lijst		
7.9	**Aantal nieuwe of verbeterde producten/ processen/diensten geïntroduceerd**	-
7.9 lijst		

8 Impact

Impact betreft het verhaal van het project: een kwalitatieve omschrijving van hoe het project heeft bijgedragen aan de missies en/of het realiseren van economische kansen. Geef aan wat er met de ontwikkelde kennis/tools uit het project wordt gedaan. Geef een toelichting op de (bredere) bijdrage van het project aan de maatschappelijke uitdaging, zoals verwoord in 1.4b. De genoemde impact kan bijvoorbeeld betrekking hebben op:

- Producten, concepten, kennis e.d. die door de partners in de praktijk worden toegepast (nu of op afzienbare termijn)
- een aansprekend voorbeeld dat onder de output (paragraaf 7) gerapporteerd is;
- (nieuw) inzicht in randvoorwaarden (buiten kennis&innovatie) die nodig zijn om de missiedoelen te realiseren (denk aan financiering, regelgeving, communicatie, etc).
- het bereiken van (nieuwe) partners en het versterken van opgebouwde netwerken;
- verbinding met (praktijkgericht) onderwijs en andere wijzen van disseminatie;

Geef een link naar de website van het project, video of infographic (indien van toepassing).

Beschrijf de impact van het project, *geef evt. ook een link naar de website van het project, een video of infographic (indien van toepassing)*
We have now demonstrated that Pt is a very effective metal at intermediate pH for the electrolysis of acetic acid to ethane and CO_2. This outcome has formed the basis for consecutive research in which the focus lies on the geometry of the Pt electrode, and study of a combination of multiple acids in the feed, leading to complications in the surface chemistry. So the impact lies on input for consecutive research and development of technology. With respect to the electroreduction of aldehydes, the Cu electrodes should also be further developed, with focus on reduction of the affinity for compounds containing C=C functionality, to enhance the conversion of e.g. butanal to 1-butanol. Alternatively, the compounds with C=C functionality need to be removed, before the pyrolysis oil is reductively treated over Cu surfaces. Also the two publications that will be shortly submitted to international journals will contribute to the successful completion of two PhD theses and two PhD graduates (De Sousa, Olde Nordkamp) and these publications also demonstrate the expertise of the PCS group at the UT in electrochemical conversion. This is useful for having future proposals on the subject granted. Finally the project has strengthened the interaction between BTG and the UT, which will lead to reduced time for development of innovative technology of relevance to the company.

Bijlage 1 TRL-categorieën

De detailcategorieën bestaan uit:
TRL 1 – basisprincipes zijn geobserveerd en gerapporteerd
TRL 2 – technologisch concept en/of toepassing is geformuleerd
TRL 3 – kritische functie of karakteristiek is analytisch en experimenteel bewezen
TRL 4 – component of experimenteel model is gevalideerd in laboratoriumomgeving
TRL 5 – component of experimenteel model is gevalideerd in relevante omgeving
TRL 6 – systeem/subsysteem model of prototype is gedemonstreerd in een relevante omgeving
TRL 7 – prototype van het systeem is gedemonstreerd in een operationele omgeving
TRL 8 – daadwerkelijk systeem is compleet en gekwalificeerd door test en demonstratie
TRL 9 – daadwerkelijk systeem is bewezen door succesvol operationeel bedrijf