Biobased Chemistry and Technology
Annual report 2014

WAGENINGEN UNIVERSITY
WAGENINGEN UR

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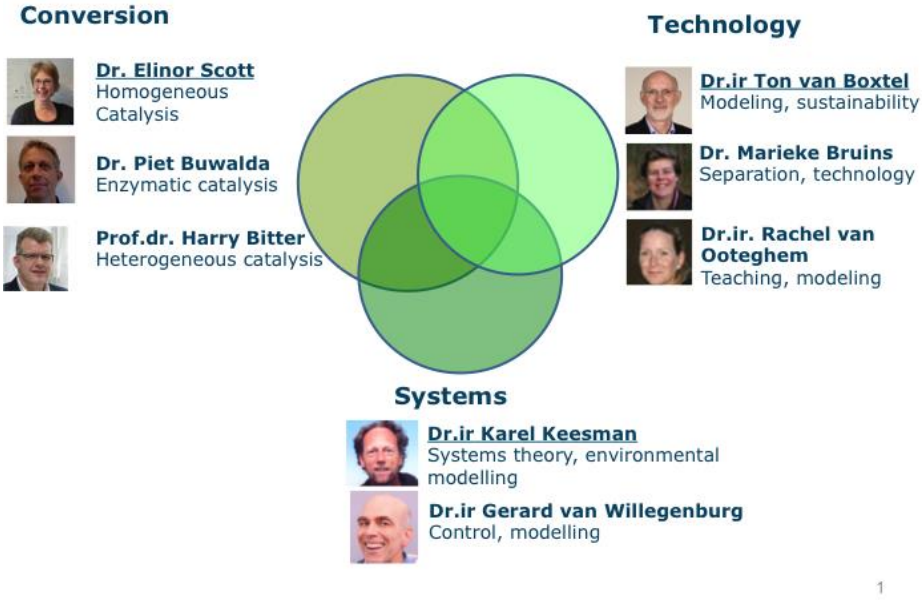
Introduction

It is my pleasure to present to you the annual report 2014 of the Biobased Chemistry and Technology group. 2014 was a year of change. The groups Biobased Commodity Chemistry (BCH) and Biomass Refinery and Process dynamics (BRD) merged to **Biobased Chemistry and Technology (BCT)**. Together we defined the mission of BCT i.e. assisting the transition of a fossil based economy to a biobased economy by investigating and developing integrated solutions on length scales ranging from a global scale (sustainability, linked networks) to a meters scale (reactors, unit operations) to a molecular scale (catalysis, conversion and reaction dynamics). Fundamental understanding is the basis for the required transition and goes hand in hand with applied research to achieve viable, applicable solutions.

We defined three focus areas for the group i.e. conversion, technology and systems which all defined their own goals to achieve the overall mission of the group.



Our research program within the focus areas combines catalytic conversion with technological advancements and (dynamic) modelling. Specific objectives of the group are:

- development of non-noble metal based catalysts
- develop catalysts stable under the specific conditions required for biomass based conversion
- integrate pretreatment, conversion and separation
- integration of sustainability indicators in design procedures for biobased conversion and separation
- design, by modelling and experimentation, processes and whole value chains for the sustainable production of chemicals and fuels from biomass
- dynamic modelling, control and optimization of reactions, reactors and separation systems

- educating young people, at BSc, MSc, PhD level, in basic sciences and applied sciences, to develop the biobased economy.

In this yearly report we give an overview of the achievements of our group with respect to research and teaching in the year 2014.
I hope you will enjoy reading it and my colleagues and I are more than happy to discuss with you on specific topics.

Prof. J.H. (Harry) Bitter
Chair holder Biobased Chemistry and Technology

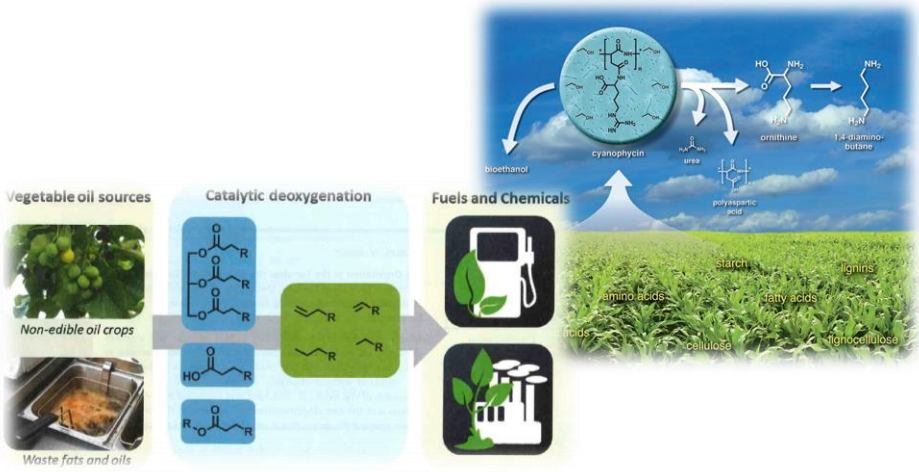
Conversion

Background and goal of this theme

Environmental concerns, fluctuating and every increasing oil prices and security of supply are drivers for the biobased production of chemicals, materials and transportation fuels. In order to achieve this, new (bio)chemical conversion routes and catalyst developments are required. As well as this bio-based molecules offer opportunities for the production of novel and functional materials.

Main topics

- The application of bio-catalysis in integrated conversions of biomass to chemicals
- Integrate pre-treatment, conversion and separation
- Development of non-noble metal based catalysts
- Develop catalysts stable under conditions required for biomass conversion
- Structure function modification of starch based materials



Staff: Dr. Elinor Scott, Dr. Piet Buwalda, Prof. Harry Bitter
PhD students and post-docs: Jurjen Spekreijse, Andrada But, Piet van der Zaal, Luana Souza Macedo, Frits van der Klis, Neus Blanch
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Selective catalytic transformations of non-edible carbohydrates

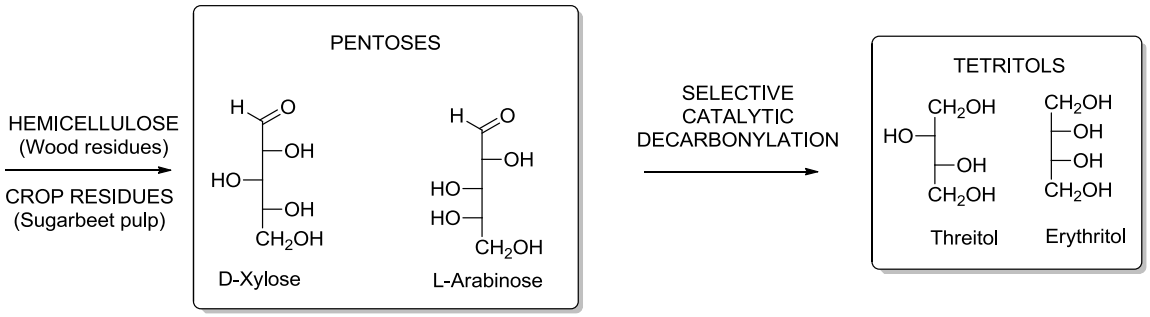
Name PhD: Frits van der Klis
Involved staff members: Prof. dr. Harry Bitter; Dr. Daan van Es;
Dr. Jacco van Haveren
Project sponsor: TKI-programs, CatchBio, EU SPLASH
Start/(expected) end date of project: October 2013 – October 2017

Background and goal of project

In the past years, carbohydrates are shown to be a suitable feedstock for the production of bio-based chemicals such as polymer building blocks. In order to avoid potential conflict with food production, it is desirable to develop novel routes to these bio-based building blocks, starting from the non-edible carbohydrates found in agro-residues, algae and seaweed. The focus of the project is therefore on the selective catalytic conversion of the carbohydrates in sugar beet pulp, a argo residue, (galacturonic acid and arabinose), and seaweeds (uronic acids and galactose).

Highlight of the past year

The C4-polyols erythritol and threitol have proven to be interesting chemical building blocks that can be used as low calorie sweeteners, in coating applications or even for the production of (bio)-butadiene. Fermentation of glucose is currently the only commercial production method for these C4-polyols. An attractive alternative route was investigated: the selective catalytic production of C4-polyols from non-edible C5-sugars (xylose and arabinose).



The aqueous conversion of xylose over a 5wt% Ru/C catalyst was investigated and optimized by using a design of experiment. It was found that an unprecedented high selectivity of 20-25% C4-polyols can be achieved under mild reaction conditions (138 ˚C, 6 bar H_2, and 24 h). A mechanistic study revealed that the dominant reaction mechanism for C5-sugar conversion involves a formal decarbonylation step leading to the initial formation of the desired C4-polyols. Subsequently the formed C4-polyols undergo further terminal C-C scissions to glycerol and ethylene glycol. Remarkably, potentially competing reactions like internal C-C chain scission (fragmentation) or hydrodeoxygenation (HDO) do not occur to any significant extent under the applied conditions.

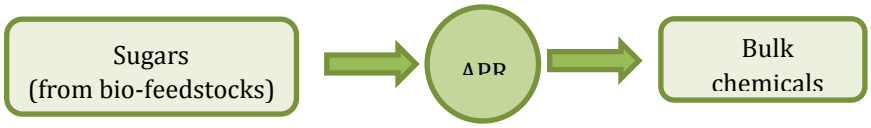
Aqueous phase reforming of Bio-feedstocks

Name Postdoc: Neus Blanch Raga
Involved staff members: Prof.dr. Harry Bitter
Project sponsor: Catchbio
Start/(expected) end date of project: 01/09/14 (2 years)

Background and goal of project
Aqueous phase reforming (APR) of biomass is an attractive method to directly produce hydrogen under mild conditions. APR can process a variety of bio-feedstocks and produces virtually CO free hydrogen using a series of reforming reactions in the water phase at typically 473 K and 25 bar. When lowering the temperature more oxygenated compounds (carboxylic acids) in the liquid phase were observed next to hydrogen in the gas phase.

APR has previously been described for substrates like glycerol, sorbitol and cellulose. Ethylene glycol is often used as model substrate for fundamental studies since it contains the same functionality as the larger polyols but gives fewer by-products. Supported (promoted) platinum-based catalysts have been investigated extensively for the production of hydrogen via APR. More recently, Ni and Cu supported on CNF materials were found to be active for the APR of glycerol and ethylene glycol.

In my research I am investigating how to steer the selectivity of these non-noble metal supported materials in the APR of sugars to bulk chemicals.



Aqueous phase reforming

Highlight of the past year
Ni supported on activated carbon (AC), carbon nanofibers (CNF) and carbon nanotubes (CNT) was prepared by incipient wetness impregnation (IWI) or wet impregnation (WI). Before testing, the catalysts were reduced ex situ at 300ºC for 2h in a H_2/Ar: 30/60 mL/min flow. Next, the reduced catalysts were loaded in an autoclave in a glove bag to prevent exposure to air.

Some reactions were performed in a six parallel autoclave reactor system in an inert atmosphere, at 150ºC and at autogenous pressure. The liquid volume was 25 mL (filling degree 50%). The reactants were 1%wt of glucose or glycerol in water, a KOH/glucose(glycerol) molar ratio of 2 and 100 mg of catalyst. Liquid phase reaction products were analyzed in an HPLC equipment (Aminex column and RID detector) previously calibrated.

With the glycerol we were able to observe oxygenated products (in addition to H_2) as reported before by the previous researcher in this project. For the glucose feedstock the results were inconclusive yet.

Haloperoxidases in the synthesis of bio-based nitriles

Name PhD: Andrada But
Involved staff members: Dr. Elinor Scott, Prof.dr. Johan Sanders
Project sponsor: Wageningen University
Start/(expected) end date of project: 11.06.2012-10.06.2016

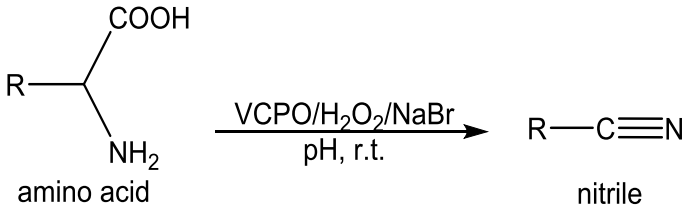
Background and goal of project

Oxygen and/or nitrogen functionalization is required for many chemicals produced from oil. The introduction of these functionalities into hydrocarbons, using reagents like oxygen and ammonia, is energy and capital intensive. Many compounds formed in plants, such as amino acids (AA), already contain these functionalities. For example, glutamic acid can be converted into 3-cyanopropanoic acid, a precursor of acrylonitrile, by a oxidative decarboxylation reaction with HOBr reagent. Vanadium chloroperoxidase (VCPO) from the haloperoxidase enzymes is producing HOBr from NaBr and H_2O_2. The use of VCPO appears to be an efficient and sustainable tool to perform the conversion of amino acids into nitriles (R-CN). The goal of this project is to investigate these reactions and to assess if the proposed route is indeed more sustainable compared to the petrochemical route.

Highlight of the past year

Production and purification of VCPO was finalised in the first part of 2014. A partially purified active VCPO sample was obtained to be further used for the oxidative decarboxylation of amino acids. It was shown that this semi-crude VCPO sample can be used to produce the nitriles and, therefore, can reduce significantly the overall production costs.

In the second part of the year, the conversion of amino acids into the corresponding nitriles by vanadium chloroperoxidase/H_2O_2/NaBr system, was studied (Scheme1.).



Scheme 1. Oxidative decarboxylation of amino acids into nitriles by vanadium chloroperoxidase (VCPO).

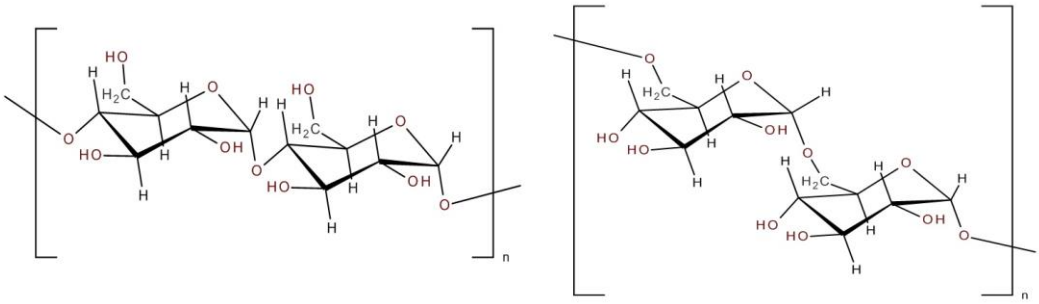
In this study, it was observed that the chemical structure and the type of functionality present in the starting material (R group, Scheme 1.) is influencing the productivity of the nitrile which is reflected by the reaction mechanism. Currently, we are elucidating, by theoretical and spectroscopic methods, the possible reaction mechanism: the interactions of starting material with reactants and/or with the reaction medium.

Novel alpha-1,4;1,6 glucans derived from starch

Name PhD: Piet van der Zaal
Involved staff members: Dr. Piet Buwalda, Prof. dr. Harry Bitter
Project sponsor: TKI/AVEBE
Start/(expected) end date of project: 01-10-2013/01-10-2017

Background

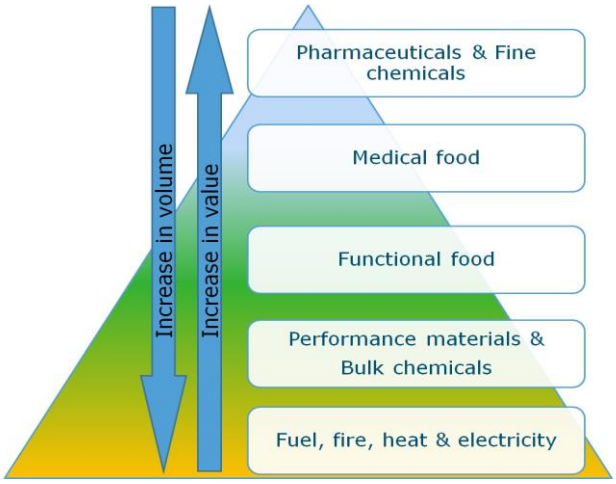
Starch is the main carbohydrate in the human diet, the compound itself is biodegradable and used in a wide variety of applications. Due to its relatively low price and its high availability starch is an attractive substrate for (enzymatic) modification. The discovery of the GtfB enzyme (4,6-α-glucano-transferase) opens up a new way to modify starch. This enzyme is able to alter the intrinsic properties of starch by cleaving α-1,4 glycosidic linkages and introducing α-1,6 glycosidic linkages to the polysaccharide.



Molecular structure of an α-1,4 linked glucose backbone (left) and an α-1,6 linked glucose backbone (right).

Goal

The goal of this project is to utilize the GtfB-enzyme for starch modification and to characterize the novel polysaccharides that are formed. The α-1,4 linkages present in starch are converted to α-1,6 linkages with the GtfB enzyme. Creating a new generation of polysaccharides with interesting properties for food fibres, pharmaceutical applications and replacement of synthetic polymers.



Highlight of the past year

The results achieved this year delivered proof that the enzyme is able to modify starch. High molecular weight products were found after modification, the distribution of α-1,6 linkages in the high and low molecular weight fractions will be the topic for further research. The extent of modification was monitored with AF4 (Asymmetric Flow Field Flow Fractionation) and ^{1}H NMR (Nuclear Magnetic Resonance). The methodology of the production and analysis techniques that were developed provide a sound foundation for further research.

Non noble metal carbides and phosphides to be developed in Brazil and the Netherlands to replace heterogeneous noble metal based catalysts

Name PhD: Luana Souza Macedo
Involved staff members: Prof. dr. Harry Bitter (WUR), Prof. dr. Victor Teixeira da Silva (UFRJ)
Project sponsor: WUR – sandwich project
Start/(expected) end date of project: 01-03-2014/01-10-2016

Background and goal of project

Catalysis is key to efficiently convert feedstocks into fuels and chemicals With the current transition from fossil sources to renewable sources new stable catalysts need to be developed. Often noble metal (Pt, Pd) based catalysts are used since these metals are stable under the reaction conditions. As support for these metals carbon is a good choice due to its inertness and stability. With the shortage of noble metals the use of more abundant non noble metals is preferred. However their stability, especially under conditions relevant for biomass based conversions, needs to be improved which is the topic of this project.

The goal of this research is investigate how the nature of the carbon support - carbon nanofibers (CNF), carbon covered alumina (ARC) and activated carbon (AC) - influences the catalytic performance (activity, stability and selectivity) of nano sized W_2C, Mo_2C and Ni_2P particles. The catalyst will be used for deoxygenation of fatty acids to yield alkanes and alkenes which can be used as fuel or bulk chemical.

Highlight of the past year

W_2C/AC, W_2C/CNF, W_2C/ARC, Mo_2C/CNF and Ni_2P/CNF were tested for the deoxygenation of stearic acid at 275 ^oC and 30 bar of H_2 in a batch autoclave system. The initial results are shown in Table 1. Clearly both the support and active phase have a significant influence on the catalytic performance. In our hands W_2C/ARC and Ni_2P/CNF were active catalysts. Why W_2C/CNF and Mo_2C/CNF which were shown before to be active catalysts were not active in our hand remains an enigma at the moment. Catalyst characterization will be performed to establish structure-performance relationships.

Table 1. Catalytic test results for deoxygenation of stearic acid at 275 ^oC and 30 bar H_2 in a batch autoclave system after 8 h of reaction.

Active phase	Support	Conversion / %
W_2C	ARC	22
W_2C	AC	0
W_2C	CNF	0
Mo_2C	CNF	0
Ni_2P	CNF	59

Waste to resource: Chemical synthesis of bulk chemicals from waste stream PHA

Name PhD: Jurjen Spekreijse
Involved staff members: Dr. Elinor Scott, Prof. dr. Harry Bitter
Project sponsor: STW
Start/(expected) end date of project: 8-2011/8-2015

Background and goal of project
With depleting fossil feedstock and the environmental problems associated with this, it will be necessary to search for green alternatives as a source of chemicals. This feedstock should be green and sustainable. For chemicals biomass is the only viable alternative. In this project waste water originated from food and agricultural industry is used as feedstock to produce biobased bulk chemicals.

Waste water can be treated by bacteria to produce an insoluble polymer polyhydroxybutyrate (PHB). PHB can be isolated as a pure compound from a water stream with diverse pollutions. However, it is challenging to use PHB as a material due fluctuating properties and processing issues. Therefore we convert PHB to a range of biobased chemicals in this project.

Highlight of the past year
One of the conversions used in the project involves an olefin metathesis reaction. The downside of the olefin metathesis reaction is the expensive Hoveyda Grubbs 2nd generation (HG2) catalyst, which should be reused in order to get an economically feasible process. Therefore we immobilized the HG2 catalyst in a Metal Organic Framework (figure 1). Metal organic frameworks are large, often porous, networks consisting of metal nodes linked by organic molecules and can be made in a single step from commercially available starting materials. Using a new immobilization technique using a mechanochemical method, we successfully immobilized the HG2 catalyst. The initial activity of the immobilized catalyst was comparable to that of the homogeneous catalyst.

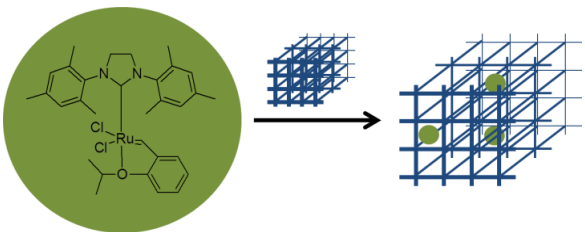


Figure 1. Immobilisation of Hoveyda-Grubbs 2nd generation catalyst (green circle) in a Metal Organic Framework (blue) by mechanochemical means.

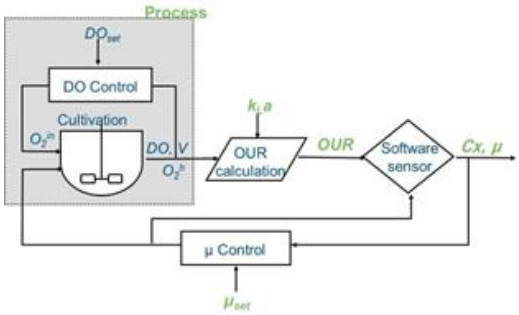
Technology

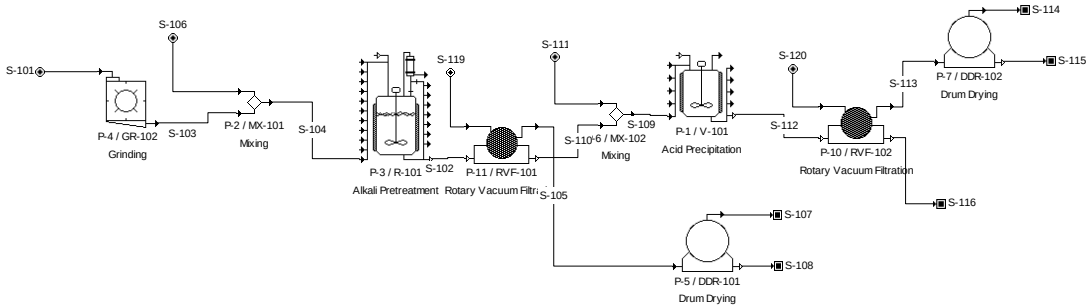
Background and goal of this theme

The biobased economy requests for new solutions in cultivation, processing and control. To find such solutions, mechanisms of conversion and separation are modelled and experimentally validated. Then the models are used to predict the performance of production systems which are often a combination of several units. The connection between the units is optimized for performance and sustainability (LCA) and effective control systems are designed.

Main topics

- Mechanisms and models for preprocessing of biomass
- Component (protein, carbohydrate etc.) recovery from waste streams using new techniques
- Integrated sustainable biorefineries (algae, lignocellulosic biomass, milk-to-powder)
- Life Cycle Analysis (LCA) combined with process design
- Processing in the region (system analysis and control)
- Control of individual and integrated processing steps in biorefineries
- Energy efficient processing (for example drying of biomass, vegetables)





Staff: Dr. Ton van Boxtel, Dr. Marieke Bruins, Dr. Rachel Ooteghem, Prof. dr. Harry Bitter

PhD students and post-doc: Sanne Moejes, Chen Zhang, Farnoosh Fasaei, Ellen Slegers, Marja Teekens, Widyarani, Nathan Bowden

Contact: ton.vanboxtel@wur.nl

Sustainable biorefinery design

Name Postdoc: Ellen Slegers
Involved staff members: Dr. Ton van Boxtel
Project sponsor: AlgaePARC Biorefinery, EU MIRACLES
Start/(expected) end date of project: December 2013 – June 2017

Background and goal of project
One element of the circular biobased economy is to use dedicated biomass or waste biomass streams for the production of chemicals, materials, fuel, food, and animal feed. There are plenty of combinations of biomass sources and products possible. The question is which combinations are the best. This depends on the properties of the starting material, the product requirements, the processing possibilities, and the desired overall performance. The performance aim can be to maximise costs, minimise energy, or to improve the environmental sustainability in terms of e.g. using Cumulative Energy Demand, EcoProfiles, Exergy Analysis or LCA.

The focus of these research projects is on designing new biorefinery chains, using technical calculation models. The first step is to develop these models and to simulate the technical performance of process designs. From this promising biorefinery chains are suggested. In a second step these chains are optimised in terms of environmental sustainability.

Highlight of the past year
Logistics of algae biorefinery (AlgaePARC Biorefinery)

Microalgae can be grown for a variety of products. The processing of algae biomass into products can take place centrally or can be divided over several processing plants. For example, with a process where biomass is first concentrated locally and then transported to a central facility that processes the biomass further (Figure 1). In 2014 a manuscript entitled “Logistic analysis of algae cultivation” was accepted for publication in Bioresource Technology.

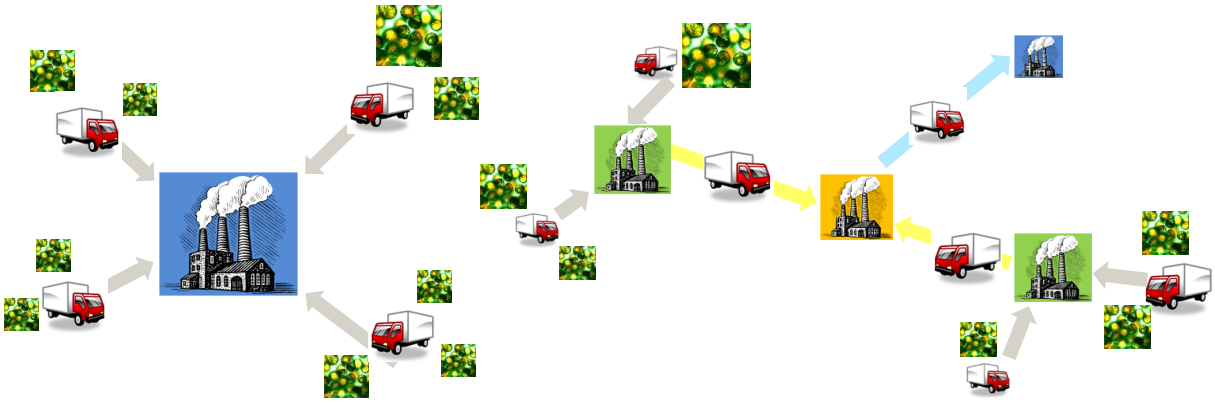


Fig 1. Central processing versus specialised processing.

The best mode of logistics is still unknown for algae biorefinery. In 2015 we will study which processing infrastructure is most suitable, to understand which characteristics and conditions lead to the selection of the specific optimal logistic network.

Modelling microalgae biorefinery (MIRACLES)

The best design of the algae biorefinery chain to the variety of products is unknown. In previous work we focussed only on lipids from algae. This work was published in Algal Research.

In a biorefinery there is also interest in the other fractions such as proteins, carbohydrates, or pigments and this leads to challenges in the disruption of cells and separation of valuable molecules. In EU MIRACLES we assess several biorefinery routes using model simulations. This year we have inventoried the harvesting, disruption and extraction/separation techniques applied within the MIRACLES community. An overview of the techniques is given in Figure 2.

A critical step in model development is to have suitable process information available. A data inventory was performed among the project partners. The technical models will be developed next year, based on the data inventory, scaling data from literature, and mechanistic models.

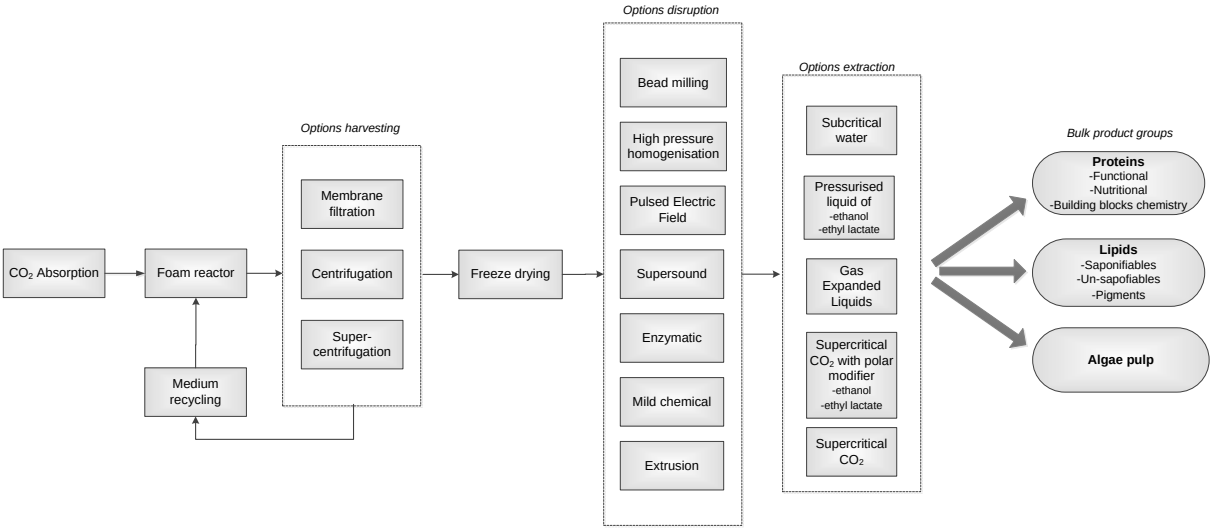
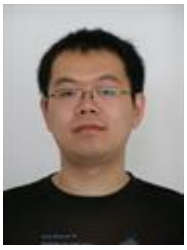


Fig 2. Laboratory process chain in MIRACLES.

Increasing the utilization of low value leaves by use of new protein extraction methods



Name PhD: Chen Zhang
Involved staff members: Dr. Marieke Bruins, Prof. dr. Johan Sanders
Project sponsor: STW/ DSM/Agrifirm/ Malibiocarburant
Start/(expected) end date of project: 1.1.2013-1.1.2016

Background and goal of project

Twice the food production at half the ecological footprint" by 2050 is a target requiring new solutions, in which high output and the complete use of agricultural products are needed. Leaf protein (LP) can serve as feed and food, but can also be hydrolysed to amino acids for other applications, however, leaf proteins are used only at limited efficiency. To develop a new, sustainable technology, preferable in small scale that can be used on location, for the extraction of leaf proteins from three major crop residue sources, grass (Europe), green tea leaves (Asia) and cassava leaves (Africa). This will include the study of the use of new technologies to pre-treat the leaf material, to open up cells to enhance extraction while keeping the protein undamaged.

Highlight of the past year

- Parameters of alkaline extraction were categorized as protein yields related and cost related. (Zhang, Sanders et al. 2014)
- Analysis how alkali aid protein extraction, and design an integrated biorefinery processes for leaves based on these analysis. (Fig.1 &2, article submitted)
- Test the effects of three pre-treatments, ethanol, viscozyme, H2O2, on anti-browning and improving digestibility of leaf protein obtained in alkaline condition.

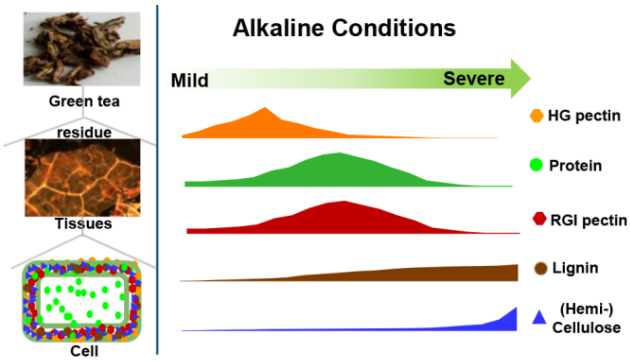


Fig.1 Extractability of leaf components in varied alkaline conditions.

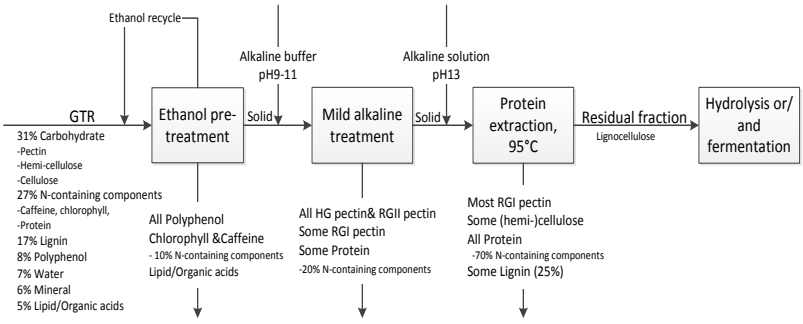


Fig.2 Integrated biorefinery design for leafy biomass.

Economics and technology of biorefinery for animal feed sources

Name PhD: Marja Teekens
Involved staff members: Prof. dr. Johan Sanders, Dr. Marieke Bruins
Project sponsor: Ministry of Economic Affairs (CBBE/ CAH Vilentum Dronten)
Start/(expected) end date of project: 01-02-2013 till 01-02-2017

Background and goal of project

Due to the growing demands for biomass, caused by an increasing world population and utilisation of biobased building blocks in industry, biomass has to be used more efficiently. Biorefinery might be a solution to the increased and versatile demand for biomass. Animal feed sources are, with their 40 million tonnes dry matter only in the Netherlands, a large biomass stream that can be used to meet the future demand.
The first goal of the project is to illustrate *if* and *how* biorefinery can deliver high feed quality and biobased products simultaneously (2014). The project also aims to determine why many feasible biorefinery initiatives are not grown into a technological innovation system yet (2015 and 2016).

Highlight of the past year

First goal of the project was to illustrate *if* and *how* biorefinery can deliver high quality feed and biobased products simultaneously from sources which are now only used for feed. Especially feed sources that are high in protein have potential for the biorefinery approach, i.e. non essential proteins will be extracted for chemicals production. The remaining feed has a better quality compared to the non extracted feed. Feed sources that are high in protein, but are currently low priced because they contain Nutritionally Active Factors (NAF's) are interesting. Since biorefinery can decrease the NAF's, high protein and low priced feed ingredients are interesting for simultaneous production of animal feed and biobased building blocks. My initial assesssment of potential feed sources for the biorefinery approach are shown in Table 1. In Table 1 feed sources are mentioned with a lower, equal or higher market price than expected when looking at its protein content. The ones with lower prices are suitable to be upgraded through biorefinery.

Table 1 Market price of heavily traded feed ingredients are not always in balance with its protein content.

Market price related to protein content				
in line	Peas (dry)	Soy bean meal	Triticale	
low	Rapeseed meal	Sunflower seed meal (not dehulled)		
high	Linseed	Maize gluten meal	Potato protein (feed)	Soy beans (heated)

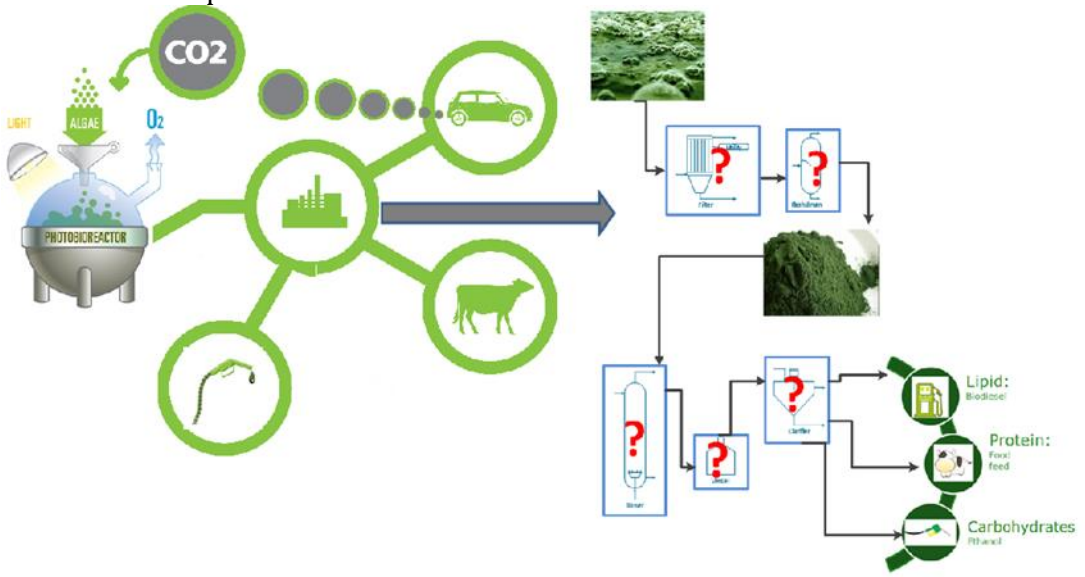
System Analysis of Algae Biorefinery

Name PhD: Farnoosh Fasaei
Involved staff members: Dr. Ton van Boxtel, Prof. dr. Harry Bitter
Start/(expected) end date of project: 01-09-2013/01-09-2017

Background and goal of project

The idea of using biobased products instead of fossil based products gains growing attention due to worldwide increasing energy demand, critical issues related to the emission from fossil based production and environmental concerns. Algal biomass is considered as a high potential source for the production of biobased products.

Algae biorefinery refers to the conversion of algae biomass into a range of valuable biobased products and energy. The technologies for algae biorefinery are still in a development phase and limited available. The algal biorefinery for the range of products consists of a sequence of operations technologies which depend on each other. The integrated biorefinery approach for a range of biobased products from algae is considered as a viable option to advance the economic feasibility and to increase the total value of the products.



Highlight of the past year

During last year selection of suitable process units for processing of microalgae has been made and library of the models for feasible unit operations has been prepared. Models are developed by including the characteristic of the flow streams like flow rate, algae concentration and internal processes and also relations inside each unit in order to quantify accurate energy consumption and yield production. By linking energy and mass balanced based models for each unit operation together, the performance of different process chains (scenarios) can be quantified. Production of lipids, proteins and carbohydrates and energy requirement are being addressed via different process design plots. Application of new technologies like Pulsed Electric Field in downstream processing design can be affected by marine algae. Desalination step is one of the additional steps to decrease the amount of salt to provide the prerequisite condition for PEF unit. This step during the last months of the last year has been introduced and optimized solution has been found. A new approach for optimization of the operation condition in framework of Matlab programing has been developed.

Redesign and optimization of the milk powder production chain

Name PhD: Sanne Moejes
Involved staff members: Dr. Ton van Boxtel, Jan-Eise Vuist MSc
Project sponsor: EU – WP1 in the FP7 ENTHALPY project
Start/ (expected) end date of project: 1-12-2013 till 30-11-2017

Background and goal of project

The dairy industry is one of the most energy consuming industries in the food sector. Mainly concentrating and drying processes are responsible for this fact. For this reason milk powder production is highly energy consuming. Introducing new technologies, which proven to be useful in other sectors, will decrease the energy demands and improve sustainability. This will influence the performance of other up- and downstream processes. Optimization of single unit operations as well as the chain as a whole will result in optimal processing conditions. Optimization via a superstructure (like in Figure 1) is a way to find the optimal combination of processes and process conditions. The challenge will be to create an optimization routine which takes both energy, water, and other LCA aspects into account.

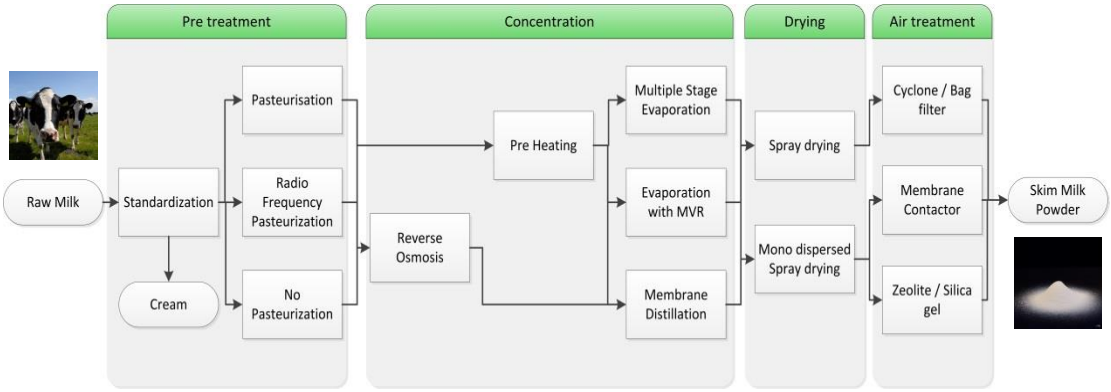


Figure 1. Superstructure of the different production routings of skim milk powder, including conventional and innovative unit operations.

Highlight of the past year

During the first year of this project it was important to start with the benchmarking, describing the state-of-art and the innovative technologies. Examples of innovative technologies are membrane distillation, radio frequency heating, mono-dispersed droplet drying and air dehumidification by zeolites. Figure 1 shows the superstructure including all unit operations, showing the different processing routings to get from raw milk to skimmed milk powder. Besides processes for the powder production, also alternative energy sources are investigated, like solar thermal collectors and photovoltaic cells.

Subsequently the mathematical models behind the different unit operations were established and programmed in MATLAB. This way the mass and energy flows within the system can be simulated, giving insight in product and energy usage. When linking the unit operations together a production scenario can be simulated. When comparing the current situation with an innovative scenario, results show an energy saving of more than 60%. This is in line with the expectations of the project. The introduction of membrane distillation as an alternative of evaporation, and the enabling to recycle the exhaust air of the dryer are responsible for these large improvements. Optimization of the operational conditions as well as heat integration is planned next, aiming to further improve this result. Methodology and results were documented and shared within the international consortium.

Isolation and valorization of peptides and amino acids from the rubber, oil palm and Jatropha tree

Name PhD: Widyarani
Involved staff members: Prof. dr. Johan Sanders, Dr. Marieke Bruins
Project sponsor: NWO/WOTRO
Start/(expected) end date of project: September 2010/September 2014

Background and goal of project

Rubber tree seeds, oil palm fruits and Jatropha seeds are potential feedstock for bio-oil, which can be further processed to biodiesel. Oil production from these biomasses results in waste streams that contain protein. Currently, these waste streams have low to no economic value. The aim of this research is to find methods for valorizing protein in bio-oil waste streams for green chemical use. Utilization of all biomass fractions, including protein, will give a higher economic value to the overall chain.

Highlight of the past year

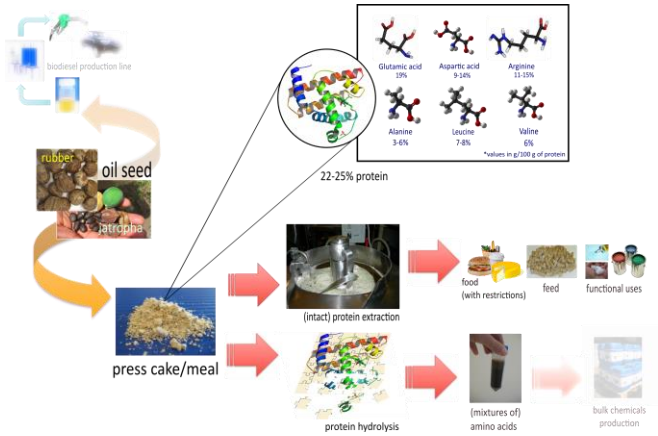


Fig. 1 – Research approach

Rubber seed was used as model biomass for this research; two routes for food/feed production and amino acids production were investigated (Fig. 1).

We have observed that the availability of protein in the press cake and meal was influenced by oil separation process. By using alkaline extraction at room temperature, protein could be extracted with high yield and preserved quality[1].

Rubber seed has a typical amino acid composition for oil seeds; high values of arginine, leucine, and valine were observed. Hydrolysis with protease enables selective hydrolysis of specific amino acid (groups), making the downstream processing easier. From experiments with several proteases, a condition that yielded in the highest hydrophobic amino acids in the hydrolysate was obtained[2].

[1] Widyarani, Ratnaningsih, E., Sanders, J.P.M., Bruins, M.E., 2014. Ind. Crops Prod. 62, 323–332.
[2] Article in preparation

Systems theory

Motivation and challenges

In the past decade, there have been strong developments in communication (internet, e- mail, smart phones, wireless), computation (Moore's exponential law - processors, memory, storage capacity), sensor networks (data warehouses) and cyber science (integration of knowledge). These developments allow the implementation of smart, high-tech, cost-effective solutions to water/energy/material related problems in a bio-based/circular economy (Fig. 1).

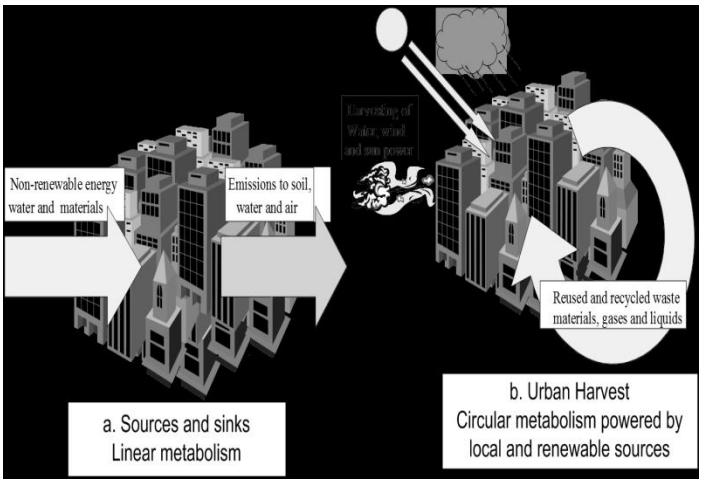


Fig. 1. From a linear towards a bio-based/circular economy

In particular, the research of the systems theory group focusses on:

(i) *Data management* with the goal to design and modify novel data processing algorithms for learning in a bio-based/circular economy

(ii) *Optimal design and operation* of dynamic, interconnected systems to optimally compose and design chains of bio-based subsystems using sustainability, energy or other possibly combined quantitative criteria

(iii) *Advanced simulation* (serious gaming) for a better exploration of future scenarios of bio-based/circular systems, for design, alarming and optimisation, at different time and spatial scales and supported by a physiologically-based modelling concept for a further understanding of S, N, P cycles.

Members

Staff: Karel Keesman, Harry Bitter and Gerard van Willigenburg.
PhD students: Nurul Khairudin, Rungnapha Khiewwijit, Elvira Bozileva, Jan Klok, Nik Grubben, Daniel Reyes Lastiri, Yu Jiang.
Contact: karel.keesman@wur.nl

Optimal Digital Control

Involved staff member: Dr. Ir. L. Gerard van Willigenburg
Start/(expected) end date of project: Continuously ongoing

Background and goal of project

The aim of this project is to develop general methodologies and algorithms for the synthesis of optimal digital controllers for non-linear, possibly infinite dimensional, systems. Applications focus on systems related to agriculture, biology, food and chemistry. Synchronous, asynchronous and random sampling schemes are accommodated as well as optimal order-reduction of the digital controller. Robustness of the controllers may be realized by introducing stochastic parameters.

Currently one line of research concerns the increase of accuracy and efficiency by U-D factorization of previously developed algorithms.

Another line concerns the detection of temporary loss of conventional system properties such as stability, stabilizability and compensatability. Detection of these temporary losses is of vital practical importance because they cause and explain the failure of control systems despite the satisfaction of associated ordinary system properties. Associated with these temporary losses is a so called temporal system structure that clarifies and reveals differences between ordinary system properties that are similar such as controllability and reachability.

Optimal control requires a reasonably well established dynamic systems model. If such a model is not (yet) obtained, active adaptive optimal controllers form an attractive alternative. A dual (active) adaptive controller structure has been proposed and studied by means of several benchmarks. The controller structure aims at enabling a cheap, fast and smooth transition from standard to advanced (multivariable optimal) digital feedback control within industrial environments. The results are very promising. Still they need some improvement before publication.

Highlight of the past year

U-D factorization of LQG controller algorithms enhances their numerical efficiency and stability. The U-D factorization algorithms for optimal reduced-order control of linear systems with white stochastic parameters has been investigated, realized and published in the International Journal of System Science.

Stabilizability and compensatability are crucial properties when designing controllers for linear systems with stochastic parameters. Temporal versions of these properties have been developed indicating the temporal loss of the associated conventional properties. They have been published in the European Journal of Control.

As part of the European project “EU Cafe” adaptive optimal scheduling and control of beer membrane filtration has been studied and published in Control Engineering Practice.

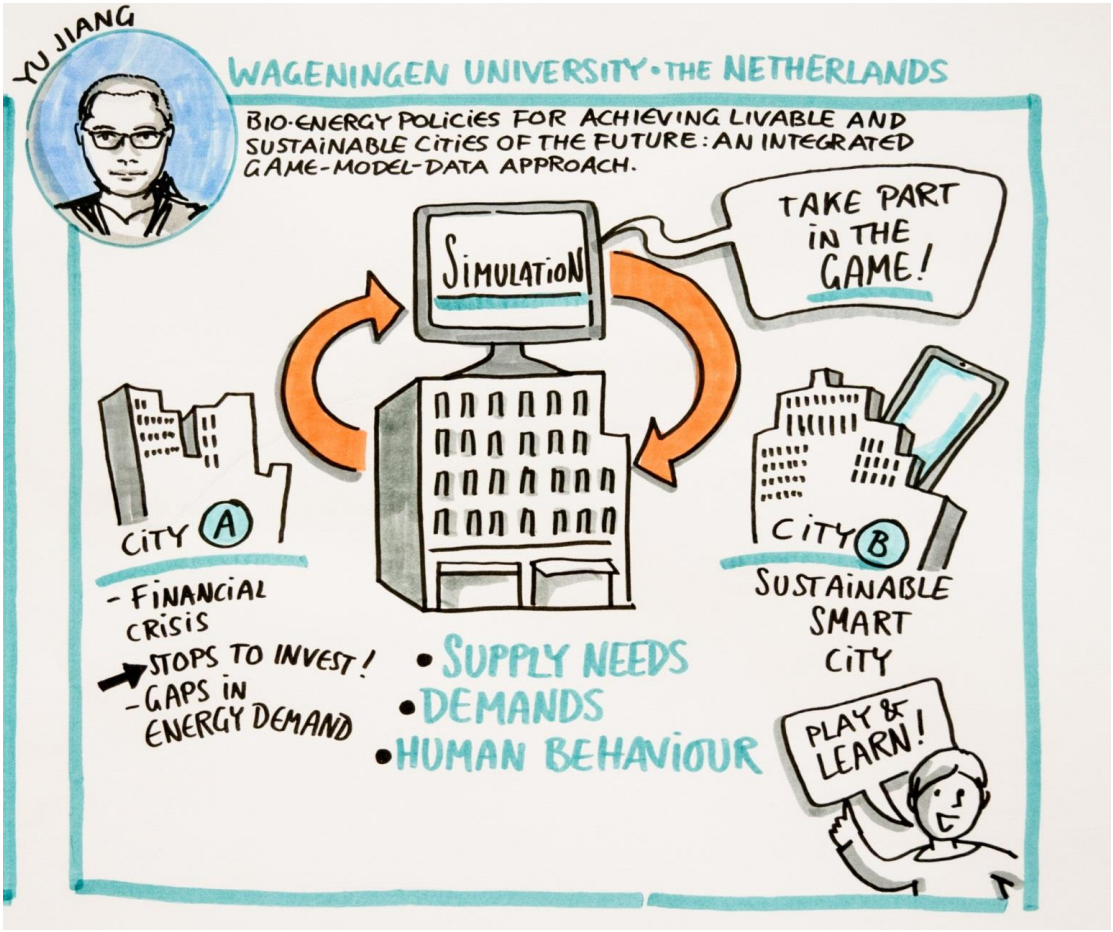
Bio-energy policies for achieving liveable and sustainable cities of the future: an integrated game-model-data approach (E-game)

Name PhD: Yu Jiang
Involved staff members: Dr. Karel Keesman
Project sponsor: Climate-KIC
Start/ (expected) end date of project:
Start: 01-09-2014
Expected end date: 01-09-2018

Background and goal of project

To investigate and develop a novel computer-aided agent-based simulation method for bio-based smart energy systems to provide scientific insights and a decision support tool to help decision makers with shaping and directing the social transition to a bio-based sustainable urban energy system

Highlight of the past year



In the past year, background study and literature review were conducted for my PhD project. Structure for the PhD thesis was determined, together with the corresponding research methods.

Modelling aquaculture-hydroponic systems

Names: Daniel Reyes Lastiri (PhD), Hans Cappon (part-time Postdoc)
Involved staff members: Dr. Karel Keesman

Project sponsor: INAPRO (EU 7th Framework Programme for Research)
Start/(expected) end date of project: Daniel - 15 June 2014/15 June 2018
Hans – 1 april 2014 – 1 april 2018

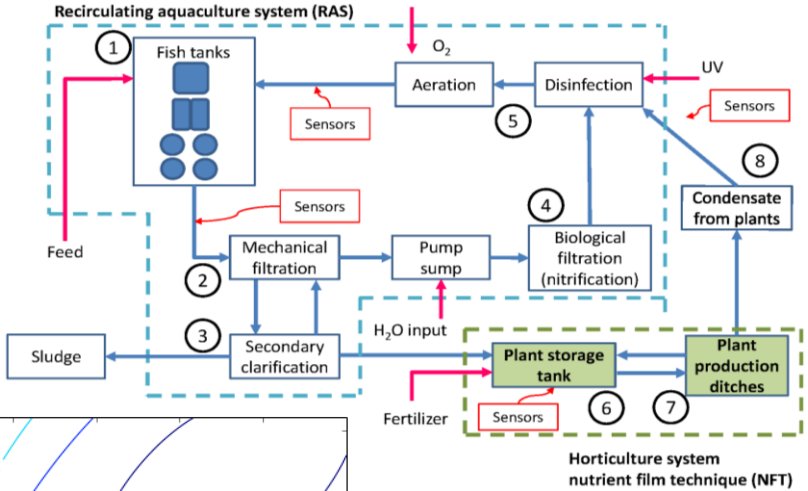
Background and goal of project

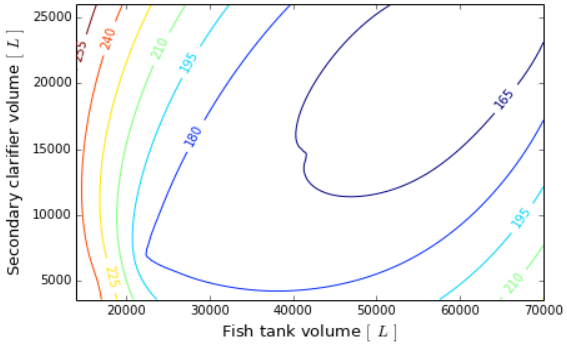
Aquaponics is a food production technique that combines aquaculture (farming of aquatic organisms) with hydroponics (farming of plants without soil). In an aquaponic system, the waste excreted by the fish can be utilised as nutrients by the plants and, in turn, the plants can help cleaning the water that is recirculated to the fish.
Our objective consists of developing a mathematical model to simulate an aquaponic system as part of INAPRO, an EU project aiming at the commercialization of aquaponics. The INAPRO system couples the production of tilapia and tomato. Understanding the system and optimising water, nutrients and energy usage is the main aim of the model. The model is generated in parallel with the construction and operation of demonstration aquaponic systems.

Highlight of the past year

The INAPRO system is shown in the diagram below (figure A). The initial model made in Excel includes nitrogen, water and energy management and its results show that it is possible to size the water buffer components, while minimising the water usage (figure B). Two reports, one on modelling and one on design specifications, were submitted as deliverables to the EU project.

A) The INAPRO aquaponic system





B) Yearly water consumption [m3/ton fish].
It is possible to size the components minimising the

Real-time accounting and simulation of dynamic energy-water-material balances for achieving liveable and sustainable cities of the future

Name PhD: Elvira Bozileva

Involved staff members: Dr. Karel Keesman

Project sponsor: Climate-KIC

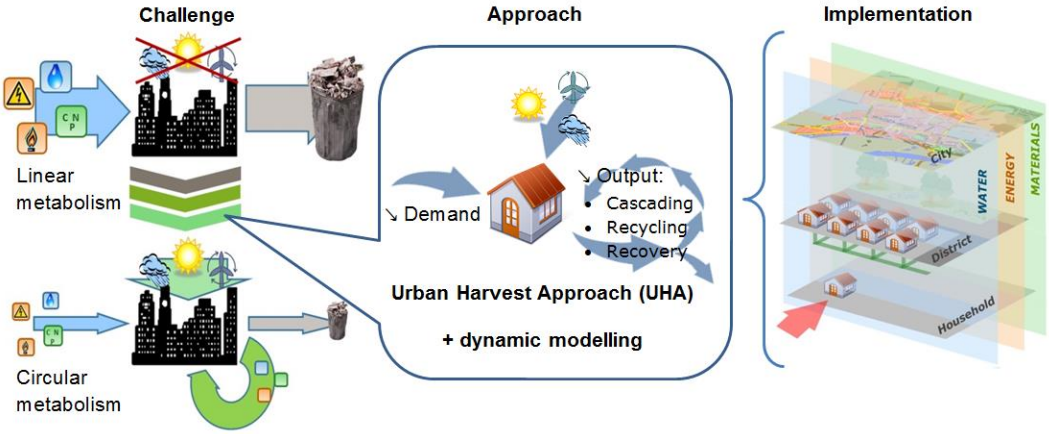
Start/(expected) end date of project: 09-2013/09-2017

Background and goal of project

In 2008 WWF, Zoological Society of London and Global Footprint Network stated that already in 2005 humanity exceeded regenerative capacity of Earth by 30%. The causes of this overshoot can be seen in a wasteful use of resources practiced today. Unsustainable resource use is especially prominent in cities – hotspots of resource conversion. As this issue attracted a lot of attention in the recent decades, a vast amount of technological concepts has been proposed that address the specific aspects of sustainability (harvesting solar energy for heat and electricity production, grey-water reuse for non-potable purposes, grey-water heat recovery, etc). The real practical question is how to systematically identify which technological solutions are the most relevant for a specific context. The goal of this project is to answer this question using a modelling approach and to describe the dynamic and spatially-distributed water-energy-materials nexus in urban systems at household-block, district and city scale.

Highlight of the past year

In order to identify the combination of technologies that have the highest impact on improving the sustainability of an urban system, a hybrid model with linear dynamics and (un) controlled switches was built in MATLAB® environment. Currently the model simulates water, gas and electricity flows in a residential multistorey building. The simulation is performed with a high temporal resolution, which allows to correctly evaluate the impact of technologies for cases when mismatch between resource supply and demand plays significant role. A good example to illustrate such mismatch is the electricity production by PV cells: electricity production peaks at noon, while the consumption mainly takes place during the morning and evening hours (for residential households). Additionally the model takes into account that different resource cycles within the system are essentially coupled, which in turn allows to account for possible trade-offs associated with implementing certain technologies.



Smart ventilation for safe and sustainable food storage

Name PhD: Nik Grubben
Involved staff members: Dr. Karel Keesman
Project sponsor: Omnivent techniek b.v.
Start/(expected) end date of project: 01/04/2014-01/04/2018

Background and goal of project

Agricultural products play an important role in life. From the very beginning, these products were used for food and feed. However, nowadays agricultural products are also used as raw material for bio-based industrial processes. Agricultural products is one of the three main categories of biomass in the upcoming bio-based economy. On the other hand, also the demand of agricultural products for food is growing under a growing world population. These trends requests for new cycles and processes to be able to supply the consumers and industry.

However, most agricultural products are season-dependent. To overcome seasonality of the harvested products and to guarantee a continuous flow of food products to the consumers and of biomass, in general, to bio-based industries, storage of primary food products and biomass is crucial.

This study focuses on the understanding and design of optimal ventilation strategies for safe and sustainable storage of primary food products.

Highlight of the past year

In current storage facilities the indoor climate is controlled in order to keep the product quality at a certain level. With computational fluid dynamics simulation (CFD) a spatially distributed link between ventilation, climate and product quality is obtained. A physical-based modelling is produced for the usage of these CFD simulations.

A review article about modelling ventilated bulk storage of agro-materials has been submitted. This includes a broad investigation on CFD simulations, used in food storage applications.

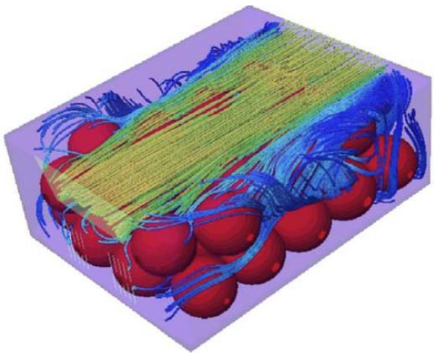


Figure 1. Air velocity profile around spherical food product obtained by CFD simulation. (Verboven, P., Flick D., Nicolai, B., Alvarez, G., 2006. Modelling transport phenomena in refrigerated food bulks, packages and stacks: basics and advances. International Journal of Refrigeration.)

To calibrate and validate the spatially-distributed model of frying potatoes a full scale test-storage facility is set up. One of the quality aspects of frying potatoes is the sugar content. For the validation of the sugar content in frying potatoes a novel procedure to measure the sugar content, with presently available measuring equipment (HPLC), is implemented.

Modelling of ammonia volatilisation in a fertilised and flooded rice field

Name PhD: Nurulhuda Khairudin
Involved staff members: Dr. Karel Keesman
Project sponsor: Ministry of Education Malaysia and Universiti Putra Malaysia
Start/(expected) end date of project: 10 January 2011 to 1 April 2015

Background and goal of project

About 20 % of the 11.8 million tons of nitrogen (N) applied in flooded rice fields globally was estimated to be lost via ammonia (NH_3) volatilisation (Bouwman et al. 2002). A mathematical model allows N loss prediction and testing of hypotheses through scenario studies. However, available secondary data sets are often small. This makes integration of small data sets with a mathematical model a challenge. To analyse NH_3 volatilisation via scenario studies using small data sets, a mathematical model with minimum number of unknown rate coefficients (parameters) is preferred, to avoid over-parameterisation.

Highlight of the past year

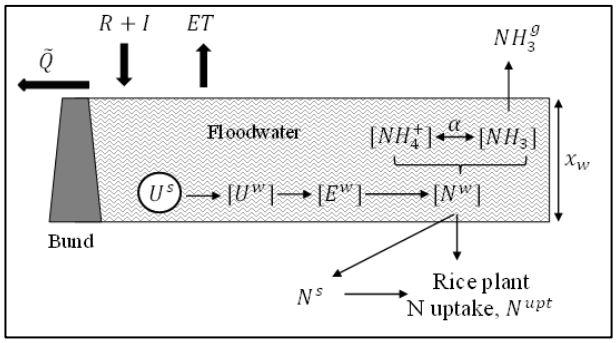


Fig. 1 Conceptualisation of the modified Jayaweera-Mikkelsen (1990) model. $\tilde{Q}$ is floodwater loss due to surface runoff and percolation, R is rainfall, I is irrigation, ET is evapotranspiration, x_w is floodwater depth, U^s is rate of urea-N applied, $[U^w]$ is concentration of dissolved urea, $[E^w]$ is slow urease activity, $[N^w]$ is concentration of ammoniacal-N, $[NH_4^+]$ is concentration of ammonium, $[NH_3]$ is concentration of ammonia, NH_3^g is ammonia volatilisation, and N^s is N in the soil.

To estimate NH_3 volatilisation in a fertilised and flooded rice field, the Jayaweera and Mikkelsen (1990) model was modified as follows; Urea hydrolysis was conceptualised as two first-order processes in series to emulate low urease activity in the floodwater. Algae activity was approximated and used to estimate floodwater pH. Direct N uptake by rice roots at floodwater-soil interface was approximated by a sigmoid curve. NH_3 volatilisation was approximated by a first-order process with time varying NH_3 volatilisation rate coefficient. The model was validated with data sets collected at Los Baños and Muñoz, Philippines, by Fillery et al. (1984).

Education

Bachelor and Master courses BCT (BCH and BRD) and contribution to other courses

Code	Course title
BCT-20306	Modelling Dynamic Systems
BCT-21306	Control Engineering
BCT-22306	Sensor Technology
BCT-22803	Physical Transport Phenomena
BCT-23306	Biorefinery
BCT-30806	Physical Modelling
BCT-31306	Systems and Control Theory
BCT-31806	Parameter Estimation and MSI
BCT-32306	Advanced Biorefinery
BCT-50306	Renewable Resources and the (Bio)Chemical Production of Industrial Chemicals
BCT-50806	Sustainability Analysis (start spring 2015)
BCT-51306	Biobased Economy

Code	Course title
BPE-10305	Process Engineering Basics
BPE-12806	Bioprocess Engineering Basics BT
BPE-60312	Bioprocess Design
FTE-12303	Introduction Biosystems Engineering part 1
FTE-12803	Introduction Biosystems Engineering part 2
FTE-13807	Engineering 2 (Electronics)
FTE-32806	Automation for Bioproduction
FTE-33306	Advanced Biosystems Engineering
MAT-24803	Mathematics for Time-dependent Systems
XWT-21305	Process Dynamics (Wetsus)

BCT: Biobased Chemistry and Technology
BCH: Biobased Commodity Chemistry
BRD: Biomass Refinery and Process Dynamics
FTE: Farm Technology
BPE: Bioprocess Engineering
MAT: Mathematics
XWT: Wetsus Academy

PhD courses

Uncertainty Analysis (2/3/4 ects)
Models are deliberate approximations of the real world and can be seen as a concise and useful representation of scientific knowledge. They serve as tools in research, in the design and control of systems, and in planning and management. Uncertainty is an important issue in all these applications. This course aims at presenting the state-of-the art in quantitative uncertainty analysis, in which much progress has been made in recent years. The course treats the problem from a systems point of view. The first part (three sessions) refreshes participants' knowledge on systems modelling and dynamics. In addition, basic notions from statistics as well as matrix calculus are dealt with and there are practical exercises to be solved within MATLAB. In the second part (three sessions) the focus is on analysis, basically using analytical and Monte Carlo-based uncertainty propagation techniques. The third part (two sessions) deals with parameter estimation with corresponding estimation uncertainty of non-linear systems. Special attention is given to non-linear least-squares techniques and Monte Carlo Markov Chain (MCMC) methods. The fourth and final part focuses on the analysis and estimation of distributed systems and is devoted to uncertainty propagation in spatial systems and the implications of an uncertainty analysis. Here, special attention is given to the effect of spatial correlation on the results of the uncertainty propagation analysis and on the interpretation of the results. The theory is supported by examples, case studies and practical exercises. This course was cancelled in 2014, but will be given again in renewed form in 2015.

BSc Theses

- Jagt, Jacob-Paul van der; The effect of vanadium chloroperoxidase purification towards the conversion of amino acids into nitrils.
- Top, Niek van den; Dynamic modelling of duckweed production on the first ECOFERM! closed-cycle farm for rose calves.
- Jansen, Maarten; Microalgae production combined with anaerobic manure digesting.
- Vos, Timo; Understanding & predicting alkaline pretreatment of Miscanthus through modelling.

MSc Theses

- Thomassen, Gijsbert; Investigating the possibilities to feed pigs individually with help of mechanistic modelling of pig growth.
- Hagen, Susanne; A model based analysis of the downstream processing of microalgae biomass into proteins.
- Galema, Titus; Membrane technology for the optimization of bioethanol production from coffee waste.
- Douwma, Folpert; Development of a new method for sugar crytallisation.
- Grubben, Nik; Agricultural storage: modelling & control.
- Palacios Martinez, Amelia; Furandicarboxylic acid production from hydroxymethylfurfural- current situation and development.
- Bouma, Eelke; Building an explorative model of the biogas production process in an anaerobic digester

- Palacios Martinez, Amelia; Catalytic oxidation of galacturonic acid to galactaric acid-kinetic study and conditions optimization.
- Zegeye, Elias; Modelling the effect of the flocculant dosage on flocculation of micro algae.
- Bouwman, Stephan; Modelling anti-solvent crystallisation.
- Zhang, Yuping; Optimisation of small-scale sugar beet biorefinery

Scientific Publications 2014

Refereed article in a journal

- Minimal heating and cooling in a modern rose greenhouse
  Beveren, P.J.M. van; Bontsema, J. ; Straten, G. van; Henten, E. van (2014)
  Applied energy 137 . - p. 97 - 109.
- The effect of harvesting on biomass production and nutrient removal in phototrophic biofilm reactors for effluent polishing
  Boelee, N.C. ; Janssen, M. ; Temmink, H. ; Taparaviciute, L. ; Khiewwijit, R. ; Janoska, A. ; Buisman, C.J.N. ; Wijffels, R.H. (2014)
  Journal of Applied Phycology 26 (3). - p. 1439 - 1452.
- Design and construction of the microalgal pilot facility AlgaePARC
  Bosma, R. ; Vree, J.H. de; Slegers, P.M. ; Janssen, M.G.J. ; Wijffels, R.H. ; Barbosa, M.J. (2014)
  Algal Research 6 (part B). - p. 160 - 169.
- Kinetics and mechanism of 5-hydroxymethylfurfural oxidation and their implications for catalyst development
  Davis, S.E. ; Benavidez, A. ; Gosselink, R.W. ; Bitter, J.H. ; Jong, K.P. de; Datye, A.K. ; Davis, R.J. (2014)
  Journal of Molecular Catalysis A: Chemical 388-389 . - p. 123 - 132.
- A framework with an integrated computer support tool to assess regional biomass delivery chains
  Elbersen, B.S. ; Annevelink, E. ; Roos Klein-Lankhorst, J. ; Lesschen, J.P. ; Staritsky, I.G. ; Langeveld, J.W.A. ; Elbersen, H.W. ; Sanders, J.P.M. (2014)
  Regional Environmental Change 14 (3). - p. 967 - 980.
- Effects of loading and synthesis method of titania-supported cobalt catalysts for Fischer–Tropsch synthesis
  Eschemann, T.O. ; Bitter, J.H. ; Jong, K.P. de (2014)
  Catalysis today 228 . - p. 89 - 95.
- Toward stable nickel catalysts for aqueous phase reforming of biomass-derived feedstock under reducing and alkaline conditions
  Haasterecht, T. van; Ludding, C.C.I. ; Jong, K.P. de; Bitter, J.H. (2014)
  Journal of Catalysis 319 . - p. 27 - 35.
- Transformations of polyols to organic acids and hydrogen in aqueous alkaline media
  Haasterecht, T. van; Deelen, T.W. van; Jong, K.P. de; Bitter, J.H. (2014)
  Catalysis Science & Technology 4 . - p. 2353 - 2366.
- Impact of different drying trajectories on degradation of nutritional compounds in broccoli (Brassica oleracea var. italica)
  Jin, X. ; Oliviero, T. ; Sman, R.G.M. van der; Verkerk, R. ; Dekker, M. ; Boxtel, A.J.B. van (2014)
  Food Science and Technology = Lebensmittel-Wissenschaft und Technologie 59 (1). - p. 189 - 195.
- Energy efficient drying strategies to retain nutritional components in broccoli broccoli (Brassica oleracea var. italica)
  Jin, X. ; Sman, R.G.M. van der; Straten, G. van; Boom, R.M. ; Boxtel, A.J.B. van (2014)
  Journal of Food Engineering 123 . - p. 172 - 178.
- Moisture Sorption Isotherms of Broccoli Interpreted with the Flory-Huggins Free Volume Theory

Jin, X. ; Sman, R.G.M. van der; Maanen, J.F.C. van; Deventer, H.C. van; Straten, G. van; Boom, R.M. ; Boxtel, A.J.B. van (2014)
Food Biophysics 9 (1). - p. 1 - 9.

- Optimal input design for model discrimination using Pontryagin's maximum principle: Application to kinetic model structures
  Keesman, K.J. ; Walter, E. (2014)
  Automatica 50 (5). - p. 1535 - 1538.
- Opportunities for small-scale biorefinery for production of sugar and ethanol in the Netherlands
  Kolfschoten, R.C. ; Bruins, M.E. ; Sanders, J.P.M. (2014)
  Biofuels Bioproducts and Biorefining 8 (4). - p. 475 - 486.
- Isomalto/Malto-Polysaccharide, A Novel Soluble Dietary Fiber Made Via Enzymatic Conversion of Starch
  Leemhuis, H. ; Dobruchowska, J.M. ; Ebbelaar, M. ; Faber, F. ; Buwalda, P.L. ; Maarel, M.J.E.J. ; Kamerling, J.P. ; Dijkhuizen, L. (2014)
  Journal of Agricultural and Food Chemistry 62 (49). - p. 12034 - 12044.
- A Fast and Accurate UPLC Method for Analysis of Proteinogenic Amino Acids
  Meussen, B.J. ; Zeeland, A.N.T. van; Bruins, M.E. ; Sanders, J.P.M. (2014)
  Food Analytical Methods 7 (5). - p. 1047 - 1055.
- Effect of biomass concentration on the productivity of Tetraselmis suecica in a pilot-scale tubular photobioreactor using natural sunlight
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