



UNIVERSITY of OULU
OULUN YLIOPISTO

Sustainable processing of natural resources (SusProc)

Academy of Finland, Sustainable Production and Products (KETJU) Programme
Annual report 2009

Project number: 118212
Responsible leader: Prof. Marja Lajunen
Research leaders: Prof. Marja Lajunen, Prof. Osmo Hormi, University of Oulu
Department of Chemistry; Doc. Eva Pongrácz, University of Oulu,
Department of Process and Environmental Engineering/Thule Institute, NorTech Oulu
Site of research: University of Oulu (UOulu)
Funding period: 01.01.2007-31.12.2010

Project abstract and objectives

The aim of SusProc project is to study, modify and process natural polymeric raw materials, cellulose and starch, in a sustainable way to new products applicable to replace detrimental materials in various fields of chemical industry. An essential aspect of these new products is non-toxicity in use and bio-degradation at the end of their life cycle. These polymeric materials are safe, non-toxic, biodegradable, economical and ubiquitous. The new materials intended to be produced from these bio-resources are environmentally benign and sustainable solutions for chemical-, pulp and paper-, medical or food industry.

The process aims at recovering maximum economic value from a natural resource while minimizing environmental risk. The project partners will investigate key aspects of sustainable production: processing safe, non-toxic raw materials, energy-efficient processes, process safety considerations, and the theoretical framework of resources use optimization.

The research methods and materials used in this project fit within principles of green chemistry. Ionic liquids (ILs), the essential reaction media of the project, are extensively evaluated as green alternatives for common organic solvents. They are non-volatile, inflammable, non-explosive and often recyclable solvents successfully used to replace volatile organic solvents. Microwave irradiation as a heating/activation method is more effective and faster than thermal heating using baths common in organic synthesis.

Some ionic liquids 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-allyl-3-methylimidazolium chloride (AMIMCl) and 2-hydroxy ethyl ammonium formate have lately proved to dissolve cellulose in powder form up to 30% dispersion. Non-enzymatic separation of starch components amylose and amylopectin in pure form was recently solved in IL.

The project includes preparation of new ionic liquids and their use as a reaction medium in preparation of new products derived from natural polymers. Modification of cellulose, starch and its components for various applications will be studied.

New compounds and methods for their preparation will also be studied from their life cycle point of view and inherent risks.

The interdisciplinary consortium consists of three research groups from two faculties of the University of Oulu, and joins expertise in pure chemistry and process and environmental engineering.

Composition of the research team:

Researchers: Ph.D. Johanna Kärkkäinen, UOulu, Department of Chemistry (on leave during 22.8.2008 - 31.12.2009)
M.Sc.(Eng.) Alli Majala, UOulu, Mass and Heat Transfer Process Laboratory (on leave during 1.3.2009 – 31.8.2010)
M.Sc. Katja Raassina, UOulu, Department of Chemistry
M.Sc. Juho Sirviö, UOulu, Department of Chemistry

Advisors: Prof. Marja Lajunen (on leave during 27.7. - 31.12.2009) and Prof. Osmo Hormi, UOulu, Department of Chemistry; Doc. Eva Pongrácz Thule Institute/NorTech Oulu and Prof. Riitta Keiski, UOulu, Mass and Heat Transfer Process Laboratory

Other researchers involved in the project:

Student Kati Haapala, UOulu, Department of Chemistry
Student Anna Sivula, UOulu, Department of Chemistry
Student Krista Kilpi, UOulu, Department of Chemistry
Student Aleksi Kolehmainen, UOulu, Department of Chemistry
Student Uula Hyväkkö, UOulu, Department of Chemistry

Collaboration partners:

Professor Kenneth R. Seddon Queen's University Ionic Liquid Laboratories (QUILL), Belfast, Ireland; Professor Ilkka Kilpeläinen, University of Helsinki; Professor Jouko Niinimäki, University of Oulu

Results of research and future goals

Task 1: Preparation of ionic liquids and their use to dissolve and degrade natural polymers cellulose and starch

- The amount of water and changes in that during the starch degradation reactions have been determined. It was found out that the amount of water does not significantly change during the degradation.
- Recycling of the ionic liquid used in the starch degradation reactions has been studied. The ionic liquid could be purified and reused in corresponding reactions.
- Reaction conditions for modifications of starch degradation products in ILs have been studied. In the optimized conditions degradation products could be acetylated with good yield. IL used in these reactions could be recycled.
- A method to purify commercial maltodextrins in ILs has been developed.
- Studies of this task include the experimental part of two M.Sc and two B.A. thesis.
- Two manuscripts from the results are under preparation.

Participation in a project financed by Tekes due to a use of a starch degradation product as a new polymeric substance for cell cultivation.

In the field of the task a search of an improved separation method of degraded products from the product mixture will continue. The study of degradation methods in ILs continues.

Task 2: Environmentally friendly oxidation process of starch and cellulose to dialdehyde starch (DAS) and dialdehyde cellulose (DAC)

Both DAC and DAS polymers are materials with great potentiality in various industrial applications. They both are more water-soluble than their native not oxidized counterparts starch and cellulose. Due to aldehyde groups in DAS and DAC they may act as environmentally friendly polymeric dialdehyde components in applications such as the manufacture of temporary cross-linked paper products. Also due to aldehyde groups they both also have potential to be used as polymer carriers for immobilization of biomolecules, Figure 1.

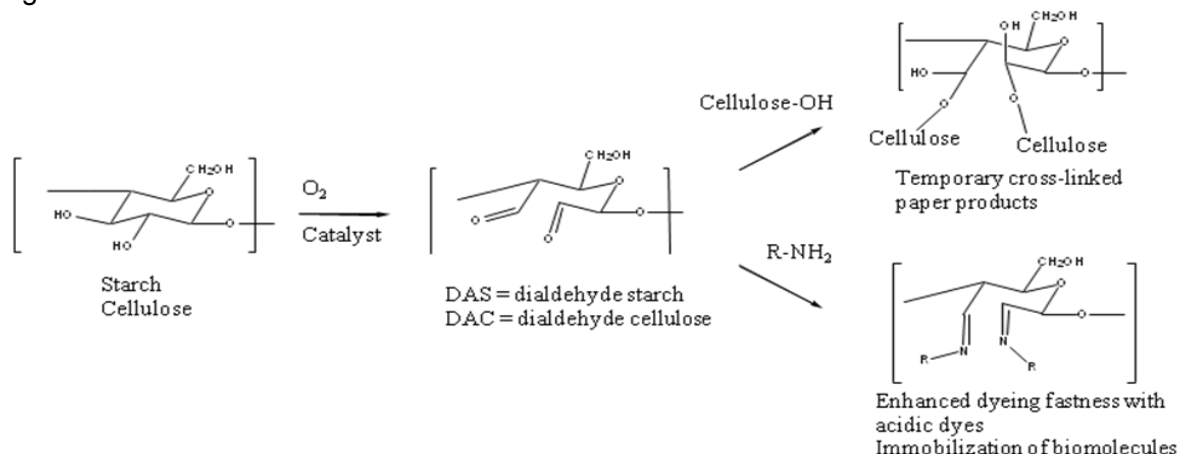


Figure 1. The oxidation of starch and cellulose to DAC and DAS and outlines of their potential utilization

- During 2009 a Forest Cluster financed project has been initiated dealing with DAC production during cellulose grinding. The project is executed in cooperation with Professor J. Niinimäki at University of Oulu, Professor I. Kilpeläinen at University of Helsinki and Heikki Pajari at VTT. Preliminary results indicate that the oxidation of cellulose to DAC in water can be accelerated considerably by using suitable metal catalysts.
- In the scope of this task, the experimental parts of additional two M.Sc. thesis works have been completed.

Task 3: Study and evaluation of environmental aspects and inherent risks related to these processes

- Literature review on the purification and recycling feasibility of ionic liquids was conducted
- Literature review on the use of membrane technologies in ionic liquid media
- Experimental design for the separation of ethanol and water from ionic liquids by pervaporation and nanofiltration on-going
- Studies for statistical experimental design carried out
- Theoretical study on Environmental Impact Assessment conducted **Impact of the research (visits, interviews, other activities)**

International collaboration

Collaboration initiated with Prof. Joao Crespo, REQUIMTE-CQFB, Department of Chemistry, Universidade Nova de Lisboa, Portugal, regarding membrane technologies and ionic liquids.

M.Sc. Katja Raassina participated in the EPNOE (European Polysaccharide Network of Excellence) conference. September 20 – 24, 2009, Turku

Results of the research (publications, posters, patents etc) in 2009

M.Sc. thesis:

Sirviö, J. *Selluloosan katalyyttinen hapetus natriumperjodaatilla*. University of Oulu

Haapala, K. *Tärkkelyksen katalyyttinen hapettaminen natriumperjodaatin avulla*. University of Oulu

Raassina K. *Tärkkelyksen hydrolyysi 1-butyyl-3-metyyli-imidatsoliumkloridissa*. University of Oulu

B.A. thesis:

Raassina, Katja. *Tärkkelyksen koostumus ja rakenne*. Oulun yliopisto

Related publications:

- Pongrácz E (2009) Through waste prevention towards corporate sustainability: Analysis of the concept of waste and a review of attitudes towards waste prevention. ***Sustainable Development***, Special issue: Paradigms of corporate sustainability. 17(2): 92-101.
- García V, Landaburu-Aguirre J, Pongrácz E, Perämäki P, Keiski R.L. (2009) Dehydration of water/dichloromethane/n-butanol mixtures by pervaporation: optimisation and modelling by response surface methodology. ***Journal of Membrane Science***, 338(1-2): 111-118.
- García V, Pongrácz E, Muurinen E and Keiski RL. (2009) Pervaporation of dichloromethane from multicomponent aqueous systems containing n-butanol and sodium chloride. ***Journal of Membrane Science***. 326(1): 92-102.
- Lajunen, Marja, (2009) Miten voi vihreä kemia? ***Natura*** 3, 50–52.

Progress of the research versus the original plan

According to the original plan starch and cellulose have been successfully modified in sustainable ways: in IL and catalytically.