



UNIVERSITY of OULU
OULUN YLIOPISTO

Sustainable processing of natural resources (SusProc)

Academy of Finland, Sustainable Production and Products (KETJU) Programme
Annual report 2008

<u>Project number:</u>	118212
<u>Responsible leader:</u>	Prof. Marja Lajunen
<u>Research leaders:</u>	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
<u>Site of research:</u>	University of Oulu (UOulu)
<u>Funding received:</u>	390.000 €
<u>Funding period:</u>	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 - 31.7.2009)

M.Sc.(Eng.) Alli Majala, UOulu, Mass and Heat Transfer Process Laboratory

Advisors: Prof. Marja Lajunen and Prof. Osmo Hormi, UOulu, Department of Chemistry; Doc. Eva Pongrácz and Prof. Riitta Keiski, UOulu, Mass and Heat Transfer Process Laboratory

Other researchers involved in the project:

Student Heidi Kemi, UOulu, Department of Chemistry

Student Ritva Nilivaara, UOulu, Department of Chemistry

Student Kati Haapala, UOulu, Department of Chemistry

Student Juho Sirviö, UOulu, Department of Chemistry

Student Katja Raassina, UOulu, Department of Chemistry

Student Anna Sivula, UOulu, Department of Chemistry

Collaboration partners:

Professor Kenneth R. Seddon Queen's University Ionic Liquid Laboratories (QUILL), Belfast, Ireland

Results of research and future goals

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

- Known ionic liquids have been prepared and used for the solubility tests of different starch species.
- New types of ionic liquids prepared in QUILL have been studied in solubility tests of starch species.
- Conditions for a degradation of different starch species in known ILs have been studied. In the optimized conditions starch species degrade yielding uniform quality products.
- Comparisons of activation methods (oil bath vs. microwaves) in the degradation of starch species have been performed.
- A method to analyze the degraded starch samples was developed. With the new method it is possible qualitatively to detect the large polysaccharides and the small sugars at the same time from a given sample.

- Studies of this task include the experimental part of one M.Sc and one B.A. thesis.

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)

- Oxidation of starch to DAS in water environment by using oxygen as the oxidizing agent has been performed. Preliminary results indicate that it is possible to oxidize starch to DAS in water environment by using oxygen as the oxidizing agent in the presence of suitable catalysts.
- The oxidation experiments on starch to obtain DAS have unambiguously shown that a 500 gram sample of starch can be oxidized in water catalytically to DAS by using a catalytic amount of NaIO_4 . The yield of DAS is about 80% it contains 8 – 10% oxidized anhydroglucose units.
- The preliminary results indicate that attempts to oxidize cellulose to DAC by using identical oxidation conditions are cumbersome.
- The results have also shown that cellulose can be oxidized in a homogenous ionic liquid solution catalytically to DAC by using NaIO_4 catalyst. The yield of DAC is about 90% and it contains 5 – 8 % of oxidized anhydroglucose units.
- In the scope of this task, the experimental parts of two M.Sc. thesis works have been completed.
- In the scope of this task, the experimental parts of additional two M.Sc. thesis works have been completed.

Both DAC and DAS polymers are materials with great potentiality in various industrial applications. 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, Figure1.

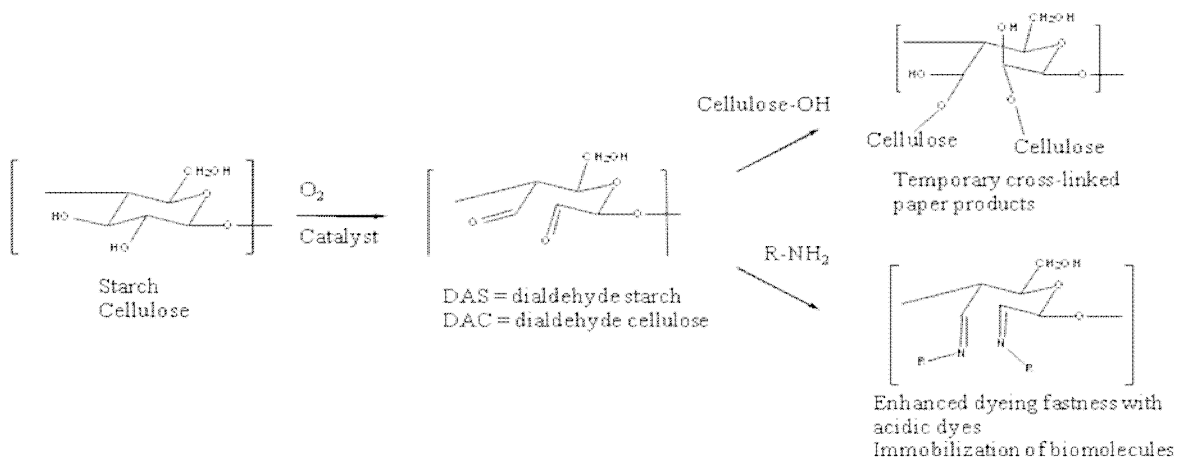


Figure 1. The oxidation of starch and cellulose to DAC and DAS and outlines of their potential utilization

In terms of environmental friendliness, the oxidation of cellulose and starch to DAC and DAS at the present moment is unattractive because it is performed by using periodate as the oxidative agent and the process results in an extremely large amounts of iodine containing byproducts.

In terms of utilization of DAS and DAC focus has been placed on their potential applications in biocomposites as a naturally occurring difunctional polymer which can create chemical bonds between the matrix and the reinforcing fibre.

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
- Experimental design for the separation of ethanol and water from ionic liquids by pervaporation and nanofiltration was commenced
- Studies for statistical experimental design carried out
- Theoretical study on Environmental Impact Assessment conducted

International collaboration

M.Sc Alli Majala spent a period of six months as a visiting researcher in QUILL (from 17.9.2007 to 31.3.2008).

Student Katja Raassina participated in the Summer School on Green Chemistry, tenth event, Safer and Innovative Solvents, Renewable-based Chemicals and Products..October 12-18, 2008, Venice.

Professor Kenneth R. Seddon Queen's University Ionic Liquid Laboratories (QUILL), Belfast, Ireland visited the group and gave a presentation (Ionic Liquids in Industrial Applications) Nov. 17-20, 2008.

Publications and presentations during 1.1.-31.12.2008

The following publications were written and published based on the research conducted during the research period of 01.01.-31.12.2008:

- Raassina, Katja; Lajunen, Marja. *Hydrolysis of starch in 1-butyl-3-methylimidazolium chloride*. The Summer School on Green Chemistry, tenth event, Safer and Innovative Solvents, Renewable-based Chemicals and Products. October 12-18, 2008, Venice.
- Niemi, Vuokko. *Luonnonpolymeerien hydrolysointi*. BA Thesis, Oulun yliopisto, 2008.
- Sivula Anna. *Tärkkelyksen koostumus ja ominaisuudet*. BA Thesis, Oulun yliopisto, 2008.
- Kemi, Heidi. *Selluloosan hapettaminen dialdehydiselluloosaksi ruteniumkatalyytin avulla*. MSc. thesis, Oulun Yliopisto 2008.
- Nilivaara, Ritva. *Tärkkelyksen katalyyttinen hapettaminen dialdehyditärkkelykseksi*. MSc. thesis, Oulun Yliopisto 2008.

Related publications

- Pongrácz, Eva. 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. In press. Accepted for publication 22.7.2008

- García, Verónica; Pongrácz, Eva; Muurinen, Esa and Keiski, Riitta Liisa. (2009) Pervaporation of dichloromethane from multicomponent aqueous systems containing n-butanol and sodium chloride. *Journal of Membrane Science*. 326(1): 92-102.
- García, Verónica; Pongrácz, Eva; Phillips, Paul S. and Keiski, Riitta Liisa. (2008) Factors Affecting Resource Use Optimisation of the Chemical Industry in the Northern Ostrobothnia Region of Finland. *Journal of Cleaner Production* 16(18): 1987-1994.