UNIVERSITY of OULU
OULUN YLIOPISTO

Sustainable processing of natural resources (SusProc)

Academy of Finland, Sustainable Production and Products (KETJU) Programme
Annual report 2007

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
Site of research:	University of Oulu (UOulu)
Funding received:	390.000 €
Funding period:	01.01.2007-31.12.2010

Project abstract

The aim of this project is to study, modify and process natural polymeric raw materials 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. Compounds to be studied are biopolymers: cellulose and starch. 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. The multidisciplinary team possesses expertise in the preparation and use of ILs, experience in working with natural polymers and in developing sustainable production processes, with the aim of recovery of maximum economic value from a resource while minimizing environmental impacts

Composition of the research team:

Researchers: Ph.D. Johanna Kärkkäinen, UOulu, Department of Chemistry (on leave during 23.3.2007 - 22.1.2008)

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 Katja Raassina, UOulu, Department of Chemistry

Collaboration partners:

Professor Kenneth R. Seddon and Dr. Nimal Gunaratne, 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 natural polymers cellulose and starch

- Known ionic liquids have been prepared for the solubility tests.
- New types of ionic liquids have been prepared and preliminary solubility tests with starch and cellulose have been performed in collaboration with QUILL.
- Various analytical methods for the detection of starch and its hydrolysis products have been studied.
- Solubilities of several commercial starches into the known ionic liquid BMIMCl assisted by microwave irradiation have been studied.

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.
- Oxidation of cellulose to DAC by using oxygen as the oxidizing agent has been performed. The preliminary results indicate that attempts to oxidize cellulose to DAC by using identical oxidation conditions are cumbersome.
- In the scope of this task, the experimental parts of two M.Sc. thesis works have been completed.

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.

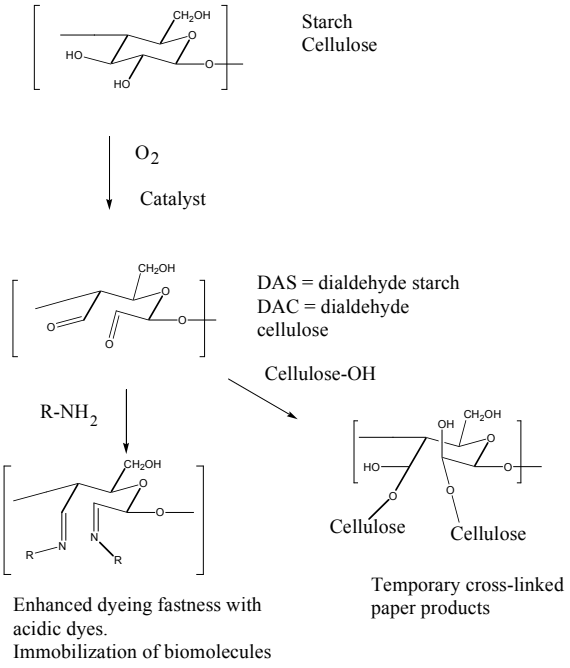

Figure 1. The oxidation of starch and cellulose to DAC and DAS and outlines of their potential utilization

In terms of environmental friendliness, the oxidation of cellulose and starch to DAC and DAS 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.

Task 3: <u>Study and evaluation of environmental aspects and inherent risks related to these processes</u>

- Theoretical study on the environmental aspects of ionic liquids was conducted.

- Researchers participated the first workshop/conference on the Biodegradability and Toxicity of Ionic Liquids (BATIL) during May 6.-8. 2007 in Berlin**,** Germany (M. Lajunen, A. Majala)

International collaboration

M.Sc. (Eng.) Alli Majala has been a visiting researcher at QUILL during 15.9. 2007 – 31.3.2008, where her work was supervised by Prof. Seddon and Dr. Gunaratne.

Publications and presentations during 1.1.-31.12.2007

The following publications were written and published based on the research conducted during the research period of 01.01.-31.12.2007:

- Majala, A., Pongrácz, E., Kärkkäinen, J., Lajunen, M. and Keiski, R.L. (2007) Environmental impacts of ionic liquids. Proc. Eight Finnish Conference of Environmental Sciences. Mikkeli, May 10-11, 2007. pp. 127-130. Extended abstract and poster presentation.
- Lajunen, M. and Tirronen, E. (2007) Kriittistä tietoa ionisista nesteistä. (Critical information about ionic liquids.) *Kemia*-Kemi, 34, **2007,** 4.
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