

SUSTAINING CARBONIC ESTERS SYNTHESIS WITH CARBON DIOXIDE FEEDSTOCK (SUSE)

Sustainable Production and Products (KETJU) Annual Report 2009

<u>Project numbers:</u>	OU: 129173 ÅA: 129170
<u>Research leaders in charge:</u>	Prof. Riitta Keiski, University of Oulu, Finland (OU) Prof. Jyri-Pekka Mikkola, Åbo Akademi University, Finland (ÅA)
<u>Funding:</u>	OU: 171.900 € ÅA: 166 530 € (total project: 608.730 €)
<u>Funding period:</u>	01.01.2009-31.12.2011

Summary of the project

Due to the continuous increase in Earth's atmosphere of carbon dioxide, under the threat of global warming, green processes based on chemical fixation of CO₂ have recently attracted much attention.

SUSE research project focuses on the development of a sustainable process for the fixation of the entire CO₂ molecule to alcohols $\text{CO}_2 + \text{ROH} \xrightleftharpoons{\text{cat.}} (\text{RO})_2\text{CO} + \text{H}_2\text{O}$ for the formation of open-chain carbonic esters such as diethyl carbonate (DEC). Organic carbonates have a high market potential, currently limited by their hazardous production technologies. Therefore, the new process elaborated within the SUSE project is aiming to waste minimization for the industry via utilizing waste-CO₂ and reducing the hazard of solvents and chemicals conventionally used for carbonic esters production. To facilitate this goal, the project intends to identify new, effective catalysts for DEC syntheses, and to explore safe and environmentally friendly reaction pathways and energy-efficient processes. Project is carried out by the University of Oulu (Finland), Åbo Akademi University (Finland), CNRS-University of Bourgogne (France) and University of Lyon (France).

Composition of the research team

Researchers funded within the project:

- M.Sc. (Eng.) Ewelina Leino (ÅA)
- M.Sc. (Chem.) Paula Saavalainen (OU) (1.9.2009-)

Other researchers involved in the project:

- M.Sc.(Eng.) Helka Turunen

Research supervisors and advisors:

- Prof. Riitta Keiski, Doc., Dr. Eva Pongrácz (OU)
- Prof. Jyri-Pekka Mikkola, Doc. Päivi Mäki-Arvela, Prof. Dmitry Yu. Murzin (ÅA)

Collaboration partners:

- Dr. Laurent Plasseraud, CNRS-University of Bourgogne, France (SYMCAAT/uB), French Coordinator
- Prof. Frédéric Bernard, CNRS-University of Bourgogne, France (MaNaPI/uB), Sub-project leader
- Prof. Henry Chermette, CNRS-University of Lyon, France (CHEMOD/UCBL), Sub-project leader

Project results during the period 01.01.-31.12.2009

In all the units of the consortium, research progress was good. During the funding period of 01.01.-31.12.2009 the following tasks were performed:

Mass and Heat Transfer Process Laboratory (OU):

- Literature review of sustainability indicators, indexes and metrics for chemical industry
- Back ground studies of sustainability methodologies
- Sustainability assessment tools (software) reviews and demo arrangements
- Existing environmental and sustainability databases evaluation

Laboratory of Industrial Chemistry (ÅA):

- Literature review of diethyl carbonate (DEC) conventional synthesis methodologies and novel technologies starting from CO₂ and ethanol
- Construction of experimental setup, development of analytical methods
- Catalyst preparation and preliminary characterisation
- Laboratory experiments to test catalyst activity and selectivity without using a chemical water trap
- Thermodynamic calculations (ΔG) and determination of equilibrium constant
- Laboratory experiments for synthesis of DEC by utilization of the chemical water trap, i.e. shifting of reaction equilibrium for enhanced conversion

Publications

The following publications were written based on the research conducted during the research period of 01.01.-31.12.2009:

Journal articles

Ewelina Leino, Päivi Mäki-Arvela, Valerie Eta, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Carbon dioxide as renewable feedstock for producing short-chain dialkylcarbonates: Insight into diethyl carbonate synthesis methods" *Energy and Environmental Sciences* (submitted)

Abstracts

Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola ” Utilization of carbon dioxide for the synthesis of organic carbonates” – submitted to The 7th European Congress of Chemical Engineering ECCE-7

Posters

Laurent Plasseraud, Danielle Ballivet-Tkatsenko, Riitta Keiski, Helka Turunen, Henry Chermette, M. Pourkhalor ”From CO₂ to dialkyl carbonates. Understanding the catalytic cycle.” – Symposium on CO₂, Toulouse, France, December 16-17, 2008.

Seminars and lectures

First six-months Meeting - SUSE Project, (ANR-08-CP2D-18), Dijon, University of Burgundy, 22-23 of June 2009

Guest lecture at Helsinki University ‘Ionic Liquids’ 13.11.2009 (invitation by Prof. Heikki Tenhu), J-P Mikkola

Mikkola, J-P, Seminar by the Finnish Society for Industrial Ecology, Geological Survey of Finland, Espoo, 28-29.04.2008 ‘Towards Sustainable Energy: the Nordic Way of Renewables ?’, invited speaker

Mikkola, J-P, BSR Baltic Sea Innonet Meeting, Örnsköldsvik, Processum; Nov. 12-13 2008, Sweden; invited speaker

Mikkola, J-P, ‘Window of Opportunity for Real Change’, The annual conference of the Finnish Society for Industrial Ecology in collaboration with the Finnish Platform on Life Cycle Assessment(FINLCA), invited speaker, December 14, Åbo Akademi, Åbo-Turku, Finland

Keiski, R. Sustainable Energy – Biofuels and Biorefinery Concept. Growth and competitiveness through renewable energy resources. Open days, Brussels, 6.10.2009. Invited speaker

Keiski, R. SUSE – Sustaining carbonic esters synthesis with carbon dioxide feedstock. KETJU annual seminar, Suomenlinna, Helsinki, 10.-11.2.2009.

Keiski, R. & Pongracz, E. SUSE – Sustaining carbonic esters synthesis with carbon dioxide feedstock. First Six-month SUSE Meeting, June 22-23, 2009, University of Burgundy, Dijon.

SUSEn annual meeting, 6-7.10.2009 Helsinki

- Prof. Jyri-Pekka Mikkola – *oral presentation*
- M.Sc. (Eng.) Ewelina Leino ”Utilization of CO₂ to organic carbonates” – *poster presentation*

Summer school: Materials – catalytic or not?, 10-12.6.2009, Hotel Kristina, Kristinestad

- Prof. Jyri-Pekka Mikkola "SILCA or SILP?- supported Ionic Liquid Catalysis-Phase"
– *oral presentation*

CO₂- SUSE seminar at Åbo Akademi Process Chemistry Centre, 8-9.10.2009, Turku

- M.Sc. (Eng.) Ewelina Leino "Novel routes for diethyl carbonate synthesis" – *oral presentation*
- Prof. Riitta Keiski "CO₂ utilization projects at UOulu" – *oral presentation*

Co-operation between SusEn & Ketju-projects

It should be pointed out that all public research projects, including those within SusEn and KETJU in progress at the Laboratory of Industrial Chemistry and Reaction Engineering, have natural interaction via researcher meetings and shared knowledge/infrastructure. Within SUSEN & KETJU the projects running are: OPTBIO, BIOGASUP, SUSFUFLEX and SUSE & CO₂UTIL. The University of Oulu is taking part in SUSFUFLEX and SUSE & CO₂UTIL.