TOWARDS UTILIZATION OF CARBON DIOXIDE AS A GREEN AND VERSATILE COMMODITY CHEMICAL: CLEAN SYNTHESIS OF METHANOL AND DIMETHYL CARBONATE (CO2UTIL)

Sustainable Production and Products (KETJU)
Annual Report 2009

Project number:	118078
Consortium leader:	Docent, Dr. Eva Pongrácz
Research leaders in charge:	Prof. Riitta Keiski, Doc., Dr. Eva Pongrácz and Prof. Kauko Leiviskä, University of Oulu (UO), Finland Prof. Jyri-Pekka Mikkola, Åbo Akademi University (ÅA), Finland Prof. Danielle Ballivet-Tkatchenko, CNRS-University of Bourgogne, France
Funding:	608.730 €
Funding period:	01.01.2007-31.12.2010

Summary of the project

CO2UTIL research project aims at developing a sustainable process for the production of methanol (CH_3OH) and dimethyl carbonate (DMC) using carbon dioxide as a raw material. The process will result in value enhancement of a secondary resource from anthropogenic source, while minimizing environmental impacts. The new process will result in waste minimization for the industry via utilizing waste CO_2 and reducing the hazard of solvents and chemicals conventionally used, while developing new innovative and sustainable products that have high economic value. To facilitate this goal, the project intends to identify new, effective catalysts for methanol and dimethyl carbonate syntheses, and explore safe and environmentally sound reaction pathways and energy-efficient processes. Project is carried out by the University of Oulu (Mass and Heat Transfer Process Laboratory and Control Engineering Laboratory), Åbo Akademi University (Laboratory of Industrial Chemistry) and CNRS-University of Bourgogne (Institut de Chimie Moléculaire).

Composition of the research team

Researchers funded within the project:

- M.Sc.(Eng.) Esa Turpeinen
- M.Sc.(Eng.) Outi Mäyrä
- M.Sc.(Eng) Valerie Eta

Other researchers involved in the project:

- M.Sc.(Eng.) Helka Turunen
- M.Sc.(Eng.) Jari Ruuska
- Docent, Dr. Päivi Mäki-Arvela

Research advisors:

- Prof. Riitta Keiski, Prof. Kauko Leiviskä, Doc., Dr. Eva Pongrácz (UO)
- Prof. Jyri-Pekka Mikkola, Prof. Tapio Salmi, Prof. Dmitry Murzin(ÅA)

Collaboration partners:

- Prof. Dr. Danielle Ballivet-Tkatchenko, Dr. Laurent Plasseraud and Dr. Michel Picquet, CNRS-University of Bourgogne, France

Project results during the period until 31.12.2009

In all the units of the consortium, research progress was good. During the funding period of 1.1.-31.12.2009 the following tasks were performed:

Mass and Heat Transfer Process Laboratory (UO):

- Identification of CO_2 containing gas streams which can be reformed and utilised in hydrogen/synthesis gas production.
- Comparing by simulations the feasibility of hydrogen production processes (reforming processes) using CO_2 containing gas streams as feedstock.
- Planning laboratory experiments concerning hydrogen production by reforming using CO_2 containing gas streams as feedstock (design of experiments, selection of catalysts and process conditions, configuration of testing equipments).
- Conducting laboratory experiments
    - testing of selected catalysts (activity, stability and selectivity)
    - testing of various gas compositions (maximization of CO_2 conversion and synthesis gas/hydrogen yield).
- Sustainability assessment of the use of secondary CO_2, waste-to-resource evaluation, resource use optimization aspects of the proposed processes.
- In addition, MHTPL/UO coordinated the project, and actively promoted networking and collaboration.

Control Engineering Laboratory (UO):

- Literature study considering the modelling of methanol synthesis.
- Development of the theoretical macroscopic models for the methanol synthesis based on the mass balances and the assumed reaction schemes.
- Development of the process simulators based on the theoretical models.
- Literature survey considering the modelling of DMC synthesis.
- Sensitivity analysis of the developed model.
- Validation of the simulator.

Laboratory of Industrial Chemistry (ÅA):

- Literature review of dimethyl carbonate (DMC) synthesis from CO_2 and methanol, process and identification of the reaction route.
- Construction of experimental setup, development of analytical methods.
- Catalyst preparation and preliminary characterisation.
- Thermodynamic calculations (ΔG) and determination of equilibrium constant.
- Laboratory experiments to test catalyst activity and selectivity, methanol conversion.
- Laboratory experiments to determine reaction conditions for DMC synthesis (temperature, pressure, time, amount of catalyst and methanol).
- A new high-end, ultra-high pressure setup equipped with sapphire windows for monitoring of reaction progress was purchased and built.
- Reaction feasibility and investigations to optimise conversion.
- Discovery of a novel route utilizing a chemical water trap for enhanced conversion.
- A candidate novel catalytic material with high selectivity and conversion discovered (preliminary results).

Collaboration:

The project team has launched an additional collaboration project titled '**Sustaining carbonic esters synthesis with carbon dioxide feedstock: a 3E criteria assessment**' (January 1, 2009 – December 31, 2011), financed by the Academy of Finland and ARN (L'Agence nationale de la recherché) joint programme.

Publications in 2009

The following publications were written and published based on the research conducted:

Articles

- Pongrácz E, Turpeinen E, Raudaskoski R, Ballivet-Tkatchenko D and Keiski RL. (2009) From waste to resource for methanol-based processes. ***Waste and Resource Management, Proceedings of the Institution of Civil Engineers***. 162(4): 215-220.
- Raudaskoski R, Turpeinen E, Lenkkeri R, Pongrácz E and Keiski RL. (2009) Catalytic activation of CO_2: Use of secondary CO_2 for the production of synthesis gas and for methanol synthesis over zirconia containing catalysts. ***Catalysis Today,*** 144(3-4): 318-323.

Conference proceedings

- Pongrácz, E.; Turpeinen, E.; Mäyrä, O.; Leiviskä, K. and Keiski, R. (2009) Chemical utilization of CO_2 in dry reforming and methanol synthesis. In: Paukkeri, A.; Ylä-Mella, J. and Pongrácz, E. (eds.) Energy research at the University of Oulu. Proceedings of the EnePro conference, June 3rd, 2009, University of Oulu, Finland. Kalevaprint, Oulu, ISBN 978-951-42-9154-8. pp. 79-82.
- Full paper submitted to the 8th World Congress of Chemical Engineering, Montreal, Quebec, Canada, Aug.23-27, 2009.

Abstracts

- Turpeinen, E. and Keiski, R.L. Reforming of CO_2 containing gases. Submitted to 9th Novel Gas Conversion Symposium, Lyon, France, May 30th - June 3rd, 2010.

Manuscripts

- Valerie Eta, Päivi Mäki-Arvela, Anne-Riikka Leino, Krisztián Kordás, Tapio Salmi, Dmitry Yu. Murzin, Jyri-Pekka Mikkola., Sustainable synthesis of dimethyl carbonate from methanol and carbon dioxide under dehydration - The effect of magnesium enhanced reactions. ***Journal of catalysis*** (submitted)

Seminars and lectures

A project meeting was kept in Oulu on 26.6.2009, where project researchers discussed sharing project data.

A joint seminar of three Academy of Finland Sustainable Production and Products (KETJU) research programme financed CO_2 projects, where participant of CO2UTIL, "Carbon dioxide as a green carbon source in transition metal catalyzed syntheses" and SUSE (Sustaining carbonic esters synthesis with carbon dioxide feedstock) projects have met and exchanged experiences during, 8.-9.10.2009 at Åbo Akademi University.

Seminar organizer:

- Prof. Jyri-Pekka Mikkola (Åbo Akademi University, Turku, Finland)

The consortium members have contributed to the seminar with the following presentations:

- Eta, V.: Recent advances in DMC synthesis
- Keiski, R.L.: CO_2 utilization projects at UOulu
- Pongrácz, E.: Chemical Utilization of CO_2: From Waste to Resource
- Prof. Em. Ballivet-Tkatchenko, D.: Mitigation of CO_2 emissions: can we make a difference?

Further, project members have given presentations and lectures based on the research conducted in this project on the following academic forums:

- Mikkola, J-P: CO2UTIL report presented at the KETJU annual seminar (Suomenlinna, Helsinki, 10.-11.2.2009)
- Guest lecture at Helsinki University 'Ionic Liquids' 13.11.2009 (invitation by Prof. Heikki Tenhu), J-P Mikkola
- '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
- Summer school: Materials – catalytic or not, 10-12.6.2009, Hotel Kristina, Kristinestad, Invited speaker
- BSR Baltic Sea Innonet Meeting, Örnsköldsvik, Processum; Nov. 12-13 2008, Sweden; invited speaker
- Valerie, Eta, Ewelina Leino., CO2-SUSE –seminar, 8-9 Oct. 2009 within the auspices of the Academy of Finland Sustainable Energy (SusEn) and Sustainable Production and Products (KETJU) research programmes, Åbo Akademi University, Finland (Poster Presentation)

- Poster presentation of CO2UTIL at the EnePro conference, June 3rd 2009, University of Oulu
- 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 report presented at the KETJU annual seminar (Suomenlinna, Helsinki, 10.-11.2.2009)