

**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 2008

<u>Project number:</u>	118078
<u>Consortium leader:</u>	Docent, Dr. Eva Pongrácz
<u>Research leaders in charge:</u>	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
<u>Funding:</u>	608.730 €
<u>Funding period:</u>	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<sub>3</sub>OH) 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<sub>2</sub> 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
- M.Sc.(Eng.) Riitta Raudaskoski (01.01.2007-31.03.2008)
- D.Sc.(Tech.) Tanja Kolli (01.07.-31.12.2008)

#### Other researchers involved in the project:

- Lic.Sc.(Tech.) Ritva Lenkkeri
- M.Sc.(Eng.) Helka Turunen
- M.Sc.(Eng.) Jari Ruuska

#### 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 01.01.-31.12.2008**

In all the units of the consortium, research progress was good. During the funding period of 01.01.-31.12.2008 the following tasks were performed:

#### Mass and Heat Transfer Process Laboratory (UO):

- Identification of CO<sub>2</sub> 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<sub>2</sub> containing gas streams as feedstocks.
- Planning of laboratory experiments concerning hydrogen production by reforming using CO<sub>2</sub> containing gas streams as feedstocks.
- Writing two articles concerning the utilisation of CO<sub>2</sub> in chemical syntheses.
- 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.

#### Laboratory of Industrial Chemistry (ÅA):

- Literature review of dimethyl carbonate (DMC) synthesis from CO<sub>2</sub> and methanol, process and identification of the reaction route.
- Construction of experimental setup, development of analytical methods
- Catalyst preparation and preliminary characterisation
- Thermodynamic calculations ( $\Delta G$ ) 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 is launching 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 ANR (L'Agence nationale de la recherche) joint programme.

### **Publications**

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

#### *Articles*

- Turpeinen E, Raudaskoski R, Pongrácz E and Keiski RL. (2008) Thermodynamic analysis of conversion of alternative hydrocarbon-based feedstocks to hydrogen. *International Journal of Hydrogen Energy*. 33(22): 6635-6643.
- Raudaskoski R, Turpeinen E, Lenkkeri R, Pongrácz E and Keiski RL. Catalytic activation of CO<sub>2</sub>: Use of secondary CO<sub>2</sub> for the production of synthesis gas and for methanol synthesis over zirconia containing catalysts. *Catalysis Today*. In press.
- Pongrácz E, Turpeinen E, Raudaskoski R, Ballivet-Tkatchenko D and Keiski RL. Chemical utilization of CO<sub>2</sub>: From waste to resource. Submitted to *Waste and Resource Management. Proceedings of the Institution of Civil Engineers*.
- Eta V, Mäki-Arvela P, Kordás K, Murzin DY, Salmi T and Mikkola J-P. The Activity of Zirconia and Other Metal Oxides in the Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide, *Heterogeneous Catalysis Research Progress* (book chapter), 2008 Nova Publishers (accepted)

#### *Abstracts*

- Turpeinen E, Raudaskoski R, Pongrácz E and Keiski RL. Hydrogen production by reforming of CO<sub>2</sub>-containing process gases. "Carbon Dioxide: a waste, a raw material. Fate or opportunity." –symposium. 16.-17.12 2008, Toulouse, France.
- Turpeinen E, Raudaskoski R, Pongrácz E and Keiski RL. CO<sub>2</sub> utilization in methanol production. "Carbon Dioxide: a waste, a raw material. Fate or opportunity." –symposium. 16.-17.12 2008, Toulouse, France

#### *Manuscripts*

- Pongrácz E, Mikkola J-P, Korhonen J, & Keiski RL. The social life-cycle of waste: Evolution of perceptions of CO<sub>2</sub>. To be submitted to *Progress in Industrial Ecology*.
- Full paper submitted to the 8<sup>th</sup> World Congress of Chemical Engineering, Montreal, Quebec, Canada, Aug.23-27, 2009

## Seminars and lectures

The project members have been actively involved in the organisation of the COST-Action 543: Summer School **Sustainable Production and Energy: Catalysis by Nanomaterials, Catalytic Microreactors** organized during June 2-6, 2008 at the University of Oulu.

Seminar coordinators

- Prof. Riitta Keiski (University of Oulu, Oulu, Finland)
- Prof. Jyri-Pekka Mikkola (Åbo Akademi University, Turku, Finland)

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

- Keiski, R.L.: Green chemistry and catalysis; Catalysis and catalysis by nanomaterials
- Leiviskä, K.: Control issues and automation in microreactor concepts
- Mikkola, J.-P.: Future integrated agro-forest biorefinery; Nanocatalysis in ionic liquids
- Pongrácz, E. : Sustainability, sustainable production and energy

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

- Eva Pongrácz, Jyri-Pekka Mikkola, Jouni Korhonen, Riitta Keiski, The social life-cycle of waste Evolution of perceptions of CO<sub>2</sub>, 14th Annual International Sustainable Research Development Conference, New Delhi, India, 21-23 Sept. 2008-10-12 (Presented by J.-P. Mikkola)
- Ballivet-Tkachenko, D., Turpeinen, E., Raudaskoski, R., Pongrácz, E. and Keiski, R.L. CO<sub>2</sub> utilization in methanol production. "Carbon Dioxide: a waste, a raw material. Fate or opportunity." –symposium. 16.-17.12.2008, Toulouse, France. (Poster presentation)
- The University of Oulu's 50<sup>th</sup> anniversary Science Days, "Global change: What is it and what can we do about it?" panel, 16.5.2008 (Pongrácz, E.)
- Nordic Recycling Day, Luleå, Sweden, 7.-8.10.2008 (Pongrácz, E.)
- Finnish TV1 Prisma science program (interv. 05.12.2007) 10.01.2008 (J.-P. Mikkola)
- Teollisuus-Nyt, 2007, interview (J.-P. Mikkola)
- SVT (Swedish TV2) RegionalNytt, 18.02.2008 (J.-P. Mikkola)
- Interviews, Kemia-kemi 06/2008; Meddelanden 31.10.2008 (J.-P. Mikkola)
- Västerbotten Kuriren 02.10.2008 (J.-P. Mikkola interview together with prof. Leif Jönsson)
- Invited lecturer, Academy of Finland, 17.-18.06.2008, 'Energy & Power' seminar, Vantaa (J.-P. Mikkola)
- Invited lecturer, Vinnova Vinnväxt Kick-off seminar, Husum, 18.09.2008 (J.-P. Mikkola)
- Invited lecturer, Processum Biorefinery Initiative, 18.03.2008 (J.-P. Mikkola)
- Invited lecturer, Helsinki University, Tvärminne seminar, 16.06.2008(J.-P. Mikkola)

## Research visits:

- Valerie Eta; Dijon, CNRS-University of Bourgogne, France, July-August 2008