# 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 2007

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| 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<br>Doc., Dr. Jyri-Pekka Mikkola, Åbo Akademi University (ÅA), Finland<br>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.) Riitta Raudaskoski
- 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
- Lic.Sc.(Tech.) Ritva Lenkkeri
- M.Sc.(Eng.) Jari Ruuska

Research advisors:

- Prof. Riitta Keiski, Prof. Kauko Leiviskä, Doc., Dr. Eva Pongrácz (UO)
- Doc., Dr. 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
- Prof. Carey Simonsson, University of Saskatchewan, Canada

**Project results during the period 01.01.-31.12.2007**

In all the units of the consortium, research has progressed as planned. During the funding period of 01.01.-31.12.2007 the following tasks were performed:

Mass and Heat Transfer Process Laboratory (UO):

- Definition and identification of processes and reactions as well as literature screening considering the research themes (methanol synthesis and reforming of $CO_2$ containing gases).

- Preliminary thermodynamic calculations with HSC Chemistry® and Aspen Plus programs for selecting proper reaction conditions for the laboratory experiments.

- Planning of laboratory experiments (activity measurements and catalyst characterization) concerning methanol synthesis reaction from carbon dioxide and hydrogen.

- Evaluating by simulations the feasibility of hydrogen production processes using different feedstock, as hydrogen is needed as raw material in the production of methanol.

Control Engineering Laboratory (UO):

- The literature study considering the modelling of the studied processes.

- Development of the theoretical macroscopic models for the methanol and DMC 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 $CO_2$ and methanol, process and identification of the reaction route.
- Construction of experimental setup, development of analytical methods
- Catalyst preparation and preliminary characterisation
- Thermodynamic calculations ($\Delta G$) 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)
- Reaction feasibility and investigations to optimise conversion

**Project organisation**

The project actively promoted networking and collaboration within the participating units and their researchers, which has resulted in further collaboration plans. The consortium members have kept the following meetings during 2007:

- 17.1. Helsinki: Catalysis research, DMC synthesis, advisor meeting (participants: Ballivet-Tkatchenko, Keiski, Mikkola, Pongrácz)
- 27.6., Oulu: Simulation of methanol synthesis and reforming, researcher meeting (Mäyrä, Pongrácz, Raudaskoski, Ruuska, Turpeinen)
- 4.12., Oulu, CO2UTIL consortium annual evaluation meeting (Eta, Keiski, Leiviskä, Mikkonen, Mäyrä, Pongrácz, Raudaskoski, Ruuska, Turpeinen)

**Publications**

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

Huuhtanen, M., Kolli, T., Pitkäaho, S., Raudaskoski, R., Turpeinen, E. and Keiski, R.L. Catalysis for Sustainable Production and Emission Control. 8th Finnish Conference of Environmental Sciences Mikkeli 10.-11.5.2007. Abstract and poster presentation.

Pongrácz, E., Raudaskoski, R., Turpeinen, E., Keiski, R.L. & Ballivet-Tkatchenko, D. Sustainability of chemical intermediates: Clean synthesis of methanol and dimethyl carbonate from carbon dioxide. In: Cerin P, Dobers P and Schwartz B (eds.) Proc. 13th Annual Sustainable Development Research Conference. 10.-12.6.2007, Västerås, Sweden. pp. 175-176. Conference paper and oral presentation.

Turpeinen, E., Pongrácz, E. & Keiski, R.L. Reforming of metallurgical industry's process gases. Europacat VIII Turku 26.-31.8.2007. CD-ROM of extended abstracts and poster presentation.

Raudaskoski, R., Turpeinen, E., Lenkkeri, R., Pongrácz, E. and Keiski, R.L. Catalytic activation of $CO_2$: Use of secondary $CO_2$ for the production of synthesis gas and for methanol synthesis over zirconia containing catalysts. Submitted to Catalysis Today.

**Seminars and lectures**

The project also initiated and the project members have been actively involved in the organisation of the first French-Finnish seminar of the Academy of Finland and Centre National de la Recherche Scientifique (CNRS) France, on 6.9.2007, titled **Chemistry for the protection of the global environment**.

Organising committee and seminar chairs:

- Aronson, Marie (Embassy of France, Helsinki);
- Ballivet-Tkatchenko, D. (CNRS-University of Bourgogne)
- Keiski R.L. & Pongrácz E., University of Oulu;

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

- Ballivet-Tkatchenko, D. : $CO_2$ to chemicals: Beyond Utopia
- Keiski, R.L.: Catalysis for sustainability
- Mikkola, J-P.: Ionic liquids, their synthesis and environmental impacts

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

- 13th Annual International Sustainable Development Research Conference, Västerås, Sweden, 10.-12.6.2007 (Pongrácz, E.)
- First Chile-Finland Renewable Energy Research Workshop, Santiago de Chile, August 8-9, 2007 (Mikkola, J-P.)
- Europacat VIII, Turku, 26.-31.8.2007 (Ballivet-Tkatchenko, D., Keiski, R.L., Mikkola, J-P., Turpeinen, E.)
- Seminar on Green Chemistry (under the auspices of KTT and Finnish Catalysis Society), Helsinki 9.10. 2007 (Keiski, R.L., Mikkola, J-P.)
- III. International Conference Catalysis: Fundamentals and Applications. 100th Anniversary of Academician G.K. Boreskov, Novosibirsk, Russia, 4.-8.7.2007 (Keiski, R.L.)
- Industrial Ecology advanced course, University of Oulu, Department of Process and Environmental Engineering, 25.9.2007 (Raudaskoski, R.)