Roadmap for CO_2 Utilization
Evaluation of the CO_2 Use as a Solvent

INTERMEDIATE REPORT

Carbon Capture and Storage Program (CCSP)

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ROADMAP FOR CO_2 UTILIZATION

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INDUSTRIAL UTILISATION OF CARBON DIOXIDE

Annual use of carbon dioxide is around 130 Mt. Approximately 70 Mt of this amount is used in urea synthesis, about 30 Mt in production of inorganic carbonates and pigments, and around 15 Mt in methanol synthesis. The utilization amounts are presented in Figure 1 (Note, the y-axis is logarithmic). The technological use includes e.g. utilization of CO2 as solvents, in fire extinguishers and in water treatment.

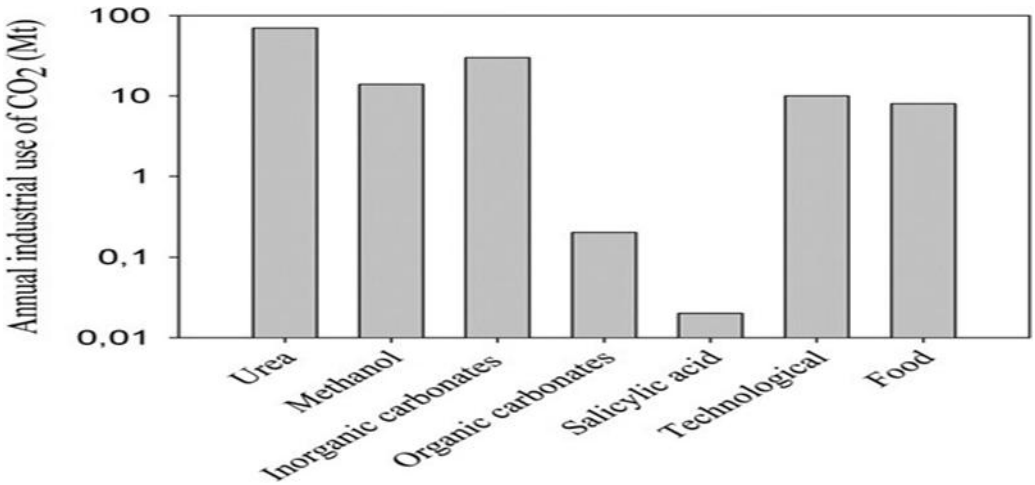


Figure 1. The use and amount of carbon dioxide at the moment [1]

In Figure 2 the technological use of carbon dioxide is presented more detailed.

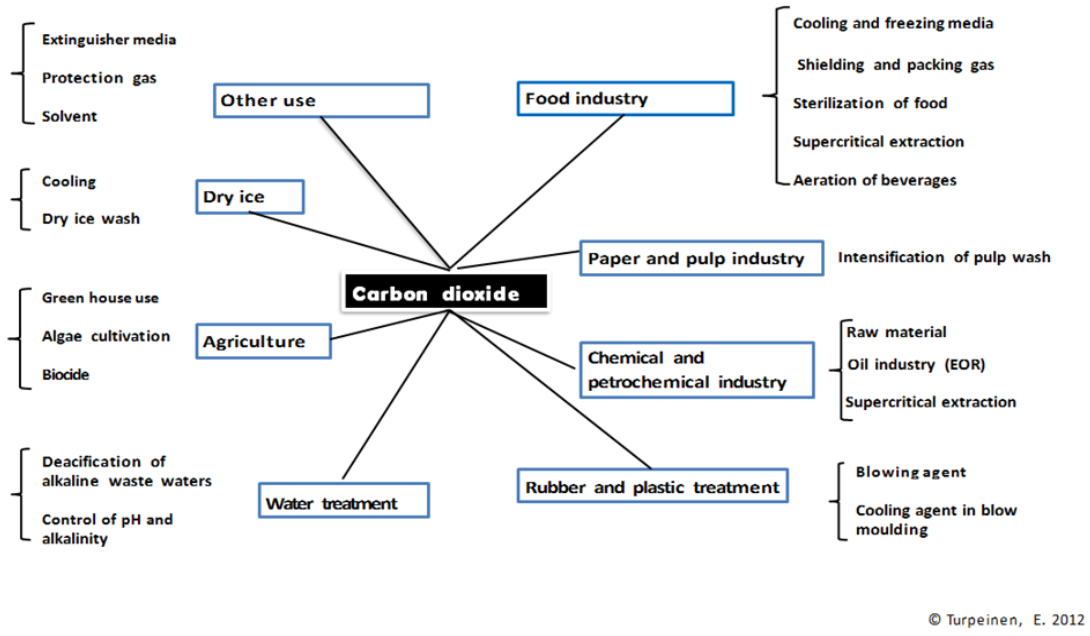


Figure 2. The utilisation subjects of carbon dioxide.

CHEMICAL UTILISATION OF CARBON DIOXIDE

As an economical, safe, and renewable carbon source, CO_2 turns out to be an attractive C1 building block for making chemicals and materials. The utilization of CO_2 as a feedstock for producing chemicals not only contributes to alleviating global climate changes caused by the increasing CO_2 emissions, but also provides a grand challenge in exploring new concepts and opportunities for catalytic and industrial development. Considerable literature has been devoted to the possibilities of CO_2 conversion as well as to the catalysis for CO_2 conversion. [2-6]

Reactions of CO_2 can be divided into two groups [7]:

- Reactions that use the entire molecule, such as fixation onto an organic substrate in which that substrate donates the needed energy. These reactions do not need much additional energy and hence occur at lower temperatures (240 - 400 K).
- Reactions that convert CO_2 into another C1 molecule or Cn molecules. These reduction reactions use hydrogen, electrons, or heat as the energy source. Because they require a large amount of energy, they occur at high temperatures (600 - 1000 K).

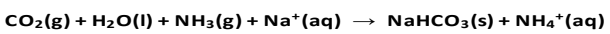
Carbon dioxide holds significant thermodynamic stability. The molecule is linear with a bond strength of 532 kJ/mol. Its Gibbs free energy of formation has a large negative value (ΔG_f = 394.6 kJ/mol), which contributes to the high inertness of CO_2 and renders its reactions energetically unfavourable. Besides requiring high energy inputs, the reduction reactions of CO_2 also need an effectively designed catalytic system that lowers the kinetic activation energy barriers.

At the moment carbon dioxide is utilised as a raw material in chemical reactions in the following five processes [1].

Urea synthesis

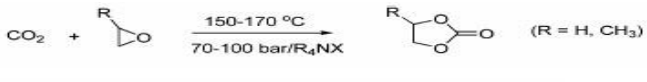
Methanol synthesis

Syntheses of inorganic carbonates
(e.g. sodiumbicarbonate, Solvay process)



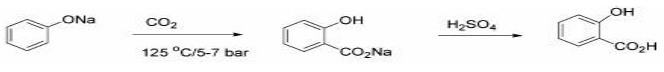
Syntheses of organic carbonates

Cyclic carbonates (e.g. propylenecarbonate)



Acyclic carbonates (e.g.. dimethylcarbonate)

Salisylic acid synthesis



In addition to the above mentioned routes several carbon dioxide based reaction routes can be identified which are under research. In Figure 3 some of these reaction routes are presented. The products are e.g. carbamates (n:o 5), acetic acid and formic acid (n:o 7), lactone (n:o 10) and ethylene (n:o 16).

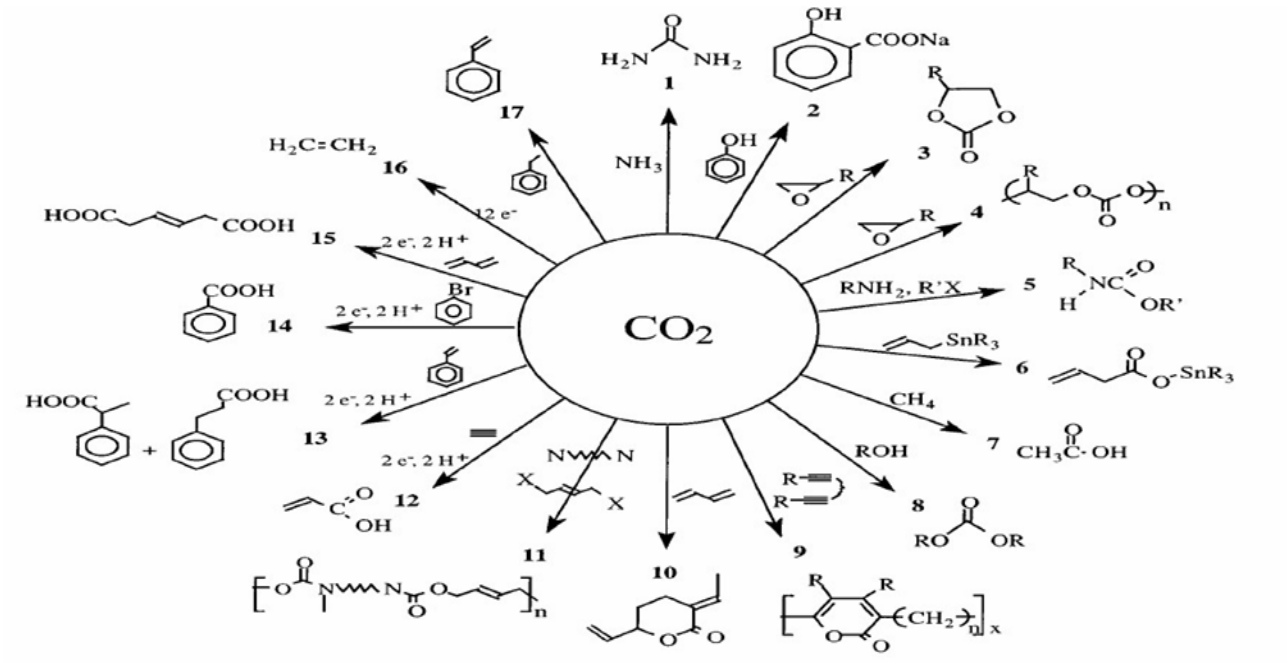


Figure 3. Reaction routes under research where carbon dioxide is a reactant [8].

Refereneces:

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2. Aresta, M. and Dibenedetto, A. (2010) Utilisation of CO_2 as a Chemical Feedstock: Opportunities and Challenges. Dalton Trans. 2975 – 2992.

3. Song, C. (2006) Global Challenges and Strategies for Control, Conversion and Utilization of CO_2 for Sustainable Development Involving Energy, Catalysis, Adsorption and Chemical Processing. Catal. Today, 115, 2 – 32.

4. Sakakura, T., Choi, J. C. and Yasuda, H. (2007) Transformation of Carbon Dioxide. Chem. Rev., 107, 2365 – 2387.

5. Centi, G. and Perathoner, S. (2009) Opportunities and Prospects in the Chemical Recycling of Carbon Dioxide to Fuels. Catal. Today, 148, 191 – 205.

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7. Aresta, M. and Dibenedetto, A. (2003) Carbon Dioxide Fixation into Organic Compounds. In Carbon Dioxide Recovery and Utilization; Kluwer Academic Publishers: Dordrecht; Boston; London.

8. Arakawa H., Aresta M. et al. (2001) Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities. Chem. Rev. 101, 953–996.

EVALUATION OF THE CO_2 USE AS A SOLVENT

INTERMEDIATE REPORT

Written for the Carbon Capture and Storage Program (CCSP)

March 30, 2012

This project will evaluate the use of carbon dioxide as a Solvent in chemical reactions. Theoretical evaluation will be done by following the ongoing research in this research area in scientific publications and on international conferences. Preparation of experimental research was started with modifying an existing laboratory reactor. The equipment changing was based on an older pressure reactor designed for low pressures. The project goal is to design a robust reactor system tolerating rather high pressures to gain supercritical conditions, e.g. $scCO_2$.

The reactor was tested (in different pressures, temperatures and heating rates) and a stable reaction feed was achieved. The online analysis was also tested but the method used so far is not satisfying. The analysis method should be further improved.

Figure 1. Former stirred batch reactor designed for low pressure experiments.

The work is done for changing the stirred batch type reactor designed for low pressures (see Fig. 1) to a robust continuous stirred tank reactor (CSTR) tolerating high pressures (see Fig. 2). The reactor itself tolerates rather high pressures and this allows modifying the system. The volume of the reactor is laboratory scale (50 cm^3).

Figure 2. Continuous stirred tank reactor equipped for tolerating high pressures.

The University of Oulu purchased a new pressure reactor from Parr Instruments (see Fig. 3). The reactor is a batch-type reactor but can be modified for continuous flows, i.e. a continuous reactor. The modified analyzing method should be connected also to this equipment to obtain online data from the process.

Figure 3. New pressure reactor.

Writing a manuscript of existing research data was done during the project. This manuscript writing was done by using and further analyzing the previously obtained research results.

One abstract was submitted to the 15th International Congress on Catalysis (ICC) 2012 that will be held on July 1–6, 2012 in Munich, Germany (http://events.dechema.de/icc2012). Congress Secretariat announced March 28 that after careful evaluation of the abstract by the members of the Scientific Committee the paper has been accepted for a poster presentation.

The first manuscript was sent to the Chemical Engineering Journal in February 2012 and it is under a review process at the moment (http://www.journals.elsevier.com/chemical-engineering-journal/). If the article will be accepted for publishing there is a plan to write and send the second article quite soon after that. These articles are planned to have continuation and the first article is planned to be used as a reference in the second article. Theoretical research has continued by using experimental results and the result will be presented in the coming articles.

In the near future the project will continue by improving the analysis method. The evaluation result for the submitted manuscript is expected and some rewriting will be done when proposed. The poster will be done according to the ICC poster instructions.

Manuscripts and presentations:

Rauli Koskinen, Riitta L. Keiski, Marja Tiitta and Helka Turunen, Comparison of microporous zeolites and a mesoporous catalyst in dimerization of 2-methyl-2-propene with the pressurized CO_2 solvent. 15th International Congress on Catalysis 2012, 01.07.-06.07.2012, Munich, Germany (accepted, poster presentation).

Rauli Koskinen, Helka Turunen, Marja Tiitta and Riitta L. Keiski, Extended Activity of Zeolite Catalysts with CO_2 as Reaction Medium. Journal of Chemical Engineering 2012 (submitted in 2012).