Chemical utilization of CO_2 in dry reforming and methanol synthesis

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1 Introduction

Open industrial systems, where too many of the natural resources end up waste and are not recycled cannot be sustained indefinitely. The current global situation suggests that we consume too many natural resources to produce the things we need, or want, while generating too many by-products that harm the environment and us. These changes threaten to upset the global environmental conditions we have adapted to and ecosystem services we depend on. Reduction in carbon dioxide (CO_2) emissions is one of the most important challenges of today. In Finland, the major contributor to greenhouse gas (GHG) emissions is CO_2 from energy generation, another major CO_2 sources are industry and transportation (Statistics Finland). Progressively reducing CO_2 emissions would require among others electricity and other energy end-use efficiency, passenger vehicle and other transport efficiency and use of renewables. In addition, every opportunity of utilizing man-made CO_2 needs to be explored. This is especially viable in the case of stationary sources such as power plants and industry. This paper reports on a research project the aim of which is chemical utilization of CO_2 from industrial sources, to produce commodity chemicals. The CO_2UTIL project (Towards utilization of carbon dioxide as a green and versatile commodity chemical: Clean synthesis of methanol and dimethyl carbonate) 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).

2 Objectives of the research

The objective of the CO_2UTIL research project is to develop a sustainable process for the production of methanol (CH_3OH) and dimethyl carbonate (DMC) using carbon dioxide (CO_2) 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. In addition, the possibilities of management and optimization of individual processes as well as the whole production chain are evaluated through modelling and simulation.

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3 Results

The investigation of industrial opportunities for CO_2 started in the 1980s, at a time when the motivation to substitute chlorinated solvents coincided with a rapid expansion of scientific interest in CO_2 (Beckman 2003). The earliest and still popular commercial target for CO_2 use is as a solvent in extraction processes in the food industry; while the highest volume use is in enhanced oil recovery. As a chemical feedstock for the production of chemicals and fuels, the foremost motivation of using CO_2 is that it provides new, more efficient and economical routes to existing chemical intermediates, and also that it can lead to totally new polymeric materials (Aresta and Dibenedetto 2004).

3.1 CO_2 reforming

Synthesis gas, an important intermediate in the chemical industry, is a mixture of hydrogen and carbon monoxide. It can be used in a number of syntheses of a wide range of chemicals and fuels, and as a source of pure hydrogen and carbon monoxide. The most preferred reforming technologies are steam reforming, partial oxidation and auto-thermal reforming (Pacheco and Marshall 1997). The most interesting way to produce synthesis gas is a process known as dry reforming, because it uses CO_2 as a feedstock. The reaction is as follows:

$$CO_2 + CH_4 \longleftrightarrow 2H_2 + 2CO$$

From the industrial viewpoint, an advantage of producing synthesis gas by this route, instead of using steam reforming, is the low H_2/CO ratio obtained, which is of particular interest in the syntheses of valuable oxygenated compounds, such as alcohols and aldehydes (Rivetti 1996).

3.2 Methanol synthesis

Methanol, or methyl alcohol (CH_3OH), is an industrially important chemical, it is an outstanding solvent with good washing capability and outstanding physical properties such as low freezing point, which makes it a good refrigerant, and it as been considered to be used as a clean synthetic fuel. The “chemical identity” of methanol was established in the 19th century, and the first commercial plant for the synthesis of methanol was built by BASF in 1923. The process involved synthesis from synthesis gas using a zinc oxide/chromium oxide catalyst at 300 °C and 200 atm. This process is also known as high-pressure methanol synthesis. (Sunggyu 1990) Later on, a number of improvements have been made to the early methanol processes, and a predominant technology now is a low pressure process ($p<100$ atm) using Cu-based catalysts (McKetta 1988).

The methanol synthesis reaction has always been expressed via the hydrogenation of carbon monoxide, i.e.:

$$CO + 2H_2 \longleftrightarrow CH_3OH$$

During the last decade, however, heterogeneous catalytic synthesis of methanol from carbon dioxide has been a subject of much research:

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$$

Hydrogen needed in the CO_2 hydrogenation reaction to methanol can be e.g. separated from synthesis gas.

3.3 Simulation for methanol synthesis

The aim is to build models for CO_2 reforming and methanol synthesis processes. The optimization of the whole process chain is also a key issue. Steady-state and dynamic process models are very useful in process engineering. They can be used in research and development, process design and plant operation. Models expand the knowledge about system behaviour and are useful in process optimization. (Luyben, 2001) Methanol synthesis has been studied widely but no mutual agreement about the reaction mechanism has been reached. During the years, different kinetic models have been proposed by many authors. The dynamic simulator has been built for the methanol synthesis (Mäyrä and Leiviskä 2009) utilizing the kinetic model proposed by Vanden Bussche and Froment (1996). The model contains the mass balances for the species present in the reactor. The behaviour of the process varies depending on different operating temperature and pressure.

The modelling scheme of different processing steps with some useful methods is illustrated in Figure 1. Sensitivity analysis is used to study how different operating conditions, e.g. temperature, pressure and feed composition affect process outputs. Also, the sensitivity of model parameters can be studied which has been done with the methanol synthesis simulator (Mäyrä and Leiviskä 2009). These results are later utilized in model parameter identification when the experimental data is available. For example, genetic algorithms can be used in parameter identification. Another possibility to utilize the experimental data is to develop data based models, such as artificial neural networks. Modelling results must be validated properly to obtain useful models for later use. The simulators of the individual processing steps are built based on the models and will be combined to simulate the whole processing chain.

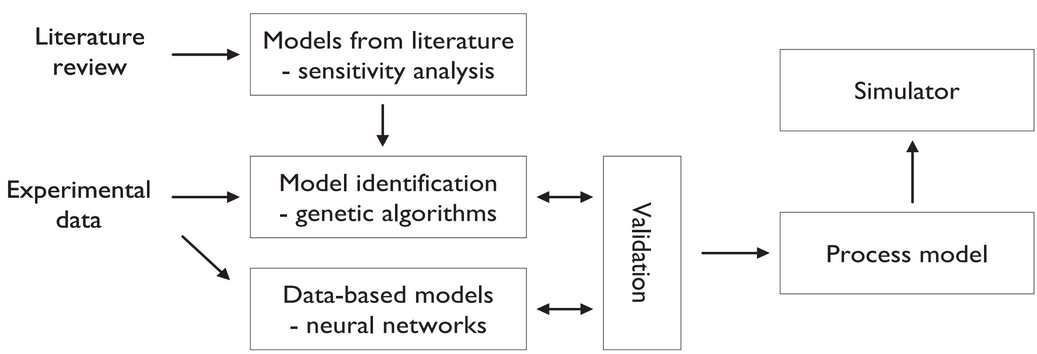

Figure 1 The overall modelling scheme

4 Relevance of the research

The conventional method for methanol production is based on fossil feedstock. The proposed new production processes will be using carbon dioxide (CO_2) as a raw material, which is non-toxic and in abundant supply as an emission of many industrial processes. The method thus transforms a secondary resource from an anthropogenic source to high volume intermediates that have substantial economic value. In addition to converting a waste material into a high-value product, the research team is developing a process using green reaction conditions and processing methods. The studied processes are also safer than conventional production methods, in terms of toxicity of intermediates, operating temperatures and pressure. Therefore, as a result of the development of this CO_2-based production process, a reduction of the use of toxic products in the chemical industry can be foreseen, with an improvement of health and safety conditions.

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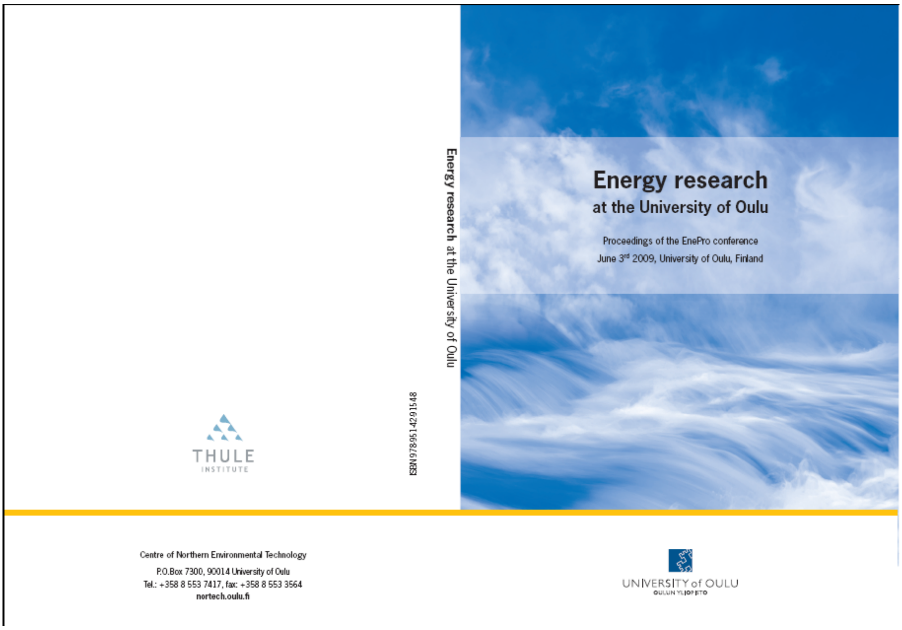

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