Chemical utilization of CO_2, sustainability assessment

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1 Introduction

Industry plays a crucial role in the transition to a sustainable society. Engineers have been in the last couple of decades working to include environmental considerations in process and product design; sustainability ideas bring additional constraints. (Sikhar 2003) Sustainable use of resources involves satisfying the three facets of sustainability: ecological, economical and social (Table 1).

Table 1 *The three facets and criteria of sustainability (Dyllick and Hockerts 2002)*

Types of sustainability	Criteria of sustainability
Ecological sustainability	Using natural resources at a rate below reproduction Using natural resources at a rate below the development of substitutes Not generating emissions at a rate beyond the capacity of the natural systems to absorb and assimilate them Not engaging in activity that degrades ecosystem services
Economical sustainability	Companies guarantee at any time a cash flow sufficient to ensure liquidity while producing a persistent above average return to their shareholders
Social sustainability	Companies add value to the communities which they operate by increasing the human capital of individual partners as well as furthering the societal capital of these communities Sustainable centric process design is about finding a process that can convert the raw materials to the desired chemical product, while satisfying the above criteria.

2 Objectives of the research

This paper reports on a continuing effort of evaluating the sustainability of chemical utilization of CO_2, conducted as part of CO2UTIL and SUSE projects. Using CO_2 as a raw material has several advantages; it is non-toxic, in abundant supply, and leads to innovative routes to producing commodity chemicals. CO2UTIL aims at developing sustainable processes for the production of methanol (CH_3OH) and dimethyl carbonate (DMC, $(CH_3)_2CO_3$) using carbon dioxide (CO_2) as a raw material. Methanol and DMC are an important product and feedstock of chemical industry. Methanol is produced commercially from synthesis gas; however it is also possible to use CO_2 as a feedstock. The conventional production methods of DMC involve the use of toxic phosgene or carbon monoxide, while the methanol-based route using CO_2 offers better atom economy and safer production. The alternative production processes using CO_2 evaluated in CO2UTIL thus transform a secondary resource from an anthropogenic source to high volume and value intermediates while reducing environmental impacts (Pongrácz et al., 2009a). The SUSE research project, in turn, focuses on the development of a sustainable process for the fixation of CO2 molecule for the formation of open-chain carbonic esters such as diethyl carbonate (DEC). Organic carbonates have a high market potential, currently limited by their hazardous production technologies. Therefore, the new

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process elaborated within the SUSE project is also aiming at reducing the hazard of solvents and chemicals conventionally used for DEC production. However, it has been recognized that, to fully evaluate the sustainability of CO_2-based chemicals, all the feedstock of the novel process has to be taken into account, and the potential applications need to be analysed (Pongrácz et al., 2009b).

3 From CO_2 to chemical resource

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, 2010).

With the estimated 120 Mt/yr total industrial CO_2 use, the impact the production of chemicals from CO_2 on global carbon balance is arguably minor (Metz et al., 2005). In order to affect the carbon balance by CO_2 utilization, another issue to be considered is the lifetime of the products obtained from CO_2. Figure 1 illustrates a number of uses of CO_2, highlighting products that are able to fix CO_2 for a long-term, such as polycarbonate plastics.

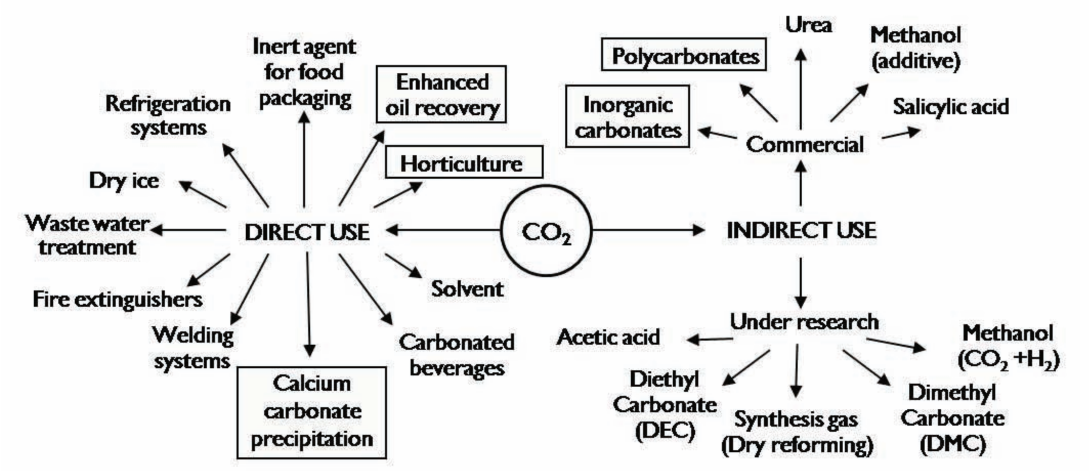

Figure 1 *Direct and indirect uses of CO_2. Only highlighted end-uses lead to long-term fixation of CO_2 (based on Raudaskoski et al. 2009).*

Most uses such as protective gas would result in carbon re-entering the atmosphere virtually immediately. The IPPC special report on carbon dioxide concludes that, in the use of captured CO_2 in industrial processes "the scale is too small, the storage times too short and the energy balance too unfavourable to become significant as a means of mitigating climate change" (Metz et al., 2005). Certainly, in the gigaton range, no application for use of CO_2 as a raw material will have much impact on the amount of anthropogenic carbon currently released into the atmosphere; however, some CO_2 sequestered as a product is better than none (Beckman, 2003). Notwithstanding, the main issue is that the driver of research into industrial uses of CO_2 is the elimination of hazardous chemical intermediates and toxic wastes, as well as the quality of CO_2-based products (Pongrácz et al., 2009b).

4 The dilemmas of CO_2 utilization processes

There are numerous challenges of CO_2 utilization. CO_2 is seldom available in pure form, it needs to be separated from flue gases and its capture, separation and transportation is rather costly. Research effort are currently explored to utilize flue gas streams of process industry directly, without separating CO_2 (Turpeinen et al., 2010). As well, since the CO_2 molecule is highly stable, considerable amounts of energy are needed for its chemical conversion. A major challenge is the availability of hydrogen, if needed for the reaction and, consequently, the issue of by what method the feedstock hydrogen is produced. This is because the process to produce hydrogen is very energy intensive, and the electricity is largely derived from fossil fuels, which produce large amounts of CO_2. There is a great need to develop non-conventional approaches to H_2 generation. The greatest opportunities with respect to greenhouse gas emission are non-fossil fuel based H_2 technologies. There are a number of alternative means of producing hydrogen, such as photocatalytic conversion of biomass (Huuhtanen et al., 2010), selective oxidation of methane, electrolysis of water using solar energy, etc. Use of solar energy for decomposition of water offers direct, non-carbon approach and, in principle, biomass use may also offer a CO_2 -neutral approach (Aresta et al, 2001). It needs to be pointed out that applications that appear at to be limited due to technical issues are (at least from a techno-optimistic standpoint) amenable to creative technical solutions (Beckman, 2003). In addition, the long-term forecast is for the overall H2 demand to increase, which may cause deficiencies between supply and demand (Odgen, 2006). Using hydrogen may eventually slash oil consumption and carbon emissions, but it will take some time. As Odgen (2006) pointed out: "Building a hydrogen economy is costly, but so is business as usual". In summation, the major technical, economical and environmental challenges are summarized in Table 2.

Table 2 *Challenges of CO_2 utilization (Pongrácz et al., 2009b).*

Technical	CO_2 needs to be separated from flue gases
	CO_2 is a highly stable molecule
	Active, selective and stable catalysts are needed
	Source of other co-reactants such as H_2
Economical	Capture, separation and transportation costs
	Energy considerations (chemical conversion of CO_2, generation of H_2)
Environmental	Source of energy
	Product life times

5 Relevance of the research

Use of CO_2 in green processing continues to evolve, in no small measure due to inclusion of researchers beyond the confines of its original base in chemical engineering (Beckman, 2003). There have been a number of large-scale commercial successes in the use of CO_2 as a green solvent. Chemical utilization of CO_2 is a means to turn this waste into a non-waste, allowing us to view CO_2 as a useful resource. The processes under research in CO2UTIL and SUSE projects aim to add value to a waste material, while reducing environmental impacts compared to conventional production methods, thus coupling economical and environmental benefits. The processes are also safer than conventional production methods, in terms of toxicity of intermediates, operating temperatures and pressure. As a result, a reduction of the use of toxic products in the chemical industry can be foreseen, with an improvement of health and safety conditions. In conclusion, chemical utilization of CO_2 meets the provisions for environmental, economic and social sustainability. One of the crucial issues in the success of this effort is finding new, effective catalysts for the synthesis reactions, which further illustrates the major role of catalysis in sustainable production.

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