Carbon dioxide utilisation

Carbon dioxide – A potential raw material for the production of fuel, fuel additives and bio-derived chemicals

Sivashunmugam Sankaranarayanan & Kannan Srinivasan*
Discipline of Inorganic Materials and Catalysis, CSIR-Central Salt and Marine Chemicals Research Institute,
Gijibhai Bhadheka Marg, Bhavnagar 364 002, India
Email: skannan@csmcri.org/ kanhem1@yahoo.com

Received 12 July 2012; revised and accepted 18 August 2012

Amongst the various greenhouse gases emitted into the atmosphere, carbon dioxide emission is the highest in terms of tonnage and has been identified as a predominant source contributing to climate change. Owing to its abundance through anthropogenic sources, it is highly desirable to utilize CO$_2$ to produce valuable products, in particular fuels and large volume chemicals, and thereby mitigate significantly its environmental impact. This review aims to cover the attempts made in utilizing CO$_2$ for the production of fuels, fuel additives and bio-derived chemicals, in particular organic carbonates. Although this review does not intend to encompass the literature in the holistic manner, it does endeavor to provide recent approaches, difficulties, challenges and offer perspective in the years to come on this important area of research.

Keywords: Carbon dioxide utilization, Raw material for fuel production, Syngas, Methane, Dimethyl carbonate, Fatty cyclic carbonate, Glycerol carbonate

Carbon dioxide (CO$_2$) is a greenhouse gas and occupies the top position (more than 80% in terms of amount for USA) in the overall emissions amongst other gases such as carbon monoxide (CO), methane (CH$_4$), chlorofluorocarbons (CFC’s), etc. Increase in the emission of greenhouse gases makes significant climate changes and will lead to consecutive effects such as increase in global temperature and changes in wind patterns. China occupies the top position in CO$_2$ emissions with 24% of world emissions, followed by United States (18%), while India contributes around 5%. Longer estimated life time of CO$_2$ in the atmosphere (50-200 years) and a profound surge in the human related emissions in recent decades cause serious concerns on its emission and impact on the environment.

Sources of CO$_2$ emissions can be broadly classified into three categories, namely, stationary, mobile and natural sources. Generally, industrial emissions belong to stationary sources, emissions from vehicles are classified as mobile sources, and emission from volcano are natural sources. Figure 1 shows the different anthropogenic sources of CO$_2$ and their sinks (based on 2010 data). Burning of fossil resources such as petroleum and coal contributes significantly to CO$_2$ emission whose rate are estimated at 22.29 and 24.65 kg C/GJ, respectively. According to the International Energy Outlook 2011, world’s energy related CO$_2$ emission is estimated to increase from 30.2 billion metric tons (BMT) in 2008 to 35.2 and 43.2 BMT in 2020 and 2035 respectively.

In the current scenario, decreasing the CO$_2$ amount in the atmosphere is the biggest challenge and needs new ideas and technologies. Possible ways to reduce the CO$_2$ concentration in the atmosphere are using renewable fuels instead of fossil fuels and by converting the emitted CO$_2$ into useful products by chemical transformations. Although sincere efforts are being made for replacing fossil fuels by renewable energy, there are several practical difficulties and limitations. Although a single solution is not going to

Fig. 1 – Anthropogenic sources of CO$_2$ and their sinks.
solve such a mega problem, an alternative approach to reduce CO\textsubscript{2} emission is by its value addition to produce large quantities of useful products. Such an approach would also create new opportunities that are hitherto not realized or known.

High abundance and low cost are the main advantages of CO\textsubscript{2} as a promising feedstock in organic synthesis.\textsuperscript{7,8} CO\textsubscript{2} is an interesting C\textsubscript{1} building block and can be an apt replacement for hazardous molecules like phosgene in many industrial processes. Efforts have been made to utilize CO\textsubscript{2} in commercial applications such as food processing and carbonated beverages. In recent years, CO\textsubscript{2} has attracted the attention of chemical industries as it can be categorized as a sustainable raw material that can be used to produce diverse products through a variety of chemical transformations. Despite such practices, currently in industries, only 110 million metric tons (MMT) of CO\textsubscript{2} are used for chemical transformation which is less than 1% of global emissions.\textsuperscript{9}

Sakakura et al.\textsuperscript{10} categorized a variety of reactions using CO\textsubscript{2} as a potential starting material resulting in many products. Figure 2 summarizes the possible reactions and some important chemicals derived using CO\textsubscript{2}. Production of chemicals like urea and carbonates using CO\textsubscript{2} is well-known and has been commercialised. Besides chemicals, energy products from CO\textsubscript{2} would make a considerable impact on its emission. The worldwide requirement of fuels is nearly two orders of magnitude higher than that of chemicals. CO\textsubscript{2} emission can be effectively reduced by its utilization as a source for fuel production. This will be advantageous not in terms of value but also in significantly curbing its emission, which in turn will mitigate greenhouse effect.

Utilization of biomass for energy and chemical production is an active research domain currently pursued all over the world because of its ecological and economic gains.\textsuperscript{11} CO\textsubscript{2} is also gaining significance in the biorefining processes of biomass to value-added bio-derived chemicals. Herein, recent attempts in the use of CO\textsubscript{2} as a raw material for fuel, fuel additives and bio-derived chemicals, in particular organic carbonates is reviewed (Fig. 3).

**CO\textsubscript{2} for the Production of Fuels**

Products obtained from CO\textsubscript{2} have applications as fuels and fuel additives. Figure 4 shows the schematic representation of production of fuel and fuel additives from CO\textsubscript{2}. Carbon dioxide is in the highly oxidized form, and hence reduction process is largely applicable to produce fuel and fuel additives. In redox reactions, high energy substances or electro-reductive processes are needed because of high thermodynamic stability and lower reactivity of CO\textsubscript{2}.\textsuperscript{12} Chemical reduction routes are being explored for the reduction processes. Very recently, a research group from University of California at Los Angeles reported a method wherein genetically engineered microorganism was deployed for the successful conversion of CO\textsubscript{2} into fuels such as iso-butanol and 3-methyl-1-butanol.\textsuperscript{13} Carbon Sciences, a California-based company is developing a bio-catalytic

---

Fig. 2 – Possible reactions and important chemicals from CO\textsubscript{2}.

Fig. 3 – Overall scheme for the utilization of CO\textsubscript{2} for the production of fuel, fuel additives and bio-derived chemicals.
process for converting CO$_2$ into hydrocarbons such as methane, ethane and propane, which can be utilized instead of gasoline and jet fuels. Generally, biocatalytic routes are more expensive and time consuming than other catalytic routes. Highly active metal catalysts have been investigated for the hydrogenation of CO$_2$ in homogenous or heterogeneous forms.

Hydrogenation of CO$_2$ results in various products of C$_1$-type and higher chain length hydrocarbons depending upon the reaction conditions. Hydrogen is generally obtained either from fossil sources or through water splitting. Development of various catalyst systems and surface science techniques has created interest in the hydrogenation of CO$_2$ in homogenous or heterogeneous forms.

The formation of CO in RWGS reaction is explained by two models, namely, redox mechanism and formate decomposition mechanism. In the case of redox mechanism it was suggested that reduction of CO$_2$ and oxidation of H$_2$ that result in the formation of CO and H$_2$O, occur due to the metal species. In the case of formate decomposition mechanism, it was suggested that association of H$_2$ with CO$_2$ results in formate species as intermediate which decomposes to give CO.

Even at 400 °C, due to the low equilibrium constants, it requires hydrogen-rich or carbon dioxide-rich reactant mixtures to yield acceptable results. Otherwise the operating temperature needs to be increased to around 750 °C. It was identified that activity of the catalysts depends on the operating temperature and both ZnO-Al and ZnO-Cr catalysts show poor activity below 600 °C. Theoretical studies...
to determine the likely reaction mechanisms augmented by instrumental techniques, is the requirement at this stage to design and develop improved catalysts that can work under energy efficient conditions.

**Hydrocarbons**

Fischer-Tropsch synthesis is a well-known reaction wherein CO is hydrogenated to give hydrocarbons. In a modified FT process, hydrocarbons can be prepared by hydrogenating syngas (CO + H₂) that contains a considerable amount of CO₂ or by hydrogenating CO₂ via CO and CH₃OH formation (Eqs 2 & 3). The main criterion for this reaction is the additional functionality of the catalyst which predominantly forms hydrocarbons. Even though catalytic FT process is well established, only a few studies are reported for catalytic hydrogenation of CO₂ for hydrocarbons production. CO₂ emission from transportation fuels can be utilized with H₂, which may be obtained from solar power, etc. This is one of the possible effective ways to maintain carbon cycle. Processes such as photochemical, electrochemical and thermochemical are applicable for the catalytic conversion of CO₂ of which the first two routes have some drawbacks. Hence, thermochemical CO₂ conversion is preferred for producing hydrocarbons with high conversions.

\[
\begin{align*}
\text{CO}_2 + H_2 & \rightarrow \text{CO} + H_2O \quad \ldots (2) \\
a\text{CO}_2 + (2a-c+b)\text{H}_2 & \rightarrow c\text{CH}_2\text{H}_b\text{O}_c + (2a-c)\text{H}_2\text{O} \quad \ldots (3)
\end{align*}
\]

Transition metal catalysts have been reported for catalytic hydrogenation of CO₂ and/or syngas to hydrocarbons. In some studies, FT process was checked with the feeding of CO₂ gas along with syngas to produce the hydrocarbons. Fe based FT catalysts are promising for hydrocarbons synthesis and various efforts have been made to increase the conversion of CO₂. Dorner et al. reported the hydrocarbons production using ceria modified iron catalysts. They have reported that addition of ceria enhances the CO₂ conversion and selectivity for C₂-C₅ hydrocarbons. Cobalt-based catalysts have also been studied for the FT process and were not found attractive for the production of long chain length hydrocarbons. Iron-based FT catalysts are reported for high temperature processes whereas cobalt-based FT catalysts are reported for low temperature processes. CO₂ and CO follow different pathways during hydrogenation that largely depend on the nature of the catalyst. For example, Fe based catalysts promote hydrocarbons production via CO formation whereas Co based catalysts convert CO₂ directly to methane due to its limited WGS reactivity. In addition, supports and promoters also play an important role in CO₂ hydrogenation. Although many efforts are being made for the production of hydrocarbon from CO₂, specific methodologies/technologies to improve the selectivity of the desired products are required.

**Methanol**

Methanol (CH₃OH) is an important chemical that finds application in various industrial processes. It was identified that worldwide consumption of methanol increased by 1 % from 2003 to 2008 and is projected to increase by 2 % from 2008 to 2013. Such robust growth obviously suggests high market potential for methanol and efforts are continuously being made to increase its production and meet global demands. Methanol can be directly used as fuel or as an additive to gasoline and can also be used as platform chemical for the synthesis of various chemicals. Currently, the focus is on methanol for the production of biodiesel (fatty acid methyl esters) by transesterification of vegetable oils. Generally, methanol can be produced from CO₂/CO and hydrogen (Eqs 4 & 5). Methanol Holdings (Trinidad) Limited (MHTL), a USA based company, is one of the largest methanol producers in the world with a total capacity of over 4 MMT/year. It is well known that CO₂ is the preferred substrate for methanol production than CO because it forms active carbonates/formates on catalyst surface which favour the reaction. Also it was evidenced that feeding small amount of CO₂ facilitates methanol production from syngas.

\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \ldots (4) \\
\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} \quad \ldots (5)
\end{align*}
\]

Methanol production by the hydrogenation of CO₂ is possible using homogeneous as well as heterogeneous catalysts. Generally, homogeneous catalysts work at lower temperature for methanol production than heterogeneous catalysts. Designing of homogeneous catalysts to improve the reactivity and selectivity is one of the main challenges being pursued for the reaction. It was reported that hydrogenation of CO₂ occurs via RWGS reaction in
which the water produced acts as an inhibitor for further conversion into methanol. Hence, it is necessary to design catalysts which show high activity at lower temperature and can tolerate the water formed during the reaction. Very recently, Leitner and co-workers have reported the first molecularly defined ruthenium phosphine complex as homogeneous catalyst for efficient hydrogenation of CO$_2$ (turnover number > 200) to methanol under mild reaction conditions. Cu based heterogeneous catalysts are effectively studied for the methanol production reactions. Precious metal supported catalysts are also reported for this reaction.

The function of the catalyst towards the selectivity and water tolerance are not yet clearly understood. Economically cheap catalyst which can overcome the process drawbacks for the conversion of CO$_2$ to CH$_3$OH is the necessity at this stage. Krossing and his team from Freiburg Materials Research Center, Germany, have developed a method for methanol production using CO$_2$ and H$_2$. The obtained methanol can be converted into gasoline through well-known MTG process. Methanol production was carried out under high pressure by combining CO$_2$ and H$_2$. Their goal is to control CO$_2$ emission in large scale along with the complete utilization for energy production and increasing the rate of chemical reaction by designing new catalyst systems and methods. Metal oxides were used to carry out the reaction at low temperature and they found that nanoparticles containing catalyst shows higher activity for methanol production. They have also attempted different preparation techniques such as catalyst impregnation with ionic liquids and covering the catalyst with a thin film of salt solutions that assist in fixing CO$_2$ and H$_2$ effectively on the catalyst and allow facile desorption of products.

**Dimethyl ether (DME)**

Dimethyl ether (CH$_3$OCH$_3$) is the first derivative of methanol effectively used as an alternative for LPGs. Traditionally, dehydration of methanol results in DME in presence of acid catalysts (Eq. 6). Care should be taken in the reaction conditions to get DME from methanol because of the equilibrium between the reactants and products.

$$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad ... (6)$$

Hydrogenation of CO$_2$ or syngas is an alternative method for the production of DME (Eqs 7-9).

One-step synthesis using bifunctional catalysts for the synthesis of methanol as well as dehydrogenation of methanol to DME is plausible. Generally, metal oxides are used for the production of methanol and acidic catalysts are used for the dehydration reactions.

$$2\text{CO}_2 + 6\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \quad ... (7)$$

$$2\text{CO} + 4\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad ... (8)$$

$$3\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{CO}_2 \quad ... (9)$$

According to 2011 data, Korea Gas Technology Corporation, Korea, received a contract from Uniteal Technologies, Inc. to build a plant for the catalytic production of DME at the scale of 300,000 tons per year by single step method using tri-reformed syngas obtained from natural gas as feedstock. They have successfully demonstrated this one-step model unit with 10 tons/day capacity.

CO$_2$ is thermodynamically more stable than H$_2$O and facilitates DME formation at higher temperature with 1:1 feed of CO$_2$/H$_2$. Generally, a two-step process is in practice because of the thermodynamic favorability of methanol which gives DME via dehydration reaction. Copper-based catalysts are known for the selective production of methanol by CO$_2$ hydrogenation, which can be converted to DME using acidic catalysts. Interestingly, Cu based core shell membrane catalysts showed direct synthesis of DME from CO$_2$. Designing highly active bifunctional catalysts which can produce DME from CO$_2$ under moderate reaction conditions, is the targeted interest of this reaction.

**Methane**

Methane has application as synthetic fuel and is produced from the hydrogenation of CO$_2$ by the Sabatier reaction. The challenges associated in the storage of hydrogen instrumental in the efforts to convert it into methane that can be stored and transported easily. Methane can be obtained by the hydrogenation of CO or CO$_2$; the latter process is less exothermic than the former. Hydrogenation of CO or CO$_2$ (Eqs 10 & 11), commonly reported as methanation, is also used in ammonia plants for the purification of syngas, reducing the residual carbon oxides in hydrogen-rich reforming gases and polymer electrolyte fuel cell anodes.
CO + 3H₂ → H₂O + CH₄  ...(10)

CO₂ + 4H₂ → 2H₂O + CH₄  ...(11)

Selective methanation of CO in CO₂-rich gas mixtures has gained interest in recent years because of its advantage as a viable alternate to selective CO oxidation. In this case, CO adsorbs strongly on the catalyst surface due to its higher adsorption energy than CO₂, resulting in surface blocking and thus inhibiting CO₂ adsorption, which in turn facilitates methanation reaction. Easy availability and low cost makes Ni based catalyst promising for industrial methanation reactions. Overheating and sintering results in problems such as decrease in the surface area due to crystallite size growth of Ni and deactivation of the catalyst. This may be overcome by choosing proper supports that are mechanically and thermally stable. Different metals such as Co, Ru and Rh containing catalysts were also studied for the methanation reactions. Particle size, operating temperature and supports play a major role in the methanation reaction. Developing a new technology that selectively makes methane from CO/CO₂ is of considerable interest. Designing active catalyst and developing a protocol to disperse the catalyst on a rationally selected support and deriving optimized reaction conditions for such systems are the hurdles which have to be overcome. Methanogens (also called as Archea) produce one billion ton of methane from CO₂ naturally every year. Hence, these microbes have been suggested as one of the effective sources for the preparation of methane and Europe has already initiated this process.

Dry reforming of methane with CO₂ is the perfect way to make syngas (ratio of H₂/CO is 1) which is one of the main building blocks for the fuels (Eq. 12). The main advantage of dry reforming process is using two greenhouse gases (CO₂ & CH₄) and this makes it superior to steam reforming or partial oxidation of methane. Fundamentally, dry reforming of methane is an endothermic process and requires high temperature (> 700 °C) to get moderate conversions.

CO₂ + CH₄ → 2CO + 2H₂  ...(12)

Methane dry reforming is a catalytic process and development of a suitable catalyst that can sustain under high temperature without deactivation and produce high yields of syngas is the key endeavor for this reaction. Ni was effectively used due to its lower cost and easier availability than noble metals such as Rh, Ru, Ir, Pd and Pt containing catalysts which are also active for this reaction. Formation of coke is the main drawback as it involves deactivation of the catalysts. The support is reported to plays a crucial role in this reaction. Ni containing catalysts were explored extensively with various supports and along with promoters. Recently, Labrecque and Lavoie studied the activity of Fe catalyst in the presence of electrical current and found that electron flow and addition of water vapour play a crucial role in methane conversion. Developing a technology that improves the resistance toward carbon deposition and designing the catalyst with proper support and/or promoter which can enable this reaction at lower temperature are the key challenges to be addressed in the CO₂ reforming of methane.

Ethanol

Ethanol (C₃H₆OH) is the one of the largest producing alternative fuel from renewables by fermentation process. Ethanol can be produced form CO₂/CO via hydrogenation process (Eqs 13 & 14). Though direct hydrogenation of CO₂ to C₃H₆OH is possible, indirect method via methanol homologation is in use only for the production of ethanol.

2CO₂ + 6H₂ ↔ C₅H₁₂O + 3H₂O  ...(13)

CH₃OH + CO + 2 H₂ → C₂H₅OH + H₂O  ...(14)

Hydrogenation of C₂ oxygenates (such as acetaldehyde and acetic acid from syngas which can be made from CO₂) to ethanol is the best possible route. Catalysts with some active centres which can reduce CO₂ to CO, promoting C-C bond formation and allowing –OH group insertion are the main criteria for this reaction. Composite catalysts satisfying the above mentioned properties were studied for this reaction due to their multifunctional nature. Potassium supported Cu based catalysts have shown high activity for this reaction; herein, potassium acts as a promoter for C-C bond forming reaction. Rh based catalysts have also been studied and it was found that promoters play a crucial role for the selectivity of ethanol. Modification of catalysts was attempted to satisfy the requirement of the reaction condition; Rh containing catalysts showed the best results. Basically, catalysts which are active
for ethanol production from syngas and RWGS are also active for methanol homologation reactions.

Ethanol has been undoubtedly proved to be the best alternative for fuels and enzymatic production predominates for its production. Designing the catalyst with highly efficient production of ethanol from CO\(_2\) is the challenging task in front of many researchers. New technology developments are required to replace and/or augment the currently practiced microbial process.

**Formic acid**

Formic acid (HCOOH) is the simplest carboxylic acid and its worldwide production was estimated to be around 720,000 tonnes/annum in 2009.\(^5\)\(^5\) It has application in various areas including fuel cells. Commercially, formic acid is produced by four different production processes, viz., methyl formate hydrolysis, oxidation of hydrocarbons, hydrolysis of formamide, and, preparation of free formic acid from formates.

Direct hydrogenation of CO\(_2\) is the best alternative method for production of formic acid (Eq. 15).

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH} \quad \text{...(15)}
\]

Mainly, homogeneous transition metal catalysts and zinc selenide/zinc telluride have been studied for this reaction.\(^5\)\(^6\) British Petroleum has developed a multistep process using Ru complex as catalyst in presence of nitrogen-containing bases.\(^5\)\(^6\) Even though efforts have been made to produce formic acid using homogeneous catalysts, recent reports suggest that formic acid can be produced from CO\(_2\) hydrogenation with high selectivity using heterogeneous catalysts.\(^5\)\(^7\)

Development of new catalytic technology to produce formic acid in attractive yields in a safe manner is the major task.

**CO\(_2\) for the Production of Fuel Additives**

Efforts have been made to produce fuel additives from CO\(_2\) without using hydrogen source. Generally, this non-hydrogenation process results in carbonates and carbamates; among these, carbonates were found to be effective fuel additives. Dimethyl carbonates are prepared by reacting methanol with CO\(_2\). Methanol, which is produced by the hydrogenation of CO\(_2\), undergoes dehydration when treated with CO\(_2\) resulting in dimethyl carbonates. Also, oxygenation of CO which is produced by the RWGS of CO\(_2\), is another way to produce dimethyl carbonate. This section discusses the non hydrogenation process of CO\(_2\) (or CO) for the production dimethyl carbonate.

Dimethyl carbonate (DMC; (CH\(_3\)O\(_2\)CO) is a linear alkyl carbonate and has been reported as a potential gasoline fuel additive.\(^5\)\(^8\) Various methods are possible for the production of DMC from methanol. High toxicity of phosgene gas and formation of hydrochloric acid as by-product are the drawbacks of the ongoing phosgene-based process. Alternative routes are utilizing CO\(_2\) or CO as reactant for the production of DMC from methanol. Lummus Technology developed a process in which reaction between methanol, carbon monoxide and oxygen in presence of Cu-based catalysts results in DMC and water (Eq. 16). A small amount of HCl is fed into the reactor to maintain the catalyst activity and the obtained byproduct CO\(_2\) can be further used for CO production.

\[
2\text{CH}_3\text{OH} + \text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CH}_3\text{OCOCH}_3 + \text{H}_2\text{O} \quad \text{...(16)}
\]

Production of DMC using CO\(_2\) with methanol is a preferred route (Eq. 17). It was found that thermodynamic limitation of the reaction, deactivation of the catalyst and hydrolysis of the DMC by the formed water results in low methanol conversion and low DMC yield. Selective synthesis of DMC is highly influenced by the presence of both acidic and basic sites on the catalyst surface.\(^6\)\(^0\) Reaction temperature is an important parameter for DMC synthesis. At higher temperatures, conversion of methanol and selectivity of DMC are decreased due to decomposition of DMC and result in unwanted products.\(^6\)\(^1\)

\[
2\text{CH}_3\text{OH} + \text{CO}_2 \rightleftharpoons \text{CH}_3\text{OCOCH}_3 + \text{H}_2\text{O} \quad \text{...(17)}
\]

Various catalysts were reported for this reaction and many diverse efforts were made to improve the selective synthesis of DMC such as catalyst modification, addition of co-reagents and dehydrating agents.\(^5\)\(^2\)-\(^5\)\(^5\) Improving the conversion of methanol along with selectivity of DMC is necessary for it to be
commercially practicable. Designing the desired catalysts and developing a new or redeploying water removal technology are the basic requirements necessary to achieve this endeavour.

**CO₂ for the Production of Bio-derived Chemicals**

Biomass mainly constitutes of lignocelluloses and related materials (70-75% of biomass), oils and fatty acids (15-20% of biomass) and proteins (5% of biomass). It is estimated that around the world approximately 170 BMT of biomass are being produced per annum. Of this barely 4% is used for food/feed and non-food purposes by the humans. Hence, biomass is perceptibly a potential alternate source for the production of fuels and chemicals. Using biomass for energy producing processes also results in the emission of CO₂, but the amount produced during this process is approximately the same as that consumed during biomass re-growth. Hence, emission of CO₂ from biomass is considered as CO₂ neutral. The combination of biomass and CO₂ in energy conversion technologies has some similarities with the combination of fossil sources and CO₂. CO₂, in the context of biomass value addition, is currently being explored as a solvent for pre-treatment of biomass for delignification, for the growth of algae in bio-reactors and for making bio-derived chemicals. The primary aim of this section is to highlight the role of CO₂ in the synthesis of biomass derived chemicals, in particular organic carbonates (Fig. 6).

**Fatty cyclic carbonate**

In recent years, fatty cyclic carbonates have gained interest in the area of renewable sources since they have been used in lubricants, fuel additives and polymer precursors, as solvents, biomedical applications and in plasticizers. Traditionally, these kinds of cyclic carbonates were prepared by using hazardous phosgene gas and organic solvents. CO₂ insertion reaction can play a profound role in the synthesis of cyclic carbonates. Generally, two step processes are carried out for the preparation of fatty cyclic carbonates such as sequential epoxidation of unsaturated centers and then carboxylation of the epoxy fatty derivatives. The main advantage of this process is insertion of CO₂ without forming any byproducts (100% atom economical). Direct oxidative carboxylation of fatty derivatives can also result in fatty cyclic carbonates (Scheme 1).

Doll and Erhan have reported the production of carbonated FAMES using supercritical CO₂. They reported a two-step reaction for the production of fatty cyclic carbonates from methyl oleate and methyl linoleate. In the first step, the unsaturated centres present in these methyl esters were converted into epoxides and then CO₂ was direct inserted in the oxirane ring using tetrabutylammonium bromide as catalyst under supercritical CO₂. The same catalyst was studied for the carbonation of epoxidized soybean oil methyl esters at atmospheric pressure and at pressurized conditions. Interestingly, Kenar and

![Figure 6 - Preparation of organic carbonates using CO₂.](image)

![Scheme 1 - Preparation of fatty cyclic carbonates from fatty derivatives.](image)
Tevis reported preparation of fatty cyclic carbonates using tetramethylammonium hydrogen carbonate as catalyst at low temperatures and in shorter reaction time by bubbling with CO₂.

Due to the renewable nature, bio-derived products have gained interest in recent years. Fatty cyclic carbonates have wide applications and researchers are attempting to produce them in economically attractive and in large volumes to replace some of the petro-derived polymeric derivatives. Further, most of the studies involve two-step processes for the production of cyclic carbonates via epoxides formation and CO₂ insertion. Unfortunately, direct oxidative carboxylation to produce fatty cyclic carbonates is scarcely studied. Appropriate design of catalyst that offers macroporosity for efficient diffusion (avoiding mass transport limitation) of the long-chain molecules which can give high yield of fatty cyclic carbonates under near ambient or energetically favorable conditions is the challenge at present. Further, production of polycarbonates and polyether carbonates from fatty derivatives/vegetable oils using CO₂ needs a more focused approach.

**Glycerol carbonate**

Glycerol is the simplest triol which has various applications due to its functionality. Glycerol can be obtained from triglycerides via hydrolysis or transesterification processes. The continuously expanding production of biodiesel from different sources results in enormous amounts of glycerol as byproduct. In order to reduce the disposal of glycerol as waste, value addition of glycerol for a variety of applications is being studied. Glycerol carbonate is important as solvent and starting material for polymers etc., due to its peculiar properties. Industrially this compound is produced by the transesterification of propylene carbonate with glycerol. Basically these carbonate derivatives are prepared by the CO₂ insertion reaction with the corresponding oxides.

Earlier studies revealed that ethylene carbonate was needed as starting material for the preparation of glycerol carbonate from glycerol and supercritical CO₂ as carbonate source. In this case ethylene carbonate can enhance the CO₂ utilization for glycerol carbonate synthesis. Very recently, Ma et al. reported the synthesis of glycerol carbonate from glycerol and CO₂ in presence of propylene oxide as the coupling agent using alkali catalysts. Some efforts were made for the direct insertion of CO₂ into glycerol moiety to form glycerol carbonate using tin based catalysts. Formation of water as byproduct prevents further conversion of glycerol due to solubility of glycerol in water and the reaction is thermodynamically limited (Scheme 2). It was further identified that addition of methanol can enhance the reaction.

Direct carboxylation of glycerol to glycerol carbonate is an important reaction not only in being industrially relevant but also in green chemistry perspective. Technology development to increase the conversion of glycerol concomitantly with high selectivity of glycerol carbonate is indispensable at this time.

**Conclusions & Perspectives**

The global atmospheric concentration of CO₂ is increasing every year and has reached 391.3 parts per million in 2011 according to the data from Worldwatch Institute. Increasing CO₂ level in the atmosphere can be controlled by utilizing it in a useful and voluminous way, given its availability in giga tons, through the production of fuels and large volume chemicals. Decreasing fuel availability has created enormous interest in the search for alternatives from different sources and various attempts are being explored. Syngas, methanol and hydrocarbons, are some of the important options for the production of fuels (or can be used as such) due to their properties. Also, possibilities of forming various products from CO₂ would be of great significance since the end-products obtained after combustion of fossil fuel can be refurbished back into the fuel chain, thus closing the energy/material loop cycle. Needless to say, the energy penalty and balance are some of the key issues that need to be sharply addressed while exploring such options. Utilizing CO₂ to develop large volume chemicals, in particular those derived from biomass, is one of the biggest opportunities in this area of research. Although not many profitable technological approaches
solutions are available at present, solutions that would not only limit the growth of CO₂ in atmosphere but also create some sustainable options for the growing population and energy/material demands of this world are expected in this century.

Acknowledgement

The authors thank CSIR, New Delhi, India, for financial support under Network Project, Clean Coal Technology (NWP-021).

References

(Accessed on 26th June 2012).