CHAPTER II
LITERATURE REVIEW

2.1 Sources of Carbon Dioxide (CO_2)

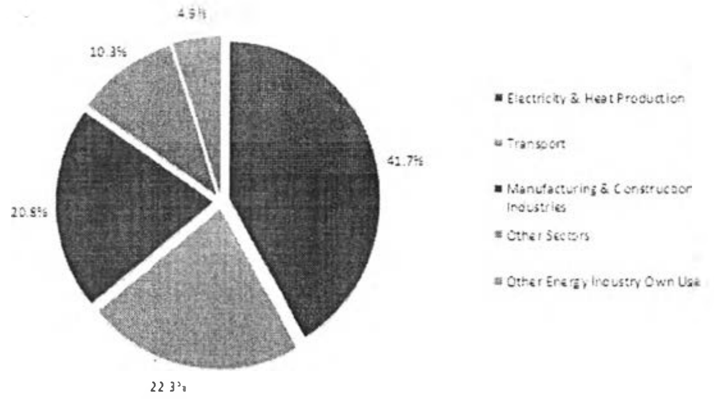
Both natural and human activities are the source of CO_2 emissions. Natural sources include decomposition, ocean release and respiration. The source of CO_2 from human activities results from different stationary and mobile energy systems as the activities from industrial plants as well. Almost all of the elevation in greenhouse gases (GHGs) in the atmosphere not seen in the last 3 million years is associated with human activities. Compared with natural emissions, the emitted amount of CO_2 from human sources is much smaller but it is disrupting the natural balance of carbon neutral cycle. Human activities are changing the carbon cycle - both by emitting more CO_2 to the air and by affecting the potential of natural sinks such as forests, to capture CO_2 from the atmosphere (Matson *et al.*, 2010). Table 2.1 suggests the major sources of CO_2.

Table 2.1 Sources of CO_2 emissions (Song, 2006)

Stationary Sources	Mobile Sources	Natural Sources
Fossil fuel-based electric power plants	Cars, and sports utility vehicles	Humans
Independent power producers	Trucks and buses	Animals
Manufacturing plants in industry	Aircrafts	Plants and animal decay
Commercial and residential buildings	Trains and ships	Land emission/leakage
Flares of gas at field	Construction vehicles	Volcano
Military and government facilities	Military vehicles & devices	Earthquake

Regarding to human activities, the sources that account for the largest CO_2 emitted are the burning of fossil fuels for energy and transportation. 87 percent of CO_2

emitted by human beings results from the combustion of coal, natural gas and oil. The rest comes from the deforestation and other land-use changes (9 percent), as industrial operation as well (4 percent) (Le Quéré *et al.*, 2013) as observed in Figure 2.1 and 2.2.



Note: Other sectors include residential

Figure 2.1 CO_2 emissions by sector (IEA, 2013a).

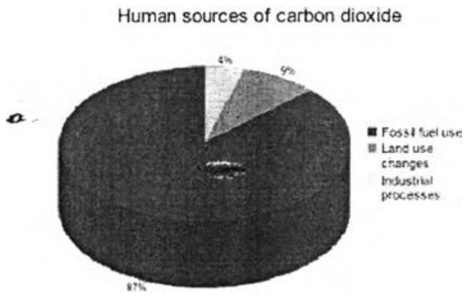


Figure 2.2 Human sources of CO_2 (Le Quéré *et al.*, 2013).

2.1.1 Fossil Fuel Combustion/Use

With 87 percent of human CO_2 emissions, combustion of fossil fuels is the largest producing source (Le Quéré *et al.*, 2013). Heat, electricity and power for transportation are the major applications for energy from burning. Power plants, cars, planes and industrial facilities can be taken as an example. In 2011, 33.2 billion tons of CO_2 was created in the world (IEA, 2013b). Coal, natural gas and oil are the most used fossil fuels. Coal is in charge of 43 percent of CO_2 emissions, followed by 36 percent produced by oil and 20 percent from natural gas (IEA, 2013a). The three main economic sectors using fossil fuels are electricity/heat, transportation and industry while the first two sectors created around two-thirds of total CO_2 emissions in 2010 (IEA, 2013b).

2.1.1.1 Electricity/Heat Sector

The largest producing of CO_2 comes from electricity and heat generation with 41 percent of fossil fuels used in 2010 (IEA, 2013a). Burning fossil fuels supports electricity to almost all industrialized nations (around 60-90 percent), excluding Canada and France. The industrial, residential and commercial sectors consume the biggest usage of electricity of 92 percent (IEA, 2013b). Industry is the largest consumer because of extremely intensive energy. Specifically, the production of chemicals, iron/steel, cement, aluminum as well as pulp and paper are the main users of industrial electricity use (IEA, 2013b). The residential and commercial sectors are also deeply dependent on electricity for their energy needs such as lighting, heating, air conditioning and appliances.

2.1.1.2 Transportation Sector

The second largest of CO_2 emission is the transportation sector with 22 percent produced via transporting goods and people worldwide in 2010 (IEA, 2013a). This sector is very energy intensive and reliant on petroleum products (gasoline, diesel, kerosene, etc.). In this sector, 74 percent comes from road transport (IEA, 2013a). Automobiles, freight and light-duty trucks are regarded as the main sources to emit CO_2 in the whole transport sector. Marine shipping produces 14 percent of all transport CO_2 emissions (IEA, 2013b). Although the number of ships are smaller than that of road vehicles, ships use the dirtiest fuel that is not refined clearly and transformed to solid across at room temperature. This is the reason why over 1 billion tons of CO_2 is emitted by marine shipping (IEA, 2013b). Global aviation constitutes 11 percent of all CO_2 emitted of transport section (IEA, 2013b). 62 percent results from international flights while domestic flights make up 38 percent (IEA, 2013b). During last 10 years, aviation has becoming one of the fastest rising sources of CO_2 emissions (IEA, 2013b).

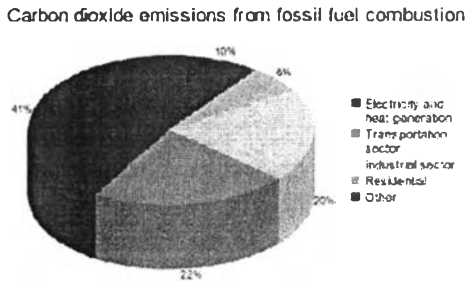


Figure 2.3 CO_2 emissions from fuel combustion (IEA, 2013a).

Emissions caused by the transportation have surpassed that from the industry, which has had a huge impact on climate change. Emissions from transportation can be categorized into direct and indirect emission. Transportation of goods causes indirect emission whilst emission created by transporting people (by car, plane, etc.) is an example of direct emission.

2.1.1.3 *Industrial Sector*

Third largest source of CO_2 emitted is the industrial sector. 20 percent results from combusting fossil fuel to supply to this sector in 2010 (IEA, 2013a). The industrial sector involves manufacturing, construction, mining, and agriculture. Manufacturing can be classified into 5 subsections: paper, food, petroleum refineries, chemicals, and metal/mineral products. Those are responsible for the most CO_2 released by this sector. Because of the need of heat and steam at various stages of production that directly combusting fossil fuels, manufacturing and industrial processes all have discharged large amount of GHGs, especially CO_2.

2.1.2 Land Use Changes

Land use changes also have adverse effects on global warming with 9 percent of CO_2 emission or 3.3 billion tons in 2011 (Le Quéré *et al.*, 2013). Land use changes include all human activities to convert natural environment into areas for human beings such as agricultural land or settlements. From 1850 to 2000, around 28-40 percent of total human-produced CO_2 or 396-690 billion tons of CO_2 comes from land use changes (Le Quéré *et al.*, 2013).

Deforestation which removes standing forests permanently is considered as the main reason for these emissions, resulting in adverse effects on the environment. When forests are removed to create farms and pastures, large volume of GHGs is emitted and it contributes to the rise of CO_2 levels in three various routes. Firstly, forests perform as a carbon sink which adsorbs CO_2 from air for photosynthesis. When trees are cut down or burnt, it will release more CO_2 to air. Secondly, because clearing forests declines the number of trees, this will decrease the amount of CO_2 adsorbed by the Earth's forests. Despite the fact that crops from new agricultural land can take CO_2 from air, the efficiency of them is not as much effective as that from forests. Finally, the quantities of CO_2 stored in the soil will reduce as a result of deforestation. Clearing forests results in soil disturbance and decomposition, which in turn creates more CO_2 emissions. Additionally, soil erosion and nutrient leaching which are also outcomes from deforestation will further lessen the CO_2 adsorption ability of soil.

2.1.3 Industrial Processes

Although only 4 percent or 1.7 billion tons of CO_2 released in 2011 comes from industrial processes (Le Quéré *et al.*, 2013), many industrial processes emit substantial quantities of CO_2 to the environment. CO_2 sources in industrial processes are either direct through fossil fuel burning or indirect by electricity usage. Four main types of industrial processes that discharge a considerable amount of CO_2 include the mineral production and consumption like cement, metal production like iron and steel as well as chemical and petrochemical production.

The vast majority of CO_2 of industrial processes is created by cement production in which calcium oxide and limestone are heated at high temperatures to transform into main ingredients in cement. As a result, large amount of CO_2 is produced as a byproduct. 1000 kg of cement produced will release 900 kg of CO_2. The process to reduce carbon content in steel production by combining oxygen with carbon in iron is also an important source of CO_2 emitted. It is estimated that 1.9 tons of CO_2 generated are a result of producing every ton of steel (Le Quéré *et al.*, 2013). Furthermore, making chemicals and petrochemical products from fossil fuels used as feedstock results in CO_2 emissions. Natural gas or other fossil fuels is exploited to produce ammonia and hydrogen with creating CO_2 in the process. Petroleum is utilized to produce plastics, solvents and lubricants which will emit CO_2 when evaporating, dissolving or wearing out over time.

2.2 Carbon Capture and Utilization

The unique physical and chemical properties of CO_2 (Table 2.2) have to be considered to find out the strategy for CO_2 utilization. One or more of targets for CO_2 conversion and utilization can be combined, including: (1) Apply CO_2 to friendly environmental physical/chemical processes that adds value to the process, (2) Make use of CO_2 to synthesize industrially profitable chemicals and materials that increase products' value, (3) Employ CO_2 as a helpful fluid or as a medium for energy recovery, contaminant removal, and emission reduction, (4) Utilize CO_2 recycling including renewable sources of energy to preserve carb for sustainable development (Song, 2006). The following figure 2.4 shows some of the important transformations of CO_2 that have been reported to date.

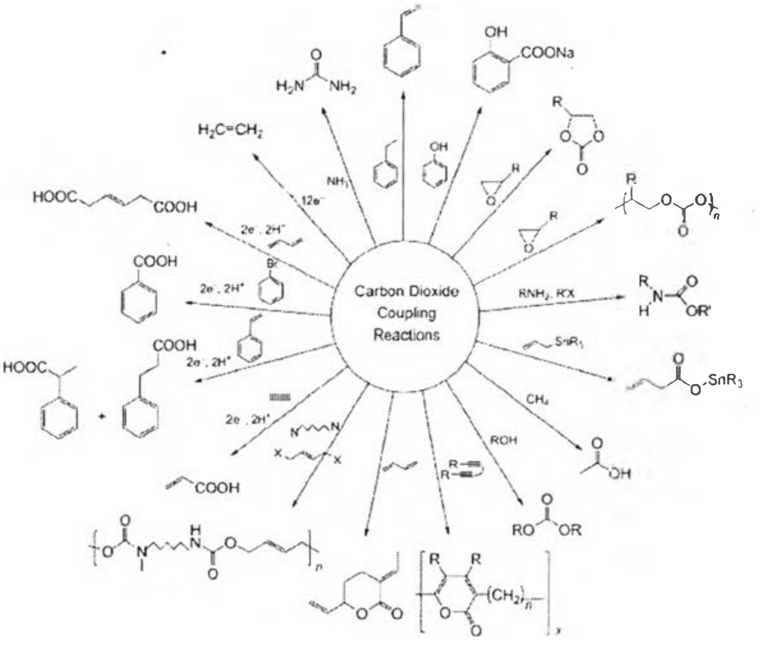


Figure 2.4 Useful chemicals from CO_2 (Yu *et al.*, 2008).

Table 2.2 The physical and chemical properties of CO_2 (Song, 2006)

Property	**Value and Unit**
Molecular weight	44.01 g/mol
Heat of formation at 25°C, $\Delta H°gas$	-393.5 kJ/mol
Entropy of formation at 25°C, $S°gas$	213.6 J/K mol
Gibbs free energy of formation at 25°C, $\Delta G°gas$	-394.3 kJ/mol
Viscosity at 25°C and 1 atm (101.3 kPa)	0.015 cP (mPas)
Liquid density at 25°C and 1 atm (101.3 kPa)	0.712 vol/vol
Gas density at 0°C and 1 atm (101.3 kPa)	1.976 g/L

2.2.1 CO_2 Fixation into Organic Compounds

Table 2.3 Use of CO_2 in the chemical industry for the synthesis of organic compounds

Chemical Product or Application	**Industrial Volume Per Year**	**Amount of Fixed CO_2 Per Year**	**Reference**
Urea	100 Mt	70 Mt	Mikkelsen *et al.* (2010)
Methanol	40 Mt	14 Mt	Mikkelsen *et al.* (2010)
Salicylic acid	70 kt	25 kt	Aresta (2003)
Inorganic carbonates	80 Mt	30 Mt	Mikkelsen *et al.* (2010)
Cylic carbonates	80 kt	ca. 40 kt	Aresta (2003)
Poly (propylene carbonate)	70 kt	ca. 30 kt	Aresta (2003)

The utilization of CO_2 via chemical synthesis is the effective way to avoid CO_2 emission and, it is regarded as an outstanding example of "carbon recycling". CO_2 fixation utilizes the entire CO_2 molecule to create organic compounds, which consume very low excess energy. The products from CO_2 fixation contain several functionalities including: -C(O)O-acids, esters, lactones; -O-C(O)O-organic carbonates; -N-C(O)O-carbonates; -N-C(O)-urea, and amides. Although the world volume of these compounds is currently about 120 Mt/yr (Aresta, 2003), only few processes using CO_2 are on stream. However, once carbonates, especially dimethyl carbonate (DMC), are exploited as additives for gasoline, an unforeseeable rise in production will occur. Several tens Mt/yr of CO_2 will be used more when CO_2-based synthesis technologies are introduced. 7-10 percent of CO_2 in air will be reduced via CO_2 recycling (Aresta, 2003). Table 2.3 indicates how much CO_2 is used in different industrial sectors.

2.2.1.1 Industrial Processes that Utilize CO_2 as Raw Material

2.2.1.1.1 Urea

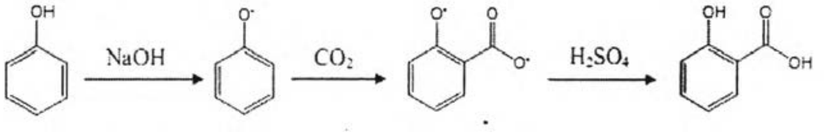
Urea, $C(O)(NH_2)_2$ is the chemical that consumes the largest amount of CO_2 during its synthesis. Urea is a main source of fixed nitrogen that works as a crop fertilizer and as a protein food for livestock. Adhesives, plastics and resins can be manufactured from urea as a feedstock.

Urea is created by the high pressure reaction of ammonia NH_3 and CO_2 to form ammonium carbonate, then carbonate is decomposed to yield urea and water. 99 percent of CO_2 and NH_3 will be converted to urea if there is a recycle and an excess of feed components, as presented in Equation 2.1. Therefore, there is no need for alternative technologies in urea production. However, if urea can be employed as a raw material for the synthesis of other chemicals, the market of urea will increase remarkably.

$$8NH_3 + 4CO_2 \rightarrow 3NH_2COONH_4 + NH_2COONH_4 + 3H_2O \qquad (2.1)$$

2.2.1.1.2 Salicylic Acid

Along with the urea synthesis, the salicylic acid production by Kolbe-Schmitt reaction has been employed in the industry for over a century, as showed in Equation 2.2. Despite how long this reaction has been used, fully understanding of the reaction mechanism to increase the yield and selectivity is always taken into account. The biggest producer in Europe is Rhone Poulenc while in USA that is Dow Chemical Company. Besides using Kolbe-Schmitt reaction to produce salicylic, some different methods can be exploited, including: (1) Air oxidation of o-cresolate at 230°C in presence of a copper catalyst; (2) Synthesis of phenol from toluene to form benzoyl-salicylic acid by the Dow Chemical's process; (3) Fermentation of polycyclic aromatic compounds (Aresta, 2003). Except Kolbe-Schmitt reaction being the most largely used technology, others have not been put into practice.



(2.2)

No major technological changes can be seen in Salicylic acid production. The main interest is developing new types of catalyst which either minimizes the loss of sodium hydroxide per mole of product or works at less severe operational conditions.

2.2.1.1.3 4-Hydroxybenzoic Acid

Although plastics, pharmaceuticals, pesticides and dyes are produced from 4-Hydroxybenzoic acid, the most important role of 4-Hydroxybenzoic acid is emulsifier and corrosion-protection agent. 4-hydroxybenzoic acid is also a precursor of polymers, either as a component in polyesters production, or as an ingredient of liquid crystals. Major part of 250 kt/yr of 4-Hydroxybenzoic acid in the world market is used for captive use (Aresta, 2003).

Aresta *et al.* (1998) reported the production of 4-Hydroxybenzoic acid by means of enzymatic synthesis. The new method showed that phenol is transformed into 4-Hydroxybenzoic with 100 percent of selectivity. This makes the process lessen difficulties in separation and lower strict operational conditions.

2.2.1.1.4 Organic Carbonates

Organic carbonates (Figure 2.5) are compounds that contain the OC(O)O functionality and include the following: (1) linear carbonates: dimethyl carbonate (DMC), diallyl carbonate (Adachi *et al.*, 2000), diethyl carbonate (DEC), diphenyl carbonate (DPC); (2) cyclic carbonates: ethylene carbonate (EC), propylene carbonate (PC), cyclohexene carbonate (CC), and styrene carbonate (SC); (3) polycarbonates: poly-(propylene carbonate) and bis-phenol A-polycarbonate (BPA-PC).

Carbonates are of various chemical industrial applications such as solvents, reagents, precursors of polymers and element of specific materials. 1.8 Mt/yr carbonates is produced in the world market while 1.5 Mt/yr is BPA-PC that makes it become the largest proportion. 38 percent of BPA-PC is exploited in the electrical and electronics, followed by the construction, automotive, optical and information storage systems, medical, and packing (Evans *et al.*, 1991). General Electric Plastics is the largest manufacture of BPA-PC in the world with 0.6 Mt/yr, 0.5 Mt/yr comes from Bayer and the rest is from Dow Chemicals (Aresta, 2003).

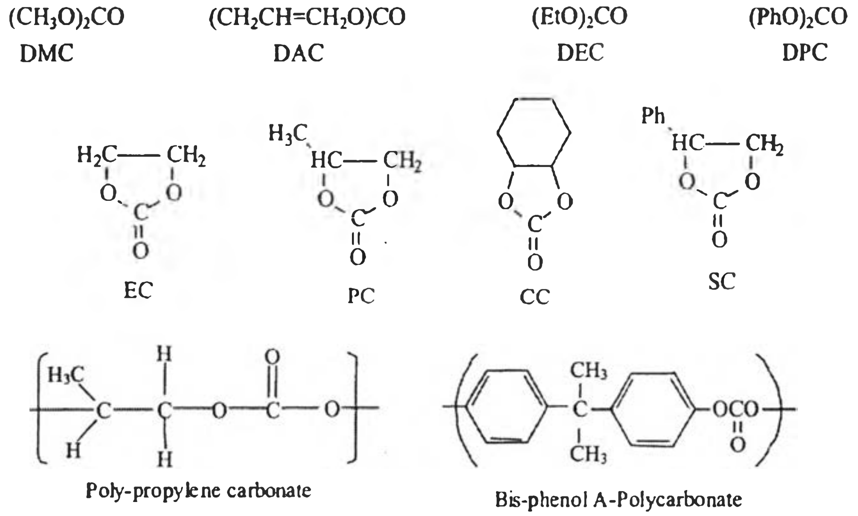


Figure 2.5 Different carbonate compounds.

Usage of DMC as gasoline additive can give an opportunity to expand the market for linear carbonates. If it happens, existing synthetic technologies cannot meet the demanding amounts required. The current productivity of DMC is around 100 kt/yr (Aresta, 2003). This situation will change to several Mt/yr when increasingly popular usage of DMC is as non-toxic solvent, green reagent or gasoline additive. Comparing with other additives, DMC when promotes the combustion of gasoline will release low quantities of CO_2 and increase the burning's efficiency due to its high oxygen content.

Cyclic carbonates are used as solvents for macromolecules and in the production of polymers (Song, 2006) such as a reaction between DMC and methanol via transesterification. Lithium batteries, extractants and reagents are also real practice of cyclic carbonates usage. The current market is in the level of 100 kt/yr with two major producers - Huntsman from USA and BASF from Europe (Aresta, 2003).

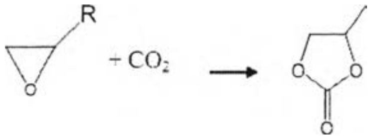
It is a fact that most quantities of carbonates in the world are synthesized through phosgene which is becoming a major disadvantage nowadays. Oxidative carbonylation of methanol or via the epoxide carboxylation only makes up a small portion of carbonates produced. Therefore, there is the unforeseeable necessity to provide large quantities of carbonates with new pathways using nontoxic and cheap reagents.

2.2.1.1.4.1 Cyclic Carbonates

Phosgenation and carboxylation of epoxides using CO_2 are two commercial synthetic routes to carbonates. Although the phosgenation of glycols has been used by SNPE since 1970, it is still the notable process until now. This process contains some drawbacks related to a harmful environmental effect. Both from the usage of phosgene as well as the release of halogenated waste such as HCl and organic solvents. Therefore, the carboxylation of epoxides has become a new interest in order to replace the older method; however, the process is still under several studies until now and it is still far from practical application. Altering from phosgene to CO_2 is two sides of the coin: on the one hand there is a chance to use safer species, on the other hand, the reactivity is lower. Ad hoc catalysts to overcome the limitation of kinetics of reaction will be the solution.

2.2.1.1.4.1.1 Carboxylation of Epoxides

The new route to produce alkylene carbonates via ethylene oxide and CO_2 by Farben has led to the rising interest in the world, as presented in Equation 2.3 (Limura *et al.*, 1995). 90-99 percent of efficiency can be achieved if alkyl ammonium-, phosphonium- and alkali metal halides catalysts are exploited. The mechanism proposed suggests that the anion which is the nucleophilic attacks at the least-hindered carbon atom of the epoxide, CO_2 addition, and intramolecular cyclization with release of the anion (Limura *et al.*, 1995).

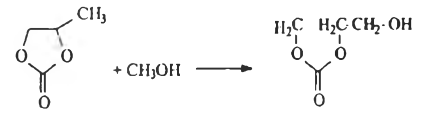


(2.3)

Catalysts for the reaction are metal halide salts (Sakai *et al.*, 1995) but in general, high concentration of catalysts is required with 5 MPa and 97 to 127°C being operational conditions. Organometallic halides RnMXm or RnMXm/Base (Darensbourg *et.al.*, 1996), where R-Me, Et, Bu, Ph; M-Sn, Te, Sb, Bi, Ge, Si; X-Cl, Br, I, are marvelous catalysts. Additionally, classical Lewis acids, organometallic complexes, e.g., $(Ph_3P)_2Ni$ (De Pasquale, 1973), heteropoly-acids and metal phtalocyanines (Ji *et al.*, 2000) (M = Co, Cr, Fe, Mn) have been considered as catalysts for reaction (Aresta *et al.*, 1995). Recently, metal oxides (MgO (Yano *et al.*, 1997), MgO/Al_2O_3 (Yamaguchi *et al.*, 1999), Nb_2O_5 (Aresta *et al.*, 2003)) have been used as heterogeneous catalysts, which considerably increase of life-time and turnover numbers (TON).

Copolymers can be synthesized from the same epoxide reagents and CO_2. Ethylene oxide, propylene oxide, cyclohexene oxide can be combined with CO_2 to create high molecular polymers. The main interest in this area is to invent selective catalysts that help produce either monomer carbonates or copolymers and prevent the mixture formation.

Transesterification reactions can be used in conversion of cyclic carbonates into linear carbonates in a two-step, as shown in Equations 2.4 and 2.5. (Frevel *et al.*, 1972).



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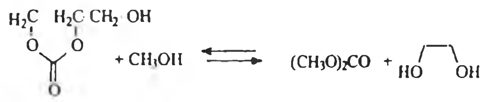
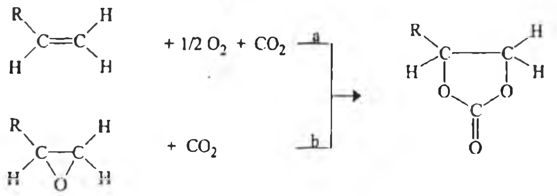


(2.5)

2.2.1.1.4.1.2 Oxidative Carboxylation of Olefins

Cyclic carbonates are straight products from the reaction of olefins with CO_2 and dioxygen, as illustrated in Equation 2.6. All these reagents are cheap and easily available. Besides promoted by both homogeneous and heterogeneous reactions, this reaction contains cheap and easily available reagents. This makes the new approach attractive to further researches. High conversion and selectivity for the new reaction become the main points to advance new catalysts.



(2.6)

2.2.1.1.4.2 *Bisphenol-A-polycarbonates (BPA-PC)*

Interfacial polymerization of BPA and phosgene is one of the common reactions to produce BPA-PC. Three steps of this process are: (1) phosgenation of BPA to bis-chloroformate; (2) Cyclization of bischloroformate to carbonate oligomers; (3) Ring condensation to produce BPA-PC (Aresta, 2003). High reactivity and efficiency under mild conditions are the benefits while phosgene usage and halogenated waste are problems of this process.

The improved synthetic process was developed to achieve high molecular mass polymers, namely the melt transesterification which include the following: (1) Formation of prepolymers at 450-530 K and 0.03-0.13 Mpa; (2) Production of oligomers; (3) Condensation of oligomers at 550-570 K and 1.3 kPa to create BPA-PC (Kim *et al.*, 2002). The new route offers better quality polymers which contain no phosgene, no chlorine as well as more stability to heat with higher molecular mass. Reducing catalytic performance is a drawback, which requires the development of a highly active catalyst. The current catalysts are lithium, sodium, potassium, tetraalkylammonium hydroxides and carbonates (Aresta, 2003).

BPA-PC which combines outstanding properties such as optical clarity, heat and impact resistance is the most broadly used aromatic polycarbonate in thermoplastic. Mixed with other polymers or copolymerized will enrich BPA-PC ability to adapt markets' special requirements. 36 percent of BPA-PC is used in electrical/electronic, followed building/construction with 24 percent while automobile accounts for 15 percent and the rest is in optical information storage (13 percent) (Evans *et al.*, 1991).

As discussed above, polymer synthesis can be conducted through molecular carbonates. Fixing CO_2 into long compounds has become the new trend in producing carbonates (linear or cyclic) and been a basement to develop CO_2-based technologies.

2.2.1.1.4.3 Aliphatic Polycarbonates (al-PC)

Oxiranes and CO_2 can be combined with the support of $ZnEt_2/H_2O$ to synthesize al-PC. This reaction was first discovered in 1969 (Inoue *et al.*, 1969) and still has been exploited to build CO_2-epoxide copolymers. The synthesis takes place at relatively mild temperatures (below 373 K) and pressures (2-8 MPa) with 10-20 percent of efficiency (Inoue *et al.*, 1969). The problem occurs due to the formation of monomer propylene carbonate and it rises along with increasing temperature. Therefore, preventing monomer as well as creating regular alternate insertion are the main interests to consider and research.

Zinc hydroxide or zinc oxide with di-carboxylic acid shows the best performance (Super *et al.*, 1997) and was commercialized through insoluble zinc catalysts. Low catalytic activity and metal contaminant which requires the removal by an acid wash are obstacles. As a result of requirement to intensify catalytic activity, soluble zinc complexes have been key issues to study. The new catalysts are based on zinc complexes with phenoxide ligands bearing bulky substituents in the 2 and 6 positions: (2,6-diphenyl phenoxide)$_2$-Zn(THF)$_2$ is a typical representative of this group of catalysts.

The most important application based on low decomposed temperature and low ash content for al-PC covers sacrificial binders for metals and ceramics in the electronics industry (Aresta *et al.*, 1995).

2.2.1.1.4.4 Linear Carbonates

Although phosgene synthesis still plays a leading position in producing many organic substances such as carbonates and polycarbonate plastics, it cannot continue affording the increasing demand for carbonate. Besides, environmental issues are the emerging interest. Due to limitations about thermodynamics and kinetics, only a few number of different pathways proposed during 30 years are put into practice.

The phosgene Route

The high reactivity and versatility under mild conditions have made phosgene still popular nowadays. The phosgene-based technology is a two-step process including the following reactions.

$$ROH + COCl_2 \rightarrow ROC(O)Cl + HCl \quad (2.7)$$

$$ROC(O)Cl + ROH \rightarrow (RO)_2CO + HCl \quad (2.8)$$

The process requires dry alcohols and anhydrous $COCl_2$ to produce carbonates. Additionally, post-treatment is necessary for halogenated solvents and HCl as byproduct has to be neutralized and disposed due to impurities. The technology also needs special equipment to evade environmental and corrosive problems.

Non-phosgene Routes

Currently, more innovative non-phosgene technologies have being processed, including the production of: (1) DMC via the oxidative carbonylation of methanol; (2) DPC by the transesterification between DMC and phenol; (3) BPA-PC through the transesterification between BPA and DPC; (4) poly(alkylene carbonate)s via the carbonation of ethylene or propylene oxide. Figure 2.6 shows some examples to synthesize linear carbonates from two various routes.

2.2.1.1.4.4.1 Dimethyl Carbonate (DMC)

One of the innovative processes for DMC production is catalytic oxidative carbonylation introduced in the 1980s by EniChem in Italy (Romano *et al.*, 1980). The reaction occurs in the liquid phase under reasonable conditions (100-130°C, 2-3 MPa) and is promoted by copper chlorides (Equation 2.9) (Romano *et al.*, 1980). While the high selectivity for DMC is the advantage, limited conversion due to deactivation of catalysts from water is a drawback. Creating an azeotropic mixture between DMC and methanol makes the process difficult to separate, besides corrosion caused by the presence of chloride. Generally, solid catalysts can be solution to corrosion problems and product recovery.

$$2CH_3OH + CO + 1/2\,O_2 \rightarrow (CH_3O)_2CO + H_2O \quad (2.9)$$

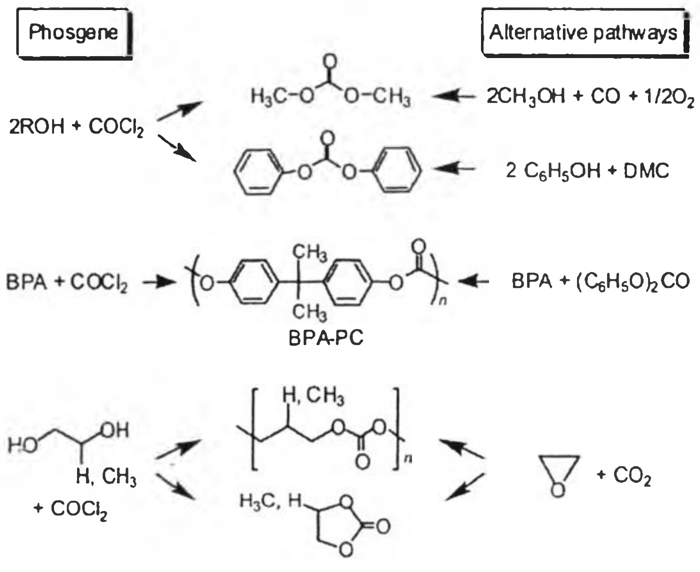


Figure 2.6 Innovative reaction pathways (Aresta, 2003).

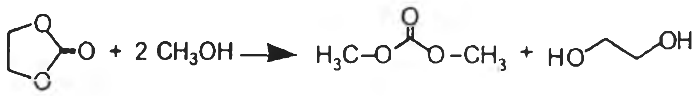
Gas phase technology was invented by UBE in the 1990s, which is supported by PdCl2-based catalyst supported on active carbon and operated at 110-150°C, 0.1-2 MPa (Uchiumi *et al.*, 1999). The selectivity of DMC is around 90-95 percent with byproducts being dimethyl oxalate, methyl formate, and methylal. Methyl nitrite and CO are combined to synthesize DMC and NO which can be recycled to regenerate methyl nitrite at 50°C, as illustrated in Equations 2.10 and 2.11.

$$2CH_3ONO + CO \rightarrow (CH_3O)_2CO + 2NO \qquad (2.10)$$

$$2CH_3OH + 2NO + 1/2O_2 \rightarrow 2CH_3ONO + H_2O \qquad (2.11)$$

Due to no formation of water, the gas-phase process enhances more catalyst stability and efficiency than that in the liquid-phase route. Besides, easier recovery is of one character in the gas-phase technology. However, corrosion which always happens in catalysts including chloride is still a difficulty but less severe than that in the liquid-phase process. The toxicity and control of methyl nitrite and NO also need to be taken into account.

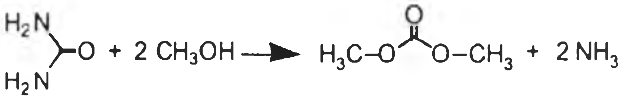
Transesterification of ethylene carbonate with methanol can be exploited to synthesize DMC with ethylene glycol as by-product, as shown in Equation 2.12.



(2.12)

The moderate conditions (60-150°C) can be conducted by both homogeneous and heterogeneous acid and base catalysts but base catalysts perform faster and more selectivity (Knifton *et al.*, 1991). Inorganic solid base such as potassium-loaded titanosilicalite (Tatsumi *et al.*, 1996) hydrotalcite-type materials (Watanabe *et al.*, 1998), and cesium-loaded zeolites (Chang *et al.*, 2002) are catalysts which can be easily separated from the reaction medium and recycled by calcination due to their thermal stability. Consideration between activity/selectivity and basicity displays that MgO is of the highest selectivity at 8 MPa and 150°C. Further improvement is to increase the yield of the reaction.

DMC can result from transesterification of urea with methanol which is promoted by tin complexes, as shown in Equation 2.13.



(2.13)

One of the major drawbacks is the formation of side products which causes poor selectivity. Catalytic deactivation and separation problems are big concerns if homogeneous catalysts are employed. By means of a reactive distillation reactor with the support of triethylene glycol dimethyl ether as solvent, the efficiency and selectivity are substantially enriched. Additionally, when integrated with urea facility the process could make ammonia recycling optimal. Such process will enable DMC to be synthesized from methanol and CO_2.

Direct synthesis of DMC from alcohols and CO_2 is currently studied by way of either organometallic compounds or inorganic oxides (Equations 2.14-2.15). Tomishige *et al.* (1999) reported that using ZrO_2 as catalysts increased selectivity and the catalytic activity was linked to acid-base pair sites in the ZrO_2 surface. Additionally, the authors established solution catalysts based on CeO_2-ZrO_2 with higher selectivity. Through usage of trimethyl orthoesters or dimethyl acetals could prevent the formation and removal of water as by -product.

$$2ROH + CO_2 \rightarrow (RO)_2CO + H_2O \qquad (2.14)$$

$$HC(OCH_3)_3 + H_2O \rightarrow 2CH_3OH + HCOOCH_3 \qquad (2.15)$$

Due to overcoming thermodynamic limitations and increasing yield, researches at near supercritical conditions have been investigated to achieve non-conventional reaction conditions. Wu and co-authors directly synthesized DMC on H_3PO_4 modified V_2O_5. With the optimum ratio of 0.15-0.5, the conversion of CH_3OH can attain 2 percent with the selectivity being around 92 percent (Ugwu *et al.*, 2005). The better outcome comes from studies of Cai *et al.* (2005). 16.2 percent of yield and 100 percent of selectivity result from the presence of CH_3OK and CH_3I under mild conditions (Cai *et al.*, 2005). The research did point out that CH_3OK plays an important role as a catalyst while CH_3I is a promoter to the creation of DME from CO_2 and CH_3OH. However, further investigation is required to understand the thermodynamic behavior under supercritical conditions.

2.2.1.1.4.4.2 Diphenyl Carbonate (DPC)

EniChem technology invented the two consecutive steps for DPC production in which methylphenyl carbonat from transesterification reaction of DMC and phenol is transformed into DPC and DMC through disproportionation (Equations 2.16-2.17). This method allows this process to overcome obstacles in thermodynamic limitation by direct transesterification.

$$C_6H_5OH + (CH_3O)_2CO \rightarrow (CH_3O)(C_6H_5O)CO + 2CH_3OH \qquad (2.16)$$

$$2(CH_3O)(C_6H_5O)CO \rightarrow (C_6H_5O)_2CO + (CH_3O)_2CO \qquad (2.17)$$

Palladium-based precursors enable the direct production of DPC from phenol, as shown in Equation 2.18 (Yanji *et al.*, 1998). Palladium plays a role as active species regenerated by oxidation by organic or inorganic oxidants which are in turn reoxidized by dioxygen (Hallgren *et al.*, 1981). The major drawbacks of these systems are ligand oxidation and aggregation of palladium (0) which are the main causes for low turnover numbers. Additionally, DPC selectivity will decrease with the appearance of side products from phenol, and CO_2 from CO (Song *et al.*, 2000).

$$2C_6H_5OH + CO + 1/2\,O_2 \rightarrow (C_6H_5O)_2CO + H_2O \qquad (2.18)$$

2.2.1.2 Perspective Use of CO_2 in the Synthesis of Carboxylates

Synthesizing organic carboxylates from CO_2 has made the CO_2 utilization become foreseeable. From the demand of the actual market, the perspective to expand CO_2 usage is arising if CO_2-based technologies are executed. While Table 2.4 makes a list of applications and markets of various carboylates, Table 2.5 exhibits current carboxylate synthesis processes and their disadvantages.

Table 2.4 Applications and market of different carboxylates

Chemical	Application	Market
Formic acid	Silage and animal feed preservation Leather and tanning Textiles Formate salts Pharmaceuticals/food chemicals Rubber chemicals (antiozonants and coagulants) Catalysts and plasticizers	324 kt/yr (Arpe *et al.*, 2010)
Acetic acid	Solvent Fragrances and perfumes manufacture Synthetic fibres and textiles manufacture Inks and dyes manufacture Clinical laboratory analysis Soft drinks bottles manufacture Rubbers and plactics manufacture Pesticides manufacture	7.8 Mt/yr (Yoneda *et al.*, 2001)
Oxalic acid	Rust remover Cleaning agent Stain lifter Bleaching agent for wood and stone Photographic film Wastewater treatment	190 Kt/yr (Aresta, 2003)
Long chain carboxylates	Surfactants (preferable to sulphonic acids due to environmental issues)	10 Mt/yr (Aresta, 2003)

Table 2.5 Current processes of carboxylate production (Aresta, 2003; Li *et al.*, 2006)

Chemical	Current Processes	Remark
Formic acid	***1) Oxidation of hydrocarbon*** $C_4H_{10} \rightarrow CH_3COOH + HCOOH$	Covering less than 20 percent of the market
	2) Hydrolysis of formamide $HCOOCH_3 + NH_3 \rightarrow HCONH_2 + H_2O$ $HCONH_2 + H_2O + 1/2\,H_2SO_4 \rightarrow HCOOH + 1/2(NH_4)_2SO_4$	Not desirable in terms of economy and environment Only constituting 6 percent of the market
	3) Methylformate hydrolysis $CH_3OH + CO \rightarrow HCOOCH_3$ $HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$	Accounting for 50 percent of the market Drawback by energy intensive in syngas production
	4) Acid hydrolysis $NaOH + CO \rightarrow HCOONa$ $HCOONa + HX \rightarrow HCOOH + NaX$	Making up 24 percent of the market
Acetic acid	***1) Liquid phase oxidation*** $C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$	Amounting to 10 percent of the market Disadvantages owing to environmental effects and separation expenses
	2) Monsanto process $CH_3OH + CO \rightarrow CH_3COOH$	The major source of acetic acid Costly due to using noble metal (Rh, Ir)
Oxalic acid	***1) Oxidation of carbohydrates*** $Carbohydrate \xrightarrow{NO_2} (COOH)_2 + other\ products$	NO_2 is toxic Separation of products
	2) Oxidation of ethylene glycol $(CH_2OH)_2 \xrightarrow{NO_2} (COOH)_2$	NO_2 is toxic
	3) Oxidation of propene $CH_3CH = CH_2 \xrightarrow{NO_2} (COOH)_2$	NO_2 is toxic
	4) Dialkyl oxalate process $2ROH + 2CO \xrightarrow{H^+, H_2O} (COOR)_2 \rightarrow (COOH)_2 + 2ROH$	CO is toxic, Corrosive to equipment by acid Separation of products
	5) Sodium formate process $CO + NaOH \rightarrow HCOONa$ $2HCOONa \xrightarrow{H_2SO_4, Ca^{2+}} (COOH)_2$	Energy intensive Sulphuric acid usage Calcium sulphate as byproduct

Table 2.5 Current processes of carboxylate production (Aresta, 2003; Li *et al.*, 2006) (con't.)

Chemical	**Current Processes**	**Remark**
Long chain carboxylates	***1) Oxidation of the corresponding alcohols*** $RCH_2OH \rightarrow RCOOH$	Harmful environmental impacts Low atom efficiency
	2) Hydrolysis of cyano-derivatives $RCN \rightarrow RCONH_2 \rightarrow RCOOH + NH_3$	

2.2.1.2.1 Formic Acid

Based on "atom economy", the new technology to synthesize formic acid from direct CO_2 and hydrogen invented by Farlow and Adkins in 1935 has been made available, as shown in Equation 2.19 (Farlow *et al.*, 1935). Zinc selenide and zinc telluride, ruthenium and palladium complexes have been employed as catalysts hydrogenation of CO_2. A multistage process was progressed by BP Chemicals (Anderson *et al.*, 1986), including: (1) an ammonium formate is a product of a nitrogen base with CO_2 and hydrogen with the support of a ruthenium complex; (2) The formate is removed from the catalyst and the low-boiling constituent; (3) Synthesis of the the ammonium formate with a high boiling base results in the new formate; (4) The new formate is thermally decomposed into formic acid that will be distillated, the low and high-boiling base are recovered .

$$CO_2 + H_2 \rightarrow HCOOH \qquad (2.19)$$

Using supercritical CO_2 for synthesis of formic acid has recently been big interests. Promoted by Ru catalysts such as $Ru(PMe_3)_4H_2$ or $Ru(PMe_3)_4Cl_2$, CO_2 itself can be hydrogenated to create formic acid (Jessop *et al.*, 1995). Methanol (MeOH) or dimethyl sulphoxide (DMSO) as co-catalysts or co-solvents can lead to higher catalytic efficiency (Jessop *et al.*, 1996). Table 2.6 shows different catalysts to synthesize formic acid from CO_2.

Table 2.6 Different catalytic systems for the hydrogenation of CO_2 to formic acid

Catalyst	**TOF (h^{-1})**	**T (°C)**	**Reference**
$[RuCl(OAc)(PMe_3)_4]$	95000	50	Munshi *et al.* (2002)
$[RuCl_2(TPPMS)_2]_2$	9600	80	Elek *et al.* (2003)
$[RuCl_2(CO)_2]n$	1300	80	Drury *et al.* (1983)
$RuH_2(PMe_3)_4$	1400	50	Jessop *et al.* (1994)
Rh(hfacac)(dcpb)	1335	25	Jessop *et al.* (1995)
$Ru_2(CO)_5(dppm)_2$	RT	103	Gao *et al.* (2000)
$RuH_2(PPh_3)_4$	698	50	Challand *et al.* (2008)

2.2.1.2.2 Acetic Acid

Acetic acid can be synthesized from CO_2 through a natural process with the help of acetogenic bacteria. Ni-systems are exploited to mimic this reaction (Aresta *et al.*, 1994; Tommasi *et al.*, 1998). In the presence of thiophenol, a thioester gave birth to form an olefin and CO_2 would be hydrolyzed to a carboxylic acid (Tommasi *et al.*, 1998).

An interesting reaction of acetic acid synthesis which is of great interests nowadays is direct combination of methane and CO_2, as illustrated in Equation 2.20. V-based catalysts is utilized to advance such reaction under mild conditions (Taniguchi *et al.*, 1998). The drawback of this reaction is mainly its low efficiency and far from practical application. However, the possibility to directly convert natural gas which is mainly CH_4 and CO_2 into acetic acid at the LNG extraction site is stimulating many researches recently.

$$CH_4 + CO_2 \rightarrow CH_3COOH \qquad (2.20)$$

In addition, acetic acid can be synthesized from CO_2 by acetogenic bacteria in nature as illustrated in Figure 2.7.

2.2.1.2.3 Oxalic Acid

Oxalic acid can be synthesized electrochemically from CO_2 in a non-aqueous media (Gressin, 1979). The radical anion $CO_2^{\cdot-}$ resulting from transferring one electron to CO_2 is a precursor of two different reactions. One reaction is the formation of oxalate dianion while the latter leads to the generation of carbonate and CO. Density, solvent and CO_2 pressure are the main factors which affects the reaction efficiency and selectivity. The low conductivity of organic media bringing about a low current density is the primary drawback (Aresta, 2003).

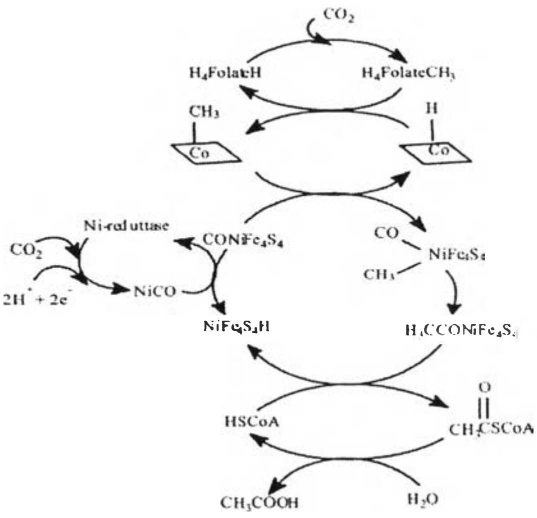
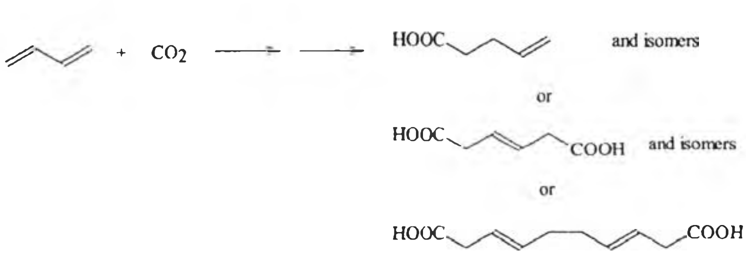


Figure 2.7 Formation of acetic acid (Aresta, 2003).

2.2.1.2.4 *Long Chain Aliphatic Carboxylic Acids, and Aromatic Mono- and Di-Carboxylic Acids*

Unsaturated carboxylic acids can be formulated from di-olefins and CO_2 with interesting efficiency and selectivity (> 90 percent) in the support of transition metal complexes as catalysts, as shown in Equation 2.21 (Hoberg *et al.*, 1984). Homo-coupling products are considered as by-products of such processes and cannot be neglected. Therefore, to exert such reactions to industry requires the control of coupling issues.



(2.21)

Aromatic compounds are also synthesized from direct carboxylation. An example of such reactions is the conversion of naphthalene into either A or B compounds below at room temperature via one-electron transfer through Group 1 metals.

Producing acrylic acid from CO_2 and ethylene promoted by Ni(0)-complexes is originating great discussions in industry (Hoberg *et al.*, 1984). The catalyst is oxidized and cannot be reused. Different diolefines can be transformed via this reaction and thus opens applicable routes to produce carboxylic acids in a large scale.

2.2.1.3 Other Possible Processes of Using CO_2 for Organic Synthesis

- Synthesis of carbamates and isocyanates.
- Synthesis of esters and other derivatives (lactones, amides).
- Insertion of CO_2 into C-C bonds.
- Electrochemical reactions that use CO_2.
- Electro-catalysis by metal complexes.
- Electrochemical reduction of CO_2.
- Radiation-induced syntheses of intermediates and fine chemicals.

2.2.2 CO_2 Reduction to C1 or Cn Molecules

While the utilization of CO_2 as a whole molecule was considered above, the next sections will assess the CO_2 usage as energy vector. Such conversion is endergonic and has high kinetic barriers as observed in Table 2.7. Therefore, it orders a considerable input of energy and catalysts to active. The main concern nowadays is finding ad hoc catalysts that may lower kinetic barriers.

2.2.2.1 CO_2 Reforming of Methane (CH_4)

The combination of CO_2 and CH_4 (often called dry reforming of CH_4) which currently has been of great interests permits to transform two greenhouse gases into syngas (H_2+CO) (Song *et al.*, 2002). Such mixture is a precursor to synthesize methanol or higher hydrocarbons, which results in achieving environmental and industrial goals.

Table 2.7 Free energy of formation of various C1 molecules (Aresta, 2003)

Species	**ΔG°f (kJ/mole)**
CH_4 (G)	-51
HCHO (L)	-102
CO (G)	-137
CH_3OH (L)	-166
HCOOH (L)	-361
CO_2 (L)	-386
CO_2 (G)	-394

Normally, the reaction is implemented at around 800-1000°C, resulting in the mixture of CO/H_2 with the ratio of 1, as illustrated in Equations 2.22-2.24 (Bradford *et al.*, 1999). Such ratio lower than that of steam reforming is appropriate for iron ore reduction and Fischer-Tropsch hydrocarbon synthesis but unfavorable to methanol synthesis.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \Delta H^0_{298K} = 247\, kJ/mol \quad (2.22)$$

$$CO + 2H_2 \rightarrow CH_3OH, \Delta H^0_{298K} = -128.6\, kJ/mol \quad (2.23)$$

$$nCO + 2nH_2 \rightarrow [CH_2]n + [H_2O]n \quad (2.24)$$

The main drawback of the dry reforming is the catalyst deactivation because of the carbon deposition, as shown in Equations 2.25 and 2.26. Coke results from either deformation of CH_4 or Baudoir equilibrium.

$$CH_4 \rightarrow C + 2H_2, \Delta H^0_{298K} = 206\, kJ/mol \quad (2.25)$$

$$2CO \rightarrow C + CO_2, \Delta H^0_{298K} = -172\, kJ/mol \quad (2.26)$$

The problem will be minimized if tri-reforming process is used (Song *et al.*, 2002). Tri-reforming process includes three following reactions, as illustrated in Equations 2.27-2.29. The new approach not only increases the ratio H_2/CO compared with the conventional process but also makes energetics of syngas production less negative.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \Delta H^0_{298K} = 247\, kJ/mol \quad (2.27)$$

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \Delta H^0_{298K} = 206\, kJ/mol \quad (2.28)$$

$$CH_4 + 1/2\, O_2 \rightarrow 2H_2 + CO, \Delta H^0_{298K} = -38\, kJ/mol \quad (2.29)$$

Coke formation can be limited when the dry-reforming works above 1230 K while the industry requires such reaction to operate at lower than 1200

K (Gadalla *et al.*, 1988). Therefore, catalysts play an important role in putting such reaction into industrial applications. Different authors have studied the heterogeneous catalysis of this reaction over catalyst like iridium, nickel, cobalt-nickel combination, ruthenium and rhodium with a combination of different supports like silica, magnesia, alumina, ultra-fine zirconia and lanthanum oxide (Song *et al.*, 2002). Due to the cost of Pt and Ru, Ni is chosen to develop Ni-based catalysts which permit to operate at low temperature and decrease coke formation. Noble metal, such as Pt, Rh, Ir, are active catalysts for dry reforming. The difference from them and Ni is less active towards CH_4 dissociative adsorption compared with Ni. An important factor which affects not only the adsorption and dissociation of CO_2 but also the creation of CO and hydrogen is the supports such as MgO, Al_2O_3 and TiO_2 (Wang *et al.*, 1996). Table 2.8 summarizes some catalysts used in dry reforming of CO_2.

Table 2.8 Summary of catalytic reforming of CO_2/CH_4 in the literature

Catalyst	Conversion (%)	T (K)	Reference
Ni/NaY	84.0	873	Kim *et al.* (1994)
KNiCa/ZSI	78	923	Park *et al.* (1995)
Rh/Al_2O_3	85.1	893	Nakamura *et al.* (1994)
Co,MgO/C	65-75	923	Guerrero-Ruiz *et al.* (1993)
$Ni/MgO-Al_2O_3$	86	1211	Gadalla *et al.* (1988)

2.2.2.2 Methanol

2.2.2.2.1 Background and Properties

Often referred to wood alcohol, methanol was first extracted from destructive distillation of wood as a by-product. Lighting, cooking and heating purposes were fundamental applications in the 19th century of methanol, followed by replacing kerosene as cheaper fuels. It is surprisingly that most methanol needed in World War I came from charcoal (Stiles, 1977). This was only ended by the development of coal and coke gasification processes which first commercially introduced by Badische Anilin und Soda Fabrik (BASF) in 1923. The process operates at 300-400°C and 250-350 atm (Cheng, 1994). In the 1940s, the appearance of steam reforming of natural gas in USA was the beginning of the new period of using natural gas to synthesize syngas because it is cleaner, cheaper and more plentiful than coal (Ott *et al.*, 2000). The initially commercial process was opened by Imperial Chemical Industries (Jitaru *et al.*) in 1966 in which low-pressure methanol process could be conducted at 100 atm (Arpe *et al.*, 2010). The new process which allowed process to operate at lower temperature and pressure (below 250°C and 50 atm) was progressed by Lurgi (Ott *et al.*, 2000). Throughout the past 40 years, significant advances have been carried out in methanol process from carbon oxides and hydrogen, which results in 99.8 percent of methanol selectivity and nearly 75 percent of energy efficiency. Current studies include the development of superior pathways to produce methanol at lower temperature and pressure with various sources of carbon oxides/hydrogen as well as at lower energy consumption. Although almost all methanol is produced from syngas in the world these days, processes without using syngas like direct production from CH_4 as well as hydrogenation of CO_2 are also being promoted. Table 2.9 shows some significant properties of methanol.

Table 2.9 Properties of methanol (Olah *et al.*, 2009a)

Property	**Value and Unit**
Molecular weight	32.04 g/mol
Melting point	-97.6°C
Boiling point	64.6°C
Density at 20°C	791 kg/m^3
Flash point	11°C
Autoignition temperature	455°C
Explosive limits in air	7-36%

2.2.2.2.2 *Uses of Methanol*

Nowadays, methanol has become a primary raw material in chemical industry and been employed to produce diverse chemicals and materials. Therefore, it is methanol produced in large scale with more than 75 million tons in 2013 (Huang *et al.*, 2014). Methanol is regarded as an intermediate in manufacturing various chemicals such as formaldehyde, methyl tert-butyl ether (MTBE) and acetic acid. In addition, methanol is a precursor of formation of chloromethanes, methylamines, methyl methacrylate (MMA), dimethyl terephthalate, and so on (Cheng, 1994). These chemicals in turn are intermediates to produce a lot of products in human life, involving paints, resins, silicones, adhesives, antifreeze and plastics. Figure 2.8 presents world market of methanol in 2007.

Formaldehyde which is the largest derivative from methanol is exploited to produce phenol-, urea- and melamine-formaldehyde and polyacetal resins as well as butanediol and methylenebis (4-phenyl isocyanate) (MDI). Because of its high octane number and reduction in air pollution, MTBE which accounts for the second largest usage of methanol is employed as a gasoline additive and a constituent for mixing. However, leakage problems of MTBE in local storages have led to severe environmental attacks. As a result, the use of MTBE has been terminated in USA and probably decreased gradually in other countries. Ethanol and ethyl tert-butyl ether (ETBE) are being considered as substitutes to MTBE.

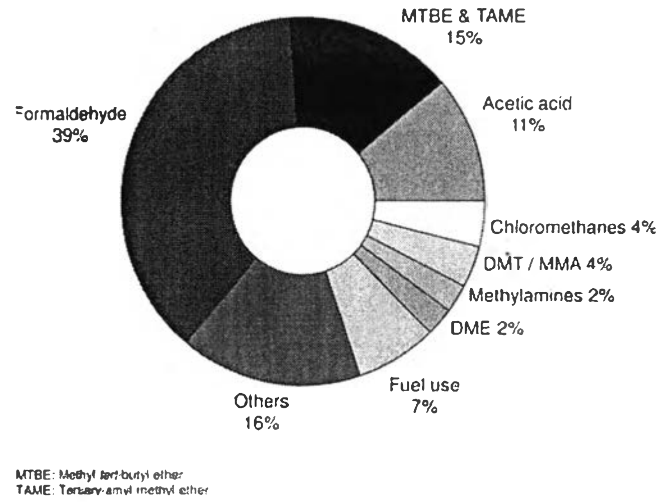


Figure 2.8 World market for methanol in 2007 (Olah *et al.*, 2009a).

Methanol and its derivative are of magnificent combustion features that make it become desirable fuels for current ICE-driven vehicles and diesel engines (Nowell, 1994). Invented by Nicholas Otto, Karl Benz and others, engines fueled by alcohol (methanol or ethanol) was used to replace steam engines (Ott *et al.*, 2000). In the early twentieth century, there was the competition between engines powered by alcohol and that by gasoline. Most European countries which were deficient in oil reserves were particularly keen on progressing ethanol as a fuel since it could be produced from diverse domestic agricultural sources. However, the situation was very different in USA which was of abundant petroleum resources and was the powerful promoter to gasoline. After the World War II, the interest in using alcohol as fuel reduced quickly over the world because of the ease of accessibility to large amount of cheap oil. Only when the oil crisis occurred in the 1970s, the concern to alternative fuels grew again, especially ethanol. Nevertheless, the new interest is currently aiming to the usage of methanol due to its flexibility. Methanol can be produced from various feeds including renewables and fossil fuels with general cost lower than ethanol. Thomas Reed was the pioneer in introducing methanol usage's advantages in 1973 (Reed *et al.*, 1973). Although various technological improvement were invented to solve methanol-related problems such as lower volatility and the deficiency of filling stations, there was a decreasing interest to methanol-based fuels until 2000. After that, however, as a consequence of the dramatic rise of world oil price and stricter standards to protect the environment, the concerns to methanol have been revised.

Methanol is a simple chemical compared with gasoline which is a complicated blend including various hydrocarbons and additives. Although being half the energy density of gasoline, methanol has higher octane number of 100 (RON = 107; MON = 92). The higher octane rating and higher compression ratio lead to a more efficiency in contrast to engine fueled by gasoline. Higher flame speed also supports the greater efficiency due to a faster and more complete combustion, which allows explaining why half the quantity of methanol is used to attain the same power result regardless of the lower energy density. Because having the higher latent heat of vaporization than gasoline, methanol can remove the more excessive heat from the engine and therefore allows using air-cooled systems instead of heavy, water-cooled processes (Nowell, 1994). Additionally, lower air pollutants of hydrocarbons, NOx and SOx are expected from methanol-optimized engines.

Owing to a high dipole moment and a high dielectric constant, methanol becomes easy to be miscible with water, acids, bases, salts that can result in corrosion problems. Aluminum, zinc and magnesium used in gasoline storage, devices and connectors can be eroded by methanol. Some plastics, rubbers and gaskets also react with methanol and therefore become fragile and fail, causing leaks or system malfunctions. Therefore, methanol requires definite systems different from those of gasoline and it makes capital costs increase. Under frigid conditions, pure methanol without highly volatile components such as butane, isobutane, propane will give rise to cold-start problems (Cheng, 1994). M85 fuel which is a mixture between methanol and gasoline of 15 percent in order to support enough vapor can be a solution to start engine with any weather conditions. Dimethyl ether (DME) are also offered to aid methanol in the beginning at low temperature (Kozole *et al.*, 1989; Green *et al.*, 1990).

The destiny of methanol fuel mainly depends on economic aspects and world oil price although energy security matters, emission concerns and other political issues also occupy a significant role. Due to declining oil and gas reserves, the call of methanol as a transportation fuel eventually accomplishes a foothold. The new era for methanol is being opened.

2.2.2.2.3 Production of Methanol

2.2.2.2.3.1 Methanol from Fossil Fuels

Today, in the world most methanol production comes from syngas which mostly contains hydrogen, CO and some CO_2 via heterogeneous catalysts according to the following reactions.

$$CO + 2H_2 \rightleftarrows CH_3OH, \Delta H^0_{298K} = -21.7\,kcal/mol \tag{2.30}$$

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O, \Delta H^0_{298K} = -11.9\,kcal/mol \tag{2.31}$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O, \Delta H^0_{298K} = 9.8\,kcal/mol \tag{2.32}$$

Coal, coke, natural gas, petroleum, heavy oils and asphalt all can become a carbonaceous source to produce the syngas by partial oxidation or reforming. Economic concerns, long-term viability of feeds, energy utilization and environmental problems will assume a crucial role in selection of raw materials.

Before World War II, coke was the main supply for methanol synthesis through coke ovens and steel factories. However, after then everything changed and the feedstock for methanol production sharply moved to natural gas, especially in USA. Natural gas became widely available because it proposes the better properties than coal including its higher hydrogen content and lower energy consumption, capital and operational costs. Fewer impurities in natural gas enable to use more active catalysts and operate at mild conditions (lower temperature and pressure). The lower the pressure, the lower the by-products such as dimethyl ether, higher alcohols, methane, etc. are obtained by the process. Most of methanol plants over the world are founded on the Johnson Matthey's process invented in 1960s and operated at low pressure of 5-10 MPa and temperature of 200-300°C (Ott *et al.*, 2000).

One of the methods to produce the syngas from natural gas is steam reforming in which methane reacts with steam at high temperatures and pressures over nickel-based catalysts (Rostrup-Nielsen, 2008). A mixture of CO, hydrogen and CO_2 is the outcome of such reactions, as illustrated in Equations 2.33-2.36. Factors that affect reactions include temperature, pressure and the ratio of CH_4/H_2O. Besides the addition of CO_2 or hydrogen to gas products to adapt to subsequent processes, the main issue is coke formation which can deactivate the catalysts due to coke deposit. Table 2.10 shows some catalysts used in steam reforming reactions.

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO, \Delta H^0_{298K} = 206\, kcal/mol \tag{2.33}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2, \Delta H^0_{298K} = -9.8\, kcal/mol \tag{2.34}$$

$$CH_4 \rightleftarrows C + 2H_2, \Delta H^0_{298K} = 18.1\, kcal/mol \tag{2.35}$$

$$2CO \rightleftarrows C + CO_2, \Delta H^0_{298K} = -40.8\, kcal/mol \tag{2.36}$$

Table 2.10 Overview of nickel-based catalysts in steam reforming

Catalyst	**T (K)**	**P (kPa)**	**X CH_4 (%)**	**Reference**
Ni/$MgAl_2O_4$ (15% Ni)	823	500	17	Xu *et al.* (1989)
Ni/CeO_2 (15% Ni)	1023	101	54	Dong *et al.* (2002)
Ni/SiO_2 (9% Ni)	873	101	75	Takahashi *et al.* (2004)
Ni/α-Al_2O (15-17% Ni)	823	120	12.5	Hou *et al.* (2001)
Ni/Ce-ZrO_2/θ-Al_2O_3 (12% Ni)	973	101	97	Oh *et al.* (2003)

Partial oxidation is also used to produce syngas by means of limited oxygen with or without a catalyst under high temperature (800-1500°C), as shown in Equations 2.37-2.39 (Choudhary *et al.*, 2008). The advantage of such reaction is the formation of desirable syngas while further oxidation of CO and hydrogen to CO_2 and water in exothermic reactions increases safety considerations. Table 2.11 exhibits some catalysts used in partial oxidation reactions.

$$CH_4 + 1/2\,O_2 \rightleftarrows CO + 2H_2, \Delta H^0_{298K} = -8.6\,kcal/mol \tag{2.37}$$

$$CO + 1/2\,O_2 \rightleftarrows CO_2, \Delta H^0_{298K} = -67.6\,kcal/mol \tag{2.38}$$

$$H_2 + 1/2\,O_2 \rightleftarrows H_2O, \Delta H^0_{298K} = -57.7\,kcal/mol \tag{2.39}$$

Table 2.11 Overview of catalysts in partial oxidation

Catalyst	**Support/Mixed Oxide with**	**Reference**
Co	$MgO\text{-}Al_2O_3$	Sokolovskii *et al.* (1998)
Co	Y_2O_3 or ZrO_2	Iwasaki *et al.* (2006)
Ni	CeO_2/TiO_2	Zhang *et al.* (2006)
Ni	Al_2O_3/clay monolith	Gómez *et al.* (1997)
Pd	Sc_2O_3	Bhattacharya *et al.* (1992)
Pd	Y_2O_3	Passos *et al.* (2006)
Rh	CeO_2/Al_2O_3	Fathi *et al.* (2000)
Rh	TiO_2/YSZ	Baranova *et al.* (2004)
Ru	CeO_2/Al_2O_3	Rabe *et al.* (2005)
Ru	MgO	Qin *et al.* (1996)

Currently, methanol plants usually employ both partial oxidation and steam reforming to produce syngas with ideal compositions and without excess heat for consuming or emitting. Because optimum conditions are exerted to each reaction, two subsequent steps are progressed in which the outflow of the reforming reactor is the feed of the partial oxidation reactor (Hansen *et al.*, 2008).

Although natural gas is currently preferred as raw materials due to easily attaining a suitable syngas with low impurities, other pathways are also employed under certain situations. Areas which are plentiful supplies of coal or heavy oils and limited sources of natural gas can recruit these resources to synthesize methanol in spite of higher capital costs for purifying syngas.

2.2.2.2.3.2 Methanol from CO_2

The combustion of fossil fuels as well as synthetic substances will produce water and CO_2 which becomes the main source to make global temperature much worse. Therefore, developing technologies to convert CO_2 into fuel is our vital mission. A promising approach is based on hydrogen reduction via catalysts to produce methanol from CO_2. As a matter of fact, two different reaction routes have been suggested: (1) reduction of CO_2 to CO with subsequent hydrogenation to methanol; (2) direct hydrogenation of CO_2 to methanol.

2.2.2.2.3.2.1 Conversion to Products via Syngas Route

CO_2 can be converted first to synthesis gas, CO/H_2, followed by reactions of the class of C1 chemistry, Fischer-Tropsch reaction, MeOH synthesis, methanation, etc. There are two ways to transfer CO_2 to syngas, being (1) with CH_4 via reforming reaction and (2) with hydrogen via reverse water gas shift reaction (RWGS). The first is discussed above while the latter is essentially the reverse of water gas shift reaction which was discovered in 1780 by Felice Fontana (Equations 2.40-2.41) (Klier, 1982).

$$CO_2 + H_2 \rightleftarrows CO + H_2O, \Delta H^0_{300K} = 41.2\, kJ/mol \qquad (2.40)$$

$$CO + 2H_2 \rightleftarrows CH_3OH, \Delta H^0_{300K} = -90.8\, kJ/mol \qquad (2.41)$$

RWGS reaction is an equilibrium reaction in which the conversion is strongly suffered by temperature while the effect from pressure does not have a significant impact. Currently, two commercial types of catalysts are used. Because of less influenced by poisons, Fe-based high-temperature-shift (HTS) catalysts is preferred to transform a large amount of CO_2 in many practical industry applications at high temperature of 350-550°C. However, Fe-based HTS catalysts are far too inactive and pose serious volume and weight restraints. Cu, Cu-ZnO and Pd based catalysts (LTS) can be selected if the lower temperature of 200-350°C is employed. Nevertheless, being unstable at high temperature and pyrophoric nature makes such catalysts less safe and inefficient during operation.

2.2.2.2.3.2.2 Direct CO_2 Hydrogenation

From the early twentieth century, scientists had known how to synthesize methanol from CO_2 and hydrogen. Metals and their oxides (notably copper and zinc) are being used to develop efficient catalysts alike to those currently employed in the fossil fuels-based methanol production, as shown in Equation 2.42 (Ostrovskii, 2002; Rozovskii *et al.*, 2003; Hansen *et al.*, 2008).

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O, \Delta H^0_{298K} = -11.9\,kcal/mol \qquad (2.42)$$

A high-activity catalyst for CO_2 conversion has been advanced by Lurgi AG which a pioneer in methanol production technology (Goehna *et al.*, 1994). The selectivity of the new process is extremely superior to that of conventional route if operating at around 260°C. The general composition of the catalysts for CO_2 hydrogenation such as $Cu/ZnO/Al_2O_3$ is similar to the ones used presently for methanol production via syngas. Palladium or gallium doped on the catalyst increases the activity of catalyst for methanol production. Additionally, the deactivation of catalysts performs at the same rate as that from catalysts practically utilized for methanol plants. A laboratory pilot scale where 50 kg methanol per day with 99.8 percent of the methanol selectivity was attained was constructed in Japan to study the efficiency of such process (Saito, 1998).

The Carbon Recycling International Company in Ireland established the first commercial plant to convert CO_2 into methanol with the usage of cheap geothermal energy (Guerrero-Ruiz *et al.*, 1993). The capacity of the plant is around 2 million liters of methanol per annum with hydrogen production by water electrolysis employing cheap geothermal-produced electricity (Shulenberger *et al.*, 2007; International, 2012). A new plant is also built in Japan by Mitsui chemicals with the annual methanol capacity of 100 tons in which hydrogen comes from photochemical splitting of water with the support of solar energy (Tremblay, 2008). Furthermore, new remarkable interests for CO_2 conversion to methanol by hydrogen are announced in China, European countries and others.

Diverse renovations to convert CO_2 and hydrogen into methanol have been reported (Goehna *et al.*, 1994; Xu *et al.*, 1996; Saito, 1998; Saito *et al.*, 2004). The capital costs to construct the methanol plant from CO_2 are estimated to be similar to that of a current methanol plant (Goehna *et al.*, 1994). The availability, the price of CO_2 and hydrogen and particularly needed energy are the main issues to prevent such process in a large scale application.

2.3 Case Studies

2.3.1 Direct CO_2 Hydrogenation into Methanol

2.3.1.1 Introduction

A lot of efforts have been conducted to convert CO_2 into methanol through hydrogenation which is a practical process to mitigate effects of greenhouse gases and technologically competitive with the conventional methanol process from syngas. Olah and co-workers (Olah, 2005; Olah *et al.*, 2009a; 2009b; 2011) are a pioneer in the introduction of alternative pathways for methanol production and its derivatives as well as their usage as fuels in the methanol economy. In such concept, CO_2 is caught from either natural and human sources or air by absorption and converted into methanol, DME and diverse products. The advantages from CO_2 to produce methanol include: (1) using renewable sources which help alleviate human reliance on fossil fuels; (2) avoiding only CO_2 separation which is quite expensive; (3) creating the chance to lessen the cause of global warming (Olah, 2005). Olah *et al.* (2009a) suggested that CO_2 conversion into methanol contributes renewable, unlimited carbon source to produce fuels, store and transport energy as well as a precursor to synthesize ethylene and propylene for the production of hydrocarbons and their products. It can fundamentally therefore replace fossil resources. It allows the lasting use of carbon-containing fuels and materials and avoids excessive CO_2 emissions causing global warming (Olah *et al.*, 2009b). CO_2 capture and storage with chemical conversion are combined to create the methanol economy concept. While water and CO_2 as raw feeds are plentiful, the required energy for methanol production can originate from any renewable energy sources solar, wind, geothermal, and nuclear energy.

CO_2 is rather inert, non-toxic, non-corrosive and non-flammable that makes it quite safe in most applications. In addition, CO_2 exists in plenty and comes from carbon capture and sequestration (CCS) as well as industrial activities such as flue gas from power plants, gaseous streams in aluminum production or a byproduct with natural gas. With the help of efficient separation methods such as membrane, redundant CO_2 from air can be exploited as a new viable alternative source. Even so, a major challenge arose is how to produce hydrogen sustainably and costly effectively (Raudaskoski *et al.*, 2009). Hydrogen is now generated from steam reforming, coal gasification and partial oxidation of light oil residues. Accordingly, the depletion of fossil fuels occurs and more CO_2 is exhausted. Methanol synthesis of CO_2 and hydrogen is considered as a friendly environment process only if it consumes more CO_2 than that emitted in hydrogen production. Dry reforming and splitting of water by renewable energy are currently becoming precious candidates to produce hydrogen although they have some drawbacks. Additionally, electrolysis of water using atomic and solar energy further represents thermo-chemical routes for hydrogen producing. Interestingly, no carbon source is employed in the thermo-chemical pathways. Nevertheless, more attempts should be progressed to find out the most feasible method to produce hydrogen.

2.3.1.2 *Thermodynamic Analysis*

The main reaction of CO_2 hydrogenation is as follows

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O, \Delta H^0_{298K} = -49.5\, kJ/mol \qquad (2.43)$$

The reaction is exothermic and involves the reduction of molecular number, which leads to the advance when increasing pressure and decreasing temperature. High efficiency also achieves if products consisting of methanol and water are separated. Although $CuO/ZnO/Al_2O_3$ catalysts are good promoters for conventional methanol production, they perform poor activity in the new process at low temperature (Saito *et al.*, 1996; Inui *et al.*, 1997). Increasing temperature will expedite the reverse water gas shift which consumes more hydrogen to form the mixture of CO and H_2O and therefore make CO_2 yield decrease (Skrzypek *et al.*, 1990). In addition, sintering and deactivation will arise if there is water in the process which enables Cu and ZnO crystallize on catalysts' surface (Wu *et al.*, 2001). Because of the formation of byproducts such as high alcohols and hydrocarbons, the high selectivity catalysts should be employed. Gallucci *et al.* (2004) conducted the research on CO_2 conversion and methanol selectivity for CO_2 hydrogenation at 250°C and 5 MPa with the ratio of CO/H_2 equal to 3. The result attainted 27 and 68 percent, respectively. To achieve the higher conversion requires the process to be run at around 30 MPa and 125°C (Mahajan *et al.*, 2003).

Compared with the conventional methanol process from syngas, the CO_2 hydrogenation requires more hydrogen because of the formation of water. Additionally, the thermodynamics from CO_2 hydrogenation are not as desirable as that from syngas. Arakawa (1998) showed that methanol yield from CO_2 is just around 40 percent whilst that from syngas can attain more than 80 percent at 200°C.

2.3.1.3 Catalysts

In the past years, several researches about catalysts for CO_2 hydrogenation have been announced. Cu, Zn, Cr, and Pd are basically employed to attain better methanol efficiency and selectivity as well as lower byproducts. Cu/ZnO catalysts are famous to achieve the high yield and selectivity. Al_2O_3 and Zr can be a good supporter to promote the activity and selectivity. Cu- and Pd-based catalysts have been of many interests recently.

2.3.1.3.1 Cu-based Catalysts

Cu-based catalysts have been extensively studied (e.g.,CuO/ZrO_2,$CuO/ZnO/ZrO_2$,$CuO/ZnO/Ga_2O_3$, modified $CuO/ZnO/Al_2O_3$ and multi-component catalysts).

Liu *et al.* (2001) realized that the method to prepare catalysts as well as the preparation's conditions significantly affect catalysts' surface structure. For example, deposition-precipitation method created the better catalysts with finer particles and higher activity than that from impregnation or co-precipitation (Moradi *et al.*, 2008). The achieved methanol efficiency is 0.36 g/(gcat hr) at 240°C and 2 MPa. ZrO_2 was added to CuO/ZnO catalyst as a promoter in the research by Yang *et al.* (2006) in which he discovered that copper was highly dispersed when adding ZrO_2. The better results were accomplished with 26.4 percent of CO_2 conversion and 0.22g/(mL hr) of methanol efficiency compared with those from just utilizing CuO/ZnO (16 percent and 0.14 g/(mL hr)) (York *et al.*, 2003). Lachowska *et al.* (2004) recognized that $CuO/ZnO/ZrO_2$ with the help of Mn performed higher catalytic activity with methanol efficiency and selectivity being 138 g/(kgcat hr) and 91 percent, respectively. Urea-nitrate combustion process was exploited to synthesize

$CuO/ZnO/ZrO_2$ catalysts by Guo *et al.* (2009) in which impacts of the urea/nitrate proportion on catalysts properties and efficiency were studied. Operated at 240°C and 3 MPa, the process showed the optimum results with 17 percent of CO_2 conversion and 56.2 percent of methanol selectivity occurs if 50 percent of stoichiometric quality of urea is utilized. By means of ultrasound irradiation, reverse co-precipitation was put into practice of synthesizing $CuO/ZnO/ZrO_2$-based catalysts. Arena *et al.* (2007) based on such new route to research total surface exposure and dispersion of active metal phase. Structure of the catalyst, especially metal dispersion, affected remarkably by ZnO and it was considered as the most important factor towards the reaction in general and turnover frequency (TOF) in particular. Additionally, the activity of such catalyst was higher than that of $CuO/ZnO/Al_2O_3$ catalyst which is used in the conventional methanol route owing to stronger affinity to water of Al_2O_3.

A zeolite membrane reactor that contains $CuO/ZnO/Al_2O_3$ showed higher performance than that in a traditional process in the research of Gallucci *et al.* (2004). Pd as a promoter which demonstrated its effects on the performance was studied by Melián-Cabrera *et al.* (2002) on $CuO/ZnO/Al_2O_3$ catalyst. The result exhibited that because Pd improved the reducibility of CuO, the inherent methanol efficiency in which 4 and 10 percent of Pd was employed at 160-200°C and 4 MPa was superior to that of the process without Pd. Mixture catalysts like $Cu/ZnO/ZrO_2/Al_2O_3$ and $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ can be a solution for cleaner methanol production in comparison with crude methanol from syngas (Saito *et al.*, 2004). Catalysts which contain Cu/Zn crystallites in a fibrous structure displayed the more desirable dispersion and stability against those from $CuO/ZnO/Al_2O_3$. Even only 5 percent of Zr was added, the methanol space time efficiency was 80 percent higher than that comes from the conventional one, which leads to the better CO_2 hydrogenation (An *et al.*, 2007).

With the usage of SiO_2 through impregnation method, Toyir *et al.* (2001) prepared $CuO/Ga_2O_3/SiO_2$ catalysts and proved they had high selectivity and stability. Nano-crystalline ZrO_2 as a promoter was employed by Liu *et al.* (2005) to prepare $CuO/Ga_2O_3/ZrO_2$ and $CuO/B_2O_3/ZrO_2$. The methanol efficiency for Ga- and B-containing catalysts was 1.93 and 1.8 mmol/(g hr), respectively (Lee *et al.*, 2004). Because of the electronic structure by nano-crystalline

ZrO_2, the relationship between the metal and supporter notably improved. Therefore, higher methanol selectivity and CO_2 conversion were the inevitable results.

2.3.1.3.2 Pd-based Catalysts

Liang *et al.* (2009) evolved Pd/ZnO catalysts for CO_2 hydrogenation into methanol with the aid of multi-walled carbon nanotubes, which leads to an outstanding performance. Higher TOF and methanol selectivity also achieved from Pd/ZnO at low pressure compared with Cu/ZnO. The study was made by Collins *et al.* (2004) to investigate the relationship between H_2/CO with β-Ga_2O_3 and Pd/β-Ga_2O_3. He suggested that adding Pd to the oxide support gave rise to the hydrogenation rate carbon-containing species. The introduction of Ga to Pd/SiO_2 was carried out by Bonivardi *et al.* (2000) while at 250°C and 3 MPa, TOF from Pd/SiO_2 and Ga_2O_3-promoted Pd/SiO_2 was 0.0017 and 0.45 1/s, respectively. 17 and 62 percent are results of methanol selectivity, respectively. The connection of Pd crystallites and reduced Ga species was assigned to explain the uncommon high catalytic behavior. The closeness of the Ga_2O_3-Pd functions and hydrogen contributed to the success of Pd/SiO_2 promoted by Ga.

2.3.1.4 Reactor Innovations

A zeolite membrane reactor utilized by Gallucci *et al.* (2004) showed the higher methanol yield due to the selective removal of products after reaction. 11.6, 75 and 8.7 percent are CO_2 conversion, methanol selectivity and yield, respectively while the corresponding ratio in the conventional reactor is 5, 48 and 2.4 percent. Barbieri *et al.* (2002) based on a simulation reactor realized that the organophilic and hydrophilic membrane result in the superior performance in comparison with the tubular reactor. The more methanol is produced, the less reactants are consumed and the lower reaction conditions operate. A two-stage catalyst bed was developed by Rahimpour (2008) to synthesize methanol from CO_2. The mission of the first bed is partially converting syngas into methanol at high temperature and yield. The second bed contributes heat to the feed to the first bed as well as increases thermodynamic equilibrium potential through steadily decreased temperature. The catalyst will be protected from sintering due to the mild temperature in the second bed. The two stage catalyst bed process can be an attractive candidate to produce methanol owing to higher performance than a single bed reactor.

2.3.1.5 Simulation Researches

Van-Dal *et al.* (2013) studied methanol production from direct hydrogenation of CO_2. The authors used Aspen Plus to construct the flowsheet and simulate the complete process including water electrolysis, CO_2 capture and methanol synthesis. CO_2 captured comes from flue gases of a coal power plant while water electrolysis supplied the used hydrogen. Although hydrogen has to be produced from carbon-free electricity source (e.g. solar, biomass or nuclear), CO_2 units are served by electricity from the coal power plant. In this research, authors employed the kinetic model from Bussche *et al.* (1996) with some arrangements to adapt to Aspen. Results showed that direct hydrogenation of CO_2 performs remarkably in abating CO_2 - 1.6 tons of CO_2 per ton of methanol produced if a byproduct is sold or 1.2 tons if it is not. Moreover, the methanol plant can be built in everywhere where the power plant from fossil fuel exists while hydrogen generated from renewable energy is transported to methanol synthesis plants.

Machado *et al.* (2014) compared the energy efficiencies and CO_2 reduction of two methanol processes-conventional process from syngas and new process from hydrogenation of CO_2. Moreover, the research found out the effect of process conditions such as pressure, H_2/CO_2 ratio and $(H_2\text{-}CO_2)/(CO_2\text{+}CO)$ on methanol production, methanol selectivity and CO_2/CO conversion. The model from Graaf *et al.* (1986) was used in this study to simulate the reactions by means of calculating equilibrium constants. The analysis concluded that new process not only consumes more utilities but also emits more CO_2 than conventional process. However, adjusting process conditions such as increasing pressure above 80 bar and maximizing $(H_2\text{-}CO_2)/(CO_2\text{+}CO)$ ratio allows the process to make the most of amount of methanol produced as well as CO and CO_2 converted.

2.3.2 Bi-reforming of CO_2 into Methanol

2.3.2.1 Introduction

Another way to exploit CO_2 more efficiently is to combine CO_2 with natural gas or other hydrocarbons to produce syngas. CO_2 reacting with natural gas via the dry reforming produces syngas with a H_2/CO ratio of 1 which is inappropriate to methanol synthesis because methanol production requires a H_2/CO_2

ratio of around 2. Hydrogen therefore from other sources must be added to syngas to achieve the suitable H_2/CO ratio. In addition, steam reforming of natural gas normally produces syngas with the H_2/CO ratio of 3, leading to complex separation requirements.

To conquer this problem and to produce a H_2/CO ratio of 2 suitable for methanol synthesis, Olah and co-workers (Olah *et al.*, 2013) has developed a new technology combining steam and dry reforming of methane, called "bi-reforming".

Bi-reforming is of advantages in the use of different natural gas sources, even significantly high concentration of CO_2. In fact, 50 to 70 percent of CO_2 can be found in some natural gas or biogas sources. In addition, bi-reforming could be employed to recycle CO_2 from emission sources such as flue gases from fossil fuel-based plants, waste gases of cement factories and other industries.

Bi-reforming is also pretty flexible for coalbed methane as well as tight gas sands. Coalbed methane from coal mining operation can be combined with CO_2 from burning coal at coal-fired power plants to produce methanol. Moreover, syngas can be obtained from bi-reforming of shale gas because dry shale gas is essentially methane (> 98 percent) or even with wet shale gas also consisting of ethane, propane and some higher hydrocarbons.

2.3.2.2 Thermodynamic Analysis

The main reactions of bi-reforming are as follows

$$CH_4 + H_2O \rightarrow 3H_2 + CO, \Delta H^0_{298K} = 206\,kJ/mol \qquad (2.44)$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO, \Delta H^0_{298K} = 247\,kJ/mol \qquad (2.45)$$

$$3CH_4 + 2H_2O + CO_2 \rightleftarrows 4CO + 8H_2 \rightleftarrows 4CH_3OH \qquad (2.46)$$

In bi-reforming, a normal ratio of methane, steam and CO_2 of 3/2/1 creates a mixture of H_2/CO with a ratio of close 2. The mixture was proposed to be called "metgas" to emphasize its difference from the conventional syngas. The mixture with 2/1 of H_2/CO ratio is suited for the synthesis of methanol and subsequently derived hydrocarbon products. The reaction is endothermic and involves the increase of molecular number, which leads to the advance when decreasing pressure and increasing temperature. Basically, bi-reforming is conducted under 5-30 atm and 830-950°C to produce metgas, which allows to directly use syngas in the methanol production (Cheng, 1994). However, most of recent research have been carried out at atmospheric pressure and with pure methane. Park *et al.* (2013) conducted the research on CO_2 and CH_4 conversion for bi-reforming at normal pressure with a range of temperature from 450 to 950°C. The author realized that increasing temperature leads to the rise of syngas production rate and the decrease of the molar ratio of H_2/CO. The molar ratio of H_2/CO of 2 attained at approximately 850°C. In order to approach to realistic applications, Olah and his colleagues (Olah *et al.*, 2013) researched bi-reforming of methane and natural gas at elevated pressures. Results showed that the H_2/CO of 2 could obtain at 830°C and 7 atm during the experiment up to 320 hr. Furthermore, the conversion of methane declined with rising pressure (71 percent at 7 atm compared with 52 percent at 28 atm). However, the H_2/CO ratio raised slightly from 1.99 at 7 atm to 2.02 at 28 atm.

2.3.2.3 Catalysts

Olah *et al.* (2013) used catalysts composed of NiO and MgO between 5 and 35 percent. Researches showed that at 15 percent of NiO on MgO, the selectivity of CO and hydrogen were 100 and 98 percent, respectively. In addition, the study indicated that steam and CO_2 reforming are of similar kinetics. With the usage of δ-Al_2O_3 as a supporter, Park *et al.* (2013) prepared a Ni/δ-Al_2O_3-Ni foam catalyst and proved it had higher CH_4 conversion than a pellet catalyst. Furthermore, the metallic foam catalyst led to a high conversion of CH_4 and CO_2 at a high space velocity. The combination of two metal including Ni and Ce was studied by Koo *et al.* (2012) while at 750°C, CH_4 and CO_2 conversion are close to thermodynamic equilibrium values.

2.3.2.4 Simulation Researches

Özkara-Aydınoğlu (2010) by means of Aspen Plus carried out a thermodynamic equilibrium research of combined CO_2 and steam reforming. With the aid of thermodynamic analysis, authors determined the most appropriate operation conditions of temperature, pressure and inlet gas composition, CO_2/CH_4 ratio in order to optimize process parameters like conversions, yields and outlet compositions. The study showed that at different operating conditions of temperature, pressure and different feed ratios the combined CO_2 and steam reforming is controlled by various reactions. The conversion efficiency and H_2/CO ratio can be managed by alternating H_2O/CO_2 ratio in the feed, temperature and pressure, depending on different purposes.

Kim *et al.* (2014) studied methanol production from combined reforming of CO_2. The authors used ProII to construct the flowsheet and simulate the complete process including natural gas separator, syngas production and methanol synthesis for FPSO (floating production, storage and off-loading). The Gibbs reactor model was used for the reformers while the Plug flow reactor was employed for the methanol reactor. The results were compared with the literature in terms of the carbon conversion to methanol. Research pointed that the use of a reverse water gas shift (RWGS) reactor provides the best results while an increase of 13.8 percent of methanol yields and a decrease of 38.7 percent of process size achieved compared with the case without RWGS. Generally, to produce 1 kg of methanol required 0.518, 0.35 and 0.956 kg of stranded gas, CO_2 and steam, respectively.

2.3.3 Tri-reforming of CO_2 into Methanol

2.3.3.1 Introduction

Normally, CO_2 has to be separated and purified from concentrated CO_2 sources through either absorption or adsorption before used for different purposes. However, the separation of CO_2 from concentrated CO_2 sources normally orders remarkable energy usage, leading to a significant reduction of net electricity output of a power plant. For example, 100 megawatts would be obligatory for a typical alkanolamine-based CO_2 capture process from a standard 500-megawatt coal power plant. Thus, directly using CO_2 from flue gases become highly appealing to CO_2 conversion. The new process, called "tri-reforming", has been developed by Song *et al.* (2004). The tri-reforming is a three-step reaction process which allows to avoid the CO_2 separation and has the potential to produce a desired H_2/CO ratios for fuels and chemicals synthesis.

2.3.3.2 Thermodynamic Analysis

Tri-reforming is a synergetic combination of endothermic CO_2 and steam reforming and exothermic partial oxidation of methane.

Tri-reforming of natural gas (Equations 2.47-2.50)

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2, \Delta H^0_{298K} = 247 kJ/mol \quad (2.47)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2, \Delta H^0_{298K} = 206 kJ/mol \quad (2.48)$$

$$CH_4 + \tfrac{1}{2}O_2 \rightleftarrows CO + 2H_2, \Delta H^0_{298K} = -36 kJ/mol \quad (2.49)$$

$$CH_4 + 2O_2 \rightleftarrows CO_2 + 2H_2O, \Delta H^0_{298K} = -880 kJ/mol \quad (2.50)$$

Reactions for coke formation and destruction (Equations 2.51-2.55)

$$CH_4 \rightleftarrows C + 2H_2, \Delta H^0_{298K} = 74.9 kJ/mol \quad (2.51)$$

$$2CO \rightleftarrows C + CO_2, \Delta H^0_{298K} = -172.2 kJ/mol \quad (2.52)$$

$$C + CO_2 \rightleftarrows 2CO, \Delta H^0_{298K} = 172.2 kJ/mol \quad (2.53)$$

$$C + H_2O \rightleftarrows CO + H_2, \Delta H^0_{298K} = 131.4 kJ/mol \quad (2.54)$$

$$C + O_2 \rightleftarrows CO_2, \Delta H^0_{298K} = -393.7 kJ/mol \quad (2.55)$$

The usage of dry and steam reforming can fulfill two important purposes: to create syngas with desired H_2/CO ratios and to alleviate the carbon formation which is remarkable for dry reforming. The combination of steam reforming and partial oxidation with CO_2 reforming could significantly diminish or eliminate carbon formation on catalysts, leading to long catalyst life and high process efficiency. O_2 plays an important role in raising energy efficiency by generating heat in situ as well as lowering carbon formation in catalysts.

Song and his teammate (Song *et al.*, 2004) calculated the equilibrium conversions and H_2/CO ratios through HSC program at atmospheric pressure. Results showed that 95 and 80 percent of CH_4 and CO_2 conversion, respectively could accomplish at a range of 800-850°C with CO_2/H_2O ratio of 1 and O_2/CH_4 ratio of 0.1. Arab Aboosadi *et al.* (2011) built a mathematic model to simulate and optimize a tri-reforming reactor via a one-dimensional heterogeneous model. Optimal conditions with 1100K and the ratio of $CH_4/CO_2/H_2O/O_2$ of 1/1.3/2.46/0.47 allows to attain 97.9 percent, 1.84 and 1.7 of methane conversion, hydrogen yield and H_2/CO ratio, respectively.

2.3.3.3 *Catalysts*

Most of recent studies with pure gases pointed out with the help of oxygen in CO_2 or steam reforming, the energy efficiency and alleviation of coke formation were dramatically improved. Inui and coworkers (Inui *et al.*, 1995) researched energy-efficient H_2 production from the combination of partial oxidation and CO_2-H_2O reforming with the support of Ni-based three component catalysts such as Ni-La_2O_3-Ru. The authors proved the addition of methane combustion enables higher hydrogen production rate even at elevated flow rate conditions (Inui *et al.*, 1995). Choudhary prepared a Ni/CaO (Choudhary *et al.*, 1994) or Ni/MgO-SA (Choudhary *et al.*, 1998) catalyst for the steam and CO_2 reforming with the attendance of oxygen at normal pressure. Researches showed that high conversion and selectivity of CO and hydrogen could obtain if O_2 presents in reforming reactions. Hegarty and his colleagues (Hegarty *et al.*, 1998) confirmed positive effects of a Pt/ZrO_2 catalyst on steam and CO_2 reforming in the presence of O_2. Song and his colleagues (Song *et al.*, 2004) are pioneers in applying the tri-reforming process for flue gas directly. The authors prepared different catalysts by wet impregnation technique to study tri-reforming experiments. The catalysts are the combination of Ni with MgO, ZrO_2, CeO_2-ZrO_2 and Mg-CeO_2-ZrO_2 supports. Results demonstrated that 97 and 80 percent of CH_4 and CO_2 conversion, respectively could attain with desired H_2/CO ratios at 800-850°C under normal pressure.

2.3.3.4 *Simulation Researches*

Zhang *et al.* (2013) also had an interest in converting CO_2 of flue stack gases into methanol through tri-reforming process. With the help of simulation tool, authors studied the optimum operating conditions of temperature, CH_4/Flue gas ratio and pressure in obtaining target ratio of syngas and maximum CO_2 conversion. Operating at 850°C, 1 atm and 0.4 CH_4/Flue gas ratio would give rise to 99% of CO_2 converted and a syngas ratio (H_2/CO) of 2. Besides, the heat integration was performed in this study to achieve energy savings by using GAMS program in which results from this program was validated by Aspen Energy Analyzer. In addition, the economic analysis disclosed that the process after heat integration could present economic viability. The CO_2-based process showed that it is a strategy to economically convert green gas emission into fuels and chemical feedstock and one tool for the long-term global management of carbon.