Ali Ahmadian
Ali Elkamel
Ali Almansoori *Editors*

Carbon Capture, Utilization, and Storage Technologies

Towards More Sustainable Cities

Springer

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Ali Ahmadian • Ali Elkamel • Ali Almansoori
Editors

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Editors
Ali Ahmadian 🆔
Department of Electrical Engineering
University of Bonab
Bonab, Iran

Department of Chemical Engineering
University of Waterloo
Waterloo, ON, Canada

Ali Almansoori 🆔
Department of Chemical Engineering
Khalifa University
Abu Dhabi, United Arab Emirates

Ali Elkamel 🆔
Department of Chemical Engineering
University of Waterloo
Waterloo, ON, Canada

Department of Chemical Engineering
Khalifa University
Abu Dhabi, United Arab Emirates

Preface

Despite the consideration of alternative energy resources and increasing the energy efficiency in the systems to decrease the amount of CO_2 emissions, the cumulative rate of CO_2 in the atmosphere needs to be decreased to limit the detrimental effects of climate change. Therefore, regardless of the extension of clean and more efficient energy systems, carbon-removing technologies need to be implemented. Carbon Capture, Utilization, and Storage (CCUS) is a novel technology that captures CO_2 from facilities including power plants, the transportation systems, and industrial sectors. The CCUS technologies can deliver 'negative emissions' by removing CO_2 directly from the atmosphere or from biomass-based energy and storing the CO_2. Therefore, CCUS technologies need to be implemented in the smart sustainable cities.

This book is an attempt to bring together the experts from the different disciplines related to carbon capture, utilization, and storage process and its impact on sustainable cities development. It contains eight chapters in which numerous researchers and experts from academia and industries are collaborated. The breakdown of the chapters is as follows:

- Chapter 1 describes the important fuels and chemicals and the synthesis methods of each. The use of carbon dioxide in the beverage and food industry is therefore considered. Moreover, the two types of carbon mineralization – in situ and ex situ, which are thought to be the most recent and efficient techniques for carbon utilization – are covered and the applications, products, challenges and risks of each of these techniques are clearly discussed.
- Chapter 2 evaluates the capabilities of CO_2 detection satellites as objective, independent, potential, low-cost and external data sources for monitoring CO_2 emissions from human activities.
- Chapter 3 discusses a much more general framework which allows different capacities for the booster stations. Furthermore, the boosters can be installed at any location, depending on pressure losses along the pipeline.

- Chapter 4 reviews the concept of Power-to-X technologies and the electrification of the chemical industry.
- Chapter 5 provides an overview of machine learning concepts and general model architectures in the context of post-combustion carbon capture. Also, this chapter presents and compares different machine learning models within the field of absorption-based carbon capture. The strengths and limitation of the strategies used in the creation of past models are discussed.
- Chapter 6 presents a design and optimization framework for a tidal power generation plant in the Bay of Fundy, Canada, in order to reduce the operation's cost and emission pollution.
- Chapter 7 presents a systematic framework to integrate renewable energy technologies for the oil and gas industry focusing on solar energy use to meet hydrogen requirements of the crude oil upgrading process for bitumen feedstock in tar sands processing.
- Chapter 8 represents a comprehensive review on CO_2 monitoring satellites.

The editors of the book warmly thank all the contributors for their valuable works. Also, we would like to thank the respected reviewers who improved the quality of the book by the valuable and important comments.

Waterloo, ON, Canada   Ali Ahmadian
Waterloo, ON, Canada   Ali Elkamel
Abu Dhabi, United Arab Emirates   Ali Almansoori

Contents

Chapter 1
Carbon Utilization Technologies & Methods

Reza Mahmoudi Kouhi, Mohammad Milad Jebrailvand Moghaddam, Faramarz Doulati Ardejani, Aida Mirheydari, Soroush Maghsoudy, Fereshte Gholizadeh, and Behrooz Ghobadipour

1.1 Introduction

Carbon utilization is the process of using captured CO_2 as a resource to make value-added products, and it is also an important aspect of climate mitigation. Generally, there are three categories carbon utilization technologies can be divided into: chemical technologies, biological technologies, and mineralization processes (Fig. 1.1).

CO_2 is utilized in chemical processes to produce polymers as well as organic compounds such as acyclic carbonates and cyclic carbonates. The production of energy carriers and transportation fuels such as methanol opens more opportunities for the capturing of CO_2. Liquid fuels are not considered long-term alternatives since they ultimately burn out. In biological technology, microorganisms like algae, cyanobacteria, and proteobacteria are utilized to convert CO_2 into a range of useful chemicals, such as ethylene and ethanol. High-value chemicals may also be produced in the pharmaceutical and food sectors. In the approach like chemical methods, CO_2 is not permanently stored, as it is released back into the atmosphere when the biofuel is burned. But the fuel is a carbon-free product since first it captures carbon from the atmosphere before entering it again by burning. The third group of

R. Mahmoudi Kouhi · M. M. Jebrailvand Moghaddam · F. Doulati Ardejani (✉) ·
A. Mirheydari · S. Maghsoudy · F. Gholizadeh
School of Mining, College of Engineering, University of Tehran, Tehran, Iran

Climate Change Group, Mine Environment & Hydrogeology Research Laboratory (MEHR Lab.), University of Tehran, Tehran, Iran
e-mail: reza_mahmoudi@ut.ac.ir; milad.jebrailvand@ut.ac.ir; fdoulati@ut.ac.ir; aida.mirheidari@ut.ac.ir; s.maghsoudy@ut.ac.ir; fereshtegholizade@ut.ac.ir

B. Ghobadipour
Climate Change Group, Mine Environment & Hydrogeology Research Laboratory (MEHR Lab.), University of Tehran, Tehran, Iran

School of Civil Engineering, Iran University of Science & Technology, Tehran, Iran
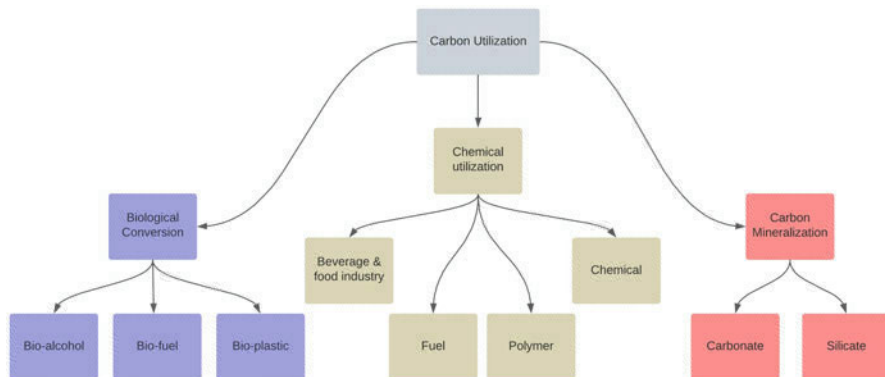
Fig. 1.1 Carbon utilization categories and products

carbon utilization technologies is the mineralization process which is classified into two types: in situ and ex situ mineralization. Mineral trapping or in situ mineralization is underground geological sequestration where a fraction of injected CO_2 reacts with alkaline rocks in the target formation and it forms solid carbonate species. In ex situ mineralization, CO_2 reaction takes place in an industrial process. The final product obtained by this technology can store CO_2 for a long time.

The most important challenges facing carbon utilization technologies are high energy consumption, long-term effects, and the cost of raw materials required. Economic issues regarding different methods, durability over time, and insufficient maturity of the technologies are the other issues that should be considered. One of the most important advantages of using carbon utilization is its ability to be used in sectors that are responsible for around 53% of carbon dioxide emitted into the air (Fig. 1.2). The usage of alternative fuels leads to a reduction in carbon emissions in the transport and electricity and heat sectors. In addition, the construction and industrial sectors reduce their carbon emissions through the manufacturing of carbonates from industrial wastes. Utilization approaches have the potential to reduce about one-fifth of the emissions necessary in the industrial sectors. It is the only option for significantly reducing direct emissions from other industrial point sources, and it will play a significant role in reducing CO_2 emissions from fossil fuel–based power plants. It is estimated that the use of carbon utilization will help cut CO_2 emissions by up to 32% by 2050. Up to 2060, industrial operations may accumulate more than 28 Gt of CO_2, with the chemical, steel, and cement subsectors accounting for the majority of this [2].
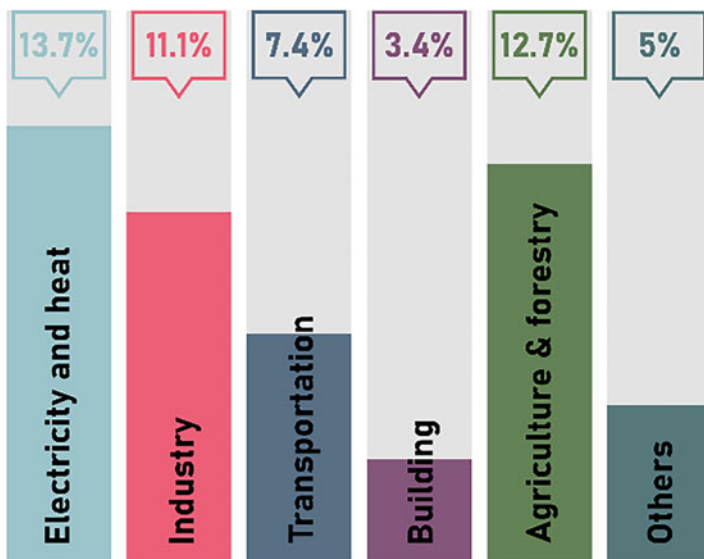
Fig. 1.2 Gross estimate of greenhouse gas emissions by various segments. (Modified after [1])

1.2 CCS Versus CCU

Carbon capture and storage (CCS) and carbon capture and utilization (CCU) refer to technologies that capture CO_2. In CCS methods, CO_2 is permanently stored while the major purpose of CCU is to convert it into valuable products such as fuels and chemicals. Both CCS and CCU are based on carbon capture, but the difference is what happens after the capture phase. Figure 1.3 shows the scope of each of these technologies' effects, as well as their similarities. As can be observed, the method of in situ mineralization is the borders between the usage of CCU and CCS technologies, implying that these two approaches can be classed in both.

1.3 Fuels and Chemicals

The main source of energy used in current energy systems is fossil fuels, which result in the generation of large amounts of carbon dioxide when used in transportation and industry. Therefore, it is necessary to find alternatives for them. Carbon dioxide conversion into fuels and chemicals reduces greenhouse gas emissions and dependence on petrochemicals. The utilization of CO_2 as a feedstock for fuel synthesis as well as chemicals has shown many potential environmental and economic benefits. Several industries, including fuel cells, power plants, and transportation, can utilize the produced fuel. CO_2 is a thermodynamically stable molecule; thus in order to utilize it and produce high fuel yields, a lot of heat and catalyst inventory must be
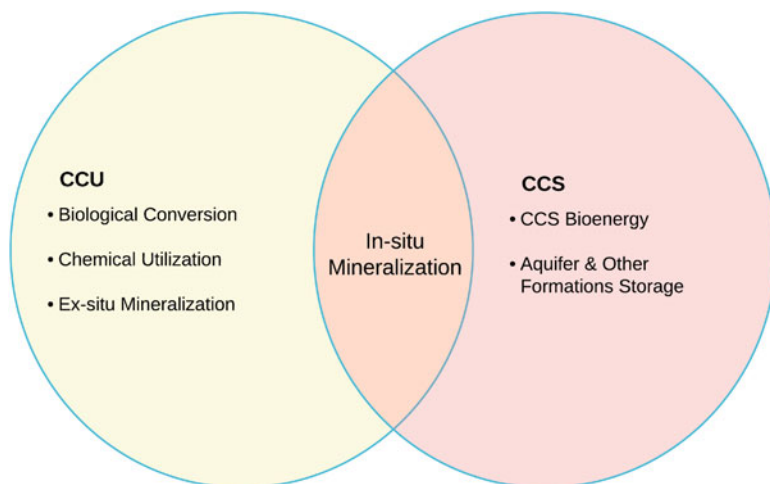
Fig. 1.3 The relations of CCU and CCS technologies

Table 1.1 Main chemicals and fuels that are now manufactured from CO_2 on a worldwide scale [3, 4]

Product		Production (Mt/year)	CO_2 utilization (tCO_2/t product)	Technology readiness level
Methane		1100–1500	2.750	CO_2 methanation: 7
Methanol		65.00	1.373	Hydrogenation of CO_2: 8–9
Formic acid		1.00	0.956	Electrochemical reduction of CO_2: 6
Dimethyl ether		11.40	1.911	1–3
Liquid fuels		–	2.6	5–9
Urea		180.00	0.735	9
Salicylic acid		0.17	0.319	9
Polycarbonate		5.00	0.173	9
Polyurethane		15.00	0.300	8–9
Cyclic carbonates	Ethylene carbonate	0.20	0.499	4–5
	Propylene carbonate	0.20	0.431	
Dimethyl carbonate		1.60	1.466	8–9

applied. Carbon dioxide can be utilized to produce energy carriers and transportation fuels such as methane, methanol, formic acid, dimethyl ether, carbon monoxide or synthesis gas (syngas), and Fischer-Tropsch fuels. In addition to synthetic fuels, it is also possible to produce various chemicals such as urea, polymers, formic acid, salicylic acid, acyclic carbonates, cyclic carbonates, and fine chemicals such as biotin using carbon dioxide. Table 1.1 summarizes some chemicals and fuels that are currently being manufactured industrially from CO_2.

1.3.1 Methane Production

One of the most significant energy sources is methane (CH_4), which is mostly obtained from natural gas, a fossil fuel source with relatively low costs, and is used to generate heat, power, and value-added chemicals [5]. CO_2 methanation has recently attracted considerable interest, due to its use in Power-to-Gas (PtG) technology and the upgrading of biogas [6]. In order to effectively incorporate renewable energy sources, such as wind and solar energy, into the current energy mix, PtG processes are viewed as a potential and intriguing solution [7]. In this technology, hydrogen generated from surplus renewable energy is chemically changed into methane, which can be stor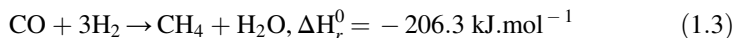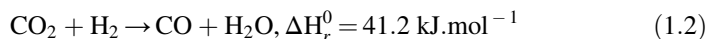ed and transported using the already-existing, highly developed natural gas infrastructure, by reacting with CO_2 [6].

Among the several PtM techniques already in use, catalytic CO_2 hydrogenation (methanation) has received the most attention, and demonstration units are already in operation in a number of nations [5]. At the beginning of the twentieth century, Sabatier and Senderens conducted the first studies of the methanation reaction, also known as the Sabatier reaction. Through this reaction, CO_2 and H_2 are converted into CH_4 and H_2O (Eq. 1.1) [8].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H = -165 \text{ kJ.mol}^{-1} \tag{1.1}$$
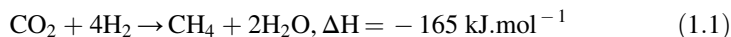
Due to the exothermic nature of this reaction, products with low temperature and high pressure are preferred in terms of thermodynamics [8]. CO_2 hydrogenation can be thought of as a result of combining reverse water gas shift (RWGS) reaction and CO hydrogenation (Eqs. 1.2 and 1.3) [9].

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_r^0 = 41.2 \text{ kJ.mol}^{-1} \tag{1.2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O, \Delta H_r^0 = -206.3 \text{ kJ.mol}^{-1} \tag{1.3}$$

Reactors for methanation might be either biological or catalytic (Fig. 1.4). Methanogenic microorganisms function as biocatalysts in biological methanation [9]. A biogas plant's fermenter or a separate bioreactor can be used to conduct this process [10].

Metals from group VIII of the periodic table catalyze the methanation reaction. Ru was shown to be the most active metal catalyst, followed by Fe, Ni, and Co. Ni is typically chosen as the active component because of its high selectivity and reactivity, and because it is reasonably priced [11]. Despite having advantages over Ni systems, Ru catalysts are more expensive. Given the low cost and wide availability of methane from natural gas, hydrogenation of CO_2 to methane is not now feasible on a big scale and is not anticipated to be in the near future. Furthermore, methane has a significantly lower economic value than the conversion of CO_2 into a variety of other compounds [12].
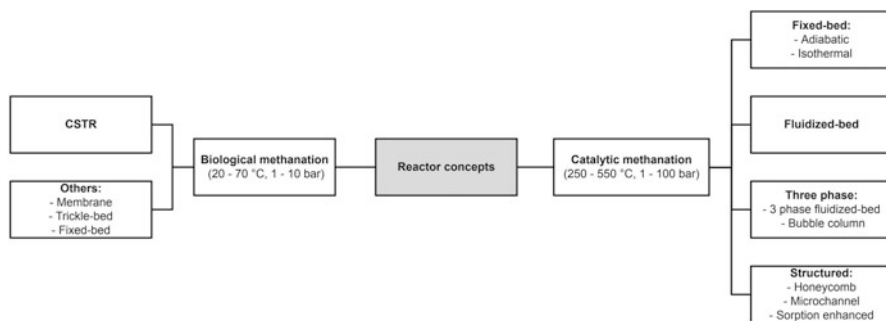
Fig. 1.4 Concepts for reactors that produce substitute natural gas [9]

The electrochemical reduction of CO_2 is another potential method for producing methane from CO_2. This technique is still being validated in the lab. However, recent results have emphasized the attractive characteristics of this path [5]. Currently, only copper is capable of catalyzing the conversion of CO_2 into hydrocarbons, particularly methane, in an aqueous solution. Higher overpotentials, low activity, and poor product selectivity are problems with conventional Cu electrodes [13]. To create catalysts with improved methane selectivity, more research is still required.

1.3.2 Methanol Production

The most basic liquid hydrocarbon that can be used as a fuel, a hydrogen carrier, or a feedstock for creating more intricate chemical compounds is methanol (CH_3OH) [14]. Formaldehyde, acetic acid, dimethyl ether (DME), and methyl tertiary-butyl ether (MTBE) are the primary chemical derivatives of methanol [15]. The methanol-to-olefins process creates light olefins like ethylene and propylene, which can be utilized to make polymers and hydrocarbon fuels. Additionally, methanol is converted into dimethyl carbonate in supercritical CO_2, which is a helpful intermediary for derivatives utilized in polycarbonates and polyurethanes [16].

According to Eq. (1.4), syngas, which has a CO/H_2 mixture, is being used to create methanol on an industrial scale. Currently, syngas (mixture of CO and H_2) produced mostly from natural gas reforming is transformed into methanol at temperatures between 250 and 300 °C and pressures between 5 and 10 MPa, using a $CuO/ZnO/Al_2O_3$ catalyst [15, 17].

$$CO + 2H_2 \rightarrow CH_3OH, \Delta H = -90.6 \text{ kJ.mol}^{-1} \qquad (1.4)$$
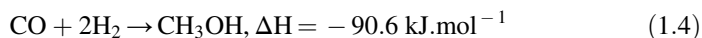
Currently, a little amount of CO_2 (up to 30%) is typically added to the syngas. The energy balance and methanol yield both considerably increase with the addition of CO_2 to the CO/H_2 feed. Syngas is low in hydrogen and high in carbon oxides (CO and CO_2). The CO in syngas is transformed to CO_2 via the water-gas shift

(WGS) reaction to increase its H_2 content and promote methanol synthesis (Eq. 1.5) [16].

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298}^0 = -41.2 \text{ kJ mol}^{-1} \tag{1.5}$$
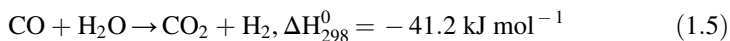
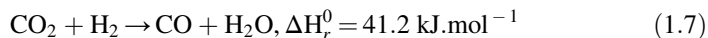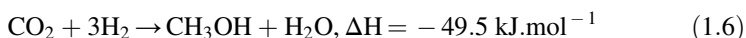The catalytic hydrogenation process shown in Eq. (1.6) is the most direct method for producing methanol from CO_2 and involves the production of H_2 using water electrolysis, ideally with the use of renewable energy, and the subsequent combination with CO_2 waste streams to create methanol, which is known as the Power-to-Methanol process. This process involves the RWGS (Eq. 1.7) as a secondary reaction and is less exothermic than the syngas-based approach. RWGS reaction is regarded unfavorable since it consumes H_2 and reduces the yield of methanol synthesis. It was discovered that the rate of the direct methanol synthesis from CO_2 was inhibited by the water produced as a byproduct. [5, 15, 16].

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H = -49.5 \text{ kJ.mol}^{-1} \tag{1.6}$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_r^0 = 41.2 \text{ kJ.mol}^{-1} \tag{1.7}$$

Hydrogenation of carbon dioxide to methanol is an efficient CO_2 utilization technique and is considered an effective sustainable development strategy. This method is technically comparable to the production of methanol from syngas for industrial use [16]. If direct hydrogenation of CO_2 to methanol is replaced with methanol production from syngas, improved catalysts are greatly needed [12]. In comparison to conventional synthesis, this method has a better water footprint, but still lacks competitive economic viability [4].

The electrochemical reduction of CO_2 using protons and electrons as a source of H_2 is another method for producing methanol. Due to its complicated kinetics, this reaction requires efficient electrocatalysts. One of the most effective materials for the electrochemical conversion of CO_2 into alcohols, including methanol, has been recognized to be copper or copper-based electrodes. In order to improve the electrochemical CO_2 reduction to CH_3OH, the usage of copper alloys has also been studied. Cu-Zn mixed oxides make up the majority of commercial catalysts used today to produce methanol, demonstrating the metals' synergistic influence on methanol synthesis [5, 12].

1.3.3 Dimethyl Ether (DME) Production

The simplest ether is dimethyl ether (DME), which has the chemical formula CH_3OCH_3. DME has physical properties similar to liquefied petroleum gases (LPG) such as propane and butane. DME has been marketed as a diesel substitute since the mid-1990s. With a high cetane number (55-60), DME has several desirable

characteristics over conventional fuels, including very low emissions of pollutants (SO_x, NO_x, CO, and particulate matter) [18, 19].

Indirect synthesis (two-stage) and direct synthesis from syngas (single-stage) are typically the two methods used to produce DME. In the single-stage method, DME is prepared directly from syngas in a single reactor [20]. Fixed-bed reactors have been used for the majority of theoretical studies on single-step DME production [21]. In the two-step process, syngas is first transformed into methanol (Eq. 1.8), which is then dehydrated to produce dimethyl ether (Eq. 1.9). Zeolites and Al_2O_3, in particular, have been suggested as acid catalysts for the dehydration of methanol to DME [22]. In a reactor, WGS reaction can occur concurrently (Eq. 1.10) [19].
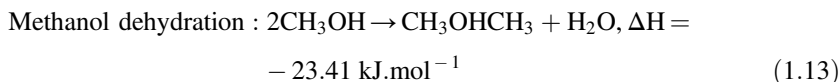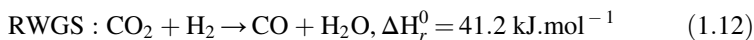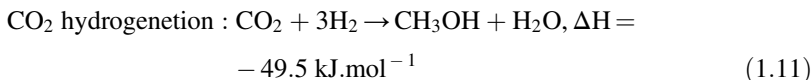
$$\text{Methanol synthesis}: CO + 2H_2 \rightarrow CH_3OH, \Delta H = -90.6 \text{ kJ.mol}^{-1} \quad (1.8)$$

$$\text{Methanol dehydration}: 2CH_3OH \rightarrow CH_3OHCH_3 + H_2O, \Delta H =$$
$$-23.41 \text{ kJ.mol}^{-1} \quad (1.9)$$

$$\text{WGS}: CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{298}^0 = -41.2 \text{ kJ mol}^{-1} \quad (1.10)$$
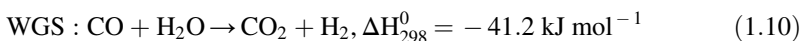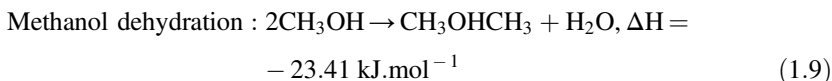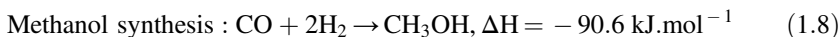
While the current technologies for both methods rely on fossil-based syngas, which again causes environmental issues, recent studies examine the possibility of replacing syngas with CO_2/H_2 feed (Eqs. 1.11 to 1.13) [22].

$$CO_2 \text{ hydrogenetion}: CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H =$$
$$-49.5 \text{ kJ.mol}^{-1} \quad (1.11)$$

$$\text{RWGS}: CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_r^0 = 41.2 \text{ kJ.mol}^{-1} \quad (1.12)$$

$$\text{Methanol dehydration}: 2CH_3OH \rightarrow CH_3OHCH_3 + H_2O, \Delta H =$$
$$-23.41 \text{ kJ.mol}^{-1} \quad (1.13)$$

The direct synthesis of DME from concentrated CO_2 and H_2 has lately gained attention due to the growing interest in CO_2 capture and valorization. The synthesis of methanol is a recognized thermodynamically limited process. As a result, using methanol immediately to create DME via a direct method has the advantageous effect of pushing the equilibrium toward higher conversions. Because of the water forming in greater quantities and the consequently more stringent thermodynamic constraints, the CO_2 to DME process is more difficult than the syngas method and hence necessitates focused attention. A strategy that has been introduced to solve this problem is the in situ removal of water produced in all individual reactions using a membrane reactor [22].

1.3.4 Formic Acid Production

Formic acid (HCOOH) serves as a platform for chemical energy storage in addition to being a valuable chemical that is frequently used as a preservative and antibacterial agent. Through its decomposition to CO_2 and H_2 and potential for reversible transition back to formic acid, this acid is a known hydrogen storage component [18]. Formic acid and its salts have a wide range of uses, including as a starting chemical for esters, alcohols, or medicinal products, as well as in the production of textiles, leather, and dyes and as a cleaning or disinfection solution [23].

Formic acid is produced industrially most frequently via a two-step process: In the first step, methyl formate is generated from methanol and CO (Eq. 1.14), and in the second step, methyl formate is hydrolyzed into formic acid (Eq. 1.15). The second step is thermodynamically unfavorable [5].
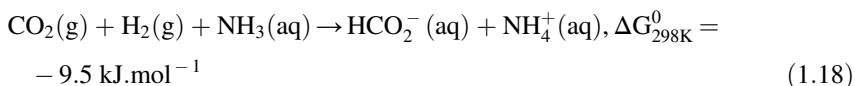
$$CH_3OH + CO \rightarrow CH_3COOH, \Delta H_r = -29 \text{ kJ.mol}^{-1} \tag{1.14}$$

$$CH_3COOH + H_2O \rightarrow HCO_2H + CH_3OH, \Delta H_r = 16.3 \text{ kJ.mol}^{-1} \tag{1.15}$$
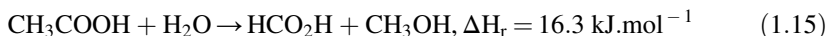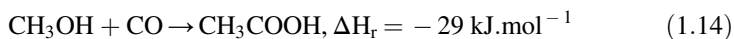
Also, formic acid can be produced through the hydrogenation of carbon dioxide (Eq. 1.16). As a result of the conversion of gases into liquids during this process, the reaction is entropically unfavorable. The reaction is therefore exergonic in the aqueous phase and endergonic in the gas phase. However, when the reaction is carried out in the aqueous phase, the presence of the solvent can change the reaction thermodynamics and makes it slightly exergonic (Eq. 1.17). By employing additives, such as specific bases like ammonia (Eq. 1.18) and triethylamine, the equilibrium can be changed in favor of the product. Carbonates, bicarbonates, and hydroxides are frequently used for the reaction in water [24, 25].

$$CO_2(g) + H_2(g) \rightarrow HCO_2H(l), \Delta G^0_{298K} = 32.9 \text{ kJ.mol}^{-1} \tag{1.16}$$

$$CO_2(aq) + H_2(aq) \rightarrow HCO_2H(aq), \Delta G^0_{298K} = -4 \text{ kJ.mol}^{-1} \tag{1.17}$$

$$CO_2(g) + H_2(g) + NH_3(aq) \rightarrow HCO_2^-(aq) + NH_4^+(aq), \Delta G^0_{298K} =$$
$$-9.5 \text{ kJ.mol}^{-1} \tag{1.18}$$

Numerous homogeneous and heterogeneous catalysts have been developed for CO_2 hydrogenation to formic acid on a lab scale. Transition metal complexes, especially those based on Ir and Ru, have been used in a tremendous amount of attempts, and the results are very remarkable. To become potentially practical, these catalysts require further improvements in selectivity to formic acid and stability. Heterogeneous catalysts, on the other hand, are less studied for this reaction; however, recently the number of examples has notably increased. The heterogeneous catalysts are characterized as follows, with clear practical advantages for continuous

operation and product separation: heterogenized molecular catalysts and unsupported and supported bulk/nanometal catalysts [18].

Because of the high market value and widespread use of formic acid, direct electrochemical reduction of carbon dioxide to this substance has emerged as a viable option. This procedure involves supplying electricity to an electrolytic cell. An electrolyte cell is made up of an anode and a cathode with catalyst-coated surfaces, as well as an electrolyte(s) that allows ions to be transferred between the electrodes. Eqs. (1.19) and (1.20) show half-reactions that take place at the anode and cathode of an electrolytic cell set up to make formic acid from CO_2.

$$\text{Cathode}: CO + 4H^+ + 4e^- \rightarrow 2HCOOH \tag{1.19}$$

$$\text{Anode}: 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1.20}$$
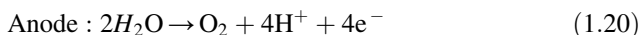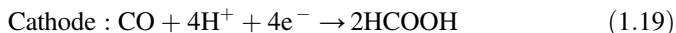
The typical operating conditions of this process are ambient temperature and pressure, which is one of its main advantages. However, the primary hurdles for the development of this method are significant overpotentials and limited product selectivity. Various catalysts based on Co, Pb, Pd, Sn, and In metal-free nitrogen-doped carbon materials have been reported for this process over the last few decades [4, 5, 26].

1.3.5   Carbon Monoxide – Syngas Production

Carbon monoxide (CO) is an important chemical product precursor (Fig. 1.5) [27]. Synthesis gas, also known as syngas, is a gaseous fuel mixture of carbon monoxide and hydrogen that is fed to a number of industrial processes, including the direct DME (dimethyl ether) synthesis, the Fischer-Tropsch (F-T) synthesis, the ammonia synthesis, the methanol synthesis, the power and heat generation
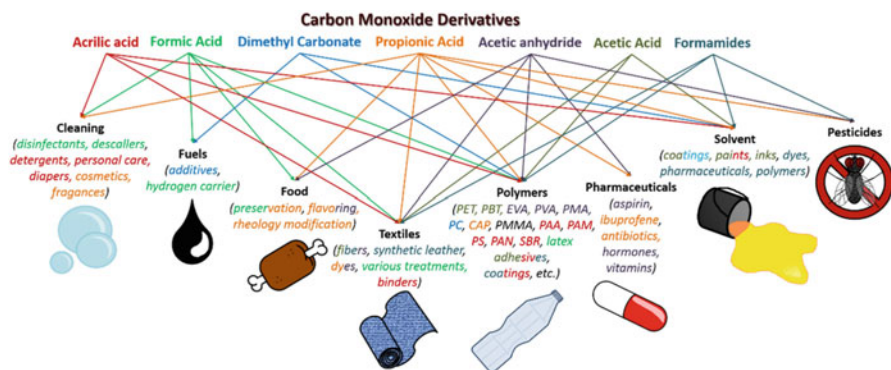

Fig. 1.5 Applications and principal derivatives of carbon monoxide [27]

processes, and the SNG (substitute natural gas) synthesis [28]. Due to its superior efficiency than the direct conversion technologies now in use, syngas remains the industrially favored technology for the indirect conversion of natural gas into higher-value chemicals and fuels for the time being. Although almost any raw material containing carbon can be utilized to produce H_2/CO mixtures, natural gas, liquid hydrocarbon sources, solid fossil carbon sources like coal or lignite, or raw materials obtained from renewable sources are now the most preferred sources [29]. Methane/natural gas is the most extensively utilized raw material for synthesis gas due to its availability, gas composition, and inexpensive cost [30].

Steam methane reforming (SMR), dry methane reforming (DRM), autothermal reforming (ATR), partial oxidation (POX), bireforming (BR), tri-reforming (TR), and combined reforming (CR) have traditionally been used to produce syngas from fossil-based natural gas and coal [28]. When methane is used to create syngas, the process involves the employment of an oxidizing agent that oxidizes methane to carbon monoxide while also creating hydrogen in a ratio that varies depending on the oxidant type. Carbon dioxide is able to function as an oxidizing agent through a procedure called dry reforming [31]. Because DRM is a highly endothermic reaction (Eq. 1.21), equilibrium conversion to syngas must occur at extremely high temperatures [32].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \Delta H_{298}^0 = 248 \text{ kJ mol}^{-1} \quad (1.21)$$
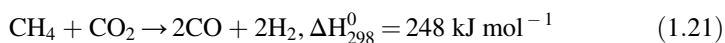
The methane dry reforming process is the most endothermic reaction when compared to SMR and ATR [33]. DRM yields syngas with a H_2 to CO ratio that is more compatible with some downstream synthesis processes, such as Fischer-Tropsch synthesis [17].

Due to the difficulty in developing catalysts with a long life-span on stream at a low price acceptable for profit-oriented commercialization, despite its economic and environmental potential, DRM is still in its infancy [34]. The formation of coke and sintering, which quickly deactivate the catalysts, is the main obstacle inhibiting the widespread use of DRM in the industry [32]. It is expected that coke will deposit on the reforming catalyst due to high working temperatures, which increase the molecular energy enough to split the C-H bonds in methane [33]. In order to be used on a large scale in industrial applications, the ideal DRM catalyst must be extremely stable and have better resistance to coke formation. Numerous experiments using supported metal catalysts and noble (ruthenium, rhodium, platinum, palladium, and iridium) and non-noble metals (nickel and cobalt) have been conducted [32].

The dry reforming reaction equilibrium is usually influenced by the co-occurrence of the RWGS reaction (Eq. 1.22) [30].

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H_{298}^0 = 41.2 \text{ kJ mol}^{-1} \quad (1.22)$$
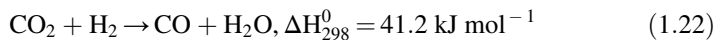
The H_2/CO molar ratio is decreased as a result of the RWGS reaction by consuming H_2 [35]. It is an endothermic reaction, so formation of CO is favored at

high temperatures [36]. Only in the presence of a suitable and sustainable source of hydrogen and thermal energy at the proper temperature level the RWGS reaction will be commercially attractive as a source for syngas [29]. For this reaction, a variety of heterogeneous catalysts have been utilized, including systems based on copper, iron, or ceria (Cerium (IV) oxide). However, in general, they have low thermal stability, and methane commonly forms as an unfavorable byproduct [12]. In designing a suitable catalyst for the RWGS reaction, criteria of high activity and high CO selectivity should be considered [36].
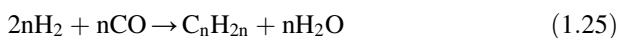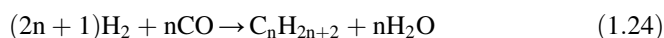
The direct electrolysis of carbon dioxide to carbon monoxide and oxygen is another method for producing CO from carbon dioxide [37]. Three electrolysis techniques are used in this procedure: solid oxide electrolysis at high temperature, molten carbonate electrolysis, and low temperature electrolysis using a solution-phase or gas diffusion electrolysis cell. The only CO_2 electrolysis method that is nearing commercialization is high-temperature electrolysis in solid oxide cells [38].
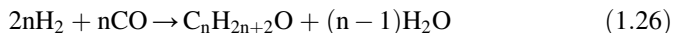
1.3.6   *Liquid Hydrocarbons Production (Fischer-Tropsch)*

A good substitute for storing renewable energy is liquid hydrocarbons. They are the main source of energy for use in aviation and transportation [20]. Carbon dioxide can also be converted to hydrocarbons through Fischer-Tropsch (FT) and methanol pathways. For the FT pathway, the intermediate product is CO (or a synthesis gas), while for the methanol pathway, it is methanol [39]. There are three steps in both pathways [17]:

- Using renewable electricity to electrolyze water to produce hydrogen.
- Conversion of CO_2 to an intermediate product, methanol or CO.
- Liquid hydrocarbon synthesis, followed by improvement or conversion to the desired fuel.

Synthesis gas can be converted into a variety of products, including synthetic fuels, lubricants, and petrochemicals, using the FT process [40]. In the Fischer-Tropsch pathway, RWGS reaction (Eq. 1.23) is used to produce syngas, which is then converted to liquid hydrocarbons via the Fischer-Tropsch reaction [39]. Synthesis of alkanes, as the main products of FT processes, alkenes, and alcohols are given in Eqs. (1.24) through (1.26) [4]. Ni, Fe, and Cu catalysts can be used in the RWGS reaction; also, Co, Fe, and Ru catalysts can be used in the Fischer-Tropsch synthesis, respectively [39].

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{1.23}$$

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{1.24}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \tag{1.25}$$

$$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O \tag{1.26}$$

In the methanol pathway, CO_2 and H_2 react over a metallic catalyst to produce methanol, which is then converted into other hydrocarbons over acidic catalysts [39]. Through a series of reactions, including DME synthesis, olefin synthesis, oligomerization, and hydrotreating, methanol is transformed into gasoline, diesel, and kerosene [17].

Currently, methanol is generated from synthesis gas using a $Cu-ZnO-Al_2O_3$ catalyst (Eq. 1.27). Recent research efforts have concentrated on the development of catalysts that support the direct conversion of CO_2 to methanol (Eq. 1.28). It is vital to utilize a very selective catalyst for this reaction because it is favored at low temperatures and high pressure and can yield a variety of byproducts [39].

$$CO + 2H_2 \rightarrow CH_3OH, \Delta H_r^{298k} = -90.6 \text{ kJ.mol}^{-1} \tag{1.27}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \Delta H_r^{298k} = -49.5 \text{ kJ.mol}^{-1} \tag{1.28}$$
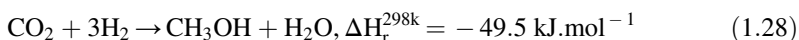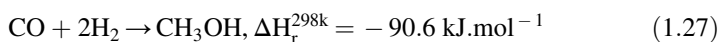
Another way to create fuel-like hydrocarbons that can be used in the current infrastructure is through electroreduction of CO_2 [41]. There are a number of systems that can produce products with new carbon-carbon bonds, even though the reduction of CO_2 to C1 feedstocks such CO, methane, formic acid, or methanol is the process that occurs most frequently [12]. Although the Faradaic efficiency is still low due to H_2O dissociation to H_2, Cu-based electrodes are perfectly suitable in activating CO_2 [41]. As mentioned above, the electroreduction of CO_2 to value-added compounds shows promise, but is still far from commercialization due to the high overpotential of this reaction and the low activity of the currently available catalysts [42].
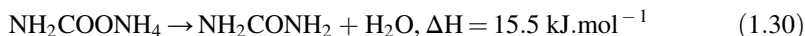
1.3.7 Urea Production

Another non-toxic product made from carbon dioxide is urea (CH_4N_2O). Liquid and solid fertilizers, urea-formaldehyde resins used to manufacture adhesives and binders, melamine for resins, livestock feeds, NO_x control from boilers and furnaces, and a variety of chemical applications are all the uses of urea [43].

Reforming natural gas to produce ammonia and carbon dioxide is the most widely used process for producing urea [44]. The production of urea results from the reaction of carbon dioxide and ammonia at a temperature between 185 and 190 °C and a pressure between 180 and 200 atm. Two equilibrium reactions known as Basaroff reactions with incomplete reactants conversion are involved in this process: Ammonium carbamate ($H_2N-COONH_4$) is generated in the first stage by the fast and exothermic reaction of liquid ammonia with gaseous CO_2 at high temperature and pressure (Eq. 1.29). In the next step, ammonium carbamate decomposes slowly

Fig. 1.6 Urea derivatives synthesis from amine and CO_2 [47]
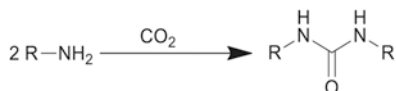
and endothermically into urea and water using the heat produced by previous reaction (Eq. 1.30) [45, 46].

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4, \Delta H = -117 \ kJ.mol^{-1} \qquad (1.29)$$

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O, \Delta H = 15.5 \ kJ.mol^{-1} \qquad (1.30)$$

The use of CO_2 in the synthesis of urea derivatives has received a lot of interest. Anti-cancer agents, plastic additives, gasoline antioxidants, agricultural pesticides, dyes, medicines, gasoline antioxidants, and corrosion inhibitors are just a few uses for urea derivatives. The traditional process for producing urea derivatives includes the reaction of amines with phosgene, carbon monoxide, or isocyanate, which has serious toxicological and environmental issues. One of the main aims of Green Chemistry nowadays is to replace these dangerous reagents in chemical processes. As a result, there has been a significant advancement in the production of urea derivatives through the reaction of amines with CO_2 either with or without the use of a dehydrating agent, using basic ionic liquids or base catalysts [47–49] (Fig. 1.6).

1.3.8 Polymers

A unique class of chemicals known as polymers is employed in the manufacturing process for plastics and resins. Polymers, such as polyurethanes and polycarbonates, are adaptable materials with several practical uses, including those in the electrical and electronic industries, the automobile sector, packaging, the medical industry, personal care goods, and the construction [50]. Up until this point, the primary raw materials used in the manufacturing of polymers were petrochemicals[51]. However, the chemical industry is under pressure to discover practical substitutes for the manufacture of renewable chemicals and polymers due to the depletion of fossil fuels and the legal demand for sustainable and renewable plastics under the circular economy [50]. As a raw material for the synthesis of polymers, CO_2 can partially replace petrochemicals. One example is the copolymerization of epoxides with CO_2 to create polycarbonates [17]. As potential, more environmentally acceptable raw materials for plastics, CO_2-based polymers have received a lot of industrial interest [52]. Additionally, using CO_2 to produce different biodegradable polymers is seen to be a cost-effective strategy from an economic perspective [20]. There are two chemical methods for including CO_2 in the production of polymers: direct and indirect methods. Both strategies have been shown to be feasible and possible [48, 49].

1.3.8.1 The Direct Method

The direct method produces high CO_2 content polymers such as polycarbonates, polyols, polyurethanes, polyureas, and polyesters by using CO_2 as a monomer in combination with proper reagents and catalysts [12].

1.3.8.1.1 Polycarbonates (PCs) from CO_2

Aromatic PCs are utilized as engineering plastics in automobiles, electrical and electronic equipment, and construction because of their great impact resistance, stiffness, toughness, superior thermal stability, transparency, and flame retardancy. The toxic and destructive phosgene reaction with 1,2-diol is the traditional method for producing polycarbonates. The copolymerization of epoxides, such as propylene oxide, cyclohexene oxide, vinyl oxide, ethylene oxide, and styrene oxide and CO_2, is an alternate method for the selective production of PCs. This process is the most promising application of CO_2. In general, transition metals or metals from the main group of elements, such as cobalt, zinc, chromium, magnesium, and aluminum, are used as homogeneous or heterogeneous catalysts for the copolymerization of CO_2 and epoxides. Compared to heterogeneous catalysts, homogeneous catalysts are more active and selective. Current CO_2 copolymerization research focuses on the development of catalysts for the production of polymers with tailored properties and derived from renewable epoxides such as limonene oxide, cyclohexadiene oxide, and α-pinene oxide [17, 51].

1.3.8.1.2 Polyurethanes (PUs) from CO_2

Polyurethanes (PUs), one of the most significant polymers, are used in a variety of products in daily life, including adhesives, sealants, coatings, elastomers and foams, heart valves, and cardiovascular catheters. They are manufactured commercially using polyaddition of diisocyanates with di- or polyols. Establishing isocyanate-free production methods has received recent attention in the field of PUs; CO_2 can play a significant role in this vital transition. When CO_2 reacts with cyclic amines like aziridines and azetidines or the N-analogs of epoxides, PUs can be produced [50].

1.3.8.1.3 Polyureas (PUA) from CO_2

Polyureas (PUAs) are polymers with urea linkages built into their backbone. They are used as linings, joint sealants, and microcapsules among other things in a variety of industries, including the building industry, the automobile industry, household products, and marine-related technology. PUAs are created commercially by the polyaddition process utilizing the reagents diisocyanate and diamine. These