CAPTURING AND CONVERSION OF CO_2 TO METHANOL IN A CHEMICAL LOOPING PACKED BED SYSTEM

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ABSTRACT

Some new efforts based on chemical-looping system for capturing and converting CO_2 into methanol are discussed in this study. In chemical-looping technology, an oxygen carrier has to be transported between circulating fluidized beds, which require additional energy and processes, like cyclone and seals. This may be one of the main drawbacks at high operating temperatures. In a new reactor concept, the oxygen carrier is not transported but kept inside a packed bed reactor and is alternately exposed to oxidizing and reducing conditions by periodic switching of the feed streams of fuel and air. In a similar operation, it is possible to convert the CO_2 to formic acid and hydrogen by using a zero-valent metal (Zn, Al, Fe, Mn)/metal oxide redox cycles under hydrothermal conditions. The oxidized metal can be regenerated by switching the feed stream to a chemical such as glycerin, which is converted to lactic acid: The overall reaction with glycerin is exothermic: Many metals (Cu, Al, Cu+Al, etc.) can react with water to produce H_2 efficiently under hydrothermal conditions. The H_2 produced by the oxidation of metals could be active to reduce the formic acid into methanol.

INTRODUCTION

Advanced, efficient, and low-emission energy technologies utilizing renewable and nonrenewable resources are vital for a sustainable energy technology which will play a major role in global climate change as well as in international politics and trade[1-4]. Sustainability has environmental, economic, and social dimensions, all of which are affected by global changes in energy use and limitations in our energy choices. Well-designed and operated systems of chemical-looping combustion/gasification of fuel/biomass offer scalable, diverse, economical, and environmentally sustainable energy pathways with inherited carbon capture[3-9]. Chemical-looping combustion (CLC) is a novel technology in which power production and CO_2 capture are intrinsically combined by the use of an oxygen carrier (OC) that transfers oxygen from the air to the fuel preventing direct contact between them. The oxygen carrier is composed of a metal oxide as an oxygen source. The fuel may be coal, natural gas, and biomass. The OC can be alternately oxidized and reduced. The product gas contains mainly CO_2 and water undiluted with nitrogen, and without the production of nitrogen oxides (NO_x) as the high temperatures associated with the use of flame is avoided. The oxidation of the OC carrier is strongly exothermic and hence can be used to heat air flow to high temperatures (1000-1200 $^{\circ}$C) and can drive a gas turbine.

Thermochemical conversions of fuel/biomass can be analyzed by using the following systems[4,7,15-17]: 1) chemical-looping combustion, 2) chemical-looping steam gasification (CLSG) for producing hydrogen (H_2), and 3) chemical-looping steam gasification for producing liquid transportation fuels of gasoline and diesel by the Fischer-Tropsch (FT) synthesis. The outcomes of such analyses would be: 1) the lowest possible energy and economic costs for the fuel/biomass conversion systems without adverse environmental/societal consequences, 2) a reduction of carbon intensity from energy conversion and use, and 3) interactions of systems and patterns at the local/regional scale with systems/patterns at the global scale. These systems combine the inherent CO_2 capture of chemical looping with the production of product gas, which can be used to capture CO_2, in fuel cells to produce electricity, and/or in transportation to replace oil. Liquid transportation fuels are catalytically synthesized from the syngas (carbon monoxide (CO) and H_2) produced from the gasification of fuels. A sensitivity analysis for system efficiency can be performed by varying fuel conversion, carbon capture, and regeneration efficiencies. This study presents a critical review of the use of chemical-looping technology in capturing and converting CO_2 into high value added chemicals and fuel such as methanol.

CAPTURING CARBON DIOXIDE

Well-designed and operated systems of chemical-looping steam combustion/gasification of fuel/biomass offer scalable, diverse, economical, and environmentally sustainable energy pathways with inherited carbon capture. Nitrogen is a major issue in restricting CO_2 capture from diluted effluent streams by solvents, such as amines, which require a substantial amount of energy for recovery and reuse. The cost of CO_2 sequestration with the chemical-looping is small (around \$4-8/tonne C) compared to the cost of separating CO_2 from typical flue gases (around \$100-200/tonne C)[3-7].

Chemical-looping Technology

Chemical-looping technology (CLT) is a novel technology in which power production and CO_2 capture are intrinsically combined by the use of an oxygen carrier (OC) that transfers oxygen from the air to the fuel preventing direct contact between them[4,7]. Interconnected fluidized bed systems are used for chemical-looping technology (Fig. 1a). The OC particles are transported between an air reactor where the oxidation of OC takes place and a fuel reactor where the OC particles are reduced with fuel. The OC can be alternately oxidized and reduced to facilitate the product gas containing mainly CO_2 and water undiluted with nitrogen. The oxidation of the OC carrier is strongly exothermic and hence can be used to heat air flow to high temperatures (1000-1200 ^{o}C) and can drive a gas turbine. During the regeneration of the OC with fuel (often natural gas) CO_2 and water are produced without nitrogen oxides (NO_x) production as the high temperatures associated with the use of flame is avoided. Oxygen carrier is composed of a metal oxide as an oxygen source and should have high reactivity in the oxidation/reduction cycles. It is this inherent ability for the separation of CO_2, which makes the CLT an invaluable tool in low-emission energy technology. The main advantages of CLT are:
- Over 90% CO_2 captures at lowest cost
- Separation of water is based on cooling/ compression of the product gas containing mainly CO_2 and water at process pressure
- No or very little thermal NO_x production because of low temperature
- Compatible with sulfur and mercury capture technologies
- Heavy metals may stay with the ash
- Higher thermodynamic efficiency
- No hot spots under fluidized bed technology

Some disadvantages are
- Dual reactors operation
- Oxygen carrier circulation between the reactors
- Solids handling
- Lower exhaust gas temperature/pressure for a direct coupling with a gas turbine

In the circulating fluidized bed systems, the oxygen carrier circulates between the fuel reactor and the air reactor. (Fig. 1a). This requires additional energy input and a cyclone to separate the particles from the hot air stream (Fig. 2a). Also the particle separation at high pressure and temperature may be difficult. Fluidized bed reactors provide excellent gas/solid mixing and operate at lower temperatures (around 800-900 ^{o}C), reducing nitrogen oxide (NO_x) emission. Fluidized bed (circulating or bubbling) reactors offer short residence time, low char/tar content, and reduced ash-related problems. The circulating fluidized bed gasifier generally operates at a higher velocity (3-5 m/s)[13-15].

An alternative to fluidized bed systems is based on packed bed chemical-looping reactor systems that contain the stationary OC particles alternately exposed to reducing and oxidizing conditions by periodic switching of the fuel feed (generally natural gas) and air streams (Fig. 1b). In this packed bed reactor technology, the circulation and separation of gas and the OC particles are avoided. This may lead to better utilization of OC with more efficient oxidation/reduction cycles[10]. For solid fuel like coal and biomass, *in situ* or separate gasification will be required. The main advantages of this reactor concept are[10-15]:
- Avoiding cyclone operation and better utilization of the oxygen carrier
- Controlling the air temperature with the amount of active material in the bed

- High thermal energy efficiencies can be realized
- The oxidation may be modeled similarly to an adsorption problem

Fixed bed reactors may produce large amounts of either tar and/or char due to the low, nonuniform heat and mass transfer between the gas and solid. The temperature of the reactor is most influential on the product gas composition[10-13]. Product gas may need extensive cleaning. However, the packed bed systems use high temperature and high flow rate of streams with switching system and require the use of large size of OC particles to avoid excessive pressure drop which may lead to slower reduction of the OC particles[10].
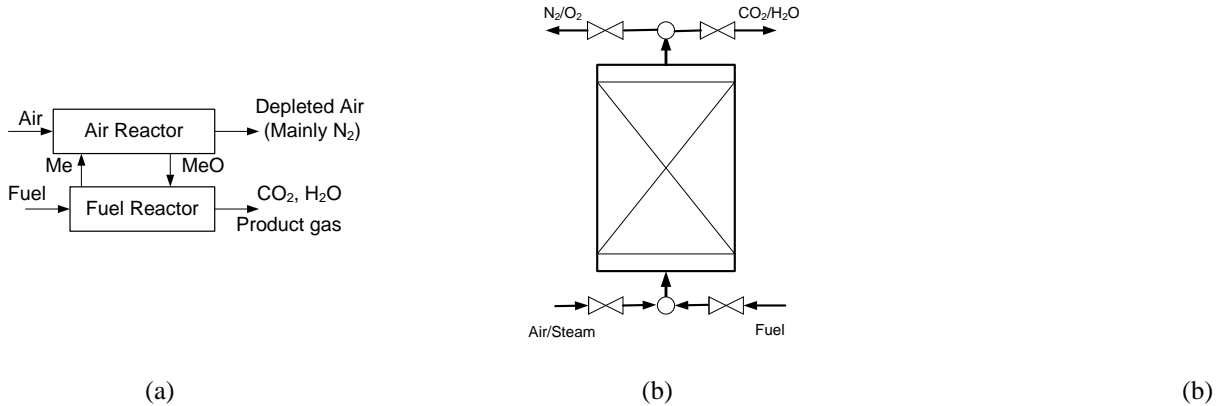

(a)   (b)   (b)

Fig. 1. Reactor configurations for chemical-looping technology: (a) Schematic of the chemical-looping combustion technology system, (b) Periodically operated chemical-looping technology in packed bed system.

In CLT, heterogeneous reactions between solid and gaseous reactants take place. Such reactions may have these rate-limiting steps: 1) external heat/mass transfer from the gas bulk phase to the outer surface of the particle, 2) diffusion of reactant gases in the particle pores, 3) chemisorption and reaction at the solid surface, and 4) diffusion of product gases in the porous solid and to the gas bulk phase. In chemical-looping system, thermal gradient may be large. Also large differences in temperature between gas bulk phase and the oxygen carrier may exist at the process conditions. Mass transfer is affected mainly by the internal mass transfer limitations rather than the external mass transfer limitations[10,11].

For theoretical modeling, two possible approaches are the shrinking core model and the homogeneous model. In the shrinking core model, the unreacted core is inert to the reactant gas, while in the homogeneous model, the porosity of the particle is constant and the effective diffusivity of the gaseous reactants does not change with the solid composition. It is usually assumed that the pseudo-steady state assumption holds and the concentration profiles of the gaseous components establish rapidly compared to the time scale of the gas solid reactions[11,12-15].

CONVERTING CARBON DIOXIDE TO OTHER CHEMICALS AND FUELS

Steam Gasification to Produce Hydrogen and Syngas

A fuel in the presence of a gasifying agent, such as steam or air, under high temperature undergoes chemical decomposition to produce a product gas containing CO_2, H_2, methane (CH_4), CO, and other chemical in small amounts. For example, the biomass undergoes the following four processes during gasification: 1) drying; 2) pyrolysis; 3) oxidation; and 4) reduction with the reactions: $C+CO_2 \rightarrow 2CO$ (Boudouard reaction), $C+H_2O \rightarrow CO+H_2$, $C+H_2 \rightarrow CH_4$; $CO+H_2O \rightarrow 2CO_2+H_2$ water-gas shift reaction[1-4]. Currently, the main research being conducted on CLSG with an oxygen carrier is to gasify the gaseous fuel, such as natural gas[4].

Many CLSG systems can be designed to produce more than one product, such as syngas (H_2, CO) and/or H_2-rich product gas[4,16-18]. The main gasification reactions may be represented by

$$C_nH_mO_p + (n-p)H_2O \rightarrow nCO + (m/2+n-p)H_2 \qquad (1)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$
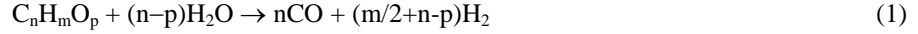
As shown in Fig. 2a, the major CLSG systems are: 1) Chemical looping partial oxidation and autothermal reforming, and 2) Chemical looping CO_2 acceptor reforming (Fig. 2b), in which the cyclic carbonization and calcination of a CaO is used to improve the selectivity of hydrogen in the product gas stream[8].

CLSG of fuel/biomass is an emerging energy technology with two attractive features: 1) it captures CO_2 during gasification and 2) it produces a product gas (CO_2, CO, H_2, H_2O, CH_4) that can have a wide range of biofuel and bioproduct applications [8-10]. CLSG can be categorized as: 1) CLSG with an oxygen carrier and 2) CLSG with a CO_2 carrier[2-4,7].

Figure 2a shows an iron (Fe)-based CLSG system, in which an equimolar H_2/steam mixture is first generated in a steam reforming reactor through chemical reactions between steam and particles of ferrous oxide (FeO). Some or all of the H_2/steam mixture is then fed into a biomass gasification reactor to produce a product gas consisting of mainly H_2, CO_2, CH_4, and CO. Part of the product gas undergoes additional processing for the removal of condensate for producing high-purity hydrogen. The remaining part of the product gas is oxidized into CO_2 and steam by hematite (Fe_2O_3) particles in the fuel reactor, while the Fe_2O_3 is mostly reduced to FeO particles. In the steam reforming reactor, the FeO particles are oxidized to magnetite (Fe_3O_4) and transported to the air reactor, where the Fe_3O_4 particles are oxidized back to Fe_2O_3. The oxidation and regeneration reactions are
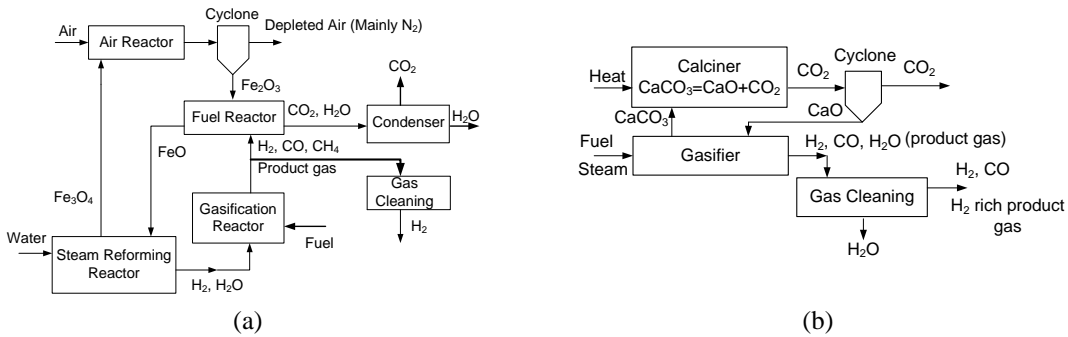
$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$	+194.3 kJ/mol	steam reforming reactor)	(3)
$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$	+314.6 kJ/mol	(air reactor)	(4)
$Fe_2O_3 + CO/H_2 \rightarrow 2FeO + H_2/H_2O$		(fuel reactor)	(5)
$4Fe_2O_3 + CH_4 \rightarrow 8FeO + 2H_2O + CO_2$	−365.5 kJ/mol (total)	(fuel reactor)	(6)

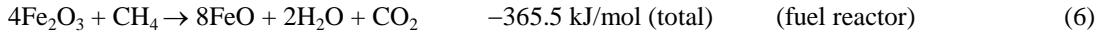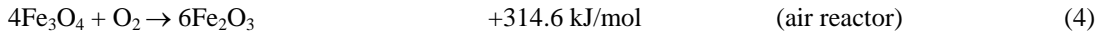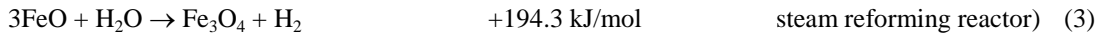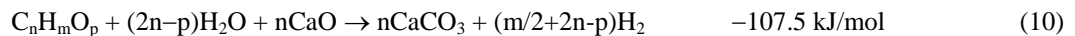(a)   (b)

Fig. 2. Hydrogen production from fuel/biomass with chemical looping steam reforming system: (a) with oxygen carrier; (b) with CO_2 carrier.

The system, shown in Fig. 2b, uses a sorbent such as calcium oxide (CaO) that carries CO_2 instead of oxygen between the two reactors: a gasifier and a regenerator (calciner)[8]. The sorbent goes through a series of calcination/carbonation cycles and captures CO_2 produced during gasification. The system produces the H_2-rich product gas, which can be used in fuel cells[7]. Typical gasifier reactions are

$C_nH_mO_p + (n-p)H_2O \rightarrow nCO + (m/2+n-p)H_2$	+112 kJ/mol	(7)
$CO + H_2O \rightarrow CO_2 + H_2$	−41.2 kJ/mol	(8)
$CaO + CO_2 \rightarrow CaCO_3$	−178.3 kJ/mol	(9)

Thus, the overall reaction in the gasifier could be written as

$$C_nH_mO_p + (2n-p)H_2O + nCaO \rightarrow nCaCO_3 + (m/2+2n-p)H_2 \qquad -107.5 \text{ kJ/mol} \qquad (10)$$

Reaction at the regenerator (calciner) is

$$CaCO_3 \rightarrow CaO + CO_2 \qquad\qquad +178.3 \text{ kJ/mol} \qquad\qquad (11)$$

Calculations are based on fuel with a composition of C, 51.13%; H, 6.10%; and O, 41.96% [13]. CaO also acts as a catalyst breaking down more tar and char into gases. Gasification with CaO maintains the temperature more or less constant. This is because the CO_2-capture (carbonization) reaction is an exothermic one; thus, the heat generated supplements the heat required for gasification. About 40% of calcium carbonate can be converted to CaO within a period of one hour when the reactor is heated at a temperature of 800°C. It is expected that the calcination rate would be much higher at a higher temperature[4,7,8].

Hydrothermal Conversion of Biomass to Chemicals

Hydrothermal reactions generally can be defined as aqueous chemical reactions under high temperature (200 - 350 °C) and high pressure (around 15-20 MPa). These hydrothermal reactions produce biocrude containing organic acids, various ketones, and phenols. No significant char/coke formation occurs during hydrothermal reactions[19,20]. The initial reaction in hydrothermal conditions is the hydrolysis of cellulose to glucose, which is the main difference to dry thermo chemical conversion. Further dehydration of the glucose hydrothermal reactions in the presence of alkali, mainly NaOH, KOH, and $Ca(OH)_2$ can be used to convert various biomass into acetic acid, formic acid, and lactic acid. Alkaline hydrothermal reaction can also be used to convert crude glycerine containing alkali into lactic acid[18-21]. Lactic acid is used to produce biodegradable lactic-acid based polymers. Glucose from any source can be converted into formic acid with a yield of 75% at a mild temperature of 250 °C in the presence of alkali as a basic output in the hydrothermal oxidation of carbohydrates according to the reaction

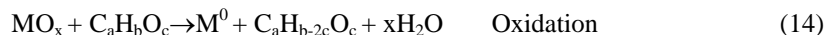$$C_6H_{12}O_6 + 3O_2 \rightarrow 6HCOOH \qquad\qquad (12)$$

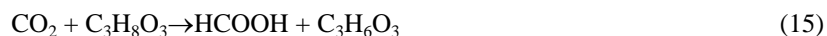## Hydrothermal Conversion of Carbon dioxide to Formic Acid

Hydrothermal conversion of biomass into chemicals is a very effective method as the high temperature properties of water are different from the water at ambient conditions. Fig. 3a shows the reduction of CO_2 to produce formic acid using the oxidation of a zero-valent metal (Zn, Al, Fe, Mn, Ni) under hydrothermal conditions in periodically operated chemical-looping packed bed system[18-21] with the following main reactions

$$M^0 + CO_2 + H_2O \rightarrow MO_x + HCOOH \qquad\qquad \text{Reduction} \qquad\qquad (13)$$

Zero-valent metals of Co and W also have catalytic activity in CO_2 reduction. With the catalysts of Ni and Cu, and small amount of $NaHCO_3$, the formic acid yield is around 48%. The reaction conditions are 573 K, and 120 minutes. Oxidized metal can be regenerated by a chemical such as crude glycerin, which is converted to lactic acid[19,20]

$$MO_x + C_aH_bO_c \rightarrow M^0 + C_aH_{b-2c}O_c + xH_2O \qquad\qquad \text{Oxidation} \qquad\qquad (14)$$

The overall reaction with glycerin is exothermic

$$CO_2 + C_3H_8O_3 \rightarrow HCOOH + C_3H_6O_3 \qquad\qquad (15)$$

Oxidation uses $FeCl_2$ $4H_2O$ and glycerin in the presence of NaOH without water to avoid reoxidation of Fe^0. The conversion of iron oxide and glycerin is around 100%. The lactic acid yield is around 82%. The overall reaction for Fe reduction with glycerin is

$$Fe(OH)_x + C_3H_8O_3 \rightarrow Fe^0 + C_3H_6O_3 + xH_2O \qquad\qquad (16)$$
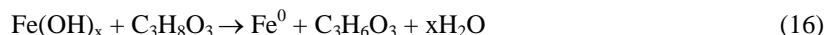
Fe(OH)$_3$, as a source of zero-valent metal, can also be used with very high rate of completion of the reduction. In the oxidation/reduction cycles, hydrogen is also produced with Fe^0 with the following possible reactions

$$Fe^0 + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \tag{17}$$
$$3FeCO_3 + H_2O \rightarrow Fe_3O_4 + H_2 + 3CO_2 \tag{18}$$
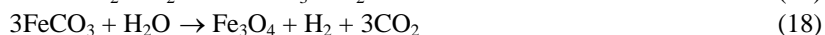
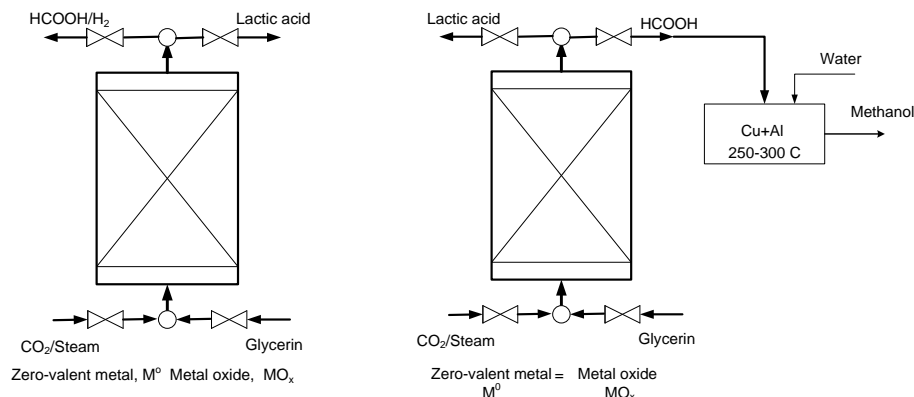The hydrogen yield is around 50%[18,19].

Fig. 3. Reactor configurations in periodically operated packed bed chemical-looping technology: (a) Packed bed system to produce formic acid (HCOOH) and hydrogen, (b) Packed bed system to produce methanol and lactic acid.

Fig. 3b shows the reduction of CO$_2$ to produce formic acid (HCOOH) by using a zero-valent metal (Zn, Al, Fe, Mn)/metal oxide redox cycles under hydrothermal conditions in a packed bed chemical-looping system operated with switching feed streams. The chemical-looping oxidation/reduction cycles have the following advantages:

- Oxygen is recycled hence there is no need for excess oxygen
- No hydrogen transportation and storage are necessary as the water supplies the hydrogen, which is reacted with CO$_2$ *in situ*
- The cycle does not require pure CO$_2$ and glycerin
- The cycle is exothermic.

Hydrothermal Conversion of Formic Acid to Methanol

Methanol is widely used as a valuable feedstock and fuel. Methanol can be separated from water more easily compared with formic acid. Using high temperature water (at 250 - 300°C) as a source of H$_2$, which can be generated using cheap metals as reductants, formic acid can be converted to methanol (CH$_3$OH) in a packed bed chemical-looping system as shown in Fig. 3b[23-25]. A possible overall reaction for such a conversion is

$$HCOOH + H_2 \rightarrow CH_3OH + H_2O \tag{19}$$

Many metals (Cu, Al, Cu+Al, etc.) can react with water to produce H$_2$ efficiently under hydrothermal conditions. The H$_2$ produced by the oxidation of metals could be active to reduce the formic acid into methanol[22-24]. Especially Cu may have high potential for reducing formic acid into methanol under hydrothermal conditions. Because of *in situ* production of H$_2$, no storage or transportation of H$_2$ would be required. Besides, the oxidative product of metals can catalyze the reduction of formic acid.

Highest yield of methanol at hydrothermal conditions using Cu (12 mmol) as catalyst in the presence of Al (4.4 mmol) was about 30.4%. The reaction takes place at 300 °C with a reaction time of 9 hours[11,12]. Methanol may be formed by the synthesis of CO$_2$ and H$_2$ from the decomposition of formic acid. This shows that there is possibility of converting CO$_2$ to methanol directly starting with CO$_2$ in a packed bed chemical-looping system.

CONCLUSIONS

Decarbonization technology needs scientific improvements in order to capture CO_2 and convert it other chemicals and fuels. This will lead to a wider use of fossil fuels deposits without carbon penalties and the renewable resources such as biomass. A matured chemical-looping technology may help improve combustion, reforming, and gasification of various fuels with the ability of capturing and converting CO_2 to valuable chemicals and fuels. Using the packed bad chemical-looping technology operated at hydrothermal conditions CO_2 can be converted to formic acid or directly to methanol using various metals. In a two stage hydrothermal process, it is possible to convert CO_2 to formic acid by using zero-valent metals in the first process, while the methanol is synthesized from formic acid in the second stage using various metals.

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