Conversion of CO_2 to Methanol in a Chemical-Looping Packed Bed System

Yaşar Demirel
Department of Chemical and Biomolecular Engineering, University of Nebraska Lincoln, Lincoln 68588;
ydemirel2@unl.edu

In the chemical looping technology (Fig. 1a), the 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.

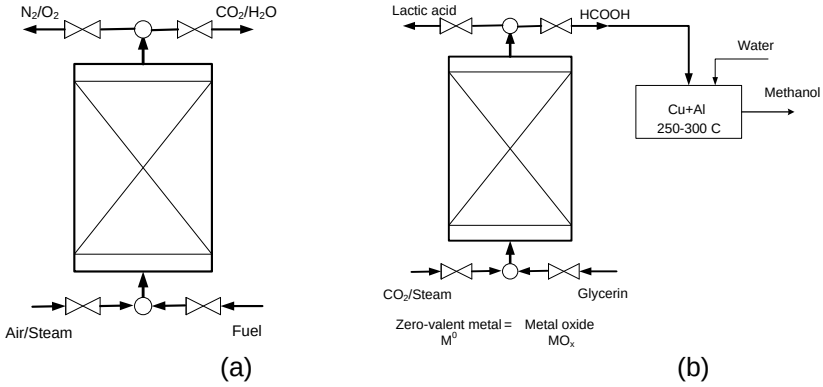

Figure 1. (a) Periodically operated CLT in packed bed system, (b) Conversion of CO_2 to methanol in a periodically operated packed bed; Cu: catalyst; Al: reductant (electron donor); yield ~30% at 300oC, in 9 hours, with 12 mmol Cu + 4.4 mmol Al.

In a new reactor concept, the oxygen carrier is kept inside a packed bed reactor and is alternately exposed to oxidizing and reducing conditions by periodic switching of the gas feed streams. Figure 1b 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 system operated with switching feed streams. The formic acid and hydrogen are produced with the feed of CO_2 and steam:

$$M^0+CO_2+H_2O \rightarrow MO_x+HCOOH$$

The oxidized metal can be regenerated by switching the feed stream to a chemical such as glycerin, which is converted to lactic acid:

$$MO_x+C_aH_bO_c \rightarrow M^0+C_aH_{b-2c}O_c+xH_2O.$$

The overall reaction with glycerin is exothermic:

$$CO_2 + C_3H_8O_3 \rightarrow HCOOH + C_3H_6O_3.$$

Using high temperature water (at 250-300^{o}C) as a source of H_2, which can be generated using cheap metals as reductants, formic acid can be converted to methanol by:

$$HCOOH + H_2 \rightarrow CH_3OH + H_2O$$

Many metals (Cu, Al, Cu+Al,) 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. Besides, the oxidative product of metals can catalyze the reduction of formic acid.

In this proposal, the operating conditions, conversion rates of CO_2 to formic acid, and conversion rates of formic acid to methanol will be investigated with a possible cooperation between the EERC and UNL.