Direct Synthesis of Organic Substances by Hydrothermal Treatment of CO_2-Rich Absorbent from CO_2 Capture Process

Summary

In order to establish an energy-saving and low-cost carbon dioxide capture and utilization (CCU) technology for CO_2 emission reduction, direct synthesis of organic substances by way of hydrothermal treatment was proposed, and the effectiveness was experimentally verified. In this process, the reaction called direct hydrothermal treatment between carbon dioxide and water which is accelerated in the presence of a reductant and a catalyst under high temperature and high pressure, is combined with CO_2 absorption by means of an alkali carbonate absorbent, to simultaneously synthesize organic compounds such as formic acid and to regenerate the absorbent. In preliminary experiments of synthesis by hydrothermal treatment of potassium bicarbonate ($KHCO_3$) solution along with a reductant and a catalyst, a formic acid yield of 32.7% and an absorbent regeneration rate of 77.8% were obtained, although 100% recycling of alkali carbonate absorbent was difficult to attain.

Proposals for Policy Development

For further examination in the future, the following research should be advanced:

- Because the absorbent solution is not 100% recyclable, a synthetic process in combination with CO_2 absorption should be designed.
- Recovery of the produced formic acid and regeneration of the oxidized reductant will also be investigated. In addition, the energy input and CO_2 emissions are evaluated to assess the feasibility of the CCU process.
- Fe powder was used as the reductant in this process, but the cost should be compared with that when hydrogen derived from renewable energy is used as a reductant. Moreover, added value by generating formic acid and hydrogen, instead of consuming Fe will be considered, and also from an economic point of view, the advantages of the proposed process over other CCU processes will be discussed and proposed.

1. The proposed process

Figure 1 shows a general CCU process. Problems to be tackled include consumption of energy when the absorbent is regenerated, and the large transportation energy and cost to the CO_2 separation and recovery site and to the site where CO_2 is converted to organic matter. The organic compound synthesis technology process by way of hydrothermal treatment (Fig. 2) remains advantageous in terms of energy and cost needed for the process and transport of CO_2.

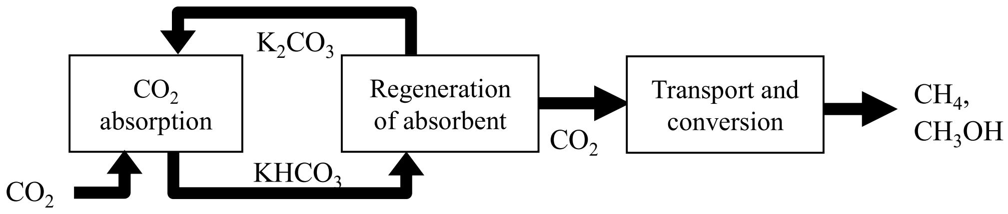

Fig. 1 Conventional CCU process using chemical absorbent

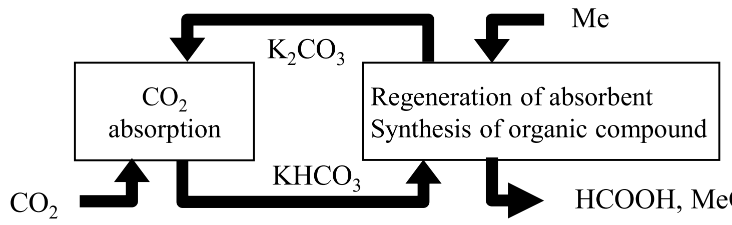

Fig. 2 CCU process using chemical absorbent, proposed in this study (Me: metal)

2. Discussion on the hydrothermal treatment of CO_2 chemical absorbent

Equation (1) shows the reaction of CO_2 when K_2CO_3 solution is used as the chemical absorbent. By heating to high temperature or reducing the pressure to release CO_2, highly pure CO_2 is captured, and the absorbent is regenerated (Equation (2)). Furthermore, by reducing CO_2 with a metal, organic compounds such as formic acid can be synthesized (Equation (3)). In this study, a process (Equation (4)) was proposed, in which reactions (2) and (3) are carried out as a one-stage process, whereby K_2CO_3 is regenerated from the absorbent by hydrothermal treatment of $KHCO_3$ solution, generated in the reaction (1), under high temperature of more than 250ºC and high pressure, and organic compounds are synthesized.

CO_2 absorption: $K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$ (1)

Regeneration of absorbent: $2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$ (2)

Synthesis of organic compound: $yCO_2 + yH_2O + xMe \rightarrow yHCOOH + Me_xO_y$ (3)

Proposed reaction: $2yKHCO_3 + xMe \rightarrow yK_2CO_3 + yHCOOH + Me_xO_y$ (4)

((2)×y + (3))

3. Experiment details, results and discussion

In the experiment, $KHCO_3$ was used as the CO_2 source, Fe powder as the reductant, and Ni powder as the catalyst. The CO_2 source concentration was varied from 0.5 to 2.0 M, the range used in the chemical absorption process, and the reaction tube was inserted into the electric tube furnace, and the reaction was continued for 120 minutes under the temperature of 300ºC. The experiment was conducted twice for each reaction condition, and the average values of the formic acid yield and the rate of regeneration of absorbent were calculated (Figs. 3 and 4).

It is recognized in Fig. 3 that the formic acid yield showed a trend of increase as the $KHCO_3$ concentration was increased, and the value of 32.7% was attained for the concentration of 1.0 M. Concerning the rate of regeneration of absorbent shown in Fig. 4, the rate of regeneration of absorbent increased as the $KHCO_3$ concentration was increased from 0.5 to 1.0 M, the maximal value of 78% was attained for the concentration of 1.0 M, and the rate of regeneration decreased as the $KHCO_3$ concentration was increased from 1.0 to 2.0 M. This finding suggests that, in the region up to 1.0 M, the consumption of CO_2 is faster than the consumption of the raw material of bicarbonate ion, thereby reaction (2) is accelerated giving rise to an increase of rate of regeneration. In the region over 1.0 M on the other hand, the consumption of HCO_3^- is faster than the consumption of CO_2, thereby the quantity of carbonate ion is reduced in the equilibrium of reaction (2) giving rise to a decrease of rate of regeneration.

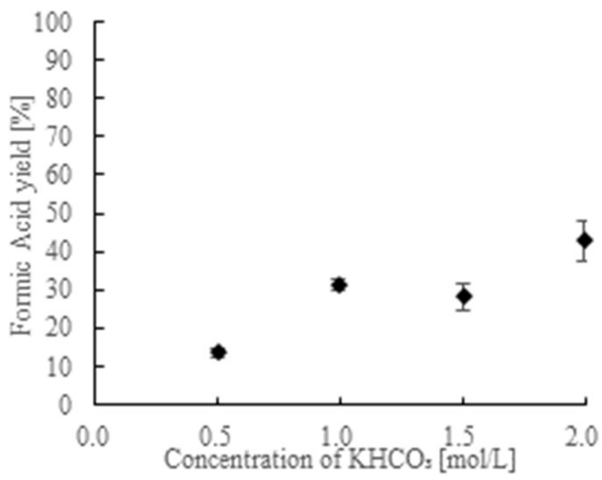

Fig. 3 Relationship between $KHCO_3$ concentration and formic acid yield (Error bar indicates standard deviation)

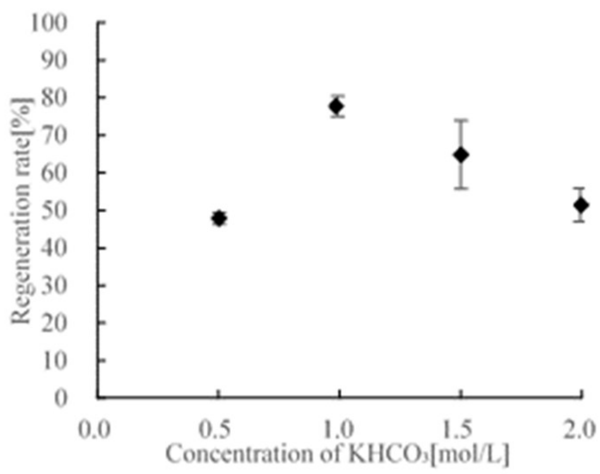

Fig. 4 Relationship between $KHCO_3$ concentration and rate of regeneration of absorbent (Error bar indicates standard deviation)

- The present proposal is compiled for policy making, using the data of the authors' conference presentation [1].

[1] Akutsu, Shimada, Nagata, Fukunaga, and Takahashi, Effects of concentration of alkali carbonate absorbent in hydrothermal synthesis of formic acid from CO_2, 52nd Autumn Meeting (Okayama), Society for Chemical Engineers, Japan, 2021.