Internal Condensation Reactor for Methanol Production from Carbon Dioxide

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Abstract: Hydrogenation of carbon dioxide to methanol is the key technology to achieve a low-carbon society. New type of reactor engineering is required to achieve high one-pass conversion to reduce energy consumption of the synthesis process. For overcoming the equilibrium limit of the reaction, "internal condensation reator (ICR)" was designed. The high boiling point products of the hydrogenation of CO_2, such as methanol and water, are eliminated from the reaction system by condensation, and the residual gases, such as H_2, CO_2 and CO, are supplied to further reaction to get almost quantitative conversion. Location of catalyst bed and diffusion zone, performance of membrane such as gas permeability and heat insulation, are important factors for the high performance of the reactor.

Keywords: carbon dioxide hydrogenation, equilibrium limit, internal condensation reactor.

1. Introduction

Methanol is an excellent fuel and a key intermediate for the matured petrochemical industry[1]. It is produced industrially from synthesis gas (mixtures of H_2, CO and CO_2) at elevated pressures (5∼10 MPa) and temperatures (200∼300°C) over Cu-Zn based catalyst[2,3]. The process suffers from the conflict between the low activity of industrial catalysts and thermodynamical equilibrium limit of the reaction. For relieving the limit, one of the effective ways is a two-stage catalyst bed reactor with high temperature in the first bed and low temperature in the second bed. Methanol formation is enhanced to high level at low temperaturet[4]. Other methods to remove methanol *in-situ* were also proposed, for instance, by means of a countercurrent stream of a selective adsorbent (such as tetraethylene glycol, n-butanol, n-hexane, etc.)[5,6]. When operation pressure as high as 20 MPa is applied at the conventional reaction temperature, *in situ* condensation of methanol also can be achieved without using adsorbents. These methods led to higher CO conversions, but have main drawbacks such as the introduction of other chemicals, complicated operation and rigorous reaction conditions.

Methanol synthesis through hydrogenation of captured CO_2 has also attracted continuous worldwide research interest because of its environmental impact to achieve low-carbon society. However, the thermodynamic limit is much more serious than those of CO hydrogenation. In this study, a system named as "Internal Condensation Reactor (ICR)" is developed, where the advantages resulting from a high per-pass conversion can be achieved under mild conditions. Such a system is based on the *in situ* separation of reaction products by condensing them on the surface of the low temperature ($<$ 100°C) condenser inside the reactor, close to the catalyst bed, which is shown in Fig. 1. The catalyst bed was placed in a porous tube and equipped with an electrical heater. The heated tube was surrounded by a membrane insulator, to prevent the heat loss, while reactants and products can pass through it freely. All is placed in a high pressure container which was submerged in a hot water bath to keep its temperature at the constant level.

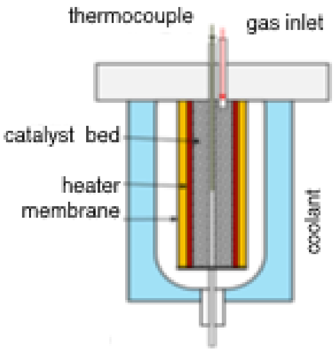

Figure 1. Schematic diagram of ICR.

2. Experimental

Home-made catalyst($Cu/ZnO/Al_2O_3$ = 4:3:3) was used in ICR reactor. The high pressure reaction was conducted in a fixed bed flow type apparatus at 2 MPa, 240°C, and H_2/CO_2=3/1. The product was analyzed with gas chromatographs. In order to simulate the reaction kinetics in ICR, (1) CO hydrogenation, (2) reverse water-gas shift reaction were considered.[7,8] Condensation rate into liquid in ICR should be proportional to partial pressures, and reaction (3) and (4) were considered to remove CH_3OH and H_2O as liquid. Direct hydrogenation of CO_2 to methanol was not necessary for the simulation.

$$(1)\ \mathrm{CO} + 2\,\mathrm{H_2} \longrightarrow \mathrm{CH_3OH}\text{: } r_1 = k_1 \cdot P_{\mathrm{CO}}^{a} \cdot P_{\mathrm{H_2}} \cdot \left(1 - \frac{P_{\mathrm{CH_3OH}}}{K_1(1 + b \cdot P_{\mathrm{CO}})P_{\mathrm{H_2}}^{2}}\right) \cdot \left(\frac{1}{1 + c \cdot P_{\mathrm{H_2O}}}\right)$$

$$(2)\ \mathrm{CO_2} + \mathrm{H_2} \longrightarrow \mathrm{CO} + \mathrm{H_2O}\text{: } r_2 = k_2 \cdot \left(1 - \frac{P_{\mathrm{CO}}P_{\mathrm{H_2O}}}{K_2 P_{\mathrm{CO_2}} P_{\mathrm{H_2}}}\right) \cdot (1 + d \cdot P_{\mathrm{H_2O}})$$

$$(3)\ \mathrm{CH_3OH} \longrightarrow \mathrm{CH_3OH(l)}\text{: } r_3 = k_3 \cdot P_{\mathrm{CH_3OH}}$$

$$(4)\ \mathrm{H_2O} \longrightarrow \mathrm{H_2O(l)}\text{: } r_4 = k_4 \cdot P_{\mathrm{H_2O}}$$

These differential equations were solved using “deSolve” library of R, to calculate CO_2 conversions, methanol yields, and CO yields. Then, reaction constants(k_1, k_2, k_3, k_4) and constants ($a \sim d$) were tuned for their fitting to the experimental results. The fitting was conducted using “rgenoud” library of R.

3. Results and discussion

In Fig.2, CO_2 conversions are compared without and with internal condensation. While CO_2 conversion levels off because of the equilibrium limit in the conventional reactor, the conversion reaches at 50% in ICR. In simulation, almost methanol was separated as liquid. The selective separation of the products (methanol and water) from the reaction mixture is based on their condensation on the surface of the reactor wall. The wall is closely located to the catalyst bed, whose temperature is lower than their dew points, in order to drive towards liquid products. The maximum CO_2 conversion reached 80% and the methanol selectivity was as high as 90%.

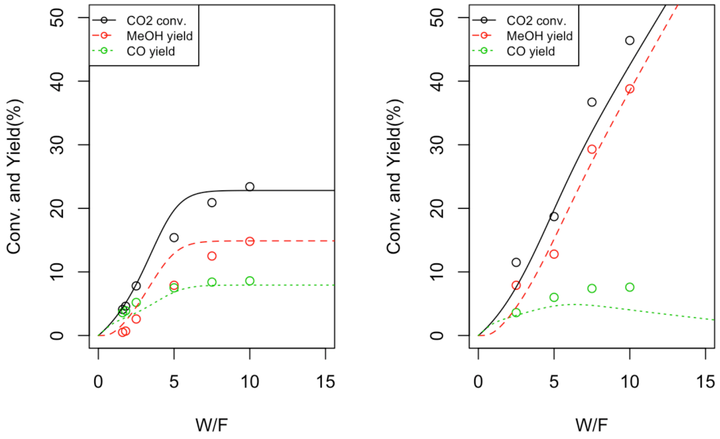

Figure 2. CO_2 conversion in the conventional reactor(left) and ICR(right).

4. Conclusions

The feasibility of the ICR for the manufacture of methanol from CO_2 hydrogenation. The condensable products are transferred from the catalyst bed to the wall through the concentration gradient. *In situ* product removal offers an attractive alternative to today'processes which requires high operation pressure or high recycle operation derived from thermodynamic equilibrium limit.

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