Diethyl carbonate (DEC) synthesize using the Pulse-quench reactor

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The Pulse-quench reactor

Solid state NMR can be efficiently utilized as a complementary analytical tool to GS/MS for characterizing catalyst reaction (see Figure 1). In order to facilitate the ongoing NMR investigation as well as to provide a constant flow reactor with the flexibility of controlling experimental parameters for the reaction, we have built a Pulse-quench Reactor depicted in Figure 2. Currently, the reactor has the following main features.

1. The maximum temperature inside the catalyst bed is about 420 °C with a temperature control stability of ±1°C.
2. Constant flow of the reagents, e.g., CH_3CH_2OH, CO and O_2 as well as the carrier gas N_2. The flow rates are controllable over a range from 0 to 200 sccm for the reactants, and 1000 sccm for the carrier N_2.
3. Pressure control over a range of 0-140 psi.
4. Pulse injection of the regents with sequence of timing under computer control.
5. Quenching of the reaction inside the catalyst bed using liquid nitrogen under computer control.

Experimental results

Figure 3 shows a typical temperature profile inside the reactor versus the quenching time with no catalyst placed inside the reactor. It is obvious that in less than 1s, the temperature can be brought from about 450 °C down to room temperature. With catalyst in place, the time needed for a complete quenching is lengthened accordingly depending on the length and the packing density of the catalyst bed.

Currently, we are using the constant flow feature of the pulse-quench reactor for the DEC catalytic reaction. A typical GS spectrum of the eluted products is given in Figure 4. Though the yield of the DEC under the specified condition is low, only 6.7 wt %, the products are simple, containing CH_3CH_2OH, DEC and only one major unknown byproduct. Preliminary results are summarized in Table 1.

Some interesting results are observed from Table 1. (1) Comparing the experiments #2, 3 and 4, the yield of DEC decreases with the increase of the flow-rate of CO in contrast to the dimethyl carbonate reaction, probably due to the side reaction of $CO + O_2 = H_2O$. So far, the best yield of DEC was observed at the balanced molar ratio condition, i.e., 6 sccm of CO and 3 sccm of O_2 (#2). (2) The wt% of the side products is increased, while the yield of DEC is decreased at decreased temperature (see #1 and #3).

Future work

1. Search the optimum conditions that give the highest yield of DEC by changing the relative ratio of CH_3CH_2OH, CO, O_2 and the carrier gas flow rates, the values of temperature and the pressure.
2. Screen different types of catalyst.
3. Investigate the effects of residence time of the reactants at the catalyst bed.
4. Once optimum experimental conditions are established using the constant flow conditions, pulse-quench experiments will be carried out to provide samples for solid state NMR to study the species adsorbed on the catalyst bed with particular emphasize on the transition period of the catalytic reaction process (see Figure 1).

Table 1. Summarize of the ending products eluted from the catalyst bed under various experimental conditions.

Experiments (#)	CH_3CH_2OH (ml/h)	**CO** (sccm)	O_2 (sccm)	Temperature (°C)	DEC (wt %)	Byproducts (wt %)
1	**1.18**	**48**	**3**	**155**	**5.0**	**4.0**
2	**1.18**	**6**	**3**	**110**	**6.7**	**2.6**
3	**1.18**	**48**	**3**	**110**	**4.3**	**6.5**
4	**1.18**	**96**	**3**	**110**	**0.8**	**4.8**

Note: The flow rate of the carrier gas N_2 and the pressure at the catalyst bed for all experiments are 48 sccm and 100 psi, respectively. The catalyst was 2.96g $CuCl_2/PdCl_2/NaOH$. The reaction time was 6 hours in order to collect sufficient liquid (2-8ml). The GS measurement was performed immediately after the reaction.

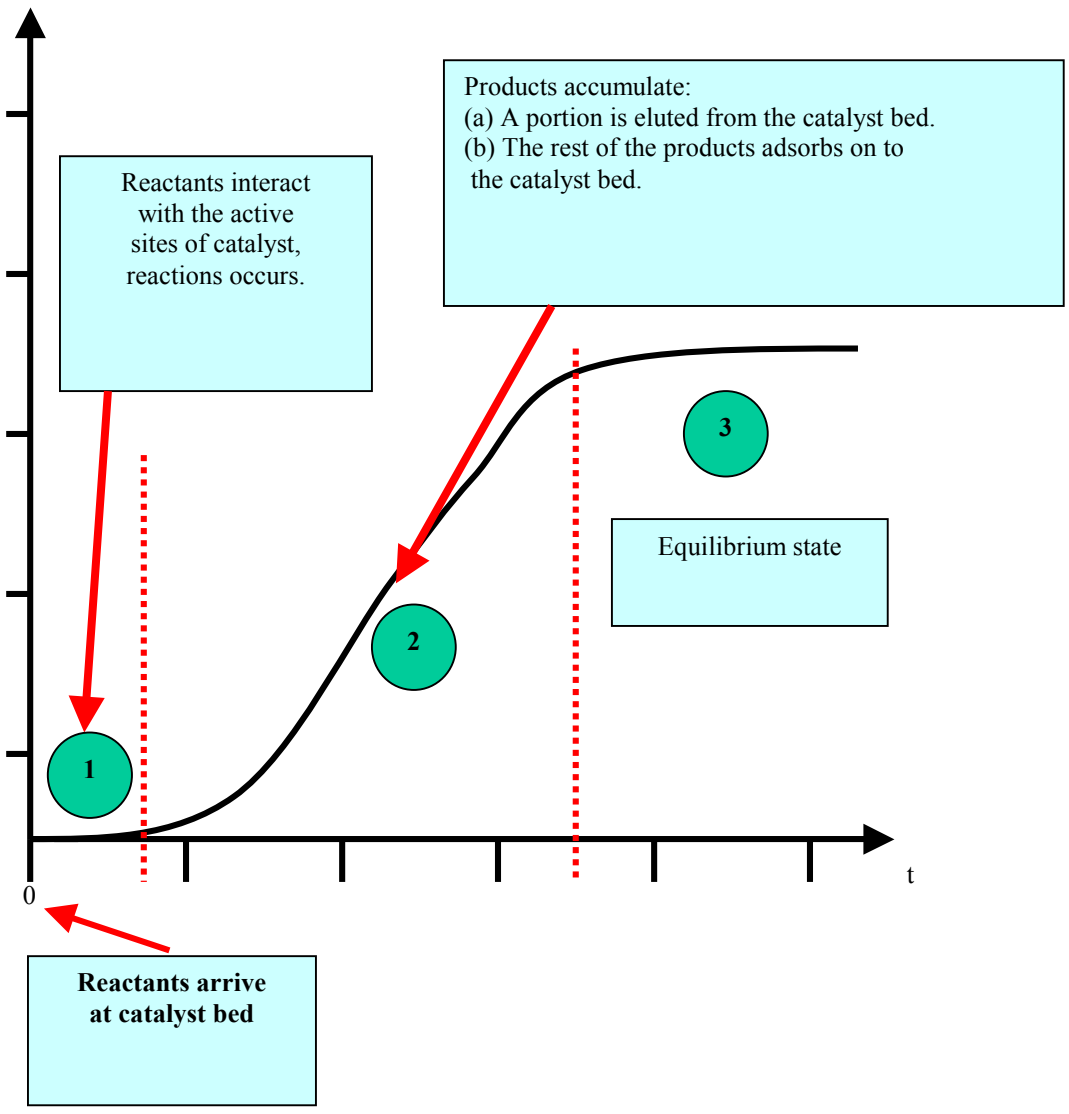
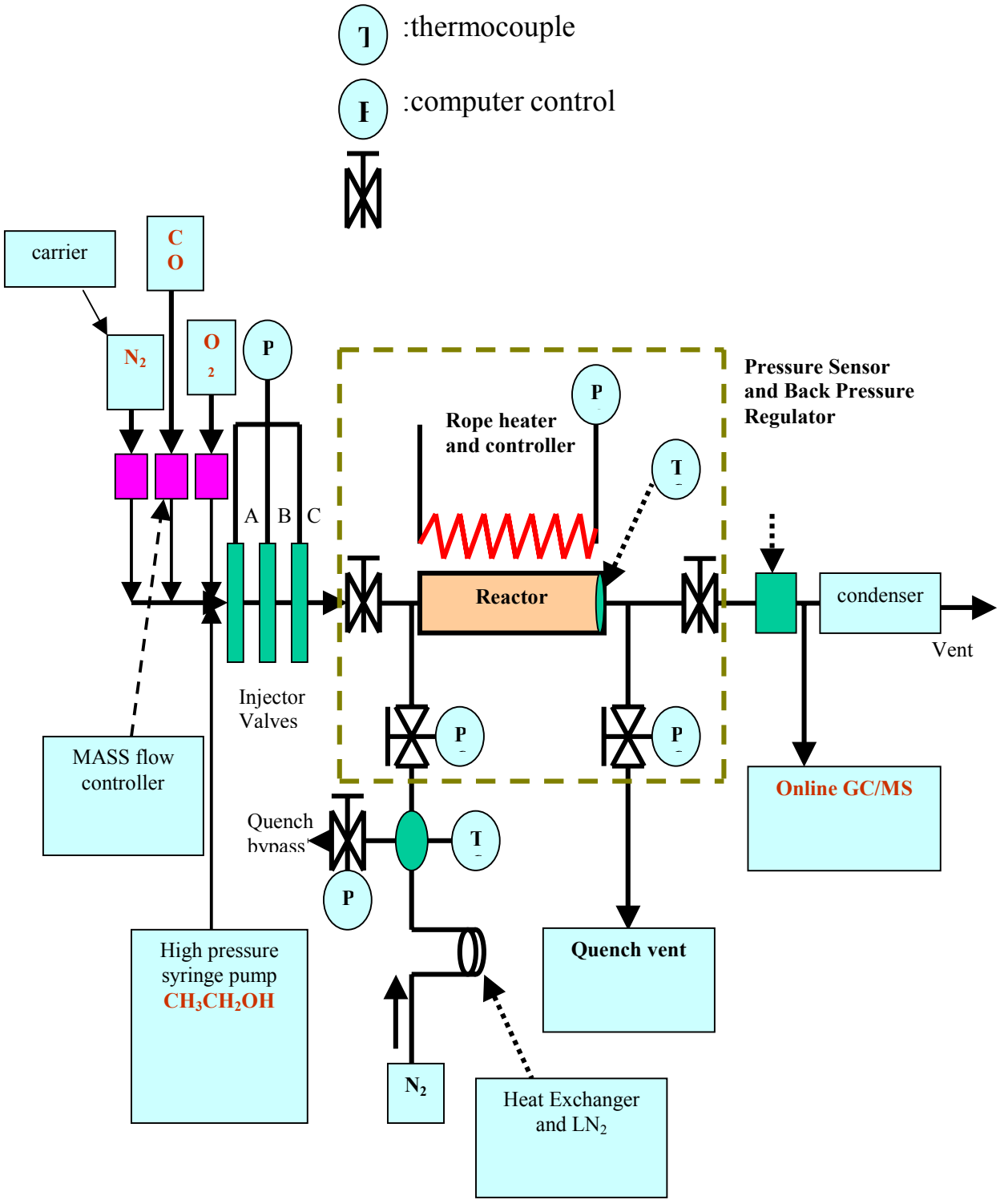


Figure 1. Postulated kinetic process in DEC reaction at constant temperature(i.e., 135 °C). NMR is good for stages (1) and (2) by investigating the product adsorbs at catalyst bed. GC/MS is useful for stages (2) and (3).

Figure 2. The diagram of pulse-quench reactor



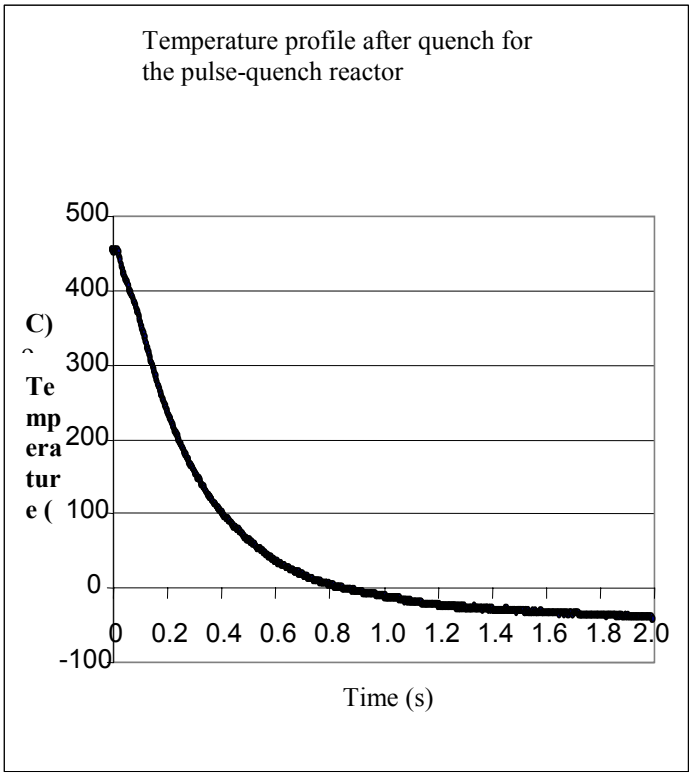


Figure 3. The temperature profile in the middle of the reactor versus the quench time. Note that the temperature can be dropped from 450 ºC to room temperature (25 ºC) in approximately 0.6s.

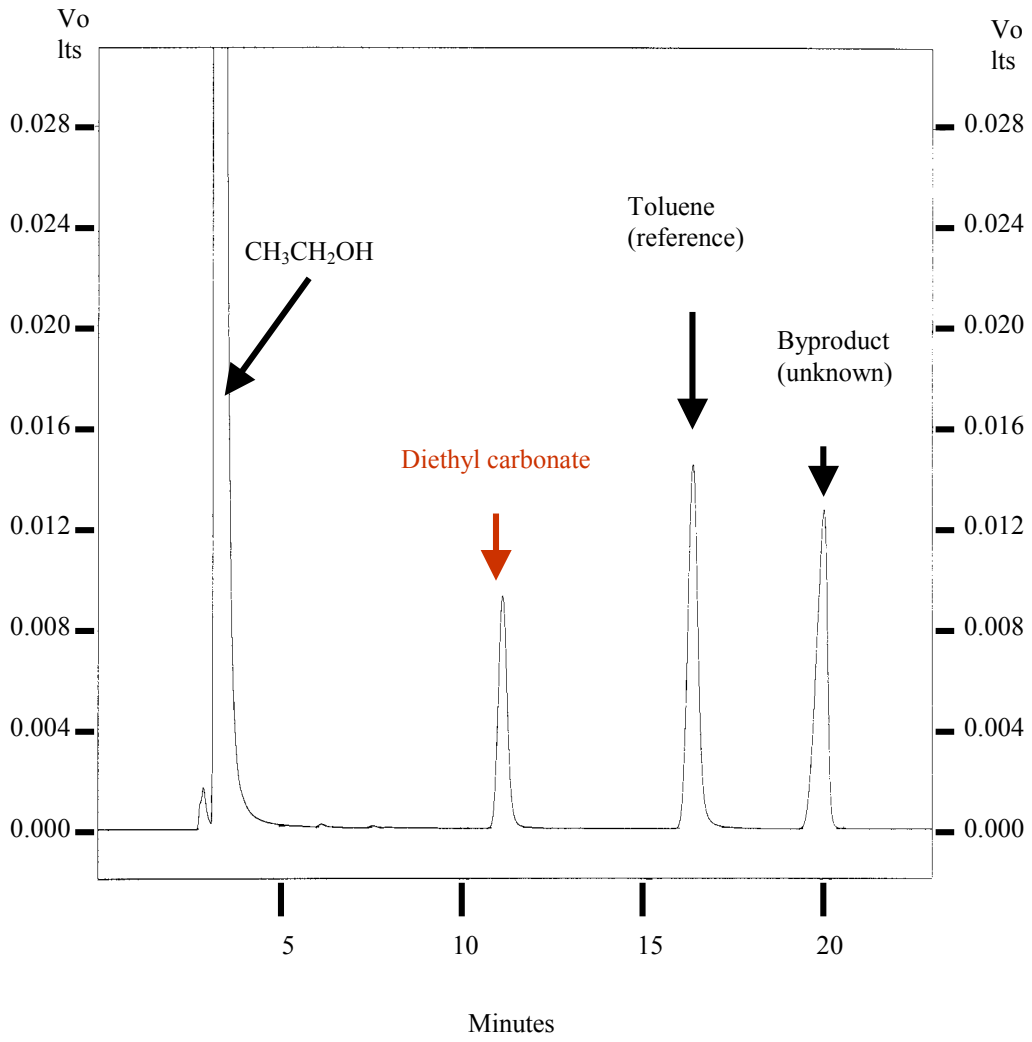


Figure 4. The GS spectrum of the ending products from the Pulse-quench reactor working at the constant flow condition in experiment #2.