



# Methanol synthesis in an integrated two-stage reactor

Wensheng Linghu, Zhenyu Liu\*, Zhenping Zhu, Jianli Yang, Bing Zhong

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, People's Republic of China

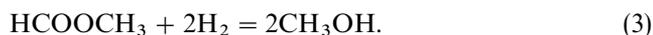
## Abstract

An alternative way for synthesis of methanol at temperatures lower than the current industrial practice is an indirect, two-step synthesis via methyl formate. An integrated two-stage reactor (ITSR) was designed and tested for the two-step synthesis to overcome problems encountered in single-slurry-reactor operation. The results show that the ITSR can be operated successfully at a broad range of conditions. For syngas conversions similar to that of the current industrial practice, the ITSR can be operated at much milder conditions. Under the conditions used in the study, the mass transfer of CO from the gas phase to the liquid phase is the rate limiting step in the transient period, and the evaporation of the intermediate, methyl formate, from the liquid phase to the gas phase is the rate limiting step at steady state. Temperature, pressure and feed flow rate showed significant influence on the synthesis reaction. © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Methanol; Low temperature synthesis; Two-stage reactor; Methyl formate; Catalysis; Reactor dynamic

## 1. Introduction

Although the synthesis of methanol from syngas (Eq. (1)) is one of the technically very well-developed industrial processes (Wender, 1996), it suffers several limitations, such as high temperature (523 K) operation and insufficient heat transfer, which result in low syngas conversion per pass. Extensive research has been carried out on the development of low temperature catalysts and on slurry phase synthesis to improve syngas conversion and reaction heat removal. An alternative way for the same objectives is an indirect, two-step synthesis via methyl formate (Marchionna et al., 1997; Liu et al., 1988), namely, carbonylation of methanol in the first step, (Eq. (2)) and hydrogenolysis of methyl formate (MeF) in the second step, (Eq. (3)):



The advantages of the two-step process are low reaction temperatures and liquid phase operation, at least for

the first step. The carbonylation can be operated at around 353 K using a homogeneous alkali methoxide catalyst, and the hydrogenolysis at around 463 K using a copper chromite catalyst. The two-step reactions have been studied individually in separate two reactors and concurrently in a single slurry reactor (Tonner et al., 1983; Liu et al., 1989; Palekar et al., 1993a, b). The advantage of the two-reactor process is the optimized reaction conditions for each step, while the disadvantages are high cost for equipment and operation. The concurrent operation, on the other hand, has advantages of low equipment cost and synergism for low catalyst deactivation, but suffers from compromised reaction conditions (not optimum for either reaction), low methanol production rate, and difficulty in natural separation of the liquid product from the slurry phase. Development of reactors which have characteristics overcoming the above problems is crucial for the further development of the two-step methanol process.

This paper presents design and test results of an integrated two-stage reactor (ITSR). Some problems encountered in the concurrent operation in a single-slurry-reactor were solved. The dynamic behavior of the reactor and the effects of reaction temperature, pressure and feed flow rate on CO conversion per pass were studied.

\*Corresponding author. Tel.: 00 86 351 4040491; fax: 00 86 351 4041153; e-mail: zyl@public.ty.sx.cn.

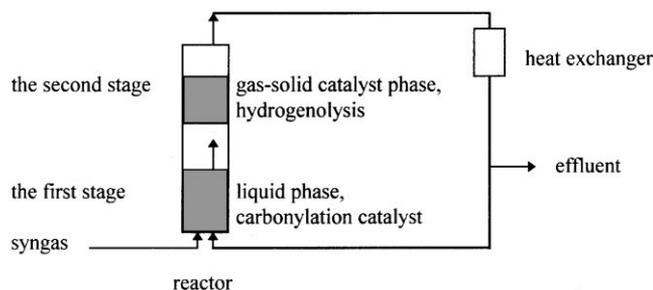


Fig. 1. A schematic diagram of the ITSR.

## 2. The ITSR

A schematic diagram of the ITSR is shown in Fig. 1. The reactor, similar to a packed distillation tower, consists of two regions, a gas–liquid region at the lower part of the tower for carbonylation of methanol (the first stage), and a gas–solid region at the upper part of the tower for hydrogenolysis of MeF (the second stage). The first stage has a liquid volume of 30 ml with a depth of 20 cm. Synthesis gas, CO + H<sub>2</sub>, is fed into the reactor through the bottom. A portion of CO is consumed in the first stage through carbonylation to form MeF, the unreacted syngas, containing less CO and more H<sub>2</sub> than the feed, along with vaporized MeF and methanol rises to the second stage. Since the vapor pressure of the intermediate MeF is higher than that of methanol, the mole ratio of MeF-to-methanol in the gas phase is higher than that in the liquid phase. The feed to the second stage, therefore, is enriched with H<sub>2</sub> and MeF compared to that in the single-slurry-reactor operation. The effluent gas of the second stage passes through a heat exchanger, where methanol is condensed. A portion of the condensed methanol is recycled to the first stage of the reactor to maintain the liquid level and the remaining portion is collected in a product tank. The non-condensable gas passes through a back pressure regulator and is measured with a wet test meter before being vented.

The design presented above makes the ITSR synthesis superior to the single-slurry-reactor operation because of: (1) optimum temperatures for both stages; (2) high hydrogenolysis rate due to high concentration of MeF and H<sub>2</sub>, and low concentration of CO; (3) natural separation of products from catalysts and (4) steady-state liquid level control for continuous operation.

## 3. Experimental

The carbonylation catalyst used in the study was an alkali methoxide, potassium methoxide (CH<sub>3</sub>OK). The hydrogenolysis catalyst used was a copper/chromite, G-89 of United Catalyst, which was reduced in situ in a mixture of 5% H<sub>2</sub> and 95% N<sub>2</sub> at 523 K for 10 h.

Table 1  
Experimental conditions used

Operating parameters	Range
Temperature	
the first stage	333–393 K
the second stage	463 K
Total pressure	1.0–4.0 MPa
Catalysts loading:	
CH <sub>3</sub> OK solution	0.5 mol/l
Copper/Chromite	0.5 g
Feed flow rate	50–200 ml/min
Feed ratio:	
H <sub>2</sub> :CO	2.0:1.0
H <sub>2</sub> :CO:Ar	2.0:1.0:0.3

After the catalyst reduction, the reactor was pressurized by syngas free of water and CO<sub>2</sub> and with a H<sub>2</sub>-to-CO ratio of 2. The two stages of the reactor were heated to the required temperatures during the same time. It is important to note that it takes about 2 h for the ITSR to reach the reaction conditions before the reaction time counting was started.

The compositions of the effluent at the exit of each stage were analyzed by a GC with a thermal conductivity detector. Some of the liquid products were subjected to GC-MS analysis. An internal standard Ar, was added to the syngas for most of the runs. The average carbon balance made for the first and the second stage at steady state was greater than 96%. Since H<sub>2</sub> was used as the carrier gas for the GC analysis, hydrogen balance was not made. Experimental conditions used are listed in Table 1.

## 4. Results and discussion

### 4.1. Dynamic behavior of ITSR

The dynamic behavior of ITSR during the initial transient period was studied using syngas with or without Ar. When Ar is used, CO conversion,  $X_{CO}$  in mol%, can be easily determined by

$$X_{CO} = \frac{R_{CO/Ar,0} - R_{CO/Ar,1}}{R_{CO/Ar,0}} \times 100, \quad (4)$$

where,  $R_{CO/Ar,0}$  and  $R_{CO/Ar,1}$  are CO-to-Ar mole ratios in the feed and in the effluent of the first stage, respectively.

The determined  $X_{CO}$  at different reaction times is shown in Fig. 2 as open circles. The  $X_{CO}$  decreased from about 56%, at zero time, to a steady state value of 8.9% in 20 h. This decrease is accompanied by a decrease of methanol concentration and an increase of MeF concentration in the liquid phase. Based on these data, an average carbonylation rate constant of 0.011 l<sup>2</sup>/mol<sup>2</sup>/min was obtained which is smaller than that (0.020 l<sup>2</sup>/

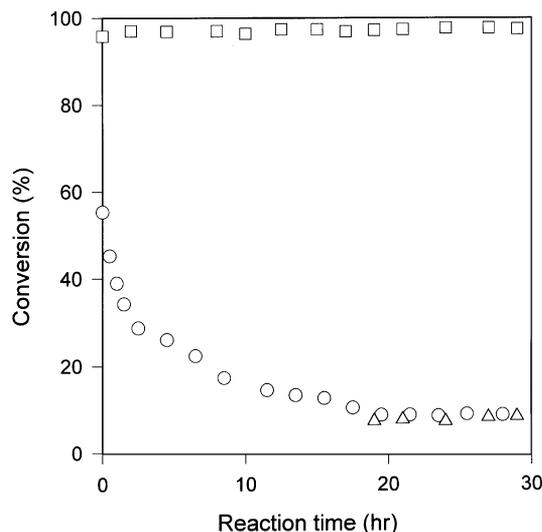


Fig. 2. Conversion-time curves for the synthesis of methanol: temperature: the first stage: 353 K; the second stage: 463 K; total pressure: 1.0 MPa; catalyst loading: the first stage: 30 ml  $\text{CH}_3\text{OK}$  (0.5 mol/l); the second stage: 0.5 g G-89; feed flow rate: 50 ml/min (○)  $X_{\text{CO}}$ , feed  $\text{H}_2:\text{CO}:\text{Ar} = 2:1:0.3$  (△)  $X_{\text{CO,ss}}$ , feed  $\text{H}_2:\text{CO} = 2:1$  (□)  $X_{\text{MeF}}$ .

$\text{mol}^2/\text{min}$ ) reported by Gormley et al. (1988) using  $\text{CH}_3\text{ONa}$  in batch autoclaves.

For syngas without Ar, only steady state CO conversion,  $X_{\text{CO,ss}}$  in mol%, can be determined (Eq. (5)),

$$X_{\text{CO,ss}} = \frac{Y_{\text{MeF},1}}{Y_{\text{CO},1} + Y_{\text{MeF},1}} \times 100, \quad (5)$$

where  $Y_{\text{CO},1}$  and  $Y_{\text{MeF},1}$  are mole fractions of CO and MeF at the exit of the first stage, respectively. The determined conversions at the steady state are shown in Fig. 2, as open triangles, in comparison with those obtained from Eq. (4). Clearly,  $X_{\text{CO,ss}}$  and  $X_{\text{CO}}$  are very close. This consistency indicates that the sampling system, the sampling procedure and the conversion calculation are reliable. This also suggests that use of an internal standard is not necessary if the steady state behavior of the reactor is to be evaluated.

The conversion of MeF in the second stage was determined using Eq. (6), in analogy to Eq. (5),

$$X_{\text{MeF}} = \frac{n_1 Y_{\text{MeF},1} - n_2 Y_{\text{MeF},2}}{n_1 Y_{\text{MeF},1}} \times 100, \quad (6)$$

where  $n_1$  and  $n_2$  are mole flow rates of the effluent for the first and the second stages, and  $Y_{\text{MeF},1}$  and  $Y_{\text{MeF},2}$  are MeF mole fractions in the effluents of the first and second stages, respectively. The determined MeF conversion, open squares in Fig. 2, are greater than 97 mol%. In fact, for all the experiments presented in this paper, MeF conversions are greater than 95 mol%. This seems to indicate that the catalyst for the second stage is very active or the catalyst loading used is too large. Under

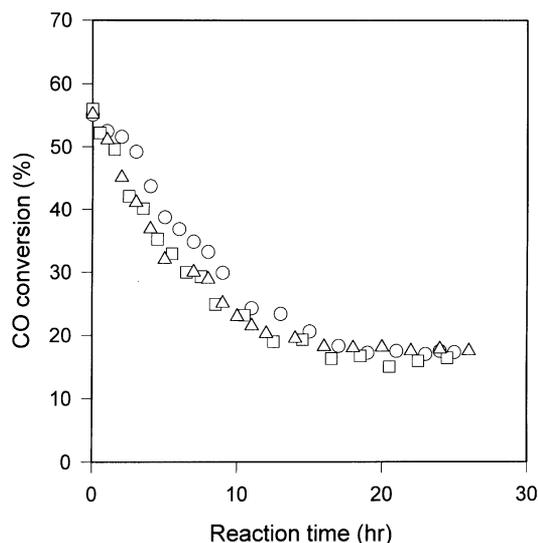


Fig. 3. Effect of carbonylation catalyst concentration on CO conversion: temperature: the first stage: 353 K; the second stage: 463 K; total pressure: 3.0 MPa; feed  $\text{H}_2:\text{CO}:\text{Ar} = 2:1:0.3$ ; feed flow rate: 50 ml/min (□) 0.5 mol/l (△) 1.0 mol/l (○) 2.0 mol/l.

these conditions, carbonylation stage is the rate limiting step for the two-stage synthesis, which is, therefore, evaluated in detail in the following content.

The effect of carbonylation catalyst concentration on  $X_{\text{CO}}$  is shown in Fig. 3. Although the  $X_{\text{CO}}$  for catalyst concentration of 2.0 mol/l is higher than that for 1.0 and 0.5 mol/l in the transient period, the difference is very small. Furthermore, the difference disappears at the steady state. Liquid analysis showed that the liquid composition at steady state is close to equilibrium values reported by Aguilo and Horlenko (1980). These phenomena indicate that the carbonylation reaction is very fast and is not the rate limiting step for the first stage either in the transient period or at the steady state. It is logical to believe that the carbonylation reaction is always at equilibrium with respect to CO concentration in the liquid phase, and the mass transfer of CO from the gas phase to the liquid phase is the slowest step in the transient period. With increasing reaction time, MeF concentration increases, which results in increase of CO concentration in the liquid phase, as determined by reaction equilibrium, and decrease of mass transfer rate of CO from the gas phase to the liquid phase. At the steady state, the liquid CO concentration is in equilibrium with CO partial pressure in the gas phase. Based on the conversion data, the mass transfer rate constant of CO from the gas phase to the liquid phase,  $k_1 a$ , was estimated to be  $0.0027 \text{ s}^{-1}$ , which is similar to the value of  $0.0016 \text{ s}^{-1}$  determined using the equation proposed by Akita and Yoshida (1973), but much smaller than  $0.12 \text{ s}^{-1}$  for a continuously stirred slurry reactor (Bai Liang et al., 1996). This indicates insufficient gas-liquid mass transfer for such bubbling systems.

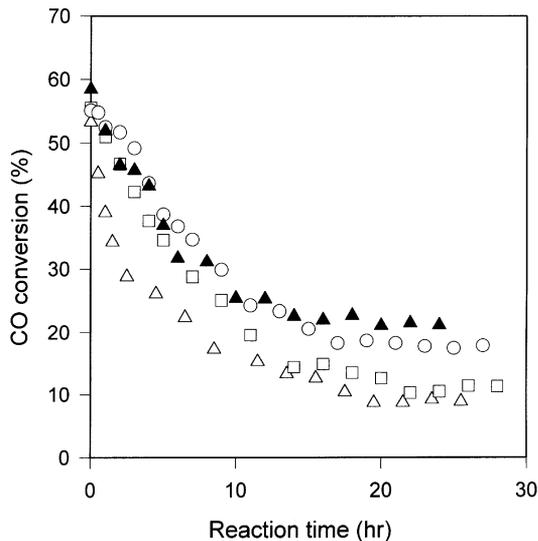


Fig. 4. Effect of total pressure on CO conversion: temperature: the first stage: 353 K, the second stage: 463 K; 30 ml  $\text{CH}_3\text{OK}$  (0.5 mol/l); feed  $\text{H}_2:\text{CO}:\text{Ar} = 2:1:0.3$ ; feed flow rate: 50 ml/min ( $\Delta$ ) 1.0 MPa ( $\square$ ) 2.0 MPa ( $\circ$ ) 3.0 MPa ( $\blacktriangle$ ) 4.0 MPa.

The effect of total pressure on  $X_{\text{CO}}$  during the initial transient period is shown in Fig. 4. Except for time zero, the CO conversion of a higher pressure is greater than that of a lower pressure, this is expected because a higher CO partial pressure results in a higher CO mass transfer rate from the gas phase to the liquid phase, and a higher CO concentration in the liquid phase. It is rather surprising to see, however, that the values of  $X_{\text{CO}}$  at time zero are similar for different pressures. The reason for this phenomenon is not clear.

#### 4.2. Steady state behavior of ITSR

The effect of temperature on the steady-state CO conversion at total pressures of 1.0 and 2.0 MPa is shown in Fig. 5. The  $X_{\text{CO}}$  increases with an increase in temperature, and approaches a maximum value of 9.4% for 1.0 MPa and 11.6% for 2.0 MPa. This trend is contradictory to that of reaction equilibrium, which shows decreasing CO conversion with increasing temperature. This behavior, however, is consistent with the analysis made earlier that the carbonylation reaction is at equilibrium and is not the rate limiting step for the overall system. This behavior suggests that the rate limiting step at the steady state is the evaporation of MeF, not the mass transfer of CO from the gas phase to the liquid phase as it was in the transient period. At the steady state, the CO concentration in the liquid is in equilibrium with CO partial pressure in the gas phase and the carbonylation is in reaction equilibrium, the carbonylation does not proceed further unless a portion of the product MeF is removed. The rate of MeF evaporation from the liquid phase is proportional to its vapor pressure and concen-

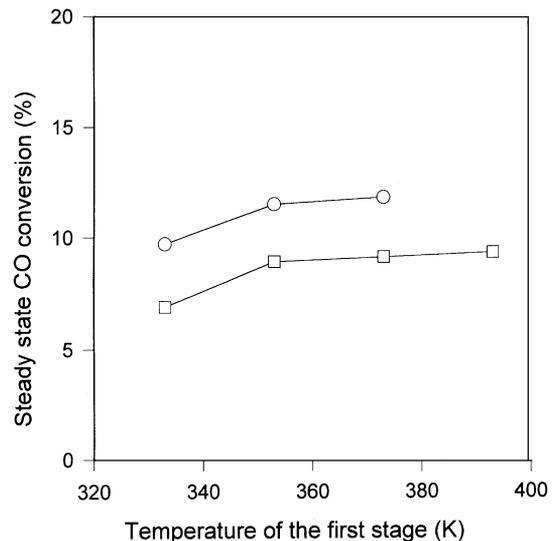


Fig. 5. Effect of temperature on steady state CO conversion: 463 K for the second stage; 30 ml  $\text{CH}_3\text{OK}$  (0.5 mol/l) (0.5 mol/l); feed  $\text{H}_2:\text{CO}:\text{Ar} = 2:1:0.3$ ; feed flow rate: 50 ml/min total pressure: ( $\square$ ) 1.0 MPa ( $\circ$ ) 2.0 MPa.

tration. The increase in temperature may result in a large increase in vapor pressure and a small decrease in liquid concentration.

The steady-state values in Fig. 4, at reaction times greater than 20 h, show the effect of total pressure on steady state CO conversion. The CO partial pressures at the total pressures of 1.0, 2.0, 3.0 and 4.0 MPa are 0.3, 0.6, 0.9 and 1.2 MPa, respectively. The increase of the steady-state CO conversion with increasing CO partial pressure is reasonable because the carbonylation is a volume decreasing reaction, and high pressure favors conversion.

The syngas feed rate has a profound effect on CO conversion and CO consumption. Table 2 shows decreasing CO conversion and increasing CO consumption with increasing feed rate. The increase in CO consumption corresponds to only a small decrease in CO conversion. The highest CO consumption is obtained at the highest pressure and the highest flow rate used, which indicates a possibility of improvement in productivity. Since the evaporation of MeF from the liquid phase is the rate-limiting step, the increased syngas flow rate certainly carries out more MeF from the liquid phase, which results in a decreased MeF concentration in the liquid and an increased driving force for carbonylation.

It is important to note that the steady-state CO conversions obtained in ITSR under the conditions used are comparable to or higher than that of current industrial practice. This is very significant because those conversions were obtained at much milder conditions than that for the current industry. For a CO conversion of 10.9%, for example, the ITSR can be operated at a total pressure of 2.0 MPa and temperatures of 353 K (for the

Table 2

Effect of feed flow rate 353 K for the first stage, 463 K for the second stage, feed H<sub>2</sub>:CO:Ar of 2:1:0.3, 30 ml methanol with CH<sub>3</sub>OK concentration of 0.5 mol/l

Total pressure, MPa	2.0				4.0	
Feed flow rate (ml/min)	50	100	150	200	50	200
CO conversion (%)	10.9	9.1	7.5	6.5	21.0	16.8
CO consumption (μmol/min)	73	122	151	173	141	450

first stage) and 463 K (for the second stage), compared to 5 MPa and 523 K for ICI technology (Tierney et al., 1993).

## 5. Conclusions

The ITSR designed and tested in this paper has characteristics superior to that of the single-slurry-reactor system for the two-step methanol synthesis. The ITSR can be operated at optimum temperatures for both carbonylation and hydrogenolysis reactions, and enables natural separation of the products from the catalysts. The increased MeF and H<sub>2</sub> concentrations and decreased CO concentration in the second stage may result in increased hydrogenolysis rate and decreased catalyst deactivation.

The ITSR can be operated successfully at a broad range of conditions. Under the conditions used, the second stage shows MeF conversions of greater than 95% and the first stage controls the overall process. Mass transfer of CO from the gas phase to the liquid phase and the evaporation of MeF from the liquid phase are the rate-limiting steps for the synthesis in the transient and steady state periods, respectively. At the steady state, an increase in either carbonylation temperature or total pressure, or a decrease in syngas flow rate results in an increase in CO conversion. The highest CO conversion obtained was 21% and the highest CO consumption rate obtained was 450 μmol/min. For syngas conversions similar to that of the current industrial practice, the ITSR can be operated at much milder conditions.

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## Notation

$R_{\text{CO/Ar},0}$	CO-to-Ar mole ratio in the feed
$R_{\text{CO/Ar},1}$	CO-to-Ar mole ratio at the exit of the first stage
$X_{\text{CO}}$	CO conversion per pass in mol%
$X_{\text{CO},SS}$	steady-state CO conversion per pass in mol%
$X_{\text{MeF}}$	MeF conversion in mol%
$n_1$	effluent mole flow rate of the first stage in mol/s
$n_2$	effluent mole flow rate of the second stage in mol/s
$Y_{\text{MeF},1}$	mole fraction of MeF at the exit of the first stage
$Y_{\text{MeF},2}$	mole fraction of MeF at the exit of the second stage

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