Progress in Development of LPDME Process: Kinetics and Catalysts

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In the Liquid Phase Di-Methyl Ether (LPDME) process under development at Air Products [1], synthesis gas (syngas) is converted into Di-Methyl Ether (DME) in a single, slurry-phase reactor using a physical mixture of a commercial methanol synthesis catalyst and a solid acid dehydration catalyst, slurried in a mineral oil. The process can be incorporated into an Integrated Gasification Combined Cycle (IGCC) to fully utilize the capacity of the gasifier(s) and increase revenue by providing an alternate product. It can also be used to produce dimethyl ether or dimethyl ether/methanol mixtures, which can be used as a diesel substitute [2], domestic fuel [3], or chemical building block [4]. The first part of this paper reports more insights we have acquired in the past year, through kinetic simulations, into (1) the chemical synergy of the reaction system, (2) the resulting process advantages (e.g., high syngas conversion per pass and the suitability for carbon monoxide-rich syngas) and their commercial implications, and (3) the limiting factors for further improvement. In the second part we report our progress in developing stable catalyst systems for the LPDME process.

1. The Chemical Synergy and the Resulting Process Advantages

A typical slurry phase bubble-column reactor performs as a continuously stirred tank reactor (CSTR). In the laboratory a CSTR is used to simulate the bubble-column reactor. Three reactions take place simultaneously in the LPDME reactor:

Methanol synthesis reaction: $CO + 2H_2 \Leftrightarrow CH_3OH$ (1)

Water gas shift reaction: $CO + H_2O \Leftrightarrow CO_2 + H_2$ (2)

Methanol dehydration reaction: $2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$ (3).

Reactions (1) and (2) are catalyzed by the methanol synthesis catalyst, and Reaction (3) by the dehydration catalyst. The dehydration reaction drives the chemical system away from the equilibrium restrictions of methanol synthesis. Water, which decreases the rate of dehydration for most dehydration catalysts, is formed in the dehydration reaction, but is consumed by the water gas shift reaction. Furthermore, hydrogen formed by the water gas shift reaction increases the rate of methanol synthesis. All these three reactions form a synergistic system.

This synergy results in higher syngas conversion and methanol equivalent productivity (MEP, defined as the productivity of methanol plus two times the productivity of DME) for LPDME. This increase has been demonstrated in the DOE 10 TPD slurry bubble-column process development unit (AFDU) at LaPorte, Texas and by the experiments conducted in our lab autoclave units [1]. Columns 6 and 7 in Table 1 compare the results from LPDME runs with those from the liquid phase methanol (LPMEOH). These runs used the feed gases that simulate the syngas compositions of three typical industrial gasifiers. In the LPDME runs γ-aluminum was the dehydration catalyst. It can be seen that LPDME gives much higher productivity than LPMEOH, clearly demonstrating the synergy.

Table 1: LPDME vs. LPMEOH for different feed gases - Experimental results[a].

Feed gas (mol%)	H_2	CO	CO_2	N_2	MEOH Equiv. Prod.[b] LPMEOH	MEOH Equiv. Prod.[b] LPDME	Gain[c]	Exit [MEOH]	$[H_2][CO_2]/[CO]$ in feed
Shell	30	66	3	1	16.4	29.4	13	1.0	1.4
Texaco	35	51	13	1	20.5	29.7	9.2	3.7	8.9
Dow	44	38	16	2	23.2	30	6.8	5.2	18.5

a: Reaction conditions: 250 °C, 750 psig, 6,000 GHSV, a pure Cu-based commercial methanol synthesis catalyst for LPMEOH, and 80 wt.% of the methanol catalyst plus 20% of γ-alumina for LPDME.

b: Defined as the methanol productivity plus two times the DME productivity in terms of moles per hour per kilogram of total catalysts.

c: Defined as the difference in the productivity between LPDME and LPMEOH.

The goal of the following work is to understand more about the synergy to provide us with guidelines in catalyst and process development. Theoretically, the maximum synergy occurs when two things happen: the reaction system reaches equilibrium and the methanol synthesis reaction becomes the rate determining step. As will be shown below, the LPDME system, for all available existing catalysts to our knowledge, will operate in the regime far below its equilibrium limitations. Therefore, the ideal case is when the reaction is run at the methanol synthesis limitation. The extent to which this limit is approached depends on several factors, including feed gas composition and dehydration activity.

Column 8 in Table 1 shows that the "gain" in the methanol equivalent productivity for LPDME is more pronounced for more CO-rich gas (e.g., Shell gas) than for more H_2-rich gas (e.g., Dow gas). In other words, there is a stronger synergy for CO-rich gas. This can be explained by the different water levels resulting from different feed gases. Water is known to retard the rate of the dehydration reaction [5]. In a CO-rich environment, water formed by dehydration can be converted by the water gas shift reaction at a high enough rate to keep the rate of methanol dehydration similar to or even greater than that of methanol synthesis. In the extreme case, the net formation rate of water and methanol will be negligible, and the overall reaction will be approximately

$$3CO + 3H_2 \Leftrightarrow CH_3OCH_3 + CO_2 \qquad (4)$$

This turns out to be the case for Shell gas at the conditions given in the table, as we observed ~500 ppmv water and less than 1 mol % methanol in the reactor effluent. When a H_2-rich gas is used, water formed from methanol dehydration cannot be shifted away because hydrogen pushes the shift reaction in the reverse direction. The dehydration step then becomes the bottleneck. An indication of this is the build-up of methanol, as shown in Column 9 in Table 1 for Dow gas. For the same reason, CO_2 in the feed gas will also prevent the synergy from reaching its full potential. In general, the ratio of $[H_2][CO_2]/[CO]$ of the feed gas (Column 10 in Table 1) serves as a good index for the water level under LPDME reaction conditions, and for the "gain" one may achieve going from LPMEOH to LPDME.

This point is illustrated by the following kinetic simulations of LPDME for feed gases of different H_2/CO ratios. The rate expressions and kinetic parameters are obtained from our lab data collected from catalyst systems containing the commercial methanol catalyst and γ-alumina. The reactor is simulated as a CSTR. As shown in Table 2, the "gain" decreases with increasing H_2/CO ratio, accompanied by increasing water and methanol concentration. The effect of water on the dehydration reaction is most evident in the case of H_2/CO ratio equal to 2. The DME productivity is smaller than that of the other two ratios even though the methanol concentration in the reactor is much greater.

Table 2: LPDME performance vs. feed gas composition - Kinetic simulations[a].

H_2:CO in feed	Gain	Exit composition (mol %)			Productivity[b]		
		H_2O	MEOH	DME	MEOH	DME	MEP[b]
0.5	17.8	0.10	0.63	8.52	1.25	16.86	35.0
1.0	16.1	0.31	4.09	9.88	7.4	17.87	43.2
2.0	7.8	0.46	8.42	7.04	15.45	12.93	41.3

a: Reaction conditions: 250 °C, 750 psig, 6,000 GHSV, methanol catalyst:dehydration catalyst = 80:20. The feed gas contains only H_2 and CO.

b: In gmol/hr/kg of total catalyst weight. MEP stands for methanol equivalent productivity.

It follows that one way to enhance the synergy is to use a dehydration catalyst of great activity. This is readily accomplished in kinetic simulations by increasing the value of the dehydration rate constant, k_d. As shown in Figure 1, when the dehydration rate constant is increased by a factor of two ($2xk_d$), the methanol equivalent productivity increased about 7% for the feed gas with H_2/CO ratio of 1 and 2, but not for the gas with 0.5 H_2/CO ratio. Increasing the rate constant by a factor of 4 only results in an additional 3.6% increase for the feed gas with 2.0 H_2/CO ratio. Further increasing k_d to 8 times its original value does not result in increased productivity (not shown). The ineffectiveness of increasing k_d on the productivity is the indication that the synergy has reached its full potential, i.e., methanol synthesis rate limits the productivity. This occurs for the 0.5 H_2/CO feed gas at the base k_d, 1.0 H_2/CO feed gas at $2xk_d$, and 2.0 H_2/CO feed gas at $4xk_d$. This is shown in Fig. 2 by the change in the methanol concentration as a function of feed gas composition and dehydration rate constant.

Also shown in Figure 1 is the equilibrium productivity for the LPDME reaction system at different feed gas compositions. There is a large gap between what the thermodynamics allows and what a typical, currently available, catalyst system can deliver. The improvement in the dehydration activity can only help to some extent before the rate of methanol synthesis becomes the bottleneck. Even with a hypothetical catalyst system of much greater activity for both methanol synthesis ($3xk_m$) and methanol dehydration ($5xk_d$), the gap between the current catalyst system and the equilibrium remains wide.

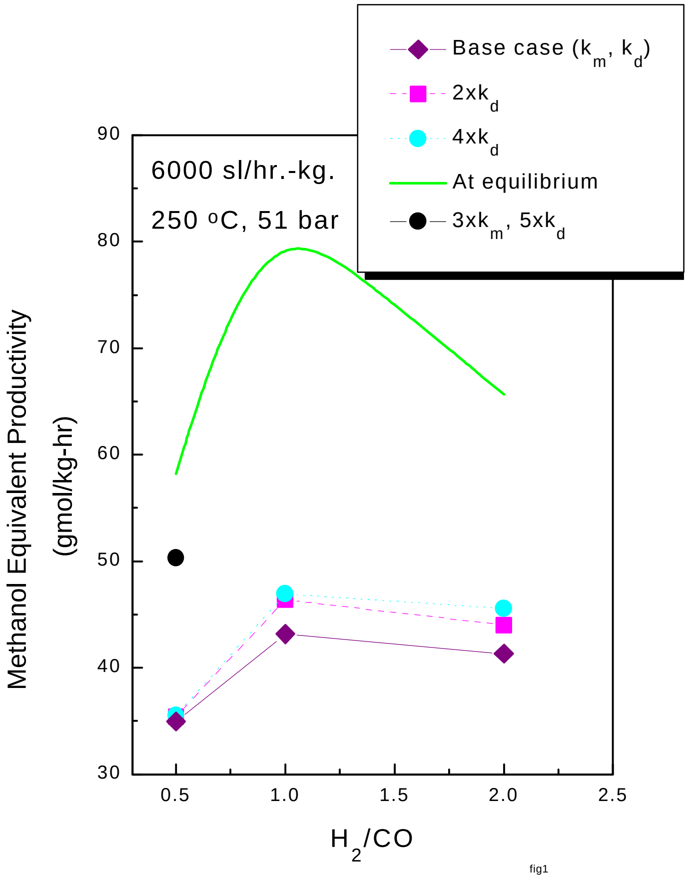


Fig. 1: The productivity as a function of feed gas composition and rate constants.

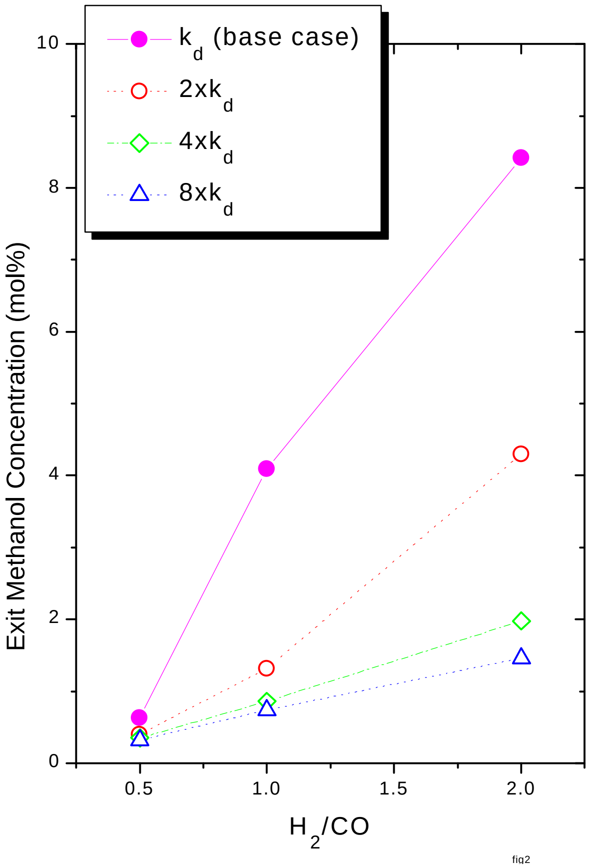


Fig. 2: The methanol concentration as a function of feed gas composition and dehydration rate constant.

It would appear that the ratio of the two catalysts could be an important parameter in optimizing the synergy. However, the simulations show that the optimal ratio is not very sensitive to the change in the gas composition or the magnitude of the rate constants. Although all trends discussed above are based on the simulations with a fixed catalyst ratio (80:20), they should hold if one optimizes the catalyst ratio for each given set of conditions.

Let us summarize the understandings we obtained from the kinetic studies and their implication to the LPDME process and commercial applications.

(1) Greater syngas conversion per pass or production rate can be obtained going from LPMEOH to LPDME due to a chemical synergy. The magnitude of the effect of the synergy depends on the feed gas composition and is most pronounced for CO-rich syngas. (The production rate is doubled in the Shell-type gas case.) A CO-rich environment allows the synergy to reach its maximum potential by maintaining a low water level.

(2) In methanol synthesis the production rate for CO-rich feed gas is much lower than that for H_2-rich feed gas. This difference is significantly narrowed in the one-step syngas to DME process because of

the stronger effect of the synergy on CO-rich syngas, making the process particularly suitable for CO-rich (e.g., coal-derived) syngas.

(3) Greater dehydration activity would allow realization of the full potential of the synergy in LPDME for H_2-rich feeds, e.g., those from natural gas.

(4) The current LPDME system is severely limited by reaction rates. The equilibrium productivity of the LPDME process would be about twice as much as what the currently available catalyst system can deliver. The improvement must await the development of more active methanol synthesis catalysts, given that catalysts with much greater dehydration activity than γ-alumina already exist.

(5) The efficient heat removal and fine temperature control provided by a slurry phase reactor makes heat management no longer the limiting factor in a syngas conversion process, which is normally highly exothermic. Thus the slurry phase reactor provides us the luxury to discuss greater syngas conversion per pass or production rate and play with the kinetics for further improvement. In the traditional gas phase methanol synthesis, the process is forced to run at H_2-rich environment with large H_2 recycle and low overall syngas conversion because of the difficult heat management. Although a gas phase single step syngas to DME process would provide the same synergy for greater production rate as in LPDME, the process is most likely to be still subject to the limitation in heat removal, therefore preventing effective realization of the synergy.

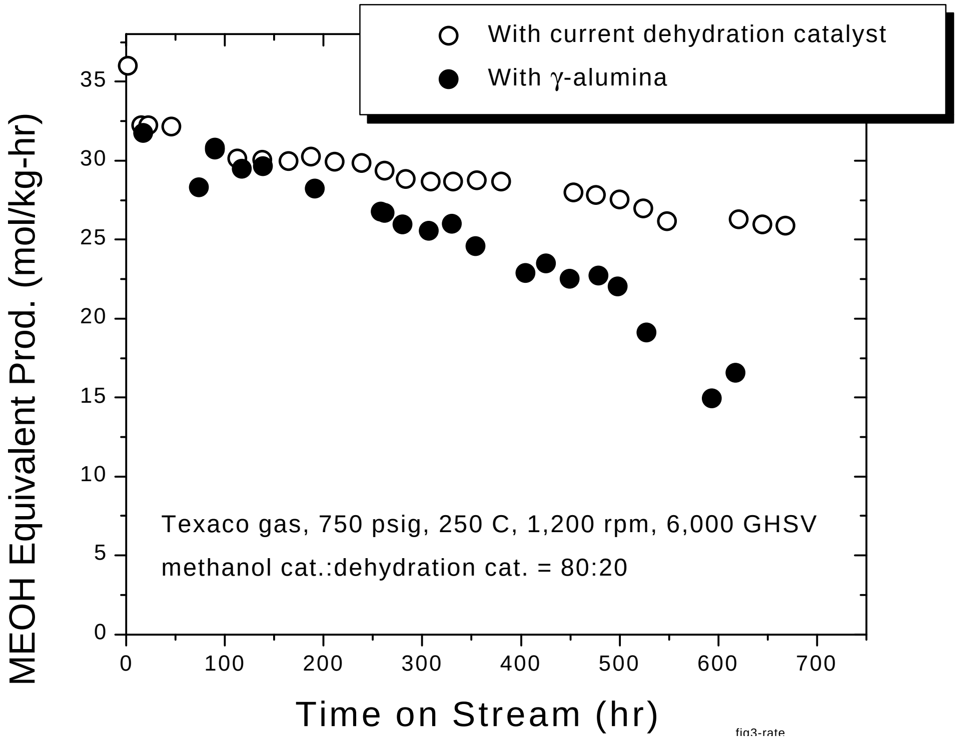
The advantages of LPDME discussed above relates directly to its potential applications. High productivity means low cost DME, especially from coal. High syngas conversion per pass is also important when LPDME is incorporated into the IGCC process, because LPDME in IGCC will be an once-through operation and high syngas conversion per pass directly enhances efficiency.

2. Development of Stable Catalyst Systems for LPDME

The previous dual catalyst system studied in our lab and demonstrated at the AFDU consists of a commercial methanol synthesis catalyst and γ-alumina. Both catalysts deactivate rapidly under LPDME conditions. The cause for this accelerated deactivation has been investigated and the results were reported previously [6]. In brief, the deactivation is caused by a detrimental interaction between the two catalysts. Intimate contact between catalyst particles in the slurry is necessary for the interaction to take place. The interaction is possibly due to inter-catalyst mass transfer or migration under the reaction conditions. For example, Zn- and/or Cu-containing species may migrate onto the alumina to poison the acid sites, therefore, destroying the dehydration activity. In the meantime, the methanol catalyst loses its activity by losing its active components. Acid sites on the dehydration catalyst also appear to play an important role in this interaction. The sites with great acidic strength result in more rapid deactivation of the methanol catalyst, while the strong sites themselves also have a higher rate of deactivation. The type of acid sites is also a factor; Brønsted acid sites are more vulnerable under LPDME conditions.

Based on these observations, dehydration catalysts of desired features have been screened. A stable dual catalyst system for LPDME has been identified and reported in the last year’s conference. This year’s work included optimization of the composition of the new dehydration catalyst, study of the preparation parameters and investigation of the catalyst stability under different reaction conditions. Further progress has been made. The performance of the current catalyst system is plotted in Figure 3. It can be seen that great improvement in stability has been achieved without sacrificing productivity, as compared with the previous system containing a commercial methanol catalyst and γ-alumina.. The stability of this catalyst system meets the requirements of our economics evaluation.

Figure 3: The performance of the current LPDME catalyst system.



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