

Kinetic mechanism of dimethyl ether production process using syngas from integrated gasification combined cycle power plant

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Abstract—In a 1-step synthesis gas-to-dimethyl ether process, synthesis gas is converted into dimethyl ether (DME) in a single reactor. Three reactions are involved in this process: methanol synthesis, methanol dehydration and water gas shift, which form an interesting reaction network. The interplay among these three reactions results in excellent syngas conversion or reactor productivity. The higher syngas conversion or reactor productivity in the syngas-to-DME reaction system, compared to that in the syngas-to-methanol reaction system, is referred to as chemical synergy. This synergy exhibits a strong dependence on the composition of the reactor feed. To demonstrate the extent of this dependence, simulations with adjusted activity for each reaction were performed to reveal the relative rate of each reaction. The results show that the water gas shift reaction is the most rapid, being practically controlled by the equilibrium. Both methanol synthesis and methanol dehydration reactions are kinetically controlled. The role of the dehydration reaction is to remove the equilibrium barrier for the methanol synthesis reaction. However, the role of the water gas shift reaction is more complex; it helps the kinetics of methanol dehydration by keeping the water concentration low, which in turn enhances methanol synthesis. It also readjusts the H_2 : CO in the reactor as the reactions proceed. In the CO-rich regime, the water gas shift reaction supplements the limiting reactant and H_2 by reacting water with CO. This enhances both the kinetics and thermodynamic driving force of the methanol synthesis reaction. In the H_2 -rich regime, water gas shift consumes the limiting reactant, CO, which harms both the kinetics and thermodynamics of methanol synthesis. An understanding of these complex roles of the methanol dehydration and water gas shift reactions and of their dependence on the syngas composition explains why the synergy is high in the CO-rich regime, but decreases with the increasing H_2 or CO_2 content in the reactor feed. The analysis shows that the optimal H_2 : CO for the LPDME reactor is around 1-to-1, in good agreement with the results from the simulation. While the 1-to-1 feed provides a good foundation for some process configurations, it does not match the composition of syngas, which typically has a H_2 : CO of 3 : 1 or greater.

Keywords: Dimethyl Ether, LPMEOH, LPDME

INTRODUCTION

The international crude oil market has been experiencing record high prices. The International Energy Agency (IEA) warned that there could be another oil market crisis within five years due to supply limit and now the oil price is going up to around 70 dollars per gallon. With high oil prices the integrated gasification combined cycle (IGCC) technology has drawn attention to be one of the alternatives available in the power generation sector. IGCC is regarded as environmentally friendly and one of the most energy-efficient power generation sources. There are many IGCC related projects being undertaken in developed countries including Korea, China and Japan for their commercialization. Those projects are utilizing more than ten years of related experience with various feedstock including coal.

Dimethyl ether (DME) seems to be a superior candidate especially for IGCC Power Plant and automotive application [1-3]. Also, DME is an important chemical intermediate for the production of chemicals such as ethylene, dimethyl sulfate, and methyl acetate. Since DME is non-toxic and non-corrosive component, it can be used as a solvent [4-7]. Therefore, it is very important as one of the

clean fuels in the 21st century, which may solve some problems originating from energy supply and environmental protection. DME is also a potential chemical feedstock and refrigerant replacement [8,9].

There are two methods for the production of DME from syngas derived from the IGCC process. One is the 2-step method: formation of methanol from synthesis gas and then production of DME by dehydration of methanol. The other is the 1-step method: direct formation of DME from syngas. DME is traditionally produced by the 2-step method. In this method, pure methanol is produced from syngas in methanol unit, and then the produced methanol is converted to DME in an adiabatic fixed bed reactor in DME unit. The cost penalties of the 2-step process are (1) limited productivity in the syngas-to-methanol reactor due to equilibrium constraints, and (2) the need for a separate dehydration reactor and associated separation units [10,11].

DME can directly be prepared from syngas in 1-step method process. In this new process, methanol production and dehydration reactions occur simultaneously on bi-functional catalysts in only one reactor, and consequently the methanol production plant can be eliminated. Therefore, the 1-step method has many advantages, for instance, cost reduction of equipment and energy saving. The main driving force for developing a 1-step syngas-to-DME process is to produce DME at a cost lower than that from the commercially available 2-step process, namely, syngas-to methanol followed by meth-

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anol dehydration in sequential reactors [12,13].

The 1-step syngas-to-DME process overcomes these two obstacles by combining the synthesis and dehydration reactions and utilizing the greater synthesis productivity made possible by a chemical synergy from the combined reactions. And, in the 1-step syngas-to-DME process, syngas is converted DME in a single reactor. Three reactions are involved in this process: methanol synthesis, methanol dehydration and water gas shift, which form an interesting reaction network. The interplay among these three reactions results in excellent syngas conversion or reactor productivity. The higher syngas conversion or reactor productivity in the syngas-to-DME reaction system, compared to that in the syngas-to-methanol reaction system, is referred to as chemical synergy. This synergy exhibits a strong dependence on the composition of the reactor feed.

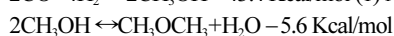
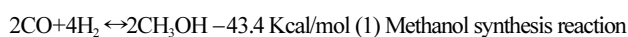
In recent years, many studies have been undertaken for the 1-step syngas-to-DME process in various reactor configurations. However, the 1-step method of DME synthesis has not yet been optimized on the face of its performance: syngas conversion and reactor productivity in DME reactor system.

In this study, we developed a simulation model through a kinetics model of the PROII simulator, performed to detect operating characteristics of the 1-step method process for the production of DME from syngas derived from the IGCC process: methanol formation and production of DME by dehydration of methanol at the same time. And, to demonstrate the extent of a dependence on the composition of the reactor feed, simulations with adjusted activity for each reaction were performed to reveal the relative rate of each reaction. This simulation results will show that there are possibilities of 1-step DME synthesis from IGCC Power Plant.

DME SYNTHESIS PROCESS WITH SYNGAS FROM IGCC

1. Mechanism for DME Synthesis Reaction

In 1-step DME synthesis process, three reactions mainly happen:



(2) Methanol dehydration reaction



Reactions (1) and (3) are catalyzed by Cu-based methanol synthesis catalyst (MSC), and reaction (2) is catalyzed by $\gamma\text{-Al}_2\text{O}_3$ methanol dehydration catalyst (MDC) [14]. MSC and MDC make up for the composite catalyst for 1-step DME synthesis by mixing them together mechanically. The presence of the dehydration reaction frees the overall synthesis gas conversion from the equilibrium constraint imposed by the thermodynamics of methanol synthesis alone. The system offers further kinetic enhancement by lowering the water level through water gas shift reaction, therefore accelerating methanol dehydration. This synergy of methanol synthesis, methanol dehydration, and water gas shift gives higher syngas conversion per pass or productivity compared to the syngas-to-methanol process. The synergy has long been recognized and demonstrated [15,16]. Experimental work has been conducted to study the performance of the reaction system as a function of various reaction parameters such as syngas composition (for example, H_2 :CO, CO_2 and H_2O content), catalyst materials and composition, space velocity, pres-

sure, and temperature [17-21]. Noticeably absent from the prior work is a fundamental and systematic analysis of the reaction system. Limited explanations have been attempted, but mostly on the basis of thermodynamics [16,19,22]. The synergy of the system is limited by the kinetics of the reaction system. Analysis based on thermodynamic equilibrium calculations is inadequate and could even be misleading. The inquiry into the mechanism of the synergy led us to a kinetic study of the reaction system, which, in turn, led to a better understanding of the process.

This study describes the kinetic understanding of this reaction system, including why the synergistic effect varies with reaction parameters, what kind of role each reaction plays in the synergy, and what the process guidelines are for optimizing the synergy.

How to accommodate the best kinetic conditions in a process is another practical matter. For example, our kinetic study demonstrates that the overall best reaction for the syngas-to-DME reactor is:



While this gives the highest reactor productivity, it also sacrifices one-third of the carbon to CO_2 . This reaction scheme poses a mismatch between the best syngas composition to the reactor (H_2 :CO ratio of 1:1) and the composition of the syngas that can be generated by commercially available conversion units. The H_2 :CO ratio from most syngas generation units is not 1:1, except for the case of the CO_2 -methane reformer. For coal-derived, CO-rich syngas, this problem can be solved readily by injecting water into the reactor to provide the extra hydrogen through water gas shift reaction.

All specific examples in this study are based on a slurry phase reactor that behaves like a single, continuously stirred tank reactor (CSTR). Therefore, the results are directly applicable to the liquid phase syngas-to-DME process (LPDME) under the development of Air Products, which consists of a slurry phase autoclave or bubble column reactor with catalyst powders suspended in an inert liquid medium.

2. Details of Simulations

All kinetic experiments were performed in 300 cc slurry phase autoclave reactors. The dual-catalyst system consisted of a powdered mixture of a commercial, copper-based methanol synthesis catalyst and γ -alumina dehydration catalyst suspended in a hydrocarbon oil. For comparison, the results from liquid phase syngas-to-methanol (LPMEOH) experiments were also used. In the LPMEOH experiments, the slurry contained only the methanol catalyst. The reactor behaved as a CSTR and was free of mass transfer limitations. Conditions used for all experiments were 250 °C, 52 MPa, 80:20 weight ratio of the methanol synthesis catalyst to the methanol dehydration catalyst. The gas hourly space velocity of 6,000 sl/kg-hr was used in all kinetic simulations, unless specified.

The kinetic simulations were based on this lab reaction system, i.e., a CSTR and the same catalyst mixture. The reaction conditions were the same as described above. The rate expressions and constants for the three reactions were obtained by using the standard reaction system. All three rate expressions were a power law form multiplied by an approach-to-equilibrium term as shown below:

Methanol synthesis reaction

$$r_m = k_m f_{\text{H}_2}^{a1} f_{\text{CO}}^{b1} (1 - \text{app}_m), \text{ app}_m = \frac{f_{\text{CH}_3\text{OH}}}{f_{\text{H}_2} f_{\text{CO}} k_m} \quad (5)$$

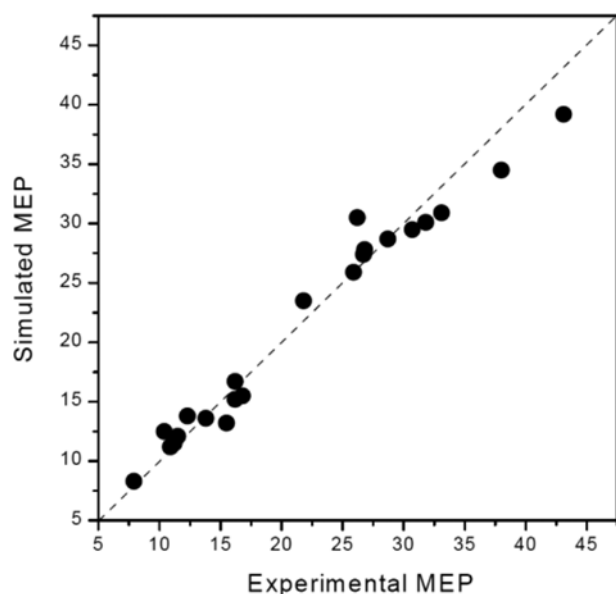


Fig. 1. Comparison of the methanol equivalent productivity (MEP) from LPDME experiments with that from kinetic simulations.

Water gas shift reaction

$$r_w = \frac{k_w f_{CO}^{a2} f_{H_2O}^{b2}}{f_{CO_2}^2} (1 - \text{app}_w), \text{app}_w = \frac{f_{CO} f_{H_2}}{f_{CO_2} f_{H_2O} k_w} \quad (6)$$

Methanol dehydration reaction

$$r_d = \frac{k_d f_{CH_3OH}^{a3}}{f_{H_2O}^{b3} f_{DME}^{c3}} (1 - \text{app}_d), \text{app}_d = \frac{f_{DME} f_{H_2O}}{f_{CH_3OH}^3 k_d} \quad (7)$$

where f_i stands for the fugacity of component i and “app.” is the approach to equilibrium. The methanol equivalent productivity (or MEP, defined as the methanol productivity plus two times the DME productivity) from various lab experiments and their corresponding simulations is plotted in Fig. 1. The good agreement indicates that the rate expressions and the process model can well serve the purpose of the current investigation.

Process simulations were used to demonstrate the technical feasibility of the process schemes described in this study. The syngas-to-DME reactor model was the same as described above, except that the ratio of the methanol catalyst to the dehydration catalyst was changed from 80 : 20 to 50 : 50. As for modeling the syngas generation unit, commercially relevant conditions were used.

RESULT AND DISCUSSION

The chemical synergy of the LPDME system is due to the interplay among methanol synthesis, methanol dehydration and water gas shift reactions. The synergy is reflected in the system's higher syngas conversion or productivity compared with methanol synthesis only. Therefore, one can use the percentage increase in the productivity from LPMEOH to LPDME under the same reaction conditions (i.e., temperature, pressure, space velocity, feed composition) as a quantitative measure of the synergy. Since one mole of DME is equivalent to two moles of methanol, one can use the MEP, defined as the methanol productivity plus two times the DME pro-

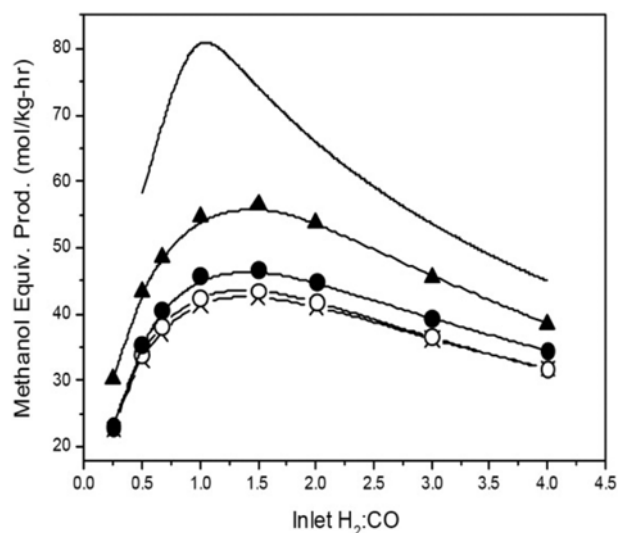


Fig. 2. The methanol equivalent productivity as a function of $H_2 : CO$ ratio in the syngas feed for catalyst systems with different activities. (X) k_m , k_d and k_w , i.e., the base catalyst system; (●), k_m , $4k_d$ and k_w ; (▲) $4k_m$, k_d and k_w ; (○) k_m , k_d and $4k_w$; (–) at equilibrium.

ductivity, to compare the productivity of the two reaction systems. In this subsection, we will discuss the dependence of the synergy on the feed gas composition (e.g., $H_2 : CO$) and the underlying mechanism.

To understand the dependence of the chemical synergy on the $H_2 : CO$ of the reactor feed, let us first determine if the reaction system is limited by thermodynamics or kinetics. If it is the latter, then what is the rate-determining reaction(s) in the system? This can be ascertained by simulating the change in MEP while varying the rate constant for each reaction. Fig. 2 depicts the MEP for (1) our base catalyst system (k_m , k_d and k_w), (2) the system with the methanol synthesis activity increased by a factor of 4 ($4k_m$, k_d and k_w), (3) the system with the dehydration activity increased by a factor of 4 (k_m , $4k_d$ and k_w), and (4) the system with the water gas shift activity increased by a factor of 4 (k_m , k_d and $4k_w$). Also shown in figure is the MEP when the system is at thermodynamic equilibrium.

An examination of Fig. 2 leads to four observations. At first, the reaction system is kinetically limited. At the maximum productivity ($H_2 : CO$ of about 1 : 1), the MEP with the base catalyst system (k_m , k_d and k_w) is only one-half of the potential maximum MEP. This observation holds true even when a space velocity as low as 2,000 is used (not shown). Therefore, to understand the reaction system, one needs to look at the kinetics. Using only thermodynamic equilibrium calculations is inadequate and possibly misleading.

Secondly, the rate of the water gas shift reaction is much greater than the rate of the other two reactions. Quadrupling the rate constant of the shift reaction (case of k_m , k_d and $4k_w$) results in little increase in MEP. The simulations also show that the water gas shift reaction is essentially thermodynamically limited over the entire range of this study. Therefore, the role of this reaction in the synergy is to re-adjust the concentration of H_2 , CO , CO_2 , and H_2O through the thermodynamic equilibrium among the four components.

Thirdly, both methanol synthesis and methanol dehydration reactions are kinetically limited. Increasing the rate constant of each of

these two reactions results in higher MEP. These two reactions are not limited by thermodynamic equilibrium because the products from each are consumed by other reactions. For methanol synthesis, the methanol produced is consumed by the dehydration reaction. For methanol dehydration, the water produced is shifted by the water gas shift reaction. Since methanol dehydration and water shift to hydrogen are in sequence, one can view the fast water gas shift reaction as the ultimate sink to drive the system away from equilibrium limitations. In this regard, the water gas shift reaction always has a positive effect on the synergy.

Finally, Fig. 2 demonstrates that increasing the methanol synthesis rate constant (k_m) produces a greater increase in MEP than increasing the dehydration rate constant (k_d). This indicates that the methanol synthesis is more rate-determining than methanol dehydration with our base catalyst system. This is completely true in the CO-rich end of the result, since increasing the dehydration rate constant has little effect on MEP. As the H_2 :CO ratio in the reactor feed increases, increasing dehydration activity starts to show positive effects on MEP. This suggests that the kinetics of the two reactions become more comparable to each other as the reactor feed becomes less CO-rich.

In summary, Fig. 2 shows that the LPDME reaction system is kinetically limited. The kinetics of the water gas shift reaction is much greater than that of the other two reactions. In terms of its effects on the other two reactions, the water gas shift reaction is essentially thermodynamically limited. This fast reaction provides the ultimate sink to drive the other two reactions away from equilibrium. It also re-adjusts the concentration of H_2 , CO , CO_2 , and H_2O as the reactions proceed. The kinetics of methanol synthesis is slower than that of methanol dehydration. Therefore, methanol synthesis is a more rate-determining step between the two kinetically controlled reactions. However, this difference becomes smaller as the H_2 :CO in the reactor feed increases.

In the LPDME system, both problems are mitigated by the dehydration and water gas shift reactions. The dehydration reaction removes its methanol product, expanding the equilibrium boundary. Most of the water formed in the dehydration reaction is converted into H_2 . This self-generated H_2 supply enhances methanol synthesis by replenishing the much-needed limiting reactant and slowing down the approach to equilibrium. In other words, the methanol dehydration and water gas shift reaction have three positive effects on methanol synthesis in the CO-rich regime: (1) consuming methanol to expand the equilibrium boundary, (2) forming H_2 to replenish the limiting reactant, and (3) forming H_2 to slow down the equilibrium. The CO-rich atmosphere enables these three effects to reach their fullest extent. The water gas shift equilibrium drives almost all water into H_2 because the atmosphere is CO-rich. The dehydration kinetics is much greater than the methanol synthesis kinetics, partly because of the lack of H_2 slows methanol synthesis, and partly because the dehydration reaction is not hindered by water. The faster dehydration kinetics keeps the methanol concentration low. Therefore, the equilibrium barrier for methanol synthesis is minimal. All of these explain why the greatest synergy is observed in the CO-rich regime.

These arguments are illustrated by the simulated results shown in Figs. 3 and 4. Fig. 3 depicts the exit composition as a function of reaction feed composition for the base catalyst system. Indeed, the

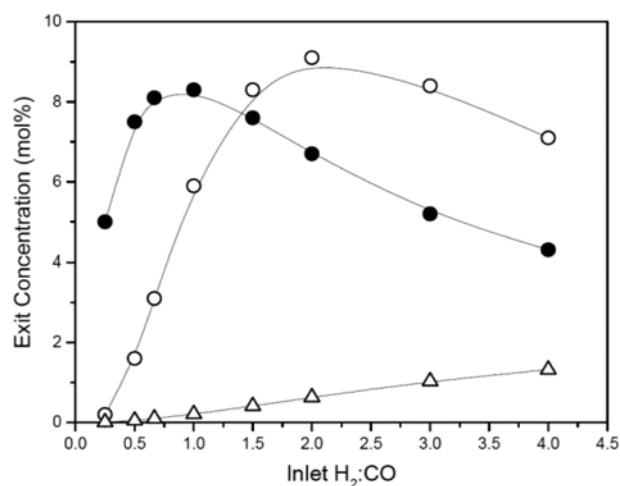


Fig. 3. The exit concentration of methanol (○), DME (●) and water (△) as a function of H_2 :CO ratio in the syngas feed for the base catalyst system. All catalyst activities are in their base values.

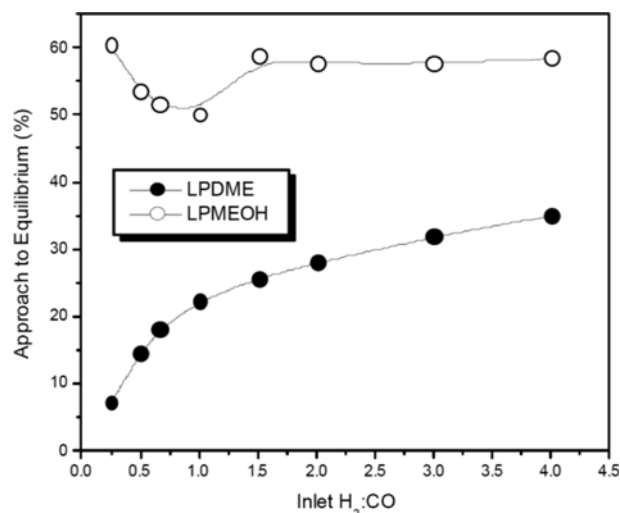


Fig. 4. The approach to methanol synthesis equilibrium for LPDMEOH (○) and LPDME (●) as a function of H_2 :CO ratio in the reactor feed.

water and methanol concentration is low in the CO-rich regime. Fig. 4 shows the approach to methanol synthesis equilibrium for both LPDMEOH and LPDME. A greater decrease in the approach is observed in the CO-rich regime from LPDMEOH to LPDME.

In the intermediate regime ($0.75 < H_2$:CO < 2), all three positive effects of the methanol dehydration and water gas shift reactions still contribute to the synergy, but to a lesser extent. First, the kinetics of methanol synthesis improves as the H_2 :CO ratio increases. The lack of H_2 is no longer sharply felt as in the CO-rich regime. Therefore, replenishing H_2 through the water gas shift reaction has less effect on methanol synthesis.

Secondly, the dehydration kinetics is less effective at removing methanol, and therefore it is less effective at expanding the equilibrium boundary for methanol synthesis. The kinetics of methanol dehydration no longer dominates that of the methanol synthesis reac-

tion, as evidenced by the increasing methanol concentration in this regime (Fig. 3). This occurs partly because the kinetics for methanol synthesis is greater due to better H_2 availability, and partly because the dehydration reaction is retarded by the increasing amount of one of its products, water, in this regime (Fig. 3). This self-restricting behavior for the methanol dehydration reaction has long been known [23] and is reflected in our kinetic model (Eq. (7)). This retardation is evidenced by the results shown in Fig. 3. Although the methanol concentration increases as the $H_2 : CO$ increases (higher reactant concentration for dehydration), the DME concentration decreases (lower dehydration rate), accompanied by increasing water concentration. The lower dehydration rate is totally due to the water retardation, because the approach to methanol dehydration equilibrium is around 1% in the regime. The increasing water concentration with increasing $H_2 : CO$ is determined by the water gas shift equilibrium. In brief, the decreasing synergy in this regime is due to the diminishing positive effects by the water gas shift and methanol dehydration reactions as the $H_2 : CO$ ratio increases.

Why is there little synergy in the H_2 -rich regime ($H_2 : CO > 2$)? With an even higher $H_2 : CO$, the effect of the methanol dehydration reaction on expanding the methanol equilibrium boundary becomes even smaller. What further diminishes the synergy is the role change of the water gas shift reaction. Note that the limiting reactant for methanol synthesis becomes CO in this regime. Shifting the water formed by dehydration depletes CO, reducing the availability of the limiting reactant for methanol synthesis. It also accelerates the approach to methanol synthesis equilibrium (the approach = $f_{CH_3OH}/f_{H_2}^2 f_{CO} k_m$). Therefore, the two positive effects of water gas shift reaction in the other two regimes become negative in the H_2 -rich regime. With the negative effects of the water gas shift reaction and smaller positive effects of the dehydration reaction, the synergy decreases.

Although these observations were made from a reactor feed containing only H_2 and CO, the understanding gained can be applied to more general cases. For example, the above discussion shows that as $H_2 : CO$ in reactor feed increases, the three positive effects of methanol dehydration and water gas shift reactions decrease. This is due to the less favorable equilibrium conditions for water conver-

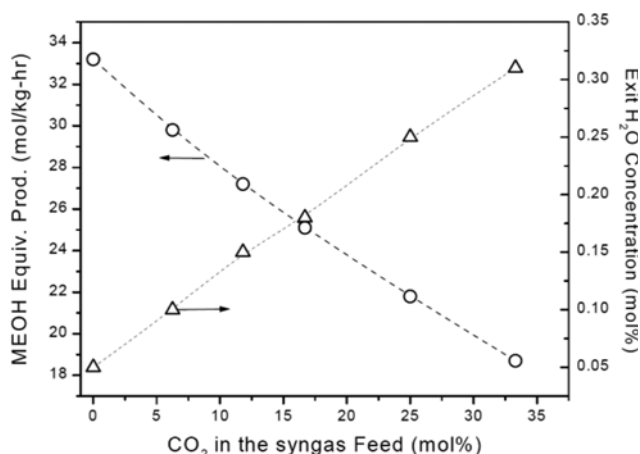


Fig. 5. The methanol equivalent productivity and the exit water concentration as a function of CO_2 concentration in the syngas feed. $H_2 : CO$ ratio is fixed at 1 : 2.

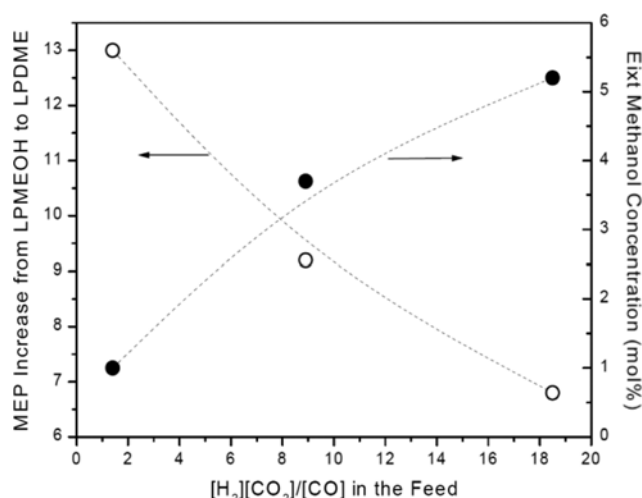


Fig. 6. The MEP increase from LPMEOH to LPDME and the exit methanol concentration as a function of the $[H_2][CO_2]/[CO]$ ratio in the syngas feed.

sion into hydrogen. It follows then that increasing the CO_2 content in the reactor feed should have a similar effect (cf., Eq. (3)). This is borne out by the simulation shown in Fig. 5: MEP decreases with increasing CO_2 concentration in the syngas feed, accompanied by an increase in the water concentration. This agrees well with the experimental observation that removing CO_2 in the syngas feed leads to higher productivity [17]. CO_2 is an undesirable component in the feed because, like H_2 , it adversely affects the synergy by building up water, but unlike H_2 , CO_2 does not contribute to methanol synthesis under syngas-to-DME conditions.

We can now explain the question asked at the beginning of this section. The feed gas in all these cases no longer contains only H_2 and CO, but also CO_2 . However, the collective effect on the synergy can be explained in terms of the $[H_2][CO_2]/[CO]$ ratio in the feed. Since the water gas shift reaction is practically equilibrium limited, the water level (not measured in these experiments) should be somehow proportional to this ratio. Then, as expected, the increase in MEP from LPMEOH to LPDME decreases with an increase in this ratio, accompanied by an increase in the experimentally measured methanol concentration (Fig. 6).

CONCLUSION

The results discussed above have the following process:

(1) There is considerable synergy under CO-rich conditions. Therefore, for a fixed CO-rich reactor feed (e.g., coal-derived syngas in a once-through operation), the syngas-to-DME process will give a much higher MEP than the syngas-to-methanol process. In practical process engineering terms, there is a potential for greater operating flexibility in an electricity-chemical co-production arrangement with IGCC.

(2) It is preferred that CO_2 in the feed be minimized.

The previous section focuses on the mechanism of the chemical synergy, i.e., comparison between LPDME and LPMEOH. As shown in Fig. 2, the maximum MEP is obtained between $H_2 : CO$ of 1 : 1 and 2 : 1, not at the CO-rich end. This can be ascribed to the trade-off between the best syngas composition for methanol synthesis

and that for the synergy, since methanol synthesis is favored by a H_2 -rich environment with the maximum rate at a $H_2 : CO$ of 2 : 1 (LPMEOH curve in Fig. 2). Through the analysis, the optimal $H_2 : CO$ for the LPDME reactor is around 1-to-1; in good agreement with the results from the simulation. While the 1-to-1 feed provides a good foundation for some process configurations, it does not match the composition of syngas, which typically has a ratio $H_2 : CO$ of 3 : 1 or greater.

NOMENCLATURE

K_d	: equilibrium constant of methanol dehydration reaction
K_m	: equilibrium constant of methanol synthesis reaction
K_w	: equilibrium constant of water gas shift reaction
f_i	: fugacity of component i
k_d	: reaction rate constant of methanol dehydration reaction
k_m	: reaction rate constant of methanol synthesis reaction
k_w	: reaction rate constant of water gas shift reaction
r_d	: reaction rate of methanol dehydration reaction [$\text{mol g}_{cat}^{-1}\text{s}^{-1}$]
r_m	: reaction rate of methanol synthesis reaction [$\text{mol g}_{cat}^{-1}\text{s}^{-1}$]
r_w	: reaction rate of water gas shift reaction [$\text{mol g}_{cat}^{-1}\text{s}^{-1}$]

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