

# Liquid phase methanol and dimethyl ether synthesis from syngas

Sunggyu Lee\* and Abhay Sardesai

University of Missouri-Columbia, Columbia, MO 65211

The Liquid Phase Methanol Synthesis (LPMeOH<sup>TM</sup>) process has been investigated in our laboratories since 1982. The reaction chemistry of liquid phase methanol synthesis over commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts, established for diverse feed gas conditions including H<sub>2</sub>-rich, CO-rich, CO<sub>2</sub>-rich, and CO-free environments, is predominantly based on the CO<sub>2</sub> hydrogenation reaction and the forward water-gas shift reaction. Important aspects of the liquid phase methanol synthesis investigated in this in-depth study include global kinetic rate expressions, external mass transfer mechanisms and rates, correlation for the overall gas-to-liquid mass transfer rate coefficient, computation of the multicomponent phase equilibrium and prediction of the ultimate and isolated chemical equilibrium compositions, thermal stability analysis of the liquid phase methanol synthesis reactor, investigation of pore diffusion in the methanol catalyst, and elucidation of catalyst deactivation/regeneration. These studies were conducted in a mechanically agitated slurry reactor as well as in a liquid entrained reactor. A novel liquid phase process for co-production of dimethyl ether (DME) and methanol has also been developed. The process is based on dual-catalytic synthesis in a single reactor stage, where the methanol synthesis and water gas shift reactions takes place over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts and the *in-situ* methanol dehydration reaction takes place over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Co-production of DME and methanol can increase the single-stage reactor productivity by as much as 80%. By varying the mass ratios of methanol synthesis catalyst to methanol dehydration catalyst, it is possible to co-produce DME and methanol in any fixed proportion, from 5% DME to 95% DME. Also, dual catalysts exhibit higher activity, and more importantly these activities are sustained for a longer catalyst on-stream life by alleviating catalyst deactivation.

**KEY WORDS:** dimethyl ether (DME); methanol; alcohol; diesel fuel; LPG; fuel cell; olefins; aerosol; syngas; natural gas; coal; biomass; methanol; oxygenates; ethers; kinetics; thermodynamics; slurry; liquid phase; catalyst deactivation.

## 1. Introduction

Synthesis gas, or syngas, is a gaseous mixture consisting of hydrogen, carbon monoxide, and carbon dioxide in varying amounts. Syngas can be produced via a variety of processes including steam reforming of natural gas and advanced gasification of coal. The catalytic synthesis of methanol from syngas has been conventionally carried out in two-phase reactors with the syngas and products in the vapor phase and the catalyst constituting the solid phase. The large exothermic heat of reactor in addition to the low heat capacity of the vapor increases the potential for thermal runaway and damage to the catalyst in the vapor phase, thus limiting the maximum operable reaction temperature. The liquid-phase methanol synthesis process (LPMeOH<sup>TM</sup>) was first developed by Chem Systems in the late 1970s [1]. The novel feature of this technology is that methanol is derived from synthesis gas over a finely powdered commercial Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst dispersed in an inert liquid. The slurry-phase operation facilitates easy heat removal, thus enabling isothermal conditions in the reactor system. High agitation rates in the reactor provide for a reaction environment devoid of temperature and concentration gradients. The salient features of the liquid phase process are (i) use of CO-rich syngas, (ii) enhanced heat transfer of exothermic heat, and (iii) high once-through conversion of syngas. A comprehensive review article on liquid-phase methanol synthesis

with emphasis on catalysts, mechanism, kinetics, chemical equilibria, vapor–liquid equilibria, and modeling is available [2].

Our research group, initially at the University of Akron and later at University of Missouri-Columbia, has carried out extensive research related to the liquid phase methanol synthesis process (LPMeOH<sup>TM</sup>) since 1982 [3–41]. Various aspects of the process have been investigated including reaction chemistry, mechanism, kinetics, pore diffusion, external mass transfer, thermodynamics, thermal stability analysis, *in-situ* catalyst reduction, catalyst deactivation, and catalyst regeneration and post-treatment.

Process development work in methanol synthesis conducted by Air Products and Chemicals has been briefly summarized [42–44]. Continued research efforts in this area have also resulted in the development of a liquid-phase single-stage dimethyl ether process from syngas. This process has been studied in great detail [45–54]. Research studies have also been conducted to examine the conversion of dimethyl ether into gasoline-range hydrocarbons [55–57], lower olefins [58–61], and methyl acetate [62]. Research efforts by Air Products and Chemicals in this area have been mentioned [63].

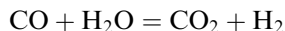
## 2. Methanol synthesis

### 2.1. Process details

The chemistry and reaction mechanisms related to methanol synthesis have been a subject of in-depth

\*To whom correspondence should be addressed.

investigation in our research [3,6,10,23]. The reactions describing methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst primarily involve the CO<sub>2</sub> hydrogenation reaction and the forward water gas shift reaction as shown below:



The liquid phase methanol synthesis reactor has been studied in a 1-liter mechanically agitated slurry reactor. A schematic of the slurry reactor system for methanol synthesis is shown in figure 1. A feed gas having the composition of H<sub>2</sub>:CO:CO<sub>2</sub>:CH<sub>4</sub> = 37.4:46.3:7.7:8.6 was used for all the experiments, unless stated otherwise. This is a typical composition of most CO-rich (unbalanced) gases from commercial gasifiers such as Koppers-Totzek and Texaco gasifiers. Methane is added to the feed in our experiments as a tie element and aids in the material balance, since methane is neither consumed nor produced at reaction conditions. The synthesis reaction takes place on the active sites of the catalyst, which is slurried in high-boiling white mineral oil. The inert oil used in the experiments is Witco 40, while other mineral oils such as Witco 70 and Freezene 100 have shown similar effectiveness. The catalyst used for methanol synthesis, in its unreduced form, consists of coprecipitated CuO and ZnO on Al<sub>2</sub>O<sub>3</sub> support. Two different commercial catalysts were used in these studies. The catalyst manufactured by United Catalysts Inc., designated as EPJ-25, had an average N<sub>2</sub> BET surface area of 80 m<sup>2</sup>/g and a specific pore volume of 0.43 cm<sup>3</sup>/g. The pore size distribution was found to be monodisperse and the average pore diameter was on the order of 200 Å. The catalyst manufactured by BASF is designated S-3-85 and has an N<sub>2</sub>-BET surface area of

86.5 m<sup>2</sup>/g and has a specific pore volume of 0.24 cm<sup>3</sup>/g. The catalysts were crushed to a size of -140 mesh (U.S. standard) in order to avoid pore diffusional limitations. The average screen opening corresponded to 106 microns. The catalysts were extremely selective, and the only products formed in experimentally significant amounts were methanol and water. The catalyst loading was influenced by the need to minimize the influence of external mass transfer limitations, and at the same time to ensure the accuracy of experimental rate measurements. A typical slurry loading consisted of 15 g catalyst in 550 mL (STP) of oil. The liquid medium chosen for the study was a mineral oil, Witco 40, a 72:28 mixture of paraffinic and naphthenic components with a mean molecular mass of about 250.

Commercially available catalysts are in the oxidized form (CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>). To make the catalyst fully active and avoid sintering during activation, a proper procedure for reduction of the catalyst must be followed [14]. Studies were carried out to conduct *in-situ* activation using hydrogen/nitrogen mixtures, whereby the temperature was increased stepwise from 122 to 207 °C. The optimum H<sub>2</sub> concentration in the mixture was determined to be approximately 5 mol% [14].

An investigation has been conducted to determine the composition of the methanol synthesis catalyst in the liquid phase methanol synthesis process [16,23]. X-ray diffraction spectra of unreduced catalysts for EPJ-25 were compared with that of the active catalyst in order to determine the state of copper in the active catalyst. In the X-ray spectrum of an unreduced (i.e., inactive) catalyst, the major phase identified is CuO, which also masks the ZnO phase present in much lesser quantity. In the spectrum of the active catalyst, the CuO peak is replaced by broader peaks, which could represent either Cu<sub>2</sub>O or ZnO. The presence of metallic Cu in the active

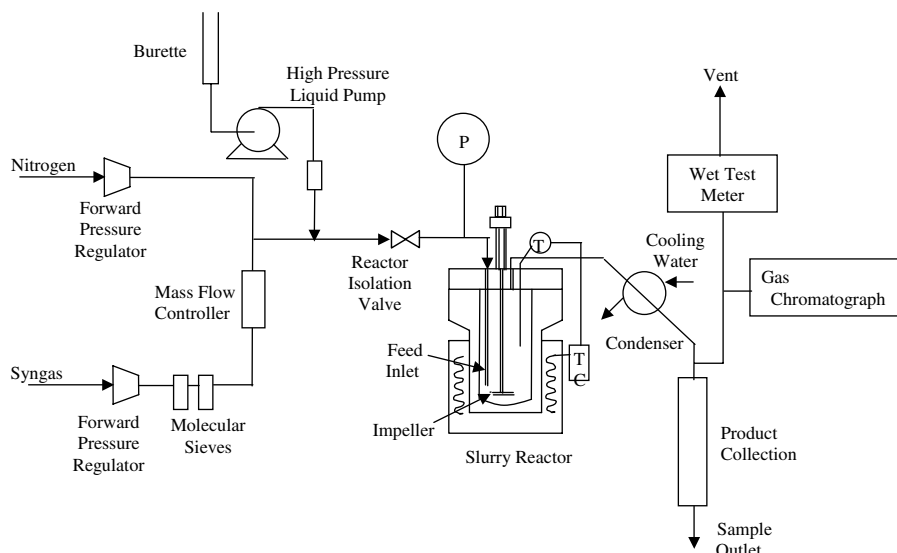


Figure 1. Process schematic of the methanol synthesis slurry reactor experimental process unit.

methanol synthesis catalyst in large amounts was confirmed by the presence of a distinct peak. In the case of X-ray spectra of fresh and active BASF-S3-85 catalyst, the peak for bare metallic Cu was prominently present while other oxidative copper peaks were absent. This establishes the fact that the active methanol synthesis catalyst contains metallic Cu and ZnO. Thus, it is confirmed that metallic Cu is the active component in the methanol synthesis catalyst. Also, at high partial pressures of CO<sub>2</sub>, ZnCO<sub>3</sub> was found to be present in significant amounts in the active catalyst.

## 2.2. Chemistry/mechanism

### 2.2.1. Role of carbon dioxide in methanol synthesis

The role of carbon dioxide on the methanol synthesis reaction is very important and was studied by carrying out different sets of experiments [11,19,21,23] using a CO-free syngas feed (H<sub>2</sub>:CO<sub>2</sub>:CH<sub>4</sub> = 63:32:5), a CO<sub>2</sub>-free syngas (H<sub>2</sub>:CO:CH<sub>4</sub> = 35:55:10) and a reference syngas (H<sub>2</sub>:CO:CO<sub>2</sub>:CH<sub>4</sub> = 36:48:7.6:8.4). These experiments were carried out at 237 °C and 63 atm. The catalyst used for this study was EPJ-25. It was determined that methanol synthesis takes place primarily by CO<sub>2</sub> hydrogenation and the presence of CO<sub>2</sub> is also important to avert catalyst deactivation, whereas CO must be present in the feed to enable the forward water gas shift reaction to take place. The optimization of carbon dioxide content in the syngas feed was studied over the BASF S3-85 catalyst suspended in the Witco-40 oil (loading of 15 g in 550 mL of oil). It was observed that the optimal loading of carbon dioxide depends upon the operating temperature. The investigations were carried out for the CO-rich gas from a Koppers–Totzek Gasifier. At 205 °C in the liquid-phase synthesis, the optimal content of CO<sub>2</sub> in the feed gas is at 4 mol% for a maximum rate of methanol formation, with the value shifting to 6.3 mol% at 225 °C, to 7.2 mol% at 237 °C, and to approximately 8 mol% at 250 °C. This trend can be explained as follows:

1. At low CO<sub>2</sub> concentrations, the rate of methanol formation is limited kinetically, that is the CO<sub>2</sub>-hydrogenation reaction cannot proceed actively in the deficiency of primary reactant, i.e., CO<sub>2</sub>. The water gas shift reaction takes place in the forward direction at low CO<sub>2</sub> concentrations, which enhances the rate of CO<sub>2</sub> hydrogenation by scavenging the byproduct, water, as well as supplies more of the primary reactant, CO<sub>2</sub>.
2. When the CO<sub>2</sub> content in the reactor feed is increased from low to moderate levels, the ratio of the rate of carbon dioxide consumption to methanol production increases. The forward water-gas shift reaction is still active. However, this causes the selectivity of methanol to decrease slightly and the net rate of water production to increase slightly.

3. When the concentration of CO<sub>2</sub> is increased to very high values, the direction of the water-gas shift reaction is altogether reversed. This not only reduces the potential for hydrogenation of CO<sub>2</sub> due to the build up of water, but also causes the reactant CO<sub>2</sub> to be competitively consumed in both the reactions. Therefore, the rate of methanol production is low, and the selectivity to methanol is extremely poor when CO is completely replaced with CO<sub>2</sub> in the reactor feed.
4. If the concentration of CO<sub>2</sub> in the feed is dropped to very low values, the potential for carbon deposition, and/or reduction of catalyst oxides is increased, thereby increasing the danger of catalyst deactivation. The catalytic activity drops significantly and progressively when it is exposed to a CO<sub>2</sub>-free syngas feed. The catalyst deactivates in the absence of carbon dioxide. It is probable that the decrease in activity is caused by the deposition of carbon on the catalyst by the Boudouard reaction (2CO = CO<sub>2</sub> + C), since there was no Cu<sup>+</sup> or Cu<sup>++</sup> in the original active catalyst.

### 2.2.2. Role of water in methanol synthesis

The role of water in determining the rate of methanol synthesis has also been investigated [11,12,20,23]. At 205 °C, a low reaction temperature, it was observed that the presence of water severely inhibits the rate of methanol formation where the methanol rates dropped from 4.7 mol/kg cat h in the absence of water, to a value of 1.2 mol/kg cat h with 1.4% water in the reactor feed. When the concentration of water is raised to 7%, the methanol formation was lowered to 0.24 mol/kg cat h. At 237 °C, a medium-high reaction temperature, a decrease in the methanol rates, albeit small, from 30.6 to 29.3 mol/kg cat h was also observed when the concentration of water in the feed gas was 1.4%. However, the rate declined from 26.8 to 23.9 mol/kg cat h with 7% water in the feed stream at that temperature. On the other hand, at a reactor temperature of 250 °C, a high reaction temperature, the rate of methanol production was higher with 7% water in the reactor feed, even though the change was not appreciable when a small quantity of water (1.4%) was present in the feed. This result indicates that water can replace carbon dioxide in reaction chemistry to some extent and there is an optimal amount of water at each temperature condition.

The water gas shift reaction plays a dominant role in determining the reaction environment. The relative rates of CO<sub>2</sub>-hydrogenation and water-gas shift reactions vary significantly within the temperature range of 205 to 250 °C. The addition of water to CO-rich syngas at low temperatures causes the methanol productivity to decrease. This is because the water gas shift reaction becomes relatively slower at lower temperatures. The formation of methanol by CO<sub>2</sub>-hydrogenation is

affected by the drop in potential for the forward reaction caused by the presence of water within the catalyst. At higher temperatures, the water-gas shift reaction is faster. This promotes the hydrogenation of CO<sub>2</sub> in two ways: by removing the byproduct water, and by providing additional CO<sub>2</sub> for the forward methanol synthesis reaction. The enhancement of reaction rates at higher temperatures is more pronounced when the concentration of CO<sub>2</sub> is very low in the syngas feed. However, this does not lend any support to the possibility that water may be substituted entirely for carbon dioxide in a CO-rich syngas, since water must first be converted to carbon dioxide before methanol production can proceed. The addition of large quantities of water would slow down the CO<sub>2</sub>-hydrogenation reaction due to a reduction in the potential for the forward reaction. Moreover, the solubility of water in the hydrocarbon oil is low. Therefore, more and more of the catalytic surface would be rendered inactive by the accumulation of water in the pores of the catalyst presenting an additional danger of catalyst deactivation and degradation. The presence of water can also cause damage to the catalyst by the promotion of hydrothermal synthesis and catalyst growth, by selective leaching of catalyst components, etc. [22].

### 2.2.3. Effect of CO<sub>2</sub> and water on the methanol synthesis catalyst

The effects of water and CO<sub>2</sub> on the metal content and the chemical constitution of the methanol synthesis catalyst have been experimentally investigated [22,23]. These experiments have been performed with only water, CO<sub>2</sub>, and N<sub>2</sub> in order to ascertain the discerning effects and have not been performed under actual conditions for methanol synthesis. Three types of analytical data were obtained from the experiments. First the amounts of metals dissolved in the water as measured by atomic absorption spectrometry were determined. Second, the extents of chemical change in the catalysts due to the action of water and CO<sub>2</sub> as measured by X-ray diffraction were determined. Third, the metal contents of catalyst pellets as examined by electron dot map analysis were determined. Results of the atomic absorption analysis show that although Cu and Al were not detected in statistically significant quantities, Zn was found in sufficient quantities. At any given temperature and pressure, the experiment performed with CO<sub>2</sub> shows significantly more zinc in the water than the experiment performed with N<sub>2</sub>. This shows that CO<sub>2</sub> has a strong leaching effect on the catalyst. Conclusions reached from the atomic absorption study are complemented by the X-ray diffraction study of the catalysts. Analysis of the catalyst subjected to a CO<sub>2</sub> atmosphere shows a much smaller CuO peak at 35.8° than usual, and also shows a new set of peaks between 15° and 25°, which are attributed to a copper-zinc compound called rosasite, with the formula

(CuZn)<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>. Thus, it is seen that CuO is transformed into rosasite by the action of water and CO<sub>2</sub>. It has been shown that the presence of CO<sub>2</sub> promotes the leaching of metals from the catalyst. Electron dot analysis shows higher dot map densities for the unused catalysts than for catalysts subjected to water and CO<sub>2</sub> environments. For example, the dot density for Cu drops from 385 to 330 and the Zn dot density drops from 490–495 to 390–410 upon exposure to these environments.

### 2.3. Kinetics

The kinetics of methanol synthesis, from synthesis gas, over a commercial Cu–Zn–Al catalyst (EPJ-25), in a three-phase slurry reactor was studied in a 1-liter, baffled autoclave [4,23]. The experimental conditions ranged as follows: temperature from 205 to 250 °C, syngas feed flow rate from 1.9 to 3.7 mol/h, H<sub>2</sub> partial pressure 25–50 atm, CO partial pressure from 10 to 30 atm, and CO<sub>2</sub> partial pressure from 3 to 6 atm. From the experimental data, the reaction rate was modeled as follows:

$$r_{\text{CH}_3\text{OH}} = A * \exp\left(\frac{-E}{RT}\right) (C_{\text{H}_2} - C_{\text{H}_2\text{eq}})$$

where Arrhenius frequency factor (A) = 1.217 × 10<sup>10</sup> L/kg cat h and the activation energy (E) = 76,837 J/mol. For a temperature of T = 227 °C, the quantity E/RT equals 19 which is close to the “thumb-rule” value (around 20) at which heterogeneous catalytic reactions are considered to be free from pore diffusional limitations [23].

A more detailed kinetic study was conducted at similar reaction conditions [34]. From the rate data on methanol formation, a Langmuir–Hinshelwood type rate expression has been developed which is sufficient for design calculations, process improvement, and optimization of operating conditions. The kinetic model developed is free from pore diffusional resistances and is not confounded by any mass transfer effects. The results of this kinetic model are in good agreement with the experimental results. The rate expression uses experimental data which covers a wide range of operating conditions and is equally valid for both H<sub>2</sub>-rich and CO-rich syngas, and is shown below as:

$$r_{\text{CH}_3\text{OH}} = \frac{k_{p,0} \exp\left(\frac{-E}{RT}\right) \left(p_{\text{H}_2}^2 p_{\text{CO}} - \frac{p_{\text{CH}_3\text{OH}}}{K_L}\right)}{\left(K_1 + K_2 \left(p_{\text{H}_2}^a + K_3 * p_{\text{CO}}^b + K_4 * p_{\text{M}}^c\right)\right)^d}$$

where

$r_{\text{CH}_3\text{OH}}$  = rate of methanol production (mol/kg cat h)  
 $p_i$  = partial pressure of species i in the product vapors (atm)

$K_L$  = liquid phase equilibrium constant

$E$  (energy of activation) = 18360 cal/mol  
or 76837 J/mol

$K_0$  (pre-exponential factor) = 965.96

$K_1 = 15.0019 * 10^{-3}$ ,  $K_2 = 1.488 * 10^{-3}$ ,

$K_3 = 3.957 * 10^{-3}$ ,  $K_4 = 0.03677 * 10^{-3}$

$a = 0.818$ ,  $b = 0.82323$ ,  $c = 2.0903$ ,  $d = 2.1598$

#### 2.4. Pore diffusional problems

The influence of pore diffusional limitations on the methanol reaction rate was analyzed and quantified for the liquid-phase methanol synthesis process using a packed bed reactor and catalyst crushed to the size of 105  $\mu\text{m}$ , suspended in Witco-40 oil [13,23]. Investigations of the kinetics were carried out under the following operating conditions: 205–250  $^{\circ}\text{C}$  and 24–50 atm. A step-wise linear regression of the reaction data indicated that the intrinsic reaction rate could be alternately expressed as follows:

$$R = k_0 \left( \exp \left[ \frac{-E}{RT} \right] \right) (C_{\text{H}_2} - C_{\text{H}_2,\text{eq}})$$

where the concentrations  $C_{\text{H}_2}$  and  $C_{\text{H}_2,\text{eq}}$  refer to the compositions of the liquid phase. The frequency factor  $k_0$  was found to be  $1.2171 \times 10^{10}$  ( $\text{dm}^3/\text{kg}$  of cat h)(mol of methanol/mol of hydrogen) and the activation energy  $E$  was 76,837 J/mol. The liquid-phase compositions were calculated on the basis of multicomponent equilibria by using the Margules equation with Henry's law standard state for the gases, and the Lewis–Randall standard state for vapors. The isolated chemical equilibrium compositions were determined by using a routine that computes the liquid-state compositions at chemical equilibrium corresponding to the values at phase equilibrium alone [8].

The overall rate was found to be limited very significantly by pore diffusion when the pellet-sized (10 mm long  $\times$  2 mm diameter) copper-based catalyst is used in the liquid phase. The limitation is partly due to the decreased liquid-phase diffusivities and larger penetration depth in the larger catalyst. In order to minimize the pore diffusional limitation in the liquid phase methanol synthesis, fine powders of catalysts must be used in a slurry mode. The actual effectiveness factors ( $\eta$ ) obtained from reactor data for pellet-sized catalysts at 205  $^{\circ}\text{C}$  range between 0.23 and 0.33 with an average of 0.29, which compares well with the theoretically estimated ( $\eta_{\tau}$ ) value of 0.32. It was also found that the theoretical approach based on the Thiele modulus can be used as an approximate predictor for the analysis of pore diffusional limitations even in a three-phase catalytic system [13].

#### 2.5. External mass transfer

The mass transfer characteristics of the liquid phase methanol synthesis process have been studied [7–9,15, 27, 35]. An experimental investigation [9] elucidates the

effects of temperature, pressure, level of oil, impeller speed, and gas flow rate on the overall gas-liquid mass transfer coefficient,  $K_{L,i}a_B$ . Results obtained indicated that the impeller speed, feed flow rate, and temperature had significant effects on the mass transfer coefficient at the experimental conditions examined. Correlations were developed for the Sherwood number based on the Reynolds number, the Schmidt number, the reciprocal gas flow number, the gas-liquid viscosity ratio, and the dimensionless temperature. A simplified power-law type approach was also used to correlate the overall gas-liquid mass transfer coefficient with the impeller speed, gas flow rate, and dimensionless temperature. At a 6 wt% slurry (corresponding to 5 g of catalyst per 100 mL of oil) in a mechanically agitated slurry reactor, the gas-liquid mass transfer does not limit the overall rate. However, at a 38.5 wt% slurry (corresponding to 50 g of catalyst per 100 mL of oil), there would be very serious gas-liquid mass transfer limitation. When the rate of external mass transfer is controlling the overall rate, the effectiveness of the reactor decreases significantly. However, it should be clearly pointed out that in order to improve the reactor productivity, commercial processes are often operated under mass transfer limited conditions.

#### 2.6. Thermodynamics

A thermodynamic study has been conducted for the multicomponent phase equilibrium that is encountered in the liquid phase methanol synthesis system [4,5,23]. The chemical species involved are  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{O}$ , and Witco-40 mineral oil. The experimental part of the investigation was carried out in a 1-liter autoclave. A model has been developed to predict multicomponent phase equilibria by using data from individual binary system experiments. The values predicted by this model were compared with the actual experimental data obtained with the corresponding multicomponent system. A computer model has been developed based on the Redlich–Kwong equation of state and a mixing rule for the analysis of experimental measurements of multicomponent gas solubilities and multicomponent phase equilibrium [8,9]. A complete program package has been developed that calculates the simultaneous phase and chemical equilibria and the isolated chemical equilibrium in the liquid phase methanol synthesis system. Vapor phase composition, pressure, temperature, and volume of oil are required as input data for this program.

#### 2.7. Thermal stability

The thermal stability of the liquid-phase methanol synthesis reactor was both experimentally and theoretically analyzed [4,23,29]. Using the “slope” and “dynamic” criteria, the liquid phase process was proven to be more stable than its counterpart vapor phase

process by an order of magnitude difference. Although the concentration driving force is of the same order of magnitude for both the liquid phase synthesis and vapor phase synthesis, the adiabatic temperature rise potential is higher by two orders of magnitude in the vapor phase than in the liquid phase, which can be attributed to an order of magnitude difference between the densities (and thermal masses) of the reaction mixture in the vapor and liquid phase synthesis. The Damköhler number and the conversion are of similar order of magnitude in both the liquid- and vapor-phase synthesis. However, the dimensionless heat transfer coefficient is an order of magnitude higher in the vapor phase than in the liquid phase due to an order of magnitude difference in the thermal mass of the reaction mixture in the vapor phase. The addition of an inert liquid such as Witco oil is instrumental in effectively controlling the heat generation rate by absorbing the heat evolved by exothermic methanol synthesis reaction. The maximum permissible temperature difference between the catalyst and the liquid for both H<sub>2</sub>-rich syngas was found to be 20 K and that for CO-rich syngas to be 18 K. From a standpoint of thermal stability in the liquid phase methanol synthesis, hydrogen-rich feed would, therefore, result in a higher production rate of methanol without significantly affecting the thermal stability of the process.

## 2.8. Catalyst deactivation/regeneration

### 2.8.1. Catalyst deactivation

The deactivation of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst during methanol synthesis [17,23,40] as well as the regeneration of deactivated catalyst [18,23,25,26,28,41] has been investigated in great detail. Long-term (120 h) methanol synthesis experiments were conducted to observe the progress of catalyst deactivation in the following environments: typical CO-rich syngas (CO, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>), feed gas mixture without CO, and feed gas mixture without CO<sub>2</sub>. It was observed that drop in catalytic activity was most serious in the CO-free feed gas as compared with the results of the other two.

X-ray powder diffraction analysis was used to compare the copper crystallite sizes of fresh and deactivated catalysts. The crystallite size distribution of a freshly reduced catalyst was nearly unimodal and the average crystallite size was found to be 37.7 Å. Analysis of the catalysts after 120-h experiments showed lesser proportion of smaller size crystallites and a greater proportion of larger size crystallites, with an average crystallite size of 47.3 Å. Crystallite size growth especially noted in the case of CO-free syngas feed, where the average size had increased significantly to 105.5 Å, the distribution curve becoming trimodal with peaks at 60, 100, and 150 Å. This experiment also produces a lot of water, thus attributing promotion of crystallite size growth to the water-rich environment.

For the CO<sub>2</sub>-free syngas feed, even though the drop in catalytic activity was almost three times more than that observed with normal syngas, the crystallite size growth was not that distinct. This indicates that catalytic activity decreased due to some other reasons as well as due to the crystallite size growth in the catalyst. This observation is consistent with the mechanistic investigation result that, in the absence of CO<sub>2</sub>, the tendency of carbon deposition is high in the liquid-phase synthesis of methanol. Thus, results from long-term methanol production experiments show that there is a strong correlation between the catalytic activity and the crystallite size in the catalyst. This led to the observation that a reduction in crystallite size in the aged catalyst would enable the lost catalytic activity to be restored.

### 2.8.2. Catalyst regeneration

In order to reduce the crystallite size in deactivated catalysts, phase redispersion experiments based on cyclic oxidation–reduction were carried out. The oxidation procedure for the oxidation–reduction scheme was based on the use of purified oxygen in low concentrations [25]. It was observed that the distribution curve shifted toward smaller crystallites sizes. The average crystallite size decreased from 47.3 to 39.6 Å after regeneration cycle, which is close to the average crystallite size of freshly reduced catalyst of 37.7 Å. The phenomenon of crystallite size reduction after regeneration becomes much more notable in the catalyst aged in a CO-free syngas feed with the disappearance of larger crystallites and a distribution shift toward smaller crystallite sizes. The average crystallite size decreased from 105.5 to 53.3 Å even with a single treatment cycle [26]. It is evident that the redispersion of the copper phase in the catalyst occurs during the oxidation–reduction cycle and as a result, the copper crystallite size is reduced. On the other hand, the cyclic oxidation–reduction treatment was not effective in regenerating the catalyst aged in CO<sub>2</sub>-free feed gas, where the size distribution did not change much.

### 2.8.3. Restoration of catalytic activity in regenerated catalysts

The catalytic activities of all the deactivated and regenerated catalysts were examined using normal syngas feed regardless of whether the catalyst was deactivated in a CO-free or CO<sub>2</sub>-free environment. The experiments were conducted at conditions where the mass transfer did not limit the overall rate and as such a measure of the actual catalytic activity by intrinsic chemical kinetics could be obtained. The catalytic activity of the deactivated catalyst before subjecting it to the regeneration cycle was 16.1 mol/kg h, while the catalyst activity of the freshly reduced and fully active catalyst was 18.9 mol/kg h under identical reaction conditions. When the deactivated catalyst was subjected

to the regeneration cycle, the catalytic activity increased to 17.3 mol/kg h after one cycle and then to 18.5 mol/kg h after two cycles (98% of the activity of the fresh unaged catalyst).

In the case of CO-free syngas, the catalytic activity of deactivated catalyst fell to 11.3 mol/kg h from fresh catalyst activity of 18.9 mol/kg h. However, the activity increased to 14.1 mol/kg h upon subjecting the catalyst to the regeneration cycle. However, a product spectrum containing 60% water in this experiment, leads us to believe that deactivation in CO-free syngas environment may be regarded as a combination of metal leaching and hydrothermal crystallite growth.

In case of the CO<sub>2</sub>-free syngas feed, the activity of the deactivated catalyst was 14.484 mol/kg h. After regeneration cycle, the activity increased merely to 14.494 mol/kg h, whose change is statistically insignificant. The lack of improvement in catalyst activity may be attributed to the fact that the mode of catalyst deactivation under the CO<sub>2</sub>-free environment involves carbon fouling and/or reduction of zinc oxide.

Leaching out of catalyst ingredients is one of the factors responsible for the deactivation. Zinc oxide is particularly vulnerable to attack by water. Large amounts of ZnCO<sub>3</sub> are formed at higher partial pressures of CO<sub>2</sub> under process conditions, as confirmed by X-ray diffraction. This would explain to some extent faster loss of activity due to leaching, since solubility of zinc carbonate in water is several times higher than that of zinc oxide. However, Cu crystallite size growth for CO<sub>2</sub>-pretreated catalyst (thus containing ZnCO<sub>3</sub>) is slower than for untreated catalyst. Zinc carbonate remains a stable phase at CO<sub>2</sub> partial pressures greater than 0.5 MPa. Water produced in pores of the catalyst can hinder the methanol synthesis, being blocked inside the pores by a hydrocarbon oil barrier. The concentration of water in the pores can then rise and approach the equilibrium value, resulting in lower rates of methanol formation and can be considered to be the cause of loss in catalytic activity.

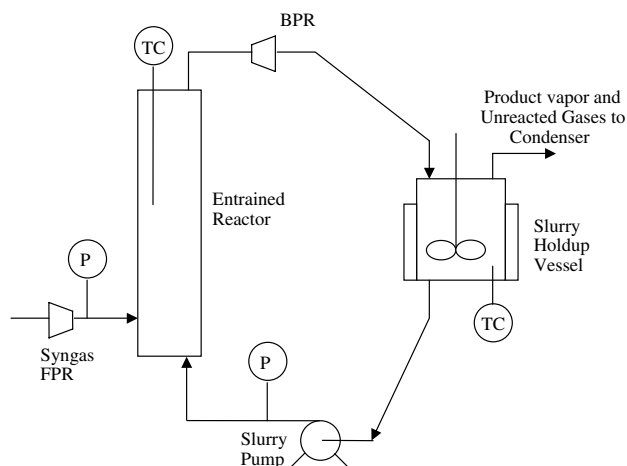


Figure 2. Liquid entrained reactor system for methanol synthesis.

## 2.9. Liquid entrained reactor

The chemical equilibrium limitation of the methanol synthesis reaction can be overcome by physically removing methanol from the slurry mixture. The design and operation of the liquid entrained reactor is based on this approach, and has been thoroughly investigated [30–33,37–39]. For methanol synthesis in the liquid entrained reactor, the catalyst-inert oil slurry is continuously circulated through the tubular reactor and syngas is fed to the reactor cocurrently with the upward flow of slurry. The catalyst particles are uniformly suspended in the liquid and catalyst agglomerates possibly formed within the reactor are broken in the pump. Recirculation of the slurry promotes catalyst distribution and improves mass transfer between the gas and the catalyst particles, especially in the case of high slurry concentrations. A schematic of the liquid entrained reactor experimental unit is shown in figure 2.

The data obtained from the experimental study involving reactor temperature, reactor pressure, slurry flow rate, syngas flow rate, slurry holdup tank pressure, and syngas composition, were used to develop a kinetic rate expression for the liquid phase methanol synthesis process in an entrained reactor. This in turn helps the scale-up and commercialization of the methanol synthesis process in an entrained reactor.

An Arrhenius-type rate expression of the following type was fit to the available data:

$$r_{\text{CH}_3\text{OH}} = k_{c,0} \exp\left(\frac{-E}{RT}\right) (C_{\text{H}_2} - C_{\text{H}_2,\text{eq}}).$$

For the CO-rich syngas, the Arrhenius-type reaction rate expression that best fits the data for the 10% catalyst loading in slurry is:

$$r_{\text{CH}_3\text{OH}} = 0.75 * 10^{10} \exp\left(\frac{-20500}{RT}\right) (C_{\text{H}_2} - C_{\text{H}_2,\text{eq}}).$$

For the H<sub>2</sub>-rich syngas, the Arrhenius-type reaction rate expression obtained was:

$$r_{\text{CH}_3\text{OH}} = 0.41 * 10^{10} \exp\left(\frac{-20500}{RT}\right) (C_{\text{H}_2} - C_{\text{H}_2,\text{eq}}).$$

Even though the kinetic model is a simple-minded, global kinetics type, it does explain the nature of chemical reactions in the liquid phase, the reversible reaction, and the thermodynamic consistency at extrapolated conditions. Data covering a wide range of practical operating conditions, including varying composition of syngas has been used to develop this kinetic rate expression.

## 2.10. Liquid phase methanol synthesis (LPMeOH™) – research and process development studies by air products and chemicals, Inc

Air Products and Chemicals (APCI) have been actively involved in research concerning liquid phase

methanol synthesis, along with Chem Systems and the Electric Power Research Institute (EPRI) since the early 1980s [42]. They have developed three different reactor configurations for methanol synthesis: a slurry bubble column reactor, a fluidized bed reactor, and a fixed bed reactor. These reactors have been tested during the process development work at U.S. DOE's 3,200 gallon-per-day Process Development Unit at LaPorte, Texas, which is operated by APCI [43].

In 1997, Air Products and Chemicals, Inc. and Eastman Chemical Company formed a partnership, namely Air Products Liquid Phase Conversion Company, L.P., to successfully demonstrate a liquid phase process for the synthesis of methanol from coal at Eastman's Kingsport, Tennessee facility [44]. This process utilizes a slurry bubble column reactor, where the micron-sized catalyst is suspended in an inert mineral oil. This novel reactor configuration offers a twofold utility of carrying out the reaction as well as conducting heat removal, which offers superior heat management pertaining to the synthesis gas conversion to methanol and thereby prolongs catalyst life. This process is versatile enough to handle a wide variety of gas feedstocks from a coal gasifier and offers on-line catalyst replacement capability as well. The process has been tested with a varied hydrogen-to-carbon monoxide ratio in the feed gas from 0.4 to 5.6 with no negative effects on performance. This process also claims higher per-pass methanol productivity with a methanol selectivity of greater than 97% and only 1% water as compared to gas phase processes whose methanol product contains 4–20% water by weight.

### 3. Dimethyl ether synthesis

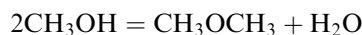
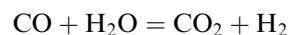
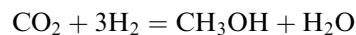
#### 3.1. Introduction

Dimethyl ether (DME) is gaining worldwide recognition as a multi-source, multi-purpose clean fuel and chemical feedstock for the 21st century [52]. DME can be produced from a variety of sources, and its end use includes a number of important applications. DME can be manufactured in large quantities from coal, natural gas, biomass and municipal solid waste. Currently, the major usage of DME is as a propellant in the aerosols industry [49]. In addition, it can be used as a clean-burning fuel in diesel engines, as a household fuel (LPG alternative) for heating and cooking, as a fuel for gas turbines in power generation, as a fuel for fuel cells, and as a chemical feedstock for higher ethers and oxygenates. Single-stage DME synthesis in the vapor phase suffers from low per-pass conversions, mandated in part by the debilitating effects of high temperature on the catalysts [49]. Gas phase DME synthesis processes, in general, suffer from the drawbacks of low hydrogen and CO conversions per pass, along with low yield and selectivity of DME, coupled with a high yield of carbon

dioxide. These processes are typically expensive due to high capital costs for reactors and heat exchangers, and high operating costs due to inefficient CO utilization and high recycle rates. Using an inert liquid as a heat sink for highly exothermic reactions offers a number of opportunities in syngas processing. Heat generated by the exothermic reactions is readily accommodated by the inert liquid medium. This enables the reaction to be run isothermally, minimizing catalyst deactivation commonly associated with the more adiabatic gas-phase technologies.

#### 3.2. Single-stage liquid phase dimethyl ether process

The single-stage, liquid phase DME synthesis process, investigated in great detail [45–51,54], incorporates the sequential reaction of methanol synthesis and methanol dehydration in a slurry phase reactor system. Combining these reversible reactions in a single step makes each reaction thermodynamically more favorable by utilizing its inhibiting products as reactants in the subsequent reaction. In addition to the superior heat management allowed by the liquid phase operation, the synergistic effect of these reactions occurring together yields higher quantities of DME than that could be obtained from sequential processing. The process is based on dual-catalytic synthesis in a single reactor stage, and also based on a combination of an equilibrium limited reaction (methanol synthesis) and an equilibrium unlimited reaction (methanol dehydration). The process chemistry is:



where the first two reactions take place over the coprecipitated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and the last one takes place over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, by varying the mass ratios of methanol synthesis catalyst to methanol dehydration catalyst, it is possible to co-produce DME and methanol in any fixed proportion, from 5% DME to 95% DME [49].

#### 3.3. Reactor productivity

The reactor productivities of methanol synthesis alone and co-production of DME and methanol were elucidated by a comparative study. The reactions were carried out at 250 °C and 70 atm in a liquid phase involving inert oil such as Witco-40 [49,51]. The nominal composition of CO-rich syngas was H<sub>2</sub>:CO:CO<sub>2</sub>:CH<sub>4</sub> = 37.4:46.3:7.7:8.6, and the syngas flow rate was set to 1 SLPM. The impeller speed in a 1-liter autoclave reactor was set to 1500 rpm. For the



case of methanol synthesis, 150 g of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst was slurried in 550 mL of oil. For the case of co-production of methanol and DME, the conditions were nominally identical except that 10 g of  $\gamma$ -alumina was also added to the slurry.

For methanol synthesis alone, 72% of H<sub>2</sub> and 38.2% of CO were converted to methanol in a single pass and the reactor productivity was 0.342 gmol of (CH<sub>3</sub>)/h. For co-production of methanol and DME, 88% of H<sub>2</sub> and 62.4% of CO were converted to methanol and DME in a single pass and the reactor productivity was increased to 0.534 gmol of (CH<sub>3</sub>)/h. Thus, the single-stage reactor productivity was increased by as much as 58% when the co-production of methanol and DME was used, as compared to methanol synthesis alone. At high slurry ratios, when methanol concentration in the liquid phase is very high, the percent increase in single-stage reactor productivity could be as high as 80%. The above fact is very significant from a commercial perspective since most commercial reactors in liquid phase synthesis are operated in the gas-to-liquid mass transfer limited region.

The effects of catalyst loadings in the slurry and the role played by carbon dioxide in dimethyl ether synthesis has been studied by conducting kinetic experiments [54]. It was observed that at 8% carbon dioxide concentration (optimal concentration for methanol synthesis) in the feed, methyl productivities are significantly higher in the co-production case as compared to methanol synthesis alone. This confirms the fact that the liquid phase dimethyl ether process can be conducted with better carbon dioxide tolerance than the liquid phase methanol synthesis process.

### 3.4. Equilibrium conversion

The maximum per-pass conversion of syngas in methanol synthesis alone is restricted by chemical equilibrium on the reversible nature of the reaction. By promoting *in-situ*, concurrent synthesis of DME in the liquid phase, the equilibrium scenario for methanol synthesis reaction is far more favorable than otherwise. At a reaction temperature of 230 °C and pressure of 52 atm, the maximum equilibrium conversion of H<sub>2</sub> for DME co-production with methanol is about 83.2%, while that for methanol synthesis alone is 67.3% [51]. It was observed that the equilibrium conversions for H<sub>2</sub> and CO are always greater for the DME production case as compared to methanol synthesis alone. This result concurs with the concentration driving force for the key chemical species, H<sub>2</sub> and CO, which follows the same trend [49]. This indicates that the available kinetic potential of the reactant is greater in the liquid phase dimethyl ether process system, which validates the over 60% increase in the syngas conversion for DME synthesis over methanol synthesis.

### 3.5. Catalyst deactivation

Analysis of the crystal growth pattern of the methanol synthesis catalyst, when used alone and when used together with  $\gamma$ -alumina, can shed light on the favorable scenario of using dual catalysts. It was observed that the rate of thermal aging and the crystal growth pattern of methanol synthesis catalyst slows down, when it is used in a co-production mode along with  $\gamma$ -alumina. This means that methanol synthesis catalyst conserves its original activity longer, when aged along with the methanol dehydration catalyst,  $\gamma$ -alumina. This means that not only do dual catalysts exhibit higher activity, but these activities would also be sustained for a longer catalyst on-stream life than those for methanol synthesis alone [49]. This indirectly implies that product methanol in the catalyst pores may be detrimental to the life of the methanol synthesis catalyst.

### 3.6. Liquid phase dimethyl ether synthesis – research by air products and chemicals

Air Products and Chemicals have developed a liquid phase process for the direct synthesis of DME (with or without coproduct methanol) from synthesis gas. This process gives higher syngas conversion per pass than can be achieved by methanol synthesis alone, with a tailored selectivity of DME and methanol that is optimized by varying reaction conditions, catalyst compositions, and/or ratios to suit specific process applications. The single-stage synthesis of DME is carried out in a slurry phase reactor, where the methanol synthesis catalysts (powdered commercial catalysts BASF S3-85 and BASF S3-86), methanol dehydration catalyst (for  $\gamma$ -alumina), and shift catalyst (copper-based BASF K3-110) are slurried in inert mineral oil, with slurry concentrations in the range of 15–30 wt% catalyst.

Process development includes three potential commercial modes of operation to produce DME. The first operating mode, which uses an oxygen-blown coal gasifier with recycle of the synthesis gas co-produces methanol and dimethyl ether, and has applications in the fuels and petrochemical industry. The second mode uses the once-through approach of coal-derived syngas, in which DME and methanol are recovered and unreacted gas is fired to a turbine. The third operating mode also uses the once-through process, but uses Basic Oxygen Furnace (BOF) off-gas as the feed stream. The hydrogen to carbon monoxide ratio of BOF off-gas is essentially zero, thereby necessitating steam to be co-fed to the reactor. This process enables the use of off-gases with unfavorable compositions, by upgrading them into value-added products.

### 3.7. Conclusion

The Liquid Phase Methanol Synthesis (LPMeOH™) process has been thoroughly investigated, both

fundamentally as well as technology-wise. These studies were conducted in a 1-liter mechanically agitated slurry reactor system and a liquid entrained reactor system. For the synthesis of methanol over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, the reaction chemistry based on the CO<sub>2</sub> hydrogenation was firmly established for diverse feed gas conditions including H<sub>2</sub>-rich, CO-rich, CO<sub>2</sub>-rich, and CO-free environments, consisting of the CO<sub>2</sub> hydrogenation reaction and the water-gas shift reaction. A global kinetic rate expression was developed that predicts the kinetic rates for various operating conditions, with good accuracy. External mass transfer mechanisms and rates were also studied with variations in operating parameters including the catalyst slurry loading. A correlation for the overall gas-to-liquid mass transfer rate coefficient was developed. A computer program was developed that computes the multicomponent phase equilibrium and also predicts the ultimate and isolated chemical equilibrium compositions corresponding to input information. Thermal stability of the liquid phase methanol synthesis reactor was both experimentally and theoretically analyzed. Analysis of pore diffusion in the methanol catalyst, when used in the liquid phase process, was also studied and a liquid entrained reactor using catalyst slurry was suggested for commercial operation for the liquid phase methanol synthesis.

A novel process for co-production of dimethyl ether (DME) and methanol was developed. The process is based on dual-catalytic synthesis in a single reactor stage, with the additional methanol dehydration reaction taking place over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. For high productivity cases using very high weight hourly space velocities of syngas, the single-stage reactor productivity could be increased by as much as 80%. By varying the mass ratios of methanol synthesis catalyst to methanol dehydration catalyst, it is possible to co-produce DME and methanol in any fixed proportion, from 5% DME to 95% DME, very easily. Not only do dual catalysts exhibit higher activity, but these activities would also be sustained for a longer catalyst on-stream life by alleviating catalyst deactivation.

### Acknowledgments

This research work was fully supported through research contracts from the Electric Power Research Institute (EPRI). The authors wish to acknowledge fellow researchers of this work namely, Dr. Ashok Sawant, Dr. Vetkav Parameswaran, Dr. Myung Ko, Dr. Byung Gwon Lee, Dr. Makarand Gogate, Dr. P. Vijayaraghavan, Dr. Timothy Tartamella, Mr. Srinivas Desirazu, Mr. Arun Gunda, Mr. Klein Rodrigues, Mr. Murthy Nishtala, Mr. Surya Varanasi, and Mr. Ramesh Gandhi.

### References

- [1] M. Sherwin and D. Blum, *Liquid Phase Methanol*, Final Report EPRI AF-1291 (Project 317-2) Electric Power Research Institute, Palo Alto, CA.
- [2] A. Cybulski, *Cat. Rev. Sci. Eng.* 36(4) (1994) 557.
- [3] S. Lee, J.M. Berty, H.L. Greene, S. Desirazu, M. Ko, V. Parameswaran and A. Sawant, *Research to Support Development of the Liquid-phase Methanol Synthesis Process Quarterly Report*, University of Akron, Jan. 7, 1984.
- [4] S. Lee, J.M. Berty, H.L. Greene, S. Desirazu, M. Ko, V. Parameswaran and A. Sawant, Thermodynamics, kinetics, and thermal stability of liquid phase methanol synthesis, Electric Power Research Institute, EPRI AP-3825-SR, *Proceedings, Ninth Annual EPRI Contractor's Conference on Coal Liquefaction*, Palo Alto, May 1984.
- [5] S. Lee, A. Sawant, V. Parameswaran and T. Sullivan, Research into thermodynamics, mass transfer, oil and catalyst degradation in liquid phase methanol, Electric Power Research Institute, *Proceedings, Ninth Annual EPRI Contractor's Conference on Clean Liquid and Solid Fuels, Special Report EPRI AP-4253-SR*, Palo Alto, 1985.
- [6] S. Lee, J. Berty, S. Desirazu, J. Gray, H. Greene, M. Ko, V. Parameswaran, F. Pelc, M. Polasky, R. Rangarajan, A. Sawant and K. Sivagnanam, Research to support development of the liquid phase methanol synthesis process, EPRI-AP-4429, 1-312, Research project 2146-2142, University of Akron, Feb. 1986.
- [7] S. Lee, V. Parameswaran, A. Sawant and M. Ko, *Mass Transfer in the Liquid Phase Methanol Synthesis Process*, Interim Report, EPRI AP-5758, 1986.
- [8] M. Ko, and S. Lee, *Energy & Fuels*, 1 (1987) 211-216.
- [9] M. Ko, *Mass Transfer Study for Liquid Phase Methanol Synthesis Process*, Ph. D. Dissertation, University of Akron, 1987.
- [10] S. Lee, V. Parameswaran, A. Sawant, M. Ko, and D. Cho, Research on once through methanol, Electric Power Research Institute, EPRI AP-5043-SR, *Proceedings, Eleventh Annual EPRI Contractor's Conference on Clean Liquid and Solid Fuels, Special Report EPRI AP-4253-SR*, Palo Alto, 1987.
- [11] V. Parameswaran, *Roles of Carbon Dioxide and Water in Liquid Phase Methanol Synthesis*, Ph. D. Dissertation, University of Akron, 1987.
- [12] A. Sawant, *Effects of Water and Thermal Aging on the Methanol Synthesis Catalyst*, Ph. D. Dissertation, University of Akron, 1987.
- [13] V. Parameswaran and S. Lee, *Energy & Fuels*, 1(2) (1987) 217.
- [14] A. Sawant, M. Ko, V. Parameswaran, S. Lee, and C. Kulik, *Fuel Science and Technology, International*, "In-situ Reduction of a Methanol Synthesis Catalyst in a Three Phase Slurry Reactor", 5(1) (1987) 77.
- [15] S. Lee, Mass Transfer Characteristics of the Liquid Phase Methanol Synthesis Process, Electric Power Research Institute, pp. 1-214, EPRI AP-5758, Palo Alto, CA, April, 1988.
- [16] A. Sawant, S. Lee and C. Kulik, *Fuel Sci. Tech. Intl.* 6(2) (1988) 151.
- [17] A. Sawant, S. Lee and A. Foos, *Fuel Sci. Tech. Intl.* 6(5) (1988) 569.
- [18] B.G. Lee, *Post-treatment and Regeneration of Methanol Synthesis Catalyst*, Ph. D. Dissertation, University of Akron, 1989.
- [19] S. Lee, B.G. Lee and V. Parameswaran, Fundamentals of methanol synthesis, Electric Power Research Institute, *Proceedings, Thirteenth Annual EPRI Contractor's Conference on Clean Liquid and Solid Fuels*, Palo Alto, Jan 1989.
- [20] V. Parameswaran, S. Lee and I. Wender, *Fuel Sci. Tech. Intl.* 7(7) (1989) 899.
- [21] V. Parameswaran, C. Kulik, I. Wender and S. Lee, *Fuel Sci. Tech. Intl.* 7(8) (1989) 1021.
- [22] A. Sawant, K. Rodrigues, S. Lee and C. J. Kulik, *Energy & Fuels*, 3(1) (1989) 2.

- [23] S. Lee, *Methanol Synthesis Technology* (CRC Press, Boca Raton, FL, 1990).
- [24] S. Lee and V. Parameswaran, Reaction Mechanism in Liquid-Phase Methanol Synthesis, Electric Power Research Institute, pp. 1–206, ER/GS-6715, Palo Alto, CA, February 1990.
- [25] S. Lee, A. Sawant and C. Kulik, Process for Methanol Catalyst Regeneration Using Crystallite Redispersion, U.S. Patent, No. 5,004,717, April 2, 1991.
- [26] B.G. Lee, S. Lee and C. J. Kulik, *Fuel Sci. Tech. Intl.*, 9(5) (1991) 587.
- [27] V. Parameswaran, M. Gogate, B.G. Lee and S. Lee, *Fuel Sci. Tech. Intl.* 9(6) (1991) 695.
- [28] B.G. Lee and S. Lee, *Fuel Sci. Tech. Intl.* 9(8) (1991) 977.
- [29] M. Gogate, S. Desirazu, J. Berty and S. Lee, *Fuel Sci. Tech. Intl.* 10(10) (1992) 1709.
- [30] P. Vijayaraghavan, S. Lee and C. J. Kulik, *Fuel Sci. Tech. Intl.* 10(9), (1992) 1501.
- [31] P. Vijayaraghavan and S. Lee, *Fuel Sci. Tech. Intl.* 11(2) (1993) 243.
- [32] P. Vijayaraghavan and S. Lee, *Fuel Sci. Tech. Intl.* 11(11) (1993) 1577.
- [33] P. Vijayaraghavan, *Entrained Reactor Studies on the Liquid Phase Methanol Synthesis Process, Ph. D. Dissertation, University of Akron*, 1994.
- [34] P. Vijayaraghavan and S. Lee, *Fuel Sci. Tech. Intl.* 11(10) (1993) 1459.
- [35] M. Gogate and S. Lee, *Fuel Sci. Tech. Intl.* 12(1) (1994) 35.
- [36] P. Vijayaraghavan, S. Lee and C. Kulik, *Fuel Sci. Tech. Intl.* 13(3) (1995) 317.
- [37] P. Vijayaraghavan and S. Lee, *Fuel Sci. Tech. Intl.* 13(3) (1995) 331.
- [38] P. Vijayaraghavan and S. Lee, *Fuel Sci. Tech. Intl.* 14(5) (1996) 685.
- [39] P. Vijayaraghavan, and S. Lee, *Fuel Sci. Tech. Intl.* 14(5) (1996) 695.
- [40] T. Tartamella and S. Lee, *Fuel Sci. Tech. Intl.* 14(5) (1996) 713.
- [41] S. Lee, V. Parameswaran and C. Kulik, Post-reduction Treatment of Alcohol Synthesis Catalysts with Carbon Dioxide, U.S. Patent No. 5,622,907, 1997.
- [42] D.M. Brown, T.H. Hsuing, D.W. Studer and J.L. Henderson, *A Novel Liquid Phase System for Methanol Synthesis, TOCAT 1, 1st Tokyo Conf. Adv. Catalytic Sci. Technol. Tokyo*, July 1–5, 1990.
- [43] G.S. Markiewicz, T.R. Tsao, E.C. Heydorn and J.L. Henderson, Design, construction, and operation of the LPMeOH process development unit, *Synfuels 4<sup>th</sup> Worldwide Symposium*, Washington D.C., Nov. 7–9, 1984.
- [44] R. Kornosky, Liquid phase methanol (LPMeOH<sup>TM</sup>) process demonstration project, [http://www.netl.doe.gov/publications/success/fetcss\\_lpmeh.html](http://www.netl.doe.gov/publications/success/fetcss_lpmeh.html).
- [45] M. Gogate, S. Lee and C. Kulik, *Fuel Sci. Tech. Intl.* 9(6) (1991) 653.
- [46] M. Gogate and S. Lee, *Fuel Sci. Tech. Intl.* 9(7) (1991) 889.
- [47] M. Gogate and S. Lee, *Fuel Sci. Tech. Intl.* 9(8) (1991) 949.
- [48] S. Lee and M. Gogate, Development of a Single Stage, Liquid Phase Synthesis Process of Dimethyl Ether from Syngas, EPRI TR-100246, pp. 1–179, EPRI, Palo Alto, CA, February, 1992.
- [49] M. Gogate, *A Novel Single-step Dimethyl Ether Synthesis Process from Syngas, Ph. D. Dissertation, University of Akron*, 1992.
- [50] M. Gogate, P. Vijayaraghavan and C. Kulik, *Fuel Sci. Tech. Intl.* 10(3) (1992) 281.
- [51] M. Gogate, C. Kulik and S. Lee, *Chem. Eng. Sci.* 47(13/14) (1992) 3769.
- [52] A. Sardesai and S. Lee, *Rev Process Chem. and Eng.* 1(2) (1998) 141.
- [53] F. Keil, *Micropor. Mesopor. Mat.* 29 (1999) 49.
- [54] A. Sardesai, A. Gunda, T. Tartamella and S. Lee, *Energy Sources* 22(1) (2000) 77.
- [55] S. Lee, M. Gogate and K. Fullerton, Dimethyl Ether to Hydrocarbons/Gasoline Process, U.S. Patent No. 5,459,166, October 17, 1995.
- [56] M. Gogate, S. Lee and C. Kulik, *Fuel Sci. Tech. Intl.* 13(8) (1995) 1039.
- [57] A. Sardesai, T. Tartamella, M. Gogate and S. Lee, *Fuel Sci. Tech. Intl.* 13(8) (1995) 1059.
- [58] A. Sardesai, T. Tartamella, C. Midha and S. Lee, *Fuel Sci. Tech. Intl.* 14(5) (1996) 669.
- [59] A. Sardesai, T. Tartamella and S. Lee, *Fuel Sci. Tech. Intl.* 14(5) (1996) 703.
- [60] A. Sardesai, *Catalytic Conversion of Dimethyl Ether to Lower Olefins: Process and Catalyst Deactivation Studies, Ph. D. Dissertation, University of Akron*, 1997.
- [61] A. Sardesai, T. Tartamella and S. Lee, *Petroleum Sci. Technol.* 17(3,4) (1999) 273.
- [62] A. Sardesai, T. Tartamella and S. Lee, *Energy Sources* 24(4) (2002) 301.
- [63] D.M. Brown, B.L. Bhatt, T.H. Hsuing, J.J. Lewnard and F.J. Waller, *Catal. Today* 8 (1991) 279.