The Direct Dimethyl Ether (DME) Synthesis Process from Syngas: Current Status and Future prospects I. Process Feasibility and Chemical Synergy in LPDME™ Process

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Submission: May 11, 2018; Published: August 06, 2018

Abstract

A novel one-step process for co-production of dimethyl ether (DME) and methanol, in the liquid phase was first conceived by the UA researchers, as an advance over the liquid phase methanol synthesis process (LPMeOH™). The one-step, direct DME process (LPDME™) is based on the application of “dual catalysis”, where 2 functionally different yet compatible catalysts are used as a physical mixture, well-dispersed in the inert liquid phase. Three different reactions, methanol synthesis (via CO and CO₂), water-gas shift, and methanol dehydration (to form DME) take place over the 2 catalysts, Cu/ZnO/Al₂O₃ and typically γ-Al₂O₃. The favorable thermodynamic and kinetic coupling of methanol dehydration reaction (very rapid and at/near thermodynamic equilibrium) with the methanol synthesis reaction (slower kinetics and highly thermodynamic) leads the beneficial “chemical synergy”. This synergy helps to overcome the limitation on thermodynamic equilibrium conversion, and increases the per-pass syngas conversion and reactor productivity. The catalyst deactivation phenomena in LPDME™ processes also greatly alleviated compared to methanol alone; the increase in syngas conversion and methyl equivalent productivity (MEP) are sustained over a longer on-stream time.

Here, we review the salient developments in the LPDME™ process since its inception, first at UA research laboratories and elsewhere including Air Products and Chemicals, Inc. First, we demonstrate the rationale of the LPDME™ process, and outline briefly the research studies in the two processes, that illustrate the chemical synergy in the LPDME™ process. This successful example of “cooperative catalysis” can be adapted in principle to many other organic reactions. We then briefly discern the intrinsic kinetics of the LPMeOH™ and LPDME™ systems, and also shed light of the catalyst deactivation phenomena in these processes. In closing, we outline the reactor design/scale-up and plant operational experience of the 3 commercial technologies, as currently practiced by JFE holdings, BP-AMOCO, and Halder-Topsoe.

Keywords: Natural gas; Steam reforming; Coal; Syngas; Methanol; DME; Bi-functional catalysts; Cu/ZnO/Al₂O₃; γ-Al₂O₃; Slurry reactors; Bubble column reactors; Chemical synergy; Methyl equivalent productivity (MEP); Intrinsic kinetics; Phase equilibrium; Chemical reaction equilibrium; Catalyst deactivation

Introduction

Figure 1: Commercial technologies that are currently available for conversion of syngas conversion to value-added chemicals. The direct DME process is the one covered in this report.
Coal and natural gas as fossil fuels continue to be at the nation’s forefront of energy conversion and power generation processes. In the United States, abundant and plentiful supply of natural gas coupled with its very low costs (~$2MM/BTU and projected to even descend further) has made it an ideal feedstock for conversion to syngas (a mixture of CO and H₂ via the highly endothermic steam reforming or auto-thermal steam reforming). Syngas is a very versatile carbon source that is the primary feedstock for further conversion to value-added chemicals (Figure 1). The recent emphasis on biomass (now primarily lignocellulosic woody feedstocks), considered to be a “renewable” and “sustainable” energy source, has made also this an appealing source of our energy needs.

Syngas generation is the first key step in further conversion to methanol and dimethyl ether (DME). The stoichiometric composition of the syngas is a strong function of the type of C source; coal (lignite, peat, or bituminous/subbituminous), natural gas, or biomass, and gasifier type. The low rank carbon sources such as coal (with low H/C ratios) result in a CO-rich syngas (H₂/CO <1), while the high CV fuels such as natural gas (with high H/C ratios) lead to stoichiometric or balanced syngas, or, a composition which reflects the stoichiometry of methanol synthesis reaction via CO hydrogenation (which requires 2 moles of H₂ per mole of CO). The syngas compositions also contain small proportions of CO₂ (from total combustion of C) and CH₄ (both typically <5%). The controlling mechanism of methanol synthesis reaction and vapor or liquid phase mode of operation governs the choice of feedstock and the H₂/CO ratio.

The introduction of a liquid phase process, in 1975, termed as “liquid phase methanol synthesis process (LPMeOH™)” by Chem Systems, Inc., has been seen as trendsetting in syngas conversion processes [1-3]. In the LPMeOH™ process, a finely powdered methanol catalyst (of the order of 100µm or less) is dispersed or slurried in high-boiling hydrocarbon solvent inert oil). Apart from the high boiling point, other key desirous characteristics of these solvents include a high solubility for syngas components, H₂, CO, CO₂, and CH₄, and a very minimal interaction between the solvent and catalyst. Some of the key advantages of the LPMeOH™ process include better heat transfer characteristics and isothermal operation, use of the CO-rich syngas (from low-cost coal sources), and a very high chemical selectivity to methanol. In the United States, the process feasibility and development studies on the new LPMeOH™ process were initially undertaken by Universities of Akron and Pittsburgh, and Air Products and Chemicals, Inc. (APCI), sponsored by Electric Power Research Institute (based in Palo Alto, Calif.) and Dept. of Energy (a United States Federal agency, with headquarters in Washington, D.C). The UA researchers, since 1985, carried out process development studies in various fundamental and applied aspects, i.e., demonstration of process feasibility, intrinsic kinetics, process chemistry, thermodynamic analysis and development of software package for combined phase and chemical reaction equilibrium for this multiphase and multicomponent system (which enables one to compute the concentrations of dissolved syngas components in the liquid solvent phase, at given reaction conditions), external mass transfer analysis, thermal stability, and scale-up [4-8]. The UA researchers’ also first conceived the direct one-step DME synthesis process, termed as LPDME™ process [9-12] and later, the DME-to-olefins and DME-to-hydrocarbons processes [13-16], both enhancements over Mobil Oil’s original methanol-to-gasoline and methanol-to-olefins process [17-20]. The APCI component has been more focused on catalyst deactivation studies and feasibility/demonstration studies on the pilot scale (5 TPD & 10 TPD scale), of the LPMeOH™ and LPDME™ processes, at its Alternative Fuels Development Unit (AFDU) in LaPorte, Texas [21-24]. Later, in 1996 Eastman Chemical Company (based in Kingsport, Tennessee) assumed a major role in the process development and pilot scale/commercial scale operation (in partnership with APCI), and formed a separate corporate entity, the Air Products Liquid Phase Conversion Company, L.P. – with support from U.S. Department of Energy [25,26].

Figure 2: A schematic diagram of the LPMeOH™ process in operation at Eastman’s Coal-to-Chemicals complex at Kingsport, Tennessee.
The LPMeOH™ Demonstration Project at the Kingsport site is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, LP, a partnership between APCI and Eastman Chemical Company. The commercial scale reactor systems at Eastman’s coal-to-chemicals complex, in Kingsport, Tennessee, are based on the bubble column slurry reactor (BCSR) designs and are one of the largest; the reactor main is 7.5 ft (or, 2.286 m) in diameter and 70 ft (21.34 m) tall, the design capacity is 260 short tons/day, at nominal conditions of 1000 psig (or, 70 atm) and 60 °F (or, 315 °C). It is interesting to note that this represents a very significant scale-up from APCI’s prior experience at the AFDU (in LaPorte, TX), where the nominal diameters were 1.5-2 ft (0.457-0.609 m).

The LPMeOH™ technology, in operation at the Eastman’s coal-to-chemicals complex, is illustrated in Figure 2. The basic reactor design of the commercial bubble column slurry reactor is given in Figure 3. The new corporate entity, Air Products Liquid Phase Conversion Company, LP, formed for this purpose (to demonstrate LPMeOH™/LPDME™ process on commercial scale) has successfully carried out demonstration runs of these processes at this complex.

Discussion

From LPMeOH™ to LPDME™ – the direct DME synthesis process

Since its discovery in 1975, the LPMeOH™ and LPDME™ processes have been illustrative examples of how a mature technology on a commercial scale (ICI low temperature methanol synthesis process) can be successfully adapted to a liquid phase operation. The LPMeOH™ process is a highly flexible process that is well-suited to process low-value CO-rich syngas feeds, uses milder reactor design conditions (of temperature and pressure), and a simple one from a process engineering standpoint. The direct, one-step DME synthesis process is based on the concept and application of so-called “dual catalysis” where 2 functionally different catalysts in a physically admixed form are finely dispersed in a slurry phase reactor system. The 2 functionally different yet compatible catalysts catalyze three parallel reactions: Methanol synthesis (from hydrogenation of CO/CO₂), water gas shift, and methanol dehydration to produce DME. The process is based on application of dual catalysis in a single reactor stage, and based on a combination of an equilibrium-limited reaction (methanol synthesis) and an equilibrium unlimited reaction (methanol dehydration). The process chemistry is represented by the following 3 equations:

\[ \text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (1) \]
\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad (2) \]
\[ 2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (3) \]

The first two reactions take place over the co-precipitated Cu/ZnO/Al₂O₃ catalyst and the third one takes place over γ-Al₂O₃ catalyst. The selective chemical removal of product methanol, from Reaction (1), via its dehydration, via Reaction (3), overcomes the chemical equilibrium barrier on methanol synthesis alone, and improves the per-pass syngas conversion and reactor productivity.

The process chemistry and dynamics of the LPDME™ process, i.e., synthesis of methanol and DME from CO/CO₂/H₂ mixtures, is very interesting and can be complicated at times. The chemical synergy in this process was first noted by researchers at Mobil Oil Company [27] and given as comparisons in a series of curve-pairs that relate the overall conversion of syngas (plotted as ordinate) to the proportion of H₂ in the feed syngas (plotted as abscissa), each at a specific T and P conditions. In these comparisons, the lower curve represents a methanol synthesis process over a standard Cu/ZnO/Al₂O₃ catalyst, with a nominal molar ratio of 60%:25%:15%. The upper curves represent the operation under a DME+ MeOH co-production mode with an identical Cu/ZnO/Al₂O₃ catalyst for methanol synthesis, but which also has a methanol dehydration component, γ-alumina, incorporated therein (10% by weight). The illustrative comparison is given in Figure 4a-4d. It is clear that the three reactions in the LPDME™ process chemistry give rise to a
very interesting interplay, based on a dual thermodynamic–kinetic coupling, which results in higher syngas conversion and per-pass volumetric reactor productivity, than in the LPMeOH™mode alone.

As stated above, this interplay and thermodynamic-kinetic coupling is often referred to as “chemical synergy”.

**Figure 4(a):** Overall syngas conversion as a function of % H2 in the feed syngas, as a comparison for DME+MEOH operation and MeOH alone (T=260 °C, P=50 atm) (Adapted from Zahner (1977)).

**Figure 4(b):** Overall syngas conversion as a function of % H2 in the feed syngas, as a comparison for DME+MEOH operation and MeOH alone (T=290 °C, P=50atm).

**Figure 4(c):** Overall syngas conversion as a function of % H2 in the feed syngas, as a comparison for DME+MEOH operation and MeOH alone (T=260 °C, P=20atm).
The chemical synergy in LPDME™ process

As noted above, the chemical synergy in the direct, one-step DME process was perhaps first noted by the researchers at Mobil Oil Corporation [27]. The researchers at University of Akron and Air Products and Chemicals, Inc., were pioneering in the LPDME™ studies, including process chemistry, process feasibility, roles of CO/CO₂/H₂, thermodynamic analysis, and intrinsic kinetics of LPMeOH™ and LPDME™ systems. We now consider the research portfolios of the University of Akron and Air Products, Inc.

Experimental studies at university of Akron

We first highlight the author’s own experimental studies on the LPDME™ process, carried out during his doctoral studies at University of Akron. We will next discuss the APCI work on process feasibility and chemical synergy. It is clear from the foregoing discussion that the forward water-gas shift, in which all primary reactants, CO, CO₂, H₂O, and H₂, participate, plays a very crucial role in the overall chemistry.

At the UA research component, the experiments were carried out in a 1-liter stirred autoclave fitted with a 6-blade turbine impeller, within a high-temperature, high-pressure slurry reactor system. The nominal temperature and pressure conditions were 250 °C and 70 atm. A feed syngas with nominal composition of H₂: CO: CO₂: CH₄ = 37.4:46.3:8.6:7.7 was used for all experiments. This composition is typical of syngas from Koppers-Totzek or Texaco gasifiers, corresponding to CO-rich syngas, with a H₂:CO ratio of 0.8. The nominal feed flowrate was 1 SLPM which corresponded to 2.678 mol/h.

The chemical synergy in the LPDME™ process system was illustrated with 3 different catalyst slurry ratios, as follows:

A. 15g Cu/ZnO/Al₂O₃ catalyst (labeled as EPJ-19, UCI/BASF) + 0.5g γ-Al₂O₃ catalyst (overall slurry ratio = 4.5%)
B. 80g Cu/ZnO/Al₂O₃ catalyst + 5g γ-Al₂O₃ catalyst (overall slurry ratio =20%)
C. 150g Cu/ZnO/Al₂O₃ catalyst + 10g γ-Al₂O₃ catalyst (overall slurry ratio =33%)

The starting volume of the catalyst slurry was 550 mL Witco-40 mineral oil (under ambient conditions). The density of Witco-40 oil is a strong function of T and compared to a R.T. value 0.773 g/cm³, its value at 250 °C is only 0.613 g/cm³. It is interesting to note that these slurry ratios cover the entire range of practical conditions of interest, from gas-to-liquid mass transfer free to gas-to-liquid mass transfer limited regions. Of course, the chemical synergy and the % increase in MEP productivity is expected to be higher for higher slurry ratios.

Table 1: The chemical synergy in the LPDME™ process as function of catalyst slurry ratio (at nominal reactor conditions of T=250 °C, P=70 atm, syngas flow=2.678 mol/h, impeller speed=1500 rpm, 1 liter stirred autoclave).

| Catalyst Slurry ratio (%) | LPMeOH™ Process | LPDME™ Process |
|---------------------------|-----------------|----------------|
|                           | H₂(%) | CO(%) | Syngas (%) | Syngas conversion(%, at chemical equilibria) | (CH₃⁻) equivalent productivity, MEP (mol/h) | H₂(%) | CO(%) | Syngas (%) | Syngas conversion(%, at chemical equilibria) | (CH₃⁻) equivalent productivity, MEP (mol/h), (Increase in MEP, %) |
| 4.5                       | 55.6  | 21.4  | 36.9       | 37.5                                       | 0.266                                       | 61.4  | 29.2  | 43.3       | 85                                         | 0.281 (5.48) |
| 20                        | 68.1  | 28.6  | 45.3       | 37.5                                       | 0.321                                       | 84.8  | 58.5  | 70.1       | 85                                         | 0.401 (24.8) |
| 33                        | 72.4  | 29.9  | 48.4       | 37.5                                       | 0.342                                       | 87.6  | 62.4  | 73.4       | 85                                         | 0.534 (56.1) |
The experimental data for the LPMeOH and LPDME process systems is given in Table 1. At the outset, it is very interesting to note that the chemical synergy “exists” in LPMeOH system, even alone. For the three catalyst slurry ratios, 4.5%, 20%, and 33%, the syngas conversion at 36.9, 45.3, and 48.3%, for LPMeOH case. The overall syngas conversion is actually higher than the syngas conversion at chemical equilibrium, 37.5%, at these conditions, T=250 °C, P=70atm, and % H₂ in feed syngas=37%. This is a reflection of very facile kinetics of forward water gas shift reaction, which also takes place at or near chemical equilibrium. At these reaction conditions, the K-value for forward WGS reaction is about 1000 times higher than either the CO or CO₂ hydrogenation reactions [28,29].

It is worth noting that, from a scientific standpoint, the shift in chemical equilibrium which results in higher syngas conversions and methanol space-time yields, can be thought to work on the basis of “phase equilibrium” or partitioning of methanol in vapor phase and liquid phase, or net condensation of methanol, even in a purely vapor phase gas-solid reaction. There are other reports that validate this working principle of phase partitioning [30]. The experimental observations indicate that methanol exhibits a rather unusual phase behavior around its critical point, 510K and 81 atm.

Research portfolio of APCI, Inc.

We now consider the research portfolio of Air Products and Chemicals on the single-step syngas to DME process. Over the past 15 years, Air Products & Chemicals, Inc., with Department of Energy (DOE) sponsorship, has been actively engaged in research and development for LPMeOH and LPDME processes, with the overall objective to produce methanol, DME, and other chemicals based on methanol/DME as feedstocks, with the ultimate goal to produce bulk chemicals/fuels/fuel additives from synthesis gas (syngas) generated from coal and natural gas. In APCI research studies, all kinetic experiments on one-step syngas to DME process (LPDME™) were carried out in 300cm³ stirred autoclave reactor systems. For the LPDME™ process, a γ-Al₂O₃ based methanol dehydration catalyst was used in a physically admixed form, with Cu/ZnO/Al₂O₃ methanol catalyst, in an 80:20 weight ratio. The experimental conditions used for all experiments were 250 °C, 5.2MPa (or, 52atm), and a gas hourly space velocity of 6,000lit/kg cat.h. Under these conditions, the experiments were free from all internal and external transport gradients, and thus under kinetic control.

A first important element of the APCI one-step DME process research is the influence of H₂: CO ratio in the feed syngas on the LPDME™ reactor productivity and comparison to LPMeOH™ productivity. A new term, called “methanol equivalent productivity”, abbreviated as MEP, was defined for the LPDME™ process, which was simply defined as the methanol productivity plus 2 times the syngas productivity. A new term, called “methanol equivalent productivity”, was defined for the LPDME™ process, which is always greater than that of LPMeOH™ processes, as a function of H₂: CO ratio in syngas, is illustrated in Figure 5. The chemical synergy is immediately seen from Figure 5. The MEP of LPDME™ (upper curve) is always greater than that of LPMeOH™ process (lower curve). However, it is clearly seen that the magnitude of the synergy varies with H₂:CO ratio. For a H₂:CO above 1.5, the percentage increase in MEP is only around 20%. However, this increase becomes 45% at a H₂:CO of 1.0 and >90% at a H₂:CO of 0.5. In other words, the chemical synergy is the highest at the CO-rich end (highly non-stoichiometric) of the syngas compositions. The LPDME™ process is also uniquely flexible and can be adapted to IGCC power production combined with once-through methanol/DME option.

![Figure 5](image_url)

Figure 5: The methanol equivalent productivity (MEP) from LPDME™ (△), the MEP from LPMeOH™ (▲), and the % increase in the MEP from LPMeOH™ to LPDME™ (•) as a function of H₂:CO ratio in the feed syngas.

To further understand the dependence of the chemical synergy on the H₂:CO ratio in feed syngas, it is instructive to examine if the system is under kinetic control: The change in MEP was assessed by numerical simulations for 4 independent cases under different regimes of kinetic control. Figure 6 depicts the MEP for the 4 cases, as follows: (a) the base catalyst system (at k_w, k_g and k_d), (b) the system with k_g increased by a factor of 4 (4 k_w, k_g, k_d), (c) the system with k_d increased by a factor of 4 (k_w, 4 k_g, k_d) and (d) the...
system with \( k_m \) increased by a factor of 4 \( (k_d, 4k_d, \ 4k_d) \). Figure 6 also shows the MEP curve for the system of 3 chemical reactions at chemical equilibrium (solid line). The cases, \( (\bullet) \ k_m, 4k_m \) and \( 4k_m \) \( (\circ) \ k_d, k_d, 4k_d \) appear as 2 curves immediately up top on the \( (x) k_m, k_d, k_m \), i.e., the base catalyst system case. In fact, the curve symbols for the base catalyst case and the \( 4k_d \) case almost overlap. It is clearly seen that quadrupling the rate constant \( k_d \) and \( k_m \) for methanol dehydration reaction and water gas shift reaction, does not exert any appreciable influence at all, on the MEP productivity. The only kinetic rate constant that profoundly influences the MEP productivity is \( k_m \), the rate constant for methanol synthesis. From the \( (\blacktriangle) \ 4k_m, k_d \) and \( k_m \) case, it is seen that increasing the kinetic rate constant for the methanol synthesis reaction raises the MEP productivity from about 40% to 55%.

**Figure 6:** The methanol equivalent productivity (MEP) as a function of \( \text{H}_2/\text{CO} \) ratio in the syngas feed. Symbol legend: \( (x) \ k_m, k_m, k_m \), i.e., base catalyst system; \( (\bullet) \ k_m, 4k_m, k_m; \ (\blacktriangle) \ 4k_m, k_m, k_m; \ (\blacklozenge) \ 4k_m, k_m, 4k_m \). The solid line over a \( \text{H}_2/\text{CO} \) ratio of 0.5-2.0 is represents MEP at equilibrium.

From Figure 6, it is clear that the overall LPDME™ system is still under “thermodynamic control”. It is thus possible to increase the MEP productivity (and % syngas conversion for LPDME™ case) if we are able to increase the kinetic rate constants of the three component reactions (with, say, design of more active and selective catalysts that are effective at low temperatures, compared to Cu/ ZnO/Al₂O₃ system, which requires 230-270 °C). These cases are denoted by 4\( k_m \), 4\( k_d \) and 4\( k_d \) respectively.

**Role of the water gas shift reaction**

We now make a few brief remarks on one of the long-standing controversial topics in methanol synthesis chemistry, the principal source of C in \( \text{CH}_3\text{OH} \), i.e., \( \text{CO} \) vs. \( \text{CO}_2 \) and the role of water gas shift reaction. We again point to the interested reader a few very important and pertinent contributions by IA researchers’ to provide unequivocal explanations to this controversial area \([4,5,9]\). The works of Lee & Parameswaran \([5]\) are the most instructive in this regard. Based on extensive experimental studies and detailed thermodynamic and kinetic analysis of the overall reaction mechanisms, it has been conclusively proven that, under a variety of syngas types (or \( \text{H}_2/\text{CO} \) ratios) – from no-\( \text{CO} \), to no-\( \text{CO} \), and balanced (or stoichiometric, with \( \text{H}_2/\text{CO}=2-2.5 \)) to \( \text{CO} \)-rich, and experimental conditions, the primary source of C in \( \text{CH}_3\text{OH} \) is the hydrogenation of \( \text{CO}_2 \).

From a historical standpoint, the early proposals on the reaction mechanisms and roles of \( \text{CO}/\text{CO}_2 \) in the vapor phase methanol process implicitly assumed that \( \text{CO} \) was the primary source for methanol (perhaps quite naively because \( \text{CO} \) was in large excess in typical feed syngas streams, compared to \( \text{CO}_2 \)), for typical process conditions of \( \text{H}_2<70\%, \text{CO}+\text{CO}_2<25-30\%, \text{CO}/\text{CO}_2<15-20\% \), \( \text{CH}_4<5\%, 70-100 \text{ bar}, \) and 500-650K. The prevailing (but erroneous) viewpoint of \( \text{CO} \) hydrogenation was pushed forward further by Klier and his team at Lehigh University \([30-34]\). However, this viewpoint was countered by the early Russian reports from Rozowski & Kagan \([35]\), who clearly showed that over \( \text{Cu} \) based catalysts under low temperature conditions, \( \text{CO}_2 \) is the primary source of methanol, i.e., methanol is produced primarily via hydrogenation of carbon dioxide, a reaction which is accompanied by the reverse water gas shift reaction, i.e., hydrogenation of \( \text{CO}_2 \). More recent isotopic labeling experiments (using labeled reactants, 14C/12C) have provided further evidence for \( \text{CO}_2 \) being the primary source, based on analysis of surface elementary reactions and rate controlling steps \([35,36]\). This theory is now confirmed by several researchers including Skryzpek \([37,38]\) and other recent works from Korean research groups \([39,40]\).

To further underscore the very important role of water gas shift reaction in the overall LPMeOH™ and LPDME™ process chemistry, we briefly invoke the kinetic rate models of Graaf et al. \([41,42]\). We refer to the interested reader to those original works for details of the kinetic model development and kinetic analysis, and some additional details are included in Part 2 of this Series on “Kinetic Studies and Catalyst Deactivation”. Here, we summarize the key findings from their work on a semi-quantitative basis. From the kinetic analysis, it is clear that the primary source of C in \( \text{CH}_3\text{OH} \) is \( \text{CO}_2 \), i.e., methanol synthesis occurs primarily via \( \text{CO}_2 \).
hydrogenation in the liquid phase process (as against vapor phase process, where up to about 30mol %C can be derived from CO; CO₂ is still the primary source, however) [43-47]. If one closely examines the kinetic parameters, it is clearly evident that the both pre-exponential factor, 7.21x10¹⁷, and apparent activation energy, 215,130J/mol, are very high for the reverse WGS reaction. In fact, the kinetics of the WGS reaction, on a first approximation based on pre-exponential factors, is faster by about a factor of 10¹² compared to CO hydrogenation and 10³⁰ compared to CO₂ hydrogenation [48-52]. This indicates that this reaction plays a very crucial role in the reaction mechanisms in the liquid phase process. Under conditions of low volumetric gas flow rates (or, low WHSV’s), the WGS reaction is even pushed further above the “equilibrium line”: This overshoot is at least 4-times higher for the WGS kinetics in the liquid phase than under corresponding conditions in the vapor phase. The forward WGS reaction, with its very rapid kinetics, is thus critical for the success of the “chemical synergy” phenomena, observed in LPMeOH™ and LPDME™ processes [53,54].

Summary

The future of DME as an alternative fuel and a chemical intermediate/commodity for targeted end use is very bright. With the right alignment and balance of the political, economic/financial, and environmental “forces”, coupled with the projections of the geopolitical climate, the future use of DME can make impactful and lasting contributions to a nation’s economy and security. By virtue of its safe, reliable, and cost-effective supply chain economics, DME can be a clean-burning alternative fuel and a “green” substitute for diesel, as well as a LPG substitute, mainly in Southeast Asia.

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