

A Novel Synthesis Route for Liquid Fuels from Coal-derived Syngas

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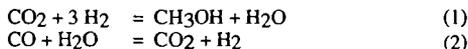
Abstract

Coal-derived syngas can be converted to methanol using Liquid Phase Methanol Synthesis Process. Methanol can be further converted to gasoline using the Mobil Methanol-To-Gasoline (MTG) process. The combination of commercial syngas-to-methanol technology with the MTG Process thus provides a ready synthetic route for liquid hydrocarbon fuels. We have developed a novel process for one-step synthesis of Dimethyl Ether (DME) from syngas. This DME Synthesis improves the reactor productivity and syngas conversion, by as much as 100%, over LPMeOH Process. One-step DME synthesis is thus an ideal front-end for further conversion to gasoline. This substitution is justified not only because DME yields an identical product distribution as methanol, DME is also a true intermediate in the Mobil MTG process. The novel integration scheme has been termed as the Dimethyl Ether-to-Gasoline (DTG) process. The advantages of the UA/EPR1 DTG Process over the conventional Methanol-to-Gasoline Process are in (a) enhanced syngas conversion, (b) superior hydrocarbon yield, (c) superior product selectivity, (d) alleviated heat duties, and (e) integrated energy efficiency. These and other salient features of this novel synthesis route for liquid fuels have been discussed.

Introduction

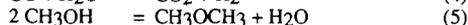
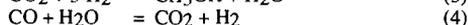
The conversion of syngas to gasoline occurs typically in two stages. Syngas is first converted to methanol over a copper-based hydrogenation catalyst. In the second stage, methanol is converted to gasoline over a ZSM-5 catalyst. These two process steps form the basis for the Mobil Methanol-To-Gasoline (MTG) Process [1-3, 12, 15]. Dimethyl Ether (DME) is a key intermediate chemical species in the second stage. Mobil's MTG process in combination with the commercial syngas to methanol technology thus provide a ready route to synthetic gasoline, i.e., with feedstocks other than petroleum.

The first stage of the MTG process is the synthesis of methanol from syngas. In a typical Liquid Phase Methanol Synthesis (LPMeOHTM) process, the synthesis catalyst (composed of CuO, ZnO, and Al₂O₃) is slurried in an inert hydrocarbon oil [14, 16]. Syngas (H₂, CO, and CO₂) reacts over the active catalyst to produce methanol in-situ. The reaction chemistry for methanol synthesis in the liquid phase from CO-rich syngas has been well-established to be [4-6, 8, 9, 13, 16, 17]:



Syngas-to-methanol conversion technology has recently been modified and improved to synthesize Dimethyl Ether (DME) directly from syngas in a single reactor stage [4-7, 10]. This process augments the per-pass syngas conversion and volumetric reactor productivity as a result of reduced chemical

equilibrium limitation governing the syngas-to-DME conversion. The reaction chemistry for typical single-stage DME synthesis from CO-rich syngas can be written as [7]:



In the Liquid Phase DME Synthesis (LP-DME) process, DME is thus directly produced from syngas, in a single reactor stage. As seen from the reaction sequence, the reaction scheme is a combination of an equilibrium limited reaction (#3, methanol synthesis) and an equilibrium unlimited reaction (#5, DME synthesis, or, methanol dehydration). Reactions #3 and #4 occur over the coprecipitated Cu/ZnO/Al₂O₃ catalyst, while reaction #5 occurs over gamma-alumina. The LP-DME synthesis is thus based on the application of dual catalysis in the liquid phase [10, 11].

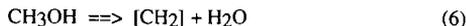
This process can be an effective substitute for the syngas-to-methanol step in the Mobil MTG Process. This substitution is justified based on the following facts (a) DME results in virtually identical hydrocarbon product distribution as methanol and (b) DME is a true intermediate in the Mobil MTG process. The single-stage conversion of syngas to DME (and methanol) thus provides an ideal front-end for further conversion to gasoline.

A novel syngas-to-gasoline process based on this unique integration scheme (Syngas-to-DME and DME-to-Gasoline) has been proven to be superior to the Mobil MTG process. Block diagrams of the conventional Syngas-to-Methanol-to-Gasoline and our novel Syngas-to-DME-to-Gasoline have been shown in Figures 1 and 2. Our novel synthesis process for hydrocarbon fuels has been termed as the UA/EPRI Dimethyl Ether -To- Gasoline (DTG) process. The DTG process merits over the Mobil MTG are in the areas of heat duty, heat of reaction, adiabatic temperature rise, space time and velocity, reactor size, hydrocarbon product yield, and selectivity. These have been conclusively validated in the following sections.

Results and Discussion

1. Heat of Reaction:

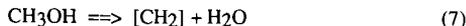
The conversion of methanol to hydrocarbons is an exothermic reaction. Depending on the nature and spectrum of the hydrocarbon product, the heat of reaction will vary. In the simple case when water is the only byproduct, the conversion can be represented stoichiometrically as:



The heat of reaction of methanol conversion to hydrocarbons is a function of the product distribution, or alternately, that of space velocity. Thus, to calculate the heat of reaction of methanol (or, DME) conversion to hydrocarbons, the product distribution spectrum at a fixed space time is necessary. These have been summarized elsewhere [1, 2]. Based on these calculations (at one sample space velocity of 108), the heat of reaction for DME conversion to hydrocarbons (-142 cal/g) was found to be 32% less than that for methanol conversion to hydrocarbons (-211 cal/g). Overall, since methanol dehydration to DME contributes about 25% to the total heat of reaction of the methanol conversion to hydrocarbons, it is expected that the heat of reaction for DME conversion to hydrocarbons at complete conversion would be about 25% lower than that for methanol conversion.

2. Selectivity and Product yield:

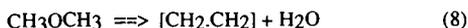
The conversion of methanol to water and hydrocarbons is essentially stoichiometric and complete. The stoichiometric representation of the reaction is:



where [CH₂] is the average composition of the hydrocarbon product comprising of paraffins and aromatics. Water is the only co-product. The final stoichiometric composition for methanol conversion then would be [12+2 = 14] atoms of [CH₂] and [2+16 = 18] atoms of [H₂O]. The stoichiometric

product ratio then becomes 14 g to 18 g. This translates to a 44:56 weight ratio basis of the hydrocarbons to water. The selectivity towards hydrocarbons for methanol conversion is then 0.44 g of hydrocarbons / g methanol.

For the conversion of DME to hydrocarbons and water, the stoichiometric representation of the reaction is:



where $[\text{CH}_2.\text{CH}_2]$ is the average composition of the hydrocarbon product. The final stoichiometric composition for DME conversion would then be $[12+2+12+2 = 28 \text{ atoms}]$ of hydrocarbons and $[2+16 = 18 \text{ atoms}]$ of water. This stoichiometric ratio then becomes 28 g to 18 g. This translates to a product ratio of 60.8 : 39.2 weight basis ratio of hydrocarbons to water. The selectivity towards hydrocarbons is then 0.61 g hydrocarbons/ g DME. The reactor productivity would then be 0.61 g/unit volume of the reactor, when compared 0.44 g for methanol case, this is 38% higher for the DME conversion.

3. Space Velocity and Reactor Size:

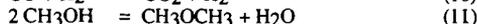
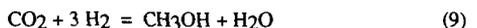
The conversion of methanol and DME to hydrocarbons is a function of space velocity (or, space time in the reactor). The reaction paths for methanol and DME conversion [2] bring out this fact in greater detail. A substantially more space time (or, contact time) is needed for complete and stoichiometric conversion of methanol to hydrocarbons when compared to that needed for DME conversion to hydrocarbons. The relative difference between the space times for these two cases is estimated at 1 magnitude of space time (1/ [g reactant/g cat. h]). Based on the reaction paths given in [1], it is estimated that for identical space time, the DTG reactor size can be about 25% lower than of the MTG reactor, for complete and stoichiometric conversion. Conversely, for identical MTG and DTG reactor size, the DTG reactor will be 25% more productive (i.e., reactor productivity per unit volume) than the MTG reactor.

4. Overall Comparison and Analysis:

Sections (1-3) have elucidated the rationale and the philosophy behind operating the novel Syngas-to-DME-to-Gasoline process, as against the conventional Syngas-to-Methanol-to-Gasoline process. The conclusive advantages of this novel synthesis route (DTG) have been summarized as follows. These advantages have also been summarized in Table I.

[1] One-step conversion of syngas to DME improves the per-pass syngas conversion and reactor productivity over syngas to methanol. The comparison of our experimental results are as follows. At 250 °C, 70 atm, 1-liter slurry reactor, per-pass syngas conversion to methanol is 53%. At nominally identical operating conditions, per-pass syngas conversion to DME is at 74%. Starting with 1 gmol of syngas, this translates to about 0.47 gmol of recycle / gmol of syngas for syngas to methanol case. The recycle load is reduced to only 0.26 gmol / gmol of syngas for the syngas to DME case. The recycle load is thus reduced by about 46%.

[2] The conversion of syngas to methanol uses copper-based $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst. This catalyst is susceptible to deactivation by crystal growth in the liquid phase rich in methanol and water. However, the conversion of syngas to DME uses a dual catalyst system based on a combination of $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst and gamma-alumina catalyst. This conversion offers a favorable scenario for crystal growth of copper catalyst because of two reasons. First, the liquid phase is lean in methanol because of in-situ conversion to DME over gamma-alumina. Second, water produced by both methanol synthesis (CO_2 hydrogenation) and DME synthesis (methanol dehydration) constantly is shifted by the forward water gas shift reaction. This is perhaps the most significant merit of the one-step conversion of syngas to DME, a fact well-proven by the research at the University of Akron. The reaction chemistry of syngas to DME conversion is as follows, starting with CO-rich or the so-called unbalanced syngas:



[3] The one-step conversion of syngas to DME improves the volumetric reactor productivity by as much as 100%, over that of syngas to methanol conversion. This is because of conversion of syngas to DME is not nearly limited by chemical equilibrium as syngas to methanol. This fact has been well-proven by the research at the University of Akron. For example, at 250 °C at 70 atm, starting with 1 gmol of unbalanced syngas, methanol yield is about 0.14 gmol, or, 0.14 gmol (CH₃) equivalent. At identical conditions, the yield of DME is about 0.12 gmol, or, 0.24 gmol of (CH₃) equivalent. This corresponds to an increase of about 72% in the reactor productivity, at identical conditions.

[4] The conversion of methanol to gasoline is highly exothermic with a heat of reaction of 398 cal/g of methanol converted. For this reason, the conversion is usually split in two parts, for exothermic heat management. In the first, methanol is converted to an equilibrium mixture of DME, water (and unconverted methanol). In the second, this mixture of methanol, DME, and water is converted to gasoline. The first step contributes to about 25% of the total exothermic heat of reaction. The conversion of DME to gasoline is thus about 25% less exothermic, with a heat of reaction of about 300 cal/g of DME converted.

[5] . As elucidated in point [4], the conversion of methanol to gasoline requires the conversion of methanol to methanol, DME, and water first, to manage the exothermic heat of reaction. The one-step conversion of syngas-to-DME followed by DME conversion to gasoline thus obviates the need for a separate methanol dehydration reactor. This contributes to significant savings in capital and operating cost.

[6] The adiabatic temperature rise in the conversion of methanol to gasoline is estimated at about 650 °C, while that for the conversion of DME to gasoline is only at about 475 °C.

[7] In methanol to gasoline conversion, equilibrium mixture of DME, water, and methanol is usually fed to the gasoline synthesis reactor. The ZSM-5 based zeolite catalyst is extremely sensitive to water in the feed (water is a catalyst poison). For this reason, water is removed from the feed. In the conversion of DME to gasoline, very little to no water is fed to the gasoline synthesis reactor, because the single-step syngas-to-DME conversion produces DME with extremely high selectivity (>99%). Catalyst life cycle in the gasoline synthesis reactor is favorable in the direct conversion of DME-to-gasoline because of (a) lower concentrations of water in the reactor and (b) about 25% reduced exothermicity of the reaction.

[8] The stoichiometric conversion of methanol to gasoline produces 44 % (w/w) to 56 % (w/w) mixture of hydrocarbons to water. For example, 1 g of methanol yields 0.44 g hydrocarbons [CH₂] and 0.56 g water, at complete and stoichiometric conversion. On the contrary, 1 g DME yields 0.61 g hydrocarbons [CH₂] and only 0.39 g water. The yield of gasoline hydrocarbons for DME conversion is thus 38 % higher than that for methanol conversion. The yield of water is concomitantly 30 % lower for the DME conversion case.

[9] Hydrocarbon product distribution is directly related to the space time for both methanol and DME conversion. For methanol conversion, the reactor space time is estimated to be 20% higher than that for DME conversion, to achieve a stable hydrocarbon product distribution. Intuitively also, this can be immediately validated considering that reaction path of methanol conversion to hydrocarbons involves DME as the intermediate. At identical space time, the DTG reactor size can be 25% lower than the conventional MTG reactor.

[10] Finally, there are important differences between two cases of syngas-to-DME-to-gasoline process, where syngas is derived from coal or from natural gas. Syngas derived from coal is CO-rich (or, unbalanced), while that derived from natural gas is H₂-rich (or, stoichiometric). These differences are in the areas of:

- (a) recycle load (about 0.34 gmol / gmol for coal vs 0.52 for NG case).
- (b) CO₂ rejection is mandatory in coal-based syngas. CO addition is necessary for NG.
- (c) overall [CH₂] productivity is about 30% higher for coal-based syngas.
- (d) overall, coal-based syngas process is more attractive. However, the availability and price of coal in comparison to NG remains a primary concern.

Conclusions

Process comparison and analysis of Syngas-to-Methanol-to-Gasoline and Syngas-to-DME-to-Gasoline conclusively proves that synthesis of gasoline via direct DME route has definitive process advantages over the synthesis via methanol route. These process merits are in the areas of higher gasoline yield, higher syngas conversion, good adaptability to coal-based syngas, and integrated energy efficiency. Further experimental investigation to establish these merits is currently underway at the University of Akron.

Acknowledgments

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Table I

Syngas-to-Methanol-to-Gasoline Vs. Syngas-to-DME-to-Gasoline

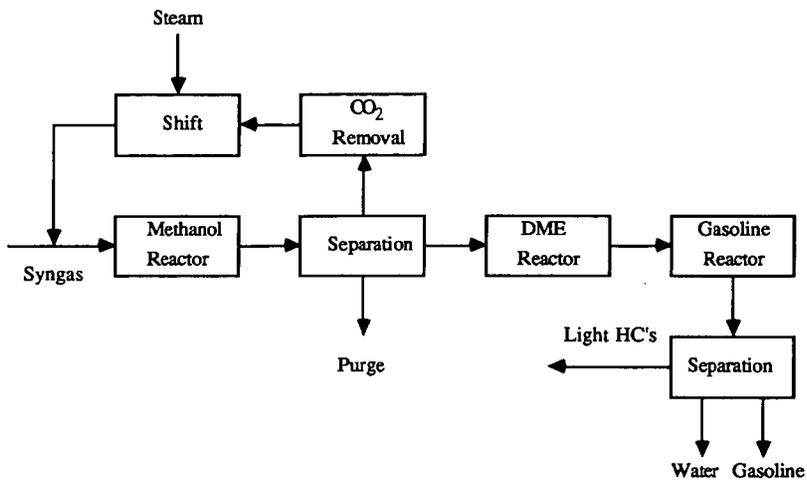
	MTG	DTG
Syngas-to-Methanol Vs. Syngas-to-DME		
1) productivity, g product [#]	10.9	11.8
2) hydrogen conversion, %	72.4	87.7
3) CO conversion, %	38.2	62.3
4) syngas conversion, %	53.0	73.4
5) recycle, gmol / gmol feed syngas	0.47	0.27
6) heat of reaction, cal (exothermic)	8008	13745
7) catalyst life	good	better

[#]On basis of experimental data, 2.68 mol (= 50 g) syngas feed, 250 °C, 70 atm, 1-Lit Autoclave.

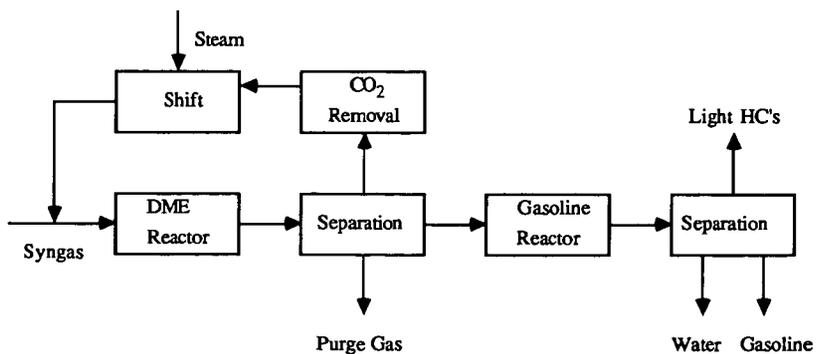
Methanol-to-Gasoline Vs. DME-to-Gasoline

8) productivity, g [CH ₂] [#]	4.79	7.46
9) conversion, %	100	100
10) heat of reaction, cal / g (exothermic)	398	300
11) adiabatic temperature rise, °C	600	475
12) reactor size at identical WHSV	1.25	1
13) catalyst life	poor	better
14) methanol dehydration reactor	necessary	not nec.
15) water concentration in the reactor	high	low
16) overall water production, g [H ₂ O]	6.16	5.15
17) [CH ₂] selectivity, g / g converted	0.44	0.61
18) [H ₂ O] selectivity, g / g converted	0.56	0.39
19) Overall hydrogen consumption, g [CH ₂] / g	3.42	4.31

[#]On basis of complete and stoichiometric conversion, 375 °C, 1 atm, feed item (1).



**Figure 1. Syngas-to-Methanol-to-Gasoline-Methanol Condensation
-Low Pressure Gasoline Reactor.**



**Figure 2. Syngas-to-DME-to-Gasoline-DME Condensation
-Low Pressure Gasoline Reactor.**