Abstract

A DOE/PETC funded study was conducted to examine the use of a liquid phase mixed alcohol synthesis (LPMAS) plant to produce gasoline blending ethers. The LPMAS plant was integrated into three utilization scenarios: a coal fed IGCC power plant, a petroleum refinery using coke as a gasification feedstock, and a standalone natural gas fed partial oxidation plant. The objective of the study was to establish targets for the development of catalysts for the LPMAS reaction.

In the IGCC scenario, syngas conversions need only be moderate because unconverted syngas is utilized by the combined cycle system. A once through LPMAS plant achieving syngas conversions in the range of 38-49% was found to be suitable. At a gas hourly space velocity of 5000 sL/Kg-hr and a methanol:isobutanol selectivity ratio of 1.03, the target catalyst productivity ranges from 370 to 460 g iBuOH/Kg-hr.

In the petroleum refinery scenario, high conversions (~95%) are required to avoid overloading the refinery fuel system with low btu content unconverted syngas. To achieve these high conversions with the low H_2/CO ratio syngas: a recycle system was required (because of the limit imposed by methanol equilibrium), steam was injected into the LPMAS reactor, and CO_2 was removed from the recycle loop. At the most economical recycle ratio, the target catalyst productivity is 265 g iBuOH/Kg-hr.

In the standalone LPMAS scenario, essentially complete conversions are required to achieve a fuel balanced plant. At the most economical recycle ratio, the target catalyst productivity is 285 g iBuOH/Kg-hr. The economics of this scenario are highly dependent on the cost of the natural gas feedstock and the location of the plant.

For all three case scenarios, the economics of a LPMAS plant is marginal at current ether market prices. Large improvements over demonstrated catalyst productivity and alcohol selectivity are required.

Introduction

1.1 Introduction

Implementation of the 1990 Clean Air Act Amendments has resulted in tremendous growth in the market for fuel oxygenates. Ethers have emerged as the oxygenates of choice for the gasoline pool because of their excellent blending properties. The prominent ethers, methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), and tertiary-amyl methyl ether (TAME), all have high blending octane, good miscibility with gasoline, and relatively low blending vapor pressure. Because MTBE is generally the least expensive ether to produce, it has emerged as the most prominent gasoline blending oxygenate. U.S. production of MTBE has increased by a factor of 13 from 1983 to 1993. Increasingly, higher alcohols, especially isobutanol, have been identified as promising additives, both for octane value and as oxygenates.

Current production of MTBE is based largely on natural gas and petroleum feedstocks. In the currently used etherification process for the production of MTBE, methanol is reacted with isobutylene in the presence of an acidic resin catalyst. The feedstock methanol is produced via synthesis gas derived from the reforming or partial oxidation of methane; while isobutylene is primarily produced as a byproduct of catalytic cracking or by butane isomerization followed by dehydrogenation.

A major thrust of the ongoing DOE-sponsored Alternative Fuels Program has been the development of a new route to MTBE based on synthesis gas derived from domestic carbonaceous feedstocks, such as coal. The route under development involves three separate chemical transformations. First, methanol and isobutanol are selectively co-produced from synthesis gas. The isobutanol is then separated from the methanol and dehydrated to isobutylene. Finally, the product isobutylene is reacted with methanol to produce MTBE.

The most significant challlenge in this overall scheme remains the production of isobutanol from synthesis gas at a high rate and selectivity. By contrast, isobutanol dehydration to isobutylene has been shown to proceed at high conversion with excellent selectivity over commercially available alumina catalysts. Thus, the efficient production of isobutanol from synthesis gas is a critical research objective in establishing a commercially viable synthesis gas-based process for the production of MTBE.

1.2 Objective

The primary objective of this study is to evaluate the use of a liquid phase mixed alcohol synthesis (LPMAS) plant to produce gasoline blending ethers. This evaluation will then be used to establish a target for catalyst development and reactor design.

The LPMAS plant was integrated into three utilization scenarios:

- Case 1 - A base-load, coal-fed integrated gasification combined cycle (IGCC) utility plant
- Case 2 - A petroleum refinery (The syngas feed is derived from gasifying petroleum coke.)
- Case 3 - A standalone natural gas-fed LPMAS plant

1.3 Background

At the time this study was conceived, the market prices of the MTBE product and methanol by-product were significantly higher than current market levels. Figure 1-1 shows that in late 1994, the MTBE price was $1.10/gallon and the methanol price was over $1.75/gallon. Currently, the market prices for MTBE

and methanol have dropped to 85 and 35 cents/gallon, repectively. Naturally, these lower prices for the downstream products from the LPMAS system make it much more difficult to achieve a sound economic basis for developing the LPMAS system.

1.4 Common Study Basis

The study was based on several assumptions that were common to all three cases.

1.4.1 LPMAS Yield -

The starting point for developing the LPMAS reactor product selectivity was a paper by Heydorn, et al.,[1] which provided data on the coproduction of methanol and isobutanol. The alcohol product distribution for a feed syngas H_2/CO ratio of 0.45 is shown in Table 1-1. Note that the methanol/isobutanol molar ratio is around 11. The demonstrated catalyst productivity from an autoclave test system at 315°C was 62 g isobutanol/Kg-hr.

The major non-alcohol organic by-products were hydrocarbons (light paraffins) and esters. It was assumed that the production of the hydrocarbon and ester by-products could be excluded in the present study because:

- The demonstrated by-product yields are low, and further catalyst development should lead to more selective conversion to alcohols.

- If these by-products were part of the product mix, they would be used as fuel and would have the same value on a BTU basis as the unconverted syngas. In other words, having a small amount of hydrocarbons and esters in the product mix would have very little effect on the overall analysis.

It was also assumed that the production of ethanol and propanol could be eliminated by using a more selective catalyst and/or by fractionating the raw product and recycling the ethanol and propanol back to the LPMAS reactor.

1.4.2 Alcohol Selectivity -

Since MTBE currently has a higher market price than methanol (85 cents/gallon vs. 35 cents/gallon), it was decided to maximize revenues and analyze the LPMAS integration at the optimum methanol/isobutanol ratio to produce ethers. This ratio is 1.03 (there is a small amount of methanol required to convert isoamylene to TAME).

Based on the above assumptions the alcohol product distribution is shown in Table 1-2. The effect of higher methanol/isobutanol ratios is studied in Case 3.

1.4.3 LPMAS Syngas Conversion

In this study, syngas conversion for the LPMAS system is defined as follows:

$$\text{Syngas conversion} = \left(1 - \left(\frac{LHV \, of \, H_2 \, and \, CO \, out}{LHV \, of \, H_2 \, and \, CO \, in}\right)\right) \times 100\%$$

Introduction

In Case 1, the LPMAS syngas conversion levels were varied from the demonstrated level of approximately 20% up to 64%. In Cases 2 and 3, the syngas conversion was maintained at a single level for each case.

1.4.4   LPMAS Reactor Design Basis -

In the LPMAS reactor, feed gas is bubbled up through an oil/catalyst slurry. Steam is generated from the heat of reaction in internal heat transfer tubes.

To show the sensitivity of capital cost to changes in syngas flow rate and conversion, the reactor size was changed to match the required heat removal capacity as the flow rate and conversion were varied. Key criteria such as operating temperature and pressure, slurry concentration and gas hourly space velocity were obtained from the Heydorn paper and kept constant. The gas inlet velocity based on the net cross-sectional area of the fluid in the reactor at the tube level was chosen by Bechtel and held constant. The overall heat transfer coefficient was calculated from a previous liquid phase methanol reactor design. With these design criteria set, the syngas feed rate determines the volume occupied by the slurry and the heat release determines the volume required for heat removal. The key design parameters were as follows:

Gas hourly space velocity, sl/Kg-hr	5000
Temperature, °C	315
Pressure, psig	1800
Catalyst slurry concentration, wt%	40
Inlet velocity, ft/sec (based on fluid area)	0.4

Using the feed syngas flow rate and the heat of reaction, the number of tubes, reactor diameter, total weight, and cost (based on weight) are calculated. The LPMAS balance-of-plant equipment costs are based on a previous EPRI report and APCI data and are factored on the basis of syngas flow.

1.4.5   Alcohol Separation

The alcohol separation step has two purposes: (1) to separate the alcohols into two streams, methanol and C_{4+} alcohols; and (2) to remove water.

A five-column system with azeotropic distillation was selected for alcohol separation and water removal. Although a detailed design for this system was not performed, a process simulator program was used to estimate column traffic and utility requirements. A capital cost for this plant was estimated for a single feed rate. Capital costs for the other cases were factored from this case.

1.4.6   Alcohol Dehydration

The estimate of the capital cost of the alcohol dehydration plant is based on an article by Armstrong et al.,[2] which provided reactor operating data. These data were used to estimate the cost of a reactor system based on a single C_{4+} alcohol feed rate. Capital costs for the other cases were factored from this case.

The key design parameters for the liquid-phase dehydration reactor are as follows:

Operating pressure, psig	25
Operating temperature, °C	300

Gas hourly space velocity, sl/Kg-hr	230
Catalyst slurry concentration, wt%	40
Inlet velocity, ft/s (based on fluid area)	0.7

1.4.7 Ether Production

The design and capital costs for the ether production facilities were based on Bechtel's in-house data.

1.5 References

1. Heydorn, E., E. Schaub, V. Stein, R. Underwood, and F. Waller, "Recent Progress on Syngas Conversion to Isobutanol," 1994 Coal Liquefaction and Gas Conversion Contractors' Review Conference, September 7-8, 1994, Pittsburgh, Pennsylvania.

2. Armstrong, P. et al., "Isobutanol Dehydration: A Key Step in Producing MTBE from Syngas," Coal Liquefaction and Gas Conversion Contractors Review Conference; September 27-29, 1993.

1.6   Tables and Figures

Table 1-1
Demonstrated Alcohol Product Distribution

Item	Wt %	Alcohol mol%
Methanol	62.5	81.74
Ethanol	3.8	3.46
Propanol	5.5	3.84
n-Butanol	1.5	0.84
i-Butanol	13.0	7.35
n-Pentanol	0.6	0.28
i-Pentanol	3.0	1.42
n-Hexanol	0.6	0.25
i-Hexanol	2.0	0.82
Misc. hydrocarbons	7.5	
Total	100.0	100.00

Table 1-2
Study Basis Alcohol Product Distribution

Component	Alcohol mol%
Methanol	48.83
Ethanol	0.00
Propanol	0.00
n-Butanol	0.84
i-Butanol	47.56
n-Pentanol	0.28
i-Pentanol	1.42
n-Hexanol	0.25
i-Hexanol	0.82
Total	100.00

Figure 1-1
MTBE/Methanol Price Survey
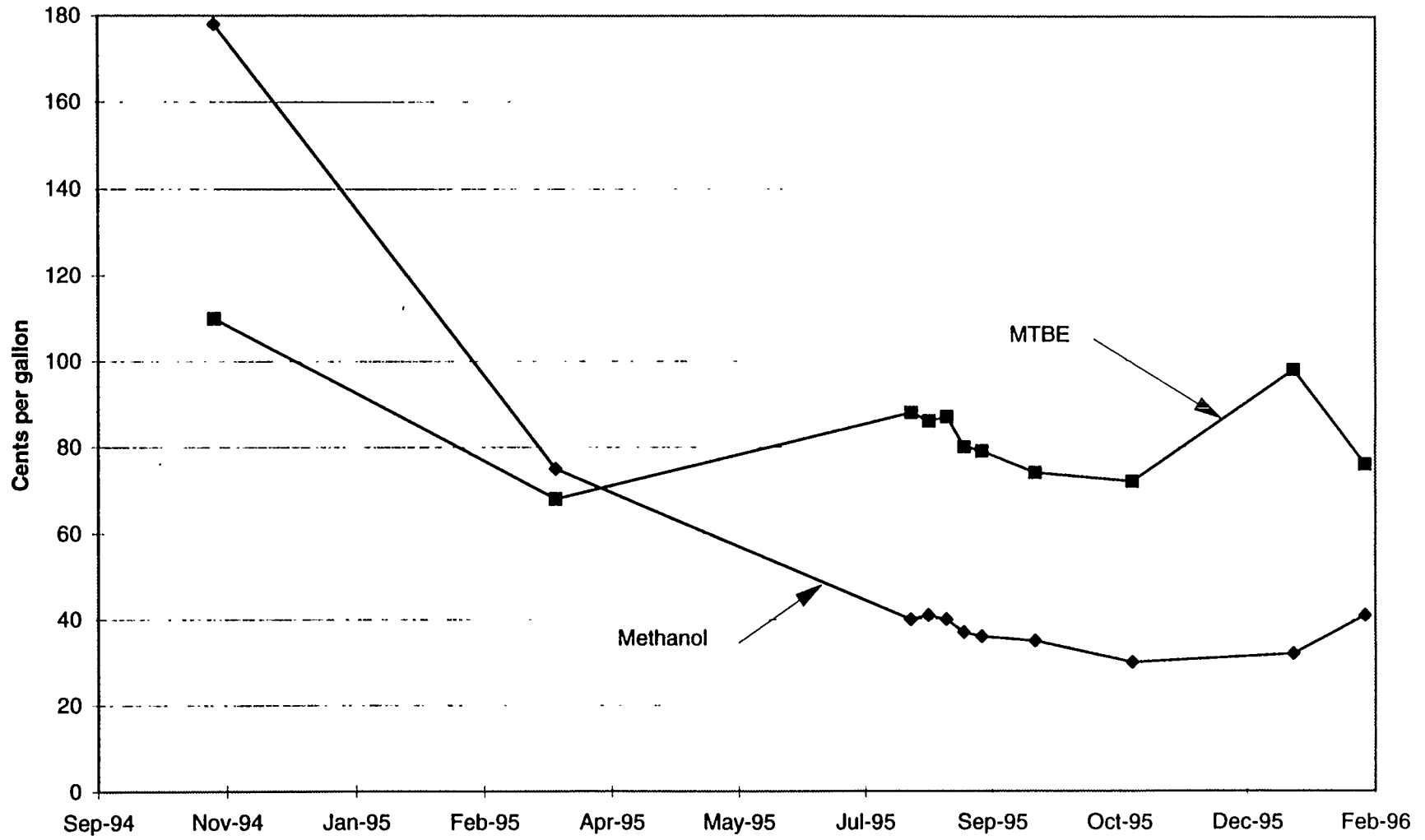
Case 1 - LPMAS/IGCC Power Plant

2.1 Background

The scenario for Case 1, a coal-fed IGCC power plant, was chosen for three reasons:

- Coal gasification produces a low H_2/CO ratio syngas which has been shown to be favorable to higher alcohol production.
- The combined cycle power plant can easily consume low btu content unconverted syngas. This allows for lower syngas conversions in the LPMAS plant.
- Higher power plant availability can be claimed since the LPMAS plant can be bypassed if there is a partial shutdown of the coal gasification section of the plant.

2.2 Study Basis

Figure 2-1 shows how the LPMAS plant was integrated into the IGCC power plant. The shaded blocks represent plants that need to be added for alcohol/ether production. Coal is gasified to produce a syngas with a H_2/CO ratio of 0.5. After cleanup, the entire syngas production is fed to the LPMAS plant where a portion of the syngas is converted into methanol and higher alcohols. The unconverted syngas is sent to the combined cycle section of the plant for power production. The mixed alcohol stream is separated into methanol and C_{4+} alcohols. The C_{4+} alcohols are dehydrated into olefins and are then sent to the ether plant. The iso-butylene and iso-amylene portions of the C_{4+} olefins are converted into MTBE and TAME, respectively.

2.2.1 Power demand level

The power production from the base-loaded IGCC plant was set at a constant 385 net MW. This was based on the production from a single 3000 stpd Shell gasifier (currently the maximum capacity) without the addition of a LPMAS system. Since the LPMAS plant consumes a portion of the syngas, the coal feed rate is higher than 3000 stpd to maintain the 385 net MW production level. This necessitates more than one gasifier train.

A load following scenario was also examined. In this scenario, the LPMAS/ether section of the plant is shutdown or bypassed at high power demand levels. This results in low stream factors for the LPMAS/ether section and poor overall economics. For this reason, the load following scenario is not presented.

2.2.2 Gasification/Combined Cycle

The syngas composition is based on a Shell gasifier fed with West Virginia coal. The analysis of the coal is shown in Table 2-1. The clean syngas composition is shown in Table 2-2.

Capital costs for the gasification (gasifier, air separation unit and acid gas removal unit) and combined cycle portions of the plant were scaled from a previous study. Single-train capital costs for the gasification plant were assumed to follow a 0.6 capacity exponent factor. Once again, the maximum gasifier train size was set at 3,000 stpd.

The impact of LPMAS conversion on project economics was evaluated based on keeping the LPMAS and combined cycle systems operating at capacity and in series. As the LPMAS syngas conversion level increases, gasifier throughput is increased in order to maintain a constant combined cycle power ouput

(385 net MW). Figure 2-2 shows how gasification requirements change as a function of syngas conversion.

A sample of a material balance for the plant is shown in Table 2-3.

Table 2-4 summarizes the operation of the IGCC and LPMAS plants. The following key points should be noted:

- The gasification capacity rises steadily from 3,860 (at 20% syngas conversion) to 7947 stpd of coal (at 64% syngas conversion).
- The design feed capacity of the LPMAS plant increases steadily (from 274 million to 563 million SCFD of syngas) as the syngas conversion level increases. The total alcohol (methanol and C_{4+} alcohols) production capacity increases from 495 to 3,199 stpd. (See Figure 2-3.)
- The production of ether rises steadily from 3,022 to 19,532 bpd. (See Figure 2-4.)

2.2.3 Syngas conversion/recycling

A block flow diagram of the LPMAS plant is shown in Figure 2-5. The clean syngas is compressed to 1800 psig and is combined with recycle gas (if required) prior to feeding into the LPMAS reactor. The raw products and unconverted syngas are cooled and separated. The liquid products are sent to the separation facilities. The unconverted gas is sent to the combined cycle system. If required, a portion of the unconverted syngas is recycled back to the reactor to achieve higher conversions.

As noted in the previous section, overall syngas conversion levels from 20 to 64% were studied. At conversion levels below 49%, a once through LPMAS system is used. Above 49%, methanol equilibrium limitations require recycling unconverted syngas back to the LPMAS reactor. Figure 2-6 shows the effect of recycling on the feed rate to the LPMAS reactor. At overall conversion levels above 60%, the costs of recycling (larger reactor/equipment, multiple trains, recycle compression, etc.) outweigh the benefit (higher ether production) of higher conversions.

2.3 Economic Analysis

The capital cost of the gasification plant was distributed between the combined cycle and the LPMAS systems by the amount of gasifier output energy (steam plus syngas heating value) used by each system. Specifically, the combined cycle consumes the energy in the high-pressure steam from the gasifier as well as the unconverted syngas.

For example, for the 40 percent syngas conversion level, 40.8 percent of the gasifier energy output is consumed by the LPMAS system. The portion of the gasifier direct capital cost attributable to the LPMAS system is, therefore, 0.408 x $306.3 million, or $125 million.

Table 2-5 summarizes estimates of the capital cost for the entire plant and for that portion of the plant attributable to the LPMAS system.

The following basis was used for the economic analysis:

- $25/short ton coal
- 4-year construction period
- 50/50 debt/equity ratio (typical ratio for the electric power industry)

Case 1 - LPMAS/IGCC Power Plant

- 9% loan

At each syngas conversion level, the required price of the ether product was determined to achieve a 13 percent rate of return based on discounted cash flow analysis. That is, the revenue from the ether product was adjusted to achieve the target rate of return. (The 13 percent rate of return is commonly used to conduct economic analysis on power industry projects.)

2.4 Results

2.4.1 Required Ether Price

Figure 2-7 shows the required price as a function of overall syngas conversion. From 20 to 49%, the required price declines as the conversion of low value syngas to high value ethers increases. At 49% conversion, there is very small increase in the required price because a recycle system is required at this point. At 51%, there is discontinuity where the number of gasifier trains increases from two to three. Above 51%, the costs of recycling start to outweigh the benefit of higher conversion levels. At 64% overall conversion, the recycle ratio (moles of recycle/moles fresh feed) is 4.7 and the per pass conversion has declined to 14%.

2.4.2 Required Catalyst Productivity

Figure 2-8 shows both the required ether price and the catalyst productivity. For a once through operation (up to 49% overall conversion), the required productivity rises steadily. Above 49%, the productivity decreases as the increase in conversion is achieved by recycling.

As noted in Section 1.3, the current market price for MTBE is about 85 cents/gallon. For a once through system, the required catalyst productivity to produce MTBE at this price is 370 g isobutanol/Kg-hr. It should be noted that the required catalyst productivities shown in Figure 2-8 are based on the study basis LPMAS reactor space velocity of 5000 sl/Kg-hr (see Section 1.4.4).

2.5 Sensitivity Study - LPMAS Space Velocity

The effect of the LPMAS reactor space velocity on the economics of an IGCC/LPMAS plant is shown in Figure 2-9. Halving or doubling the space velocity (to 2500 or 10,000 sl/Kg-hr) results in a small change in the required ether price (2-3 cents/gallon). This is because the cost of the LPMAS reactor represents a small portion of the capital cost of the overall plant. It should be noted that the required catalyst productivity is directly proportional to the space velocity. In other words, halving the space velocity also halves the required catalyst productivity.

2.6 Case 1 Conclusions

- Within the study basis parameters, a LPMAS plant could be economically integrated into a base load IGCC plant to produce gasoline blending ethers

- For an ether price of 85 cents/gal, the required catalyst productivity is over 370 g iBuOH/Kg-hr (5000 sl/Kg-hr, 1.03 MeOH/iBuOH ratio).