

3.3.2 Oxygenates via Synthesis Gas (Lehigh University)

Overall 2QFY96 Objectives

- (i) Continue studies of increasing the conversion of H₂/CO to higher alcohols by promotion of the C₁ → C₂ carbon chain growth step over Cs-promoted Cu/ZnO/Cr₂O₃ catalysts,
- (ii) Significantly enhance the C₂ → C₃ → C₄ carbon chain growth steps over Cs/Cu/ZnO/Cr₂O₃ catalysts, and
- (iii) Prepare and test high surface area Cu/ZrO₂ catalysts, both Cs-doped and undoped, that are candidates for the synthesis of C₁-C₅ alcohols, in particular branched products such as isobutanol.

Results and Discussion

Cu/ZnO₂ and Cs/Cu/ZnO₂ Catalysts for Alcohol Synthesis

During this quarter, experimental research with the Cu/ZrO₂ catalysts was completed. The Cu/ZrO₂ and Cs/Cu/ZrO₂ catalysts were previously tested, and most of the data analyses and catalyst characterization in terms of BET surface areas, X-ray photoelectron spectroscopy (XPS), and X-ray powder diffraction (XRD) have now been completed. In selected cases, electron microscopy (mainly TEM) is also being carried out.

Surface areas were obtained with a Micromeritics Gemini 2360 instrument using nitrogen as the adsorbate. A comparison of the surface areas, some of which were reported previously, is shown in Table 3.3.6 for Cu/ZrO₂ = 10/90 and 30/70 mol% catalysts.

Table 3.3.6 BET Surface Areas for the Cu/ZrO₂ = 10/90 and 30/70 mol% Catalysts, Where Each Calcination Treatment was Maintained for 3 hr

Cu/ZrO ₂ Catalyst	Calcination Temp. (°C)	BET Surface Area (m ² /g)
10/90	500	63
10/90	400	112
10/90	350	148
10/90	350, after testing	72
3% Cs/10/90	350, after testing	73
30/70	500	25
30/70	400	73
30/70	350	78
30/70	350, after testing	55

It is evident that utilizing higher calcination temperatures resulted in less surface area for the catalysts. In addition, catalytic testing resulted in the loss of surface area. These observations were also reflected by the XRD results obtained with these catalysts, in which an increase in crystallinity was directly correlated with a decrease in surface. The data in Table 3.3.6 also indicate that doping of the 10/90 catalysts with Cs did not affect the surface area of the catalyst as

observed after catalytic testing, since both the undoped and Cs-doped catalysts exhibited surface areas slightly above 70 m²/g after testing. This was approximately 50% of the surface area of the catalyst after calcination at 350°C. It is noted that the temperature of catalytic testing did not exceed 330°C.

Transmission electron micrographs and corresponding selected area diffraction patterns of the Cu/ZrO₂ = 10/90 and 30/70 catalysts after testing showed the presence of two distinct phases having different contrast properties. These phases corresponded to crystalline ZrO₂ and metallic copper. The Cu⁰ particle sizes corresponded to ≈4.0 nm and ≈5.5 nm for the 10/90 and 30/70 catalysts, respectively.

X-ray photoelectron spectra of some of the samples were obtained with a SCIENIA ESCA-300 spectrometer with a monochromatic Al Kα (1486.7 eV) X-ray source. Samples for analysis were pressed onto a sample stub, inserted into the analysis chamber, and evacuated to 10⁻⁹ torr or lower. The surface charging problem caused by the liberation of photoelectrons was minimized by flooding the sample surface with a beam of low-energy electrons (5-10 eV). For all spectra, Shirley background was subtracted, and a Voigt function was used to analyze the peaks. XPS analysis was centered on the tested 3 mol% Cs/Cu/ZrO₂ catalyst. The Zr 3d_{5/2} peak (182.5 eV) was used as a reference, and was considered a better reference than the C 1s line (284.6 eV). The NTS survey spectrum of the sample is shown in Figure 3.3.19. The Cs component was readily detected, with the Cs 3d core level peak located at 724.8 eV.

XPS spectra of regions of particular interest are shown in Figure 3.3.20. The Cu 2p peak in Figure 3.3.20a is located at 932.8 eV, while the Zr 3d_{5/2} and 3d_{3/2} peaks, separated by 238 eV, are shown in Figure 3.3.20b. The position of the Cs 3d peak shown in Figure 3.3.20c indicates that Cs was present as Cs⁺. The O 1s spectra shown in Figure 3.3.20d contains a pronounced shoulder, indicating the presence of two different states of oxygen in the catalyst. The surface composition of the catalyst was estimated by normalizing the peak areas with Scofield cross sections of the individual elements. The surface metal ratio was found to be 11/16/73 mol% Cs/Cu/Zr. The finding that the Cs content was higher than 3 mol% shows that the Cs remained as a surface dopant and that it was uniformly dispersed over the surface.

Isobutanol Synthesis Over Double Bed Catalysts

The research this quarter has been a continuation of our higher alcohol synthesis research over double-bed catalysts in a single reactor that are operated at different reaction temperatures (see quarterly reports for July-September and October-December 1995). In our previous research, the two catalysts consisted of 3% Cs/Cu/ZnO/Cr₂O₃/ZnO//4% Cs/ZnO/Cr₂O₃. We have now shown that much higher productivity of isobutanol was obtained when both beds consisted of 3 mol% Cs/Cu/ZnO/Cr₂O₃ (at different temperatures of 325 and 340°C) than when the lower catalyst bed consisted of copper-free 4% Cs/ZnO/Cr₂O₃ catalyst at 405°C.

Before further testing in the dual-bed configuration, the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst (2 g; prepared as described in the quarterly report for October-December 1995) was first tested for alcohol synthesis by itself at 7.6 MPa using H₂/CO = 0.45 synthesis gas at a gas hourly space

Figure 3.3.19 X-Ray Photoelectron Spectroscopy Survey Spectrum of the 3 mol% Cs/Cu/ZrO₂ Catalyst After Catalytic Testing

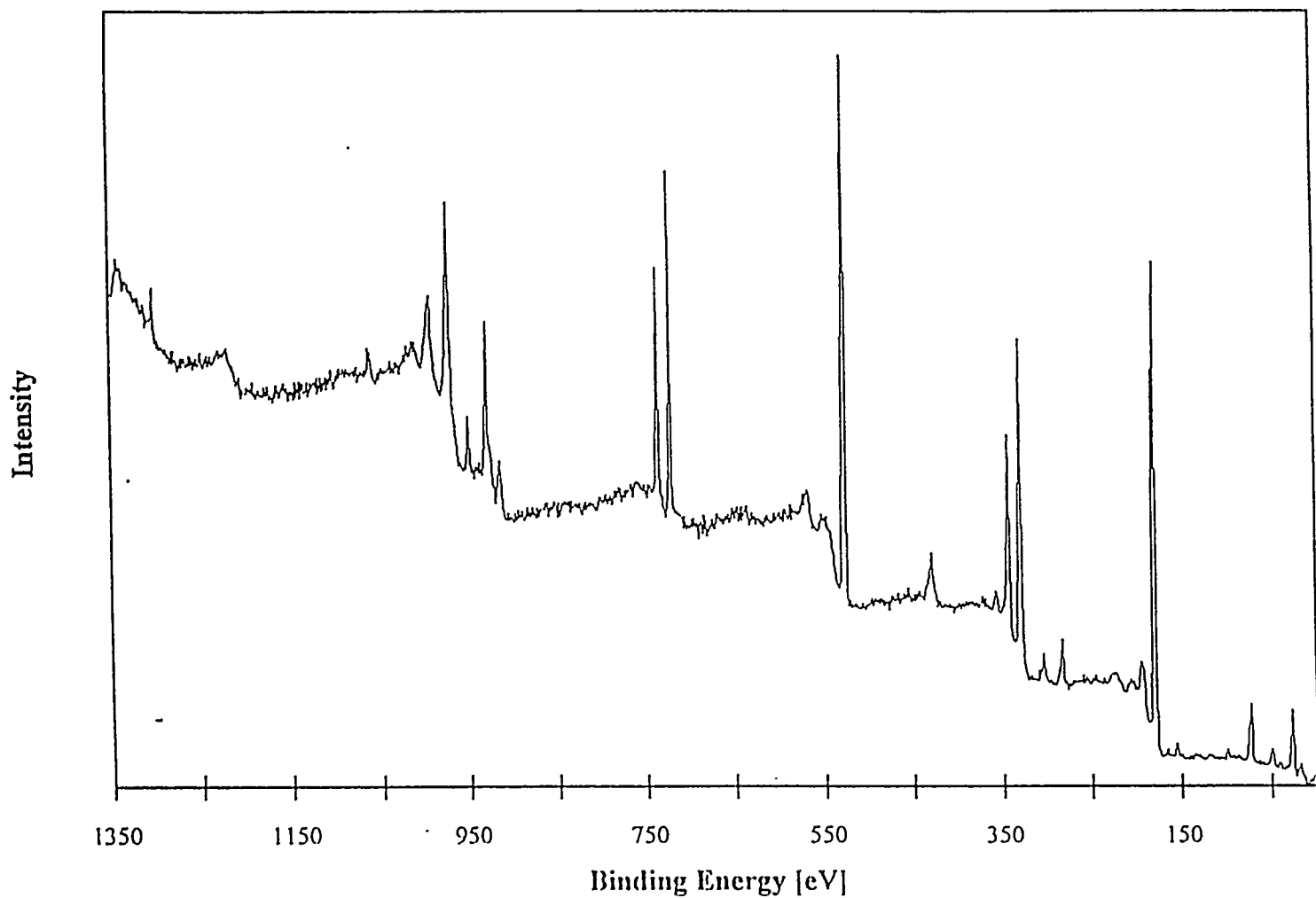
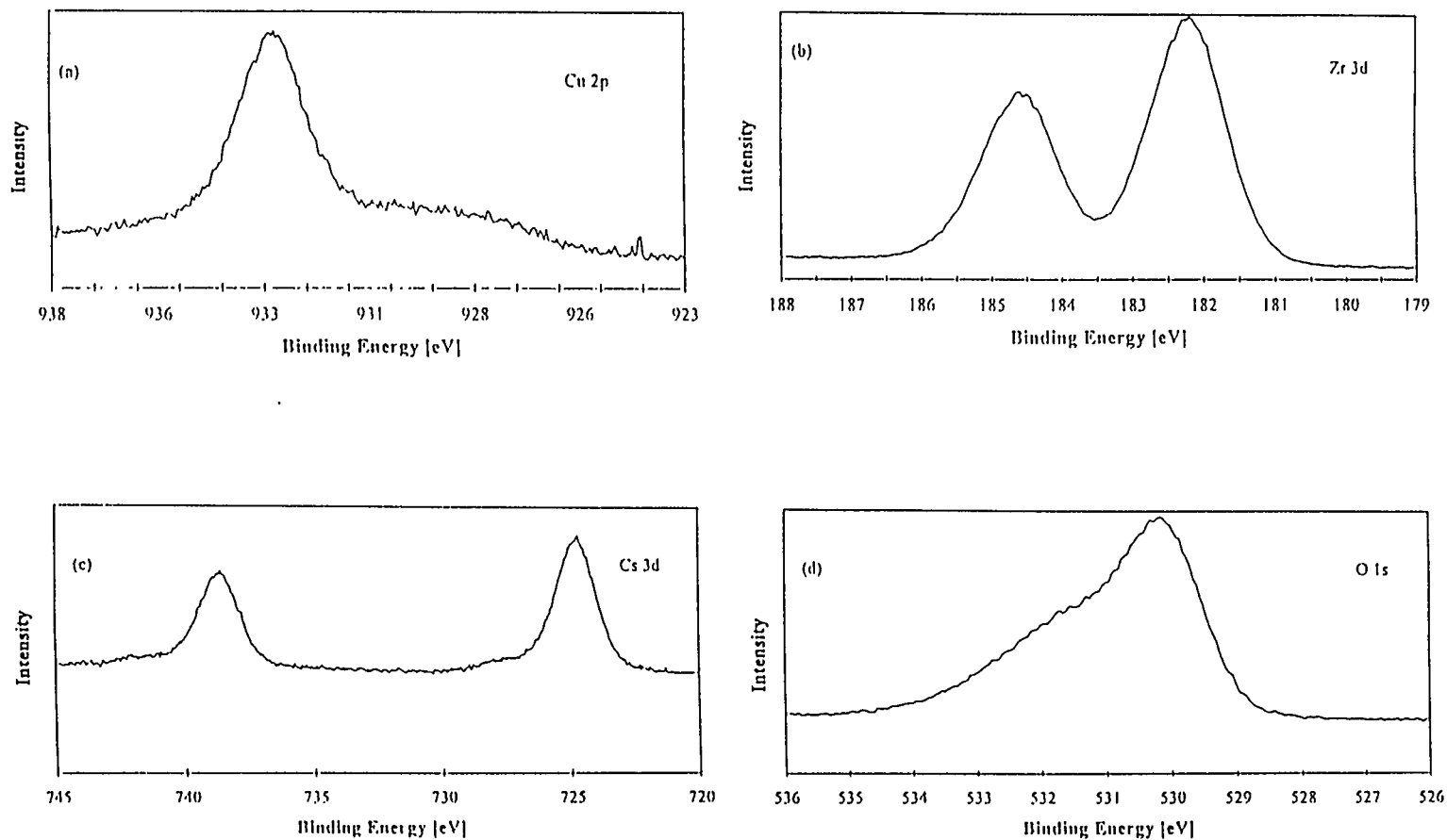


Figure 3.3.20 Photoelectron Al K α Spectra of the (a) Cu 2p, (b) Zr 3d, (c) Cs 3d, and (d) O 1s Regions of the 3 mol% Cs/Cu/ZrO₂ Catalyst after Catalytic Testing



velocity (GHSV) of 5450 liter (STP)/kg cat/hr at temperatures higher than previously employed for this copper-containing catalyst. The results of this catalytic testing, where steady-state conversions and selectivities were observed, are shown in Table 3.3.7.

By systematic testing at 340, 370, 405, and 430°C, it was shown that CO conversion decreased from 9.6 to 7.5 to 5.3 to 4.2 mol% as the temperature was sequentially increased from 340 to 430°C. Methanol productivity steadily decreased as well in the sequence of 122, 77, 29, and 19 g/kg cat/hr. At the same time, isobutanol productivity decreased from 73 to 67 to 53 to 40 g/kg cat/hr, with the decline more gradual than that for methanol. This resulted in higher isobutanol productivity than for methanol at 405 and 430°C. With methanol as a precursor to the higher alcohols, this range of high reaction temperatures under these reaction conditions is not conducive to the enhancement of isobutanol synthesis.

Catalytic testing of the dual catalysts was carried out as described in previous quarterly reports, and the double-bed experiment used 1 g of catalyst in each bed. In this experiment, two portions of the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst were utilized in a double-bed configuration, both in the lower temperature first bed and in the higher temperature second bed. A H₂/CO = 0.75 synthesis gas at GHSV = 18,375 liter (STP)/kg cat/hr and 7.6 MPa was utilized; the temperature of the first (top) catalyst bed was 325°C, while the second (bottom) bed was maintained at 340 or 370°C. The productivities and CO conversion levels are given in Table 3.3.8.

As shown in the quarterly technical progress report for October-December 1995, using the 4 mol% Cs/ZnO/Cr₂O₃ catalyst in the second bed (at 405°C, but under similar reaction conditions) resulted in a CO conversion of 6.1 mol% and an isobutanol (2m-PrOH) productivity of 125 g/kg cat/hr. Thus, using the 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst in both beds, which allows the second bed to be operated at lower temperature, resulted in a significant increase in the productivity of isobutanol, with high selectivity to methanol + isobutanol. The 202 g of isobutanol/kg cat/hr reported in Table 3.3.8 for a second catalyst bed temperature of 340°C is a significant enhancement of isobutanol productivity over the space time yields previously observed over this type of catalyst.

The selectivities shown in Table 3.3.8 are especially notable. The isobutanol/ methanol mass ratios are about 0.35 and 0.5 for the lower bed temperatures of 340 and 370°C, respectively. At the lower bed temperature of 340°C, 67% of the carbon in the products shown in Table 3.3.8 is in the isobutanol and methanol. If n-propanol is included, then 80% of the carbon in alcohol and hydrocarbon products is found in these three alcohols. This is a remarkable product distribution.

Overall 3QFY96 Objectives

Future research for Task 3 will focus on the following areas:

- (i) Complete revision of the manuscript detailing our experimental progress on the preparation of Cu/ZrO₂ catalysts, both Cs-doped and undoped, and the synthesis of methanol and dimethyl ether over these catalysts from H₂/CO synthesis gas mixtures, in which the effects of CO₂ and H₂O were determined.

Table 3.3.7 Productivities and Distribution of Products Formed Over the 3 mol% Cs/Cu/ZnO/Cr₂O₃ Catalyst (2 g) with H₂/CO = 0.45 Synthesis Gas at 7.6 MPa with GHSV = 5,450 liter(STP)/kg cat/hr as the Temperature (T) was Increased from 340 to 430°C. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols. Abbreviations used are Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pent = pentyl, 2m = 2-methyl, 3m = 3-methyl, MF = methylformate, MAC = methylacetate, DME = dimethylether, and HC = hydrocarbon.

	T = 340°C (g/kg cat/hr)	T = 370°C (g/kg cat/hr)	T = 405°C (g/kg cat/hr)	T = 430°C (g/kg cat/hr)
MeOH	122	77	29	19
EtOH	4	1	1	1
PrOH	22	13	4	3
BuOH	3	0	0	1
PentOH	3	0	1	1
2m-PrOH	73	67	53	40
2m-BuOH	20	13	8	4
2m-PentOH	12	10	4	2
2-BuOH	5	6	5	2
3m-2-BuOH	3	4	1	1
3-PentOH	5	6	4	3
2m-3-PentOH	12	10	7	6
MF	1	4	6	9
MAC	1	2	1	3
DME	2	3	3	1
C ₇ ⁺ - Oxygenates	9	9	11	10
CH ₄	7	10	14	18
C ₂ -C ₄ HC	11	10	15	15
%CO Conv. (CO ₂ -free)	9.6	7.5	5.3	4.2

Table 3.3.8 Higher Alcohol Synthesis Over Two Portions of the 3 mol% Cs/Cu/ZnO/Cr₂O₃ Catalyst Held in a Double-Bed Configuration, Where the Top Bed (1 g) was Held at 325°C and the Lower Bed (1 g) was Maintained at 340 or 370°C. The synthesis gas consisted of H₂/CO = 0.75 at 7.6 MPa with GHSV = 18,375 liter(STP)/kg cat/hr. The productivities of aldehydes and ketones have been added to those of the corresponding primary and secondary alcohols. Abbreviations used are Me = methyl Et = ethyl Pr = propyl, Bu = butyl, Pent = pentyl, 2m = 2-methyl, 3m = 3-methyl, and HC = hydrocarbon.

	Top = 325°C Bottom = 340°C (g/kg cat/hr)	Top = 325°C Bottom = 370°C (g/kg cat/hr)
MeOH	574	369
EtOH	15	5
PrOH	93	47
BuOH	0	1
PentOH	0	1
2m-PrOH	202	180
2m-BuOH	7	6
2m-PentOH	5	5
2-BuOH	26	20
3m-2-BuOH	1	0
3-PentOH	11	9
2m-3-PentOH	13	2
CH ₄	14	22
C ₂ -C ₄ HC	24	22
%CO Conv. (CO ₂ -free)	8.5	6.2

- (ii) Finish data analysis for the catalytic testing and characterization carried out with Cs/Cu/ZnO/Cr₂O₃ catalyst, both by itself and in the configuration of Cs/Cu/ZnO/Cr₂O₃||Cs/Cu/ZnO/Cr₂O₃ dual-bed catalysts at different reaction temperatures; these catalysts were systematically tested for the synthesis of methanol and isobutanol. In addition, complete the revision of a full manuscript describing this research.

3.4 Chemicals from Synthesis Gas - No progress to report this quarter.

3.5 Poison Resistant Catalyst Development and Testing

3.5.1 Alternate Fuels Field Test Unit (AFFTU)

Construction of the AFFTU, which began in June 1995, was completed, and the equipment will be ready for a shakedown run in mid April. The project has remained basically on schedule and on budget, in spite of a significant cost and time overrun in the electrical installation work.

The Air Products Hazards Review process was completed in March. The results of this review were forwarded to Eastman Chemicals for their review, in preparation for the feed tests to be performed on-site at Eastman (Kingsport, Tenn.) in May/June of this year. The safety strategy and controls have been approved by both parties, with only minor changes recommended. These have been adopted and implemented. We have had ongoing dialogue with Eastman to verify such elements as schedule, site preparation, utility tie-ins, and emergency response procedures.

Two key technical hurdles were surmounted in our analytical methods: (a) analysis of trace hydrogen sulfide, which readily reacts with tubing, valves, and other process equipment before reaching the point of analysis and (b) analysis of both DME and methanol using the GC configuration that was originally specified and supplied. The former problem was minimized by using specially passivated tubing and regulators; however this is no guarantee that temporary pulses of trace H₂S in the Eastman gas might not disappear in tie-in piping long before they reach the AFFTU. The latter problem was eventually solved by switching the methanol and DME analysis from the TCD to the FID and using a different column for the FID separation. While DME analysis is only a minor issue for the Kingsport work, it will become important for future experimentation.

In the shakedown run, stable methanol activity was observed over a 250-hour test period (Figure 3.5.1). The observed methanol productivity of 18-19 gmol/hr kg was consistent with past runs using Texaco feed gas under similar conditions (250°C, 750 psig, GHSV=6000 L/hr kg).

Additionally, the ability of the analytical system to detect and identify key catalyst poisons and the ability of the four-bed adsorption system to selectively remove these poisons from the feed stream were demonstrated (Table 3.5.1). Several critical problems with process control and data acquisition surfaced during this testing; while they were eventually solved, the schedule of the Eastman testing had to be pushed back one week. Transport of the AFFTU to Kingsport is now scheduled for 6 May; details of the workplan are given in Table 3.5.2.

Figure 3.5.1 Stability of Methanol Synthesis Over the 250 Hours Shakedown Run

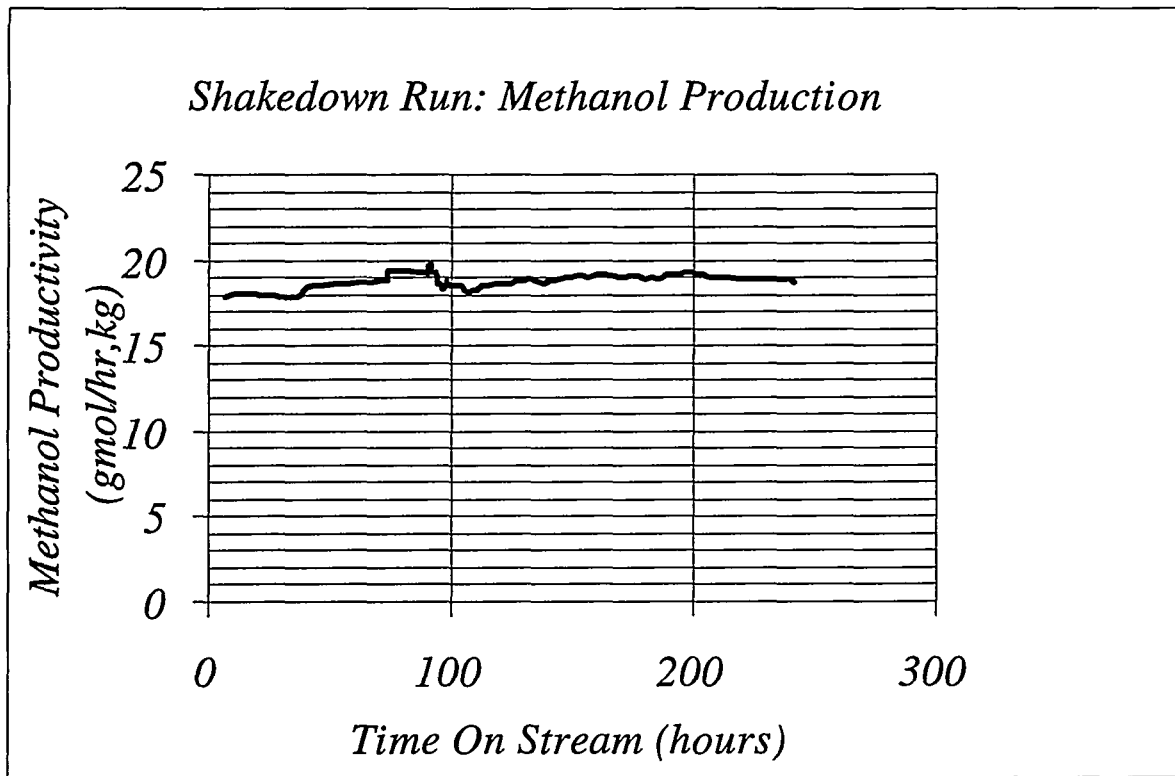


Table 3.5.1 Shakedown Run Poisons/Adsorption History

Time On Feed	0-71 hrs.	71-100 hrs.	100-180 hrs.	180-192 hrs.	192-240 hrs.
Nickel Carbonyl (1.45 ppm in Feed)	Removed on Bed#1	Breakthru Beds #1 & #2; Removed on Bed #3	Removed on Bed #3	Removed on Bed #3	Removed on Bed #3
Iron Carbonyl (2.73 ppm in Feed)	Removed on Bed#1	Removed on Bed#1	Removed on Bed#1	Removed on Bed#2	Breakthrough Bed #2; Removed on Bed#3

Bed #1 Bypassed

Table 3.5.2 AFFTU Schedule for Kingsport Tests

Now - 4/29		Final Testing of Control and Data Acquisition System
M4/29 - F5/3		Disassembly and Packing
M5/6 - W5/8		Trailer transport from Iron Run to Kingsport
W5/7,8		Arrival of Tom Dahl and Andrew Wang, Dean Chin-Fatt (GC expert) and Kevin Snyder (Electronics/IEAS) at Kingsport
W5/8 - F5/10		Kingsport safety indoctrination (AW & TD), setup and testing of equipment, alarm calibration (KS), shakedown of GC system, reactor loaded and pressure checking.
~F5/10	Day #	ORI with Eastman representatives
F5/10 - Su5/12	1,2	Reduction of Bed #1 and reactor catalyst. Dean and Kevin depart once systems are functioning satisfactorily (Friday, Saturday or Sunday).
M5/13	3	Syngas feed through full adsorption system -- complete GC analysis of feed, product and intermediate flows. Start with syngas alone, then add makeup CO.
T5/14	4	Begin feed to reactor with ramping to 250°C and 750 psig.
T5/14 - Th5/16	5,6	Reaction run using all four adsorption beds -- confirm stability of methanol production.
F5/17	7	Remove Bed #4 from feed pretreatment -- confirm stability and poison-free flows.
S5/18	8	Remove Bed #1 from feed pretreatment -- confirm stability and poison-free flows.
Su5/19	9	Remove Bed #2 from feed pretreatment -- confirm stability and poison-free flows.
M5/20	10	Remove Bed #3 from feed pretreatment -- begin long-term stability tests with no guard beds in place.
M6/10	31	Long-term stability test ends. Criteria for success are three weeks on stream with no guard beds and a final methanol productivity greater than 90% of the original "steady-state" value achieved during the guard bed phase of the run.
T6/11		System shutdown and depressurization
W6/12		Regeneration of the adsorption beds; purging of reactor.
Th6/13		Passivation of Bed #1 in 2% oxygen; emptying of Beds #2-4 with sample collection for analysis.
F6/14		Emptying of Bed #1 and reactor with sample collection.
S6/15-R6/20		Disassembly and packing.
F6/21		Target date for trailer to leave Eastman/Kingsport

Composition and Flow Rate Information

	1° Feed (Str. 30)	2° Feed (Str. 10)	Autoclave Feed
Flow Rate	2475 sccm	825 sccm	3000 sccm
Hydrogen	67.8%	2.0%	51.35%
Carbon Monoxide	27.7%	97.0%	45.02%
Nitrogen	0.5%	1.0%	0.63%
Carbon Dioxide	4.0%	0.0%	3.00%

3.5.2 Contingency Plans if Poisons Are Detected

Contingency Plan #1 -- Poisons observed via GC prior to putting reactor on line (Test Day 3)

Determine whether poison is due to primary feed, secondary feed or in-situ generation on one of the beds. Assuming that poison is in one of the feeds, work with Eastman to identify the cause and decide whether test should be continued. If poison is identified by GC (metal carbonyl or sulphide), verify that it is removed by the appropriate beds. Proceed with Test Days 4-9, but modify order of adsorbent bed removal appropriately. Verify stable operation with minimum guard beds in place. After two weeks of stable operation (assuming concentration is low enough to permit two weeks' operation), remove the last guard bed and monitor methanol activity for two additional weeks.

If poison is produced in-situ on one of the beds, remove it from the system and verify that poison is no longer observed. Proceed with operating plan as originally designed.

Contingency Plan #2 -- Poisons not observed via GC, but methanol synthesis catalyst displays deactivation.

Hopefully this problem will be detected during Test Days 5-9, so that it will be clear which adsorbent bed is needed to remove the unknown poison. The objective will become identification of this poison by collecting it either on an adsorbent bed or, if none of the beds is effective at removing it, on the catalyst itself. These materials will be brought back to Air Products for analysis using some sophisticated techniques. In this scenario, it will also be valuable to communicate with Eastman to determine whether any upsets have occurred or if they can provide any other insights into the nature of the poisoning.

During Test Days 5-9 we will need to carefully evaluate any potential signs of deactivation. Due to the occasional scatter in the data, it will be easy to have "false alarms." If we suspect deactivation after removing one of the adsorbent beds, we may follow the performance for longer than the allotted one day to confirm poisoning before making any other changes to the experiment.

Contingency Plan #3 -- Poisoning due to an upset condition

Presumably this will be seen via GC. If no guard beds are in place at the time, it will provide some data regarding how well the catalyst will respond to these excursions. If the duration of the excursion is sufficiently long, we can protect the catalyst with the appropriate guard bed for the balance of the upset.

TASK 4: PROGRAM SUPPORT

4.1 Economics of MTBE via Mixed Alcohol Synthesis (Bechtel Corporation)

Introduction

The primary objective of this DOE/PETC-funded 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 determine 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 stand-alone LPMAS plant. The syngas feed is derived from the partial oxidation of natural gas.

This paper summarizes the basis and the results for each of the case studies, and identifies the required catalyst productivities for an economical utilization.

Common Study Basis

The following assumptions were common to all three cases.

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 major nonalcohol 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 production to alcohols.

Component	Alcohol (mol%)
Methanol	48.83
Ethanol	0.0
Propanol	0.0
n-Butanol	0.84
i-Butanol	47.56
n-Pentanol	0.28
i-Pentanol	1.42
n-Hexanol	0.25
i-Hexanol	<u>0.82</u>
Total	100.00

- If these by-products were part of the product mix, they would be utilized 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.

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 small amount of methanol required to convert iso-amylene to TAME).

Based on the above assumptions, the alcohol product distribution is shown in Table 4.1.1.

3. *LPMAS Reactor Design Basis*

The design basis for the LPMAS reactor was based on Air Products' autoclave and pilot plant demonstration runs:

Gas hourly space velocity	5000 sl/kg-hr
Temperature	315°C
Pressure	1800 psig
Catalyst slurry concentration	40 wt%

Case 1 - IGCC Power Plant

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

- Coal gasification produces a low H₂/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.

Figure 4.1.1 Case 1 - IGCC/LPMAS Block Flow Diagram

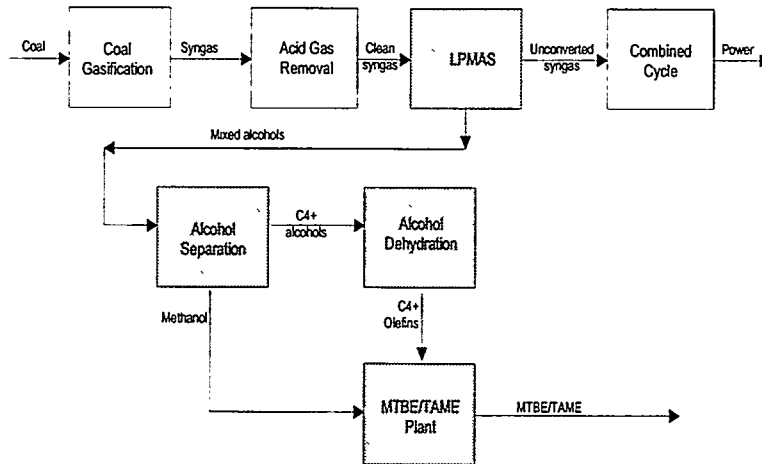
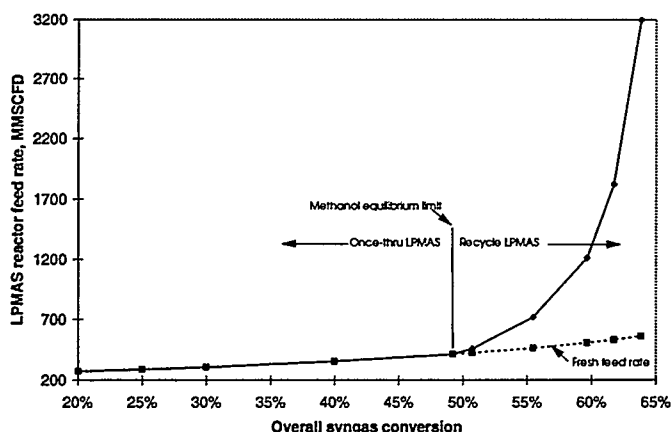


Figure 4.1.1 shows how the LPMAS plant was integrated into the IGCC power plant. The shaded blocks represent plants that need to be added for alcohol/ether production. Shell gasifiers are used to produce a syngas with a H_2/CO ratio of 0.5. After cleanup, the entire syngas production is fed to the LPMAS 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.

Power production from the IGCC plant, 385 net MW, was based on the production from a single 3000-stpd Shell gasifier 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.

In Case 1, overall syngas conversion levels ranging from 20 to 64% were studied. At conversion levels below 49%, a once-through LPMAS system is utilized. Above 49%, methanol equilibrium limitations require recycling unconverted syngas back to the LPMAS reactor. Figure 4.1.2 shows the effect of recycling on the feed rate to the LPMAS reactor. At overall conversion levels above 60%, the costs of recycling (e.g., larger equipment, multiple trains, recycle compression) become prohibitive.

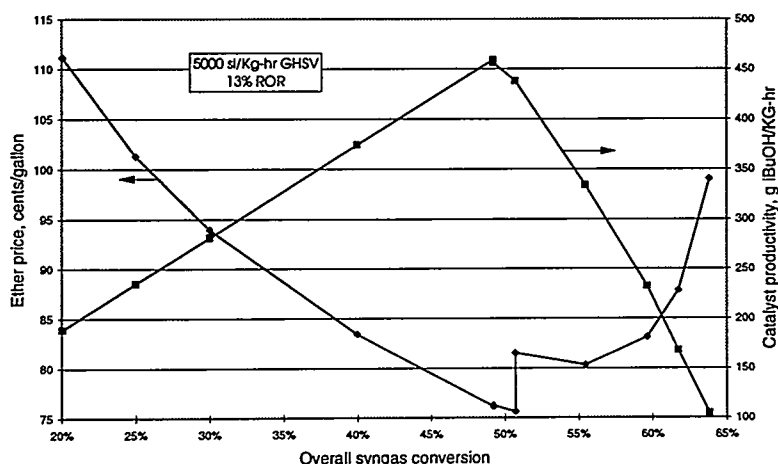
Figure 4.1.2 Case 1 - IGCC/LPMAS Reactor Feed Rate



The effect of overall syngas conversion on economic feasibility was determined by calculating the required ether price to achieve a 13% internal rate of return. Figure 4.1.3 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 a 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 jumps from two to three. Above 51%, the costs of recycle start to overwhelm 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%.

Also shown in Figure 4.1.3 is the required catalyst productivity. For once-through operation (up to 49% overall conversion), the required catalyst productivity rises steadily. Above 49%, the productivity decreases as the recycle ratio increases.

Figure 4.1.3 Case 1 - IGCC/LPMAS Required Ether Price and Catalyst Productivity



Sensitivity Study - LPMAS Space Velocity

The effect of the LPMAS reactor space velocity on the economics of an IGCC/LPMAS plant was also examined. 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 occurs because the cost of the LPMAS reactor represents a small portion of the capital cost of the overall plant.

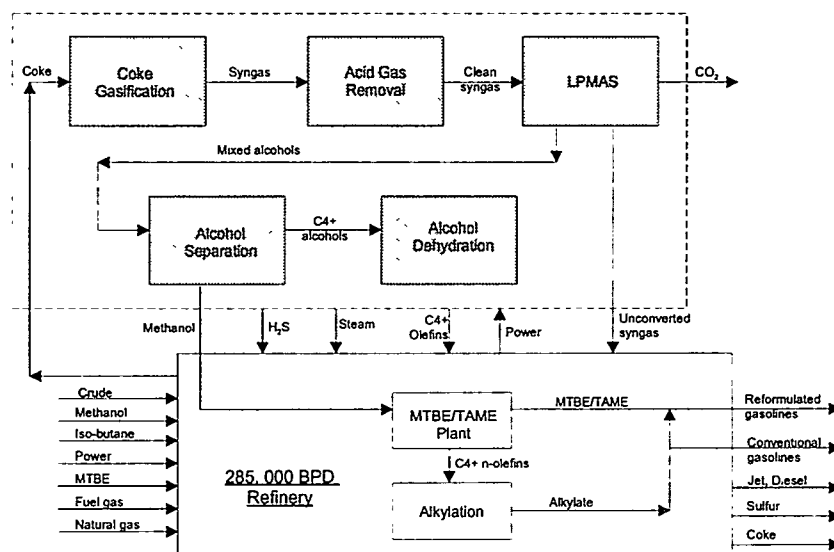
Case 2 - Petroleum Refinery

The scenario for Case 2, petroleum refinery, was chosen for four reasons:

- Coke gasification produces a low H₂/CO ratio syngas which has been shown to be favorable to higher alcohol production.
- The feedstock for syngas production--petroleum coke--has a zero or negative value.
- The refinery consumes ethers for oxygenated or reformulated gasolines.
- The refinery can consume a limited amount of unconverted syngas.

Figure 4.1.4 shows how the LPMAS plant was integrated into an existing petroleum refinery. The shaded blocks represent the new plants that are required. Syngas from an 1800-stpd coke gasification plant is sent to acid gas removal, where H₂S and CO₂ are removed. The clean syngas, having a H₂/CO ratio of 0.4, is sent to the LPMAS plant. The mixed alcohols from the LPMAS plant are separated and the C₄+ alcohols are dehydrated. The primary products from the new plants are methanol, C₄+ olefins and unconverted syngas. These products are consumed by the refinery to produce additional ethers and reduce the amount of purchased MTBE.

Figure 4.1.4 Case 2 - Petroleum Refinery/LPMAS Block Flow Diagram

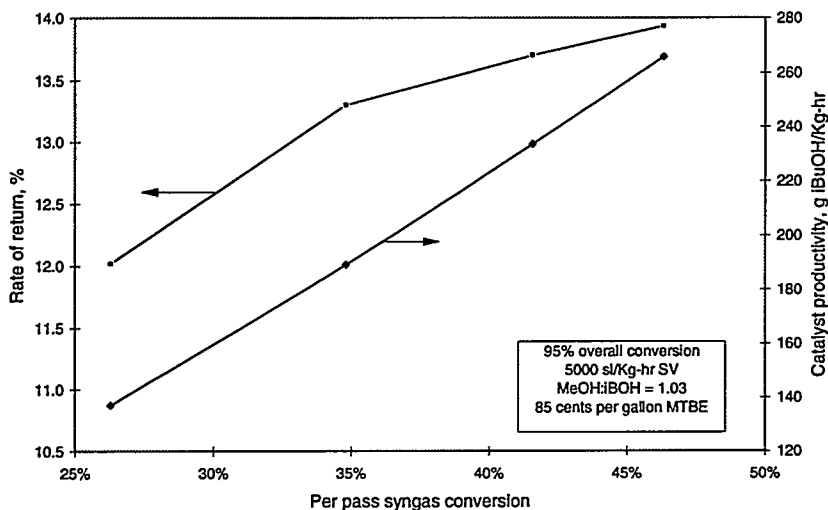


There are several key differences between Case 2 and Case 1:

- There is a single overall syngas conversion level, 95%. This level was chosen so that the refinery fuel system would not be diluted with large volumes of low-BTU unconverted syngas.

- To achieve the 95% conversion, a recycle LPMAS system is required.
- Steam is added to the LPMAS feed to provide hydrogen via internal water gas shift (WGS).
- CO₂ (generated by WGS) is removed from the LPMAS recycle loop.

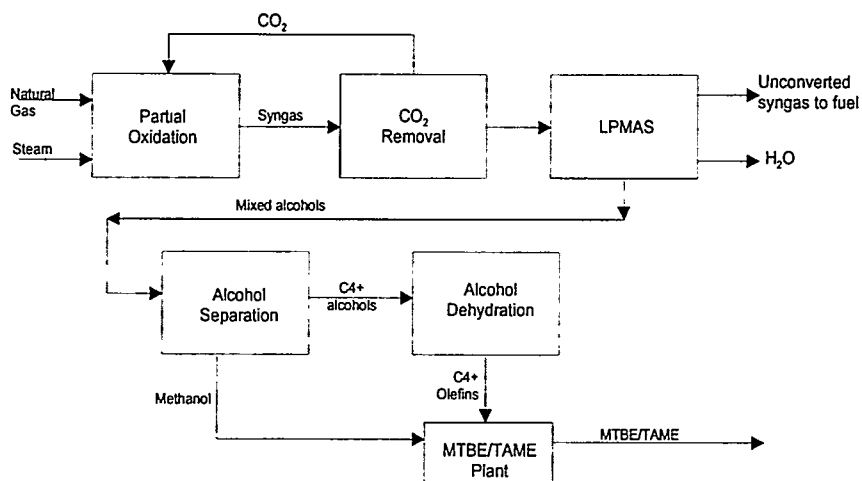
Figure 4.1.5 Case 2 - Refinery/LPMAS - Rate of Return - Catalyst Productivity



The Bechtel Process Industry Modeling System (PIMS) linear program was used to determine the rate of return at the current market MTBE price of 85 cents per gallon. Recycle ratios were varied between 2.1 and 4.7. Figure 4.1.5 shows the rate of return and the required catalyst productivity as a function of per pass conversion. Higher recycle rates are needed to achieve the 95% overall syngas conversion as the per pass conversion declines. The rate of return decreases because of the higher cost of recycling. The highest rate of return is at the methanol equilibrium limit (highest per pass conversion/lowest recycle ratio). However, higher recycle ratios do permit lower catalyst productivities.

Case 3 - Stand-Alone LPMAS

Figure 4.1.6 Case 3 - Standalone LPMAS Block Flow Diagram



The scenario for Case 3, a stand-alone LPMAS plant, was chosen because of the potential for low cost natural gas feedstock in certain situations, and because it is less expensive to produce syngas from natural gas than from coal or coke.

Figure 4.1.6 shows the key components for the stand-alone plant. 230 MMSCFD of natural gas is partially oxidized with steam and oxygen. CO₂ is recovered from the syngas and recycled back to the POX plant to reduce the H₂/CO ratio. Syngas, having a H₂/CO ratio of 1.54, is sent to the LPMAS plant. The balance of the system is similar to Case 1.

The key differences between Cases 2 and 3 are:

- To achieve a fuel balanced plant, a syngas conversion level of 98% is required.
- The natural gas feed price is \$1/MMBTU

Similar to Case 1, the required ether price to achieve a 13% rate of return was determined. As with Case 2, a recycle LPMAS system was required to achieve the 98% overall syngas conversion. Recycle ratios were varied between 2.3 and 5.7. Figure 4.1.7 shows that the lowest required ether price is at the methanol equilibrium limit (highest per pass conversion/lowest recycle ratio).

Sensitivity Study - Elimination of CO₂ Recovery System -

The CO₂ recovery system shown in Figure 4.1.6 represents about 25% of the capital cost of producing the syngas. A sensitivity study was conducted from which the CO₂ system was deleted. Aside from the cost savings, the key change is that the H₂/CO ratio increases from 1.54 to 2.02. With this syngas, it was immediately apparent that the methanol equilibrium limitation dictates a high recycle ratio (5.7) to achieve the 98% conversion requirement. Since this is a H₂-

rich syngas, it was decided to investigate the effect of increasing the methanol/isobutanol selectivity ratios. At higher selectivity ratios, overall capital costs are lower because of lower recycle ratios. However, as the selectivity ratio increases, more methanol and less MTBE is produced. At the current market price of 35 cents/gallon, methanol has a much lower product value than MTBE, and the overall revenues decrease. Figure 4.1.8 shows the effect of selectivity ratio on the required ether price. A minimum is reached at a selectivity ratio of 4.0 when the capital savings from the decline in recycle requirements is just offset by decreases in revenues because of higher methanol (lower MTBE) production.

Figure 4.1.7 Case 3 - Standalone LPMAS - Required Ether Price - Catalyst Productivity

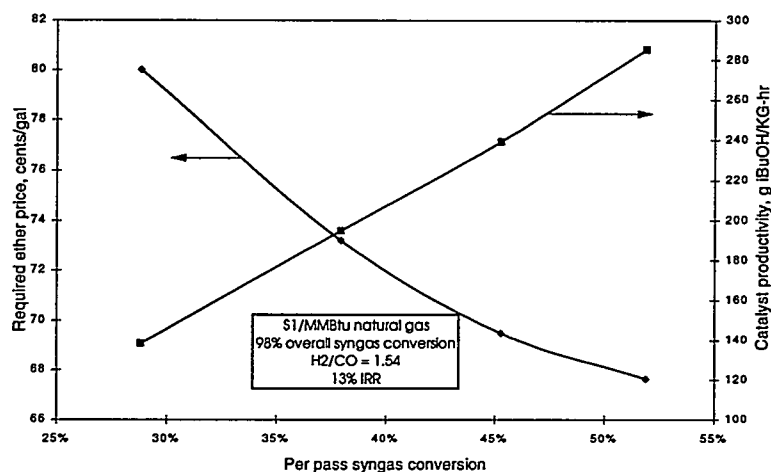
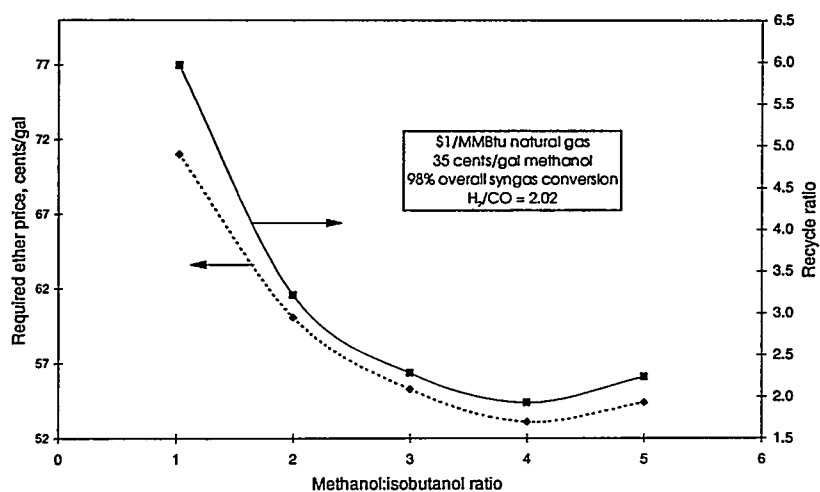


Figure 4.1.8 Case 3 - Standalone LPMAS - Sensitivity Study - Required Ether Price - Recycle Ratio @ H₂/CO = 2.02



Summary

Although not all presented in this paper, this study has examined a number of factors that had significant bearing on the results of the study:

- Methanol/isobutanol selectivity
- Syngas H₂/CO ratio

- Syngas conversion/disposition of unconverted syngas
- Recycling of syngas to LPMAS reactor
- Methanol equilibrium limitation
- LPMAS reactor space velocity
- CO₂ removal
- Steam addition
- Plant location
- Feedstock costs

In using this study, it is important to bear in mind that the results (e.g., catalyst productivity) are very specific to the selected conditions.

Table 4.1.2 summarizes the operating conditions for the most economic scenario for each case. Also included is the Case 3 sensitivity study in which the methanol/isobutanol selectivity ratio was raised from 1.03 to 4.0.

For Case 1, to produce an ether product that is at or below the current MTBE market price of 85 cents per gallon with a once-through LPMAS system, the required catalyst productivity would need to be in the range of 370-460 g iBuOH/kg-hr (methanol/isobutanol ratio - 1.03). For Case 2, the most economic case is that in which the LPMAS reaction is at methanol equilibrium. The internal rate of return is 13.9% and the required catalyst productivity is 265 g iBuOH/Kg-hr. For Case 3, the most economic case is also that in which the LPMAS reaction is at methanol equilibrium. For \$1/MMBTU natural gas feedstock, the required ether price is 68 cents/gallon. For \$2/MMBTU natural gas feedstock, the required ether price is 84 cents/gallon. Table 4.1.2 also shows that for higher H₂/CO ratio syngas, there is potential for higher returns if coproduction of methanol and ethers is an option.

Case	1	2	3	3S
Feed	Coal	Coke	NG @ \$1	NG @ \$1
Syngas H ₂ /CO ratio	0.5	0.4	1.54	2.02
LPMAS reactor feed H ₂ /CO ratio	0.5	0.5	1.8	3.3
MeOH:iBuOH ratio	1.03	1.03	1.03	4.0
LPMAS syngas recycle ratio	0	2.0	2.3	1.9
Per pass conversion, %	38-49	48	52	45
Overall conversion, %	38-49	95	98	98
Productivity, g iBuOH/kg-hr	370-460	265	285	181
g MeOH/kg-hr	165-205	118	126	314
Req'd ether price @ 13% IRR, cents/gal	85-76		68	53
IRR at 85 cents/gal ether, %		13.9		

Conclusions

For all three scenarios, economical LPMAS plants are possible even at current ether market prices. However, large improvements in catalyst productivity and alcohol selectivity must be achieved prior to commercialization of this process. If inexpensive natural gas feedstock is available, because of less demanding catalyst productivity and selectivity requirements, coproduction of methanol and ethers looks attractive.

References

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

4.2 Economic Incentive to Develop a Sulfur-Tolerant Methanol Synthesis Catalyst for Coal Gasification and Other High-Sulfur Feedstock Applications

Introduction

By developing a more sulfur-tolerant synthesis catalyst, the costs associated with the production of methanol from coal can be reduced. This cost saving has to be evaluated by catalyst developers/suppliers to determine whether there is sufficient incentive, together with market opportunity, to warrant developing such a catalyst.

This report summarizes the study work performed and presents the results of the cost savings realized by relaxing the sulfur removal specification from <0.1 ppmv total sulfur in the treated syngas to 20-30 ppmv total sulfur, for four different syngases, each using a different sulfur removal technology.

The sulfur removal technologies selected for evaluation are all "regenerable solvents" - a class of commercially proven solvents and the main technology in use today for sulfur removal. In some cases, to achieve the required sulfur specification, pre- and post-solvent processing are necessary.

This work is part of the Alternative Fuels and Chemicals from Synthesis Gas subcontract (No. PT5781B) between Air Products and Bechtel.

Need for a Sulfur-Tolerant Catalyst

- **Cost Savings** - Lower capital and operating costs for sulfur removal are a result of relaxing the sulfur removal specification. For a high-sulfur coal, with 1.5 mol% sulfur species in the raw syngas, treating to 20 ppmv total sulfur is equivalent to a three-nines reduction (99.87%), compared to the greater than five-nines reduction (99.9996%) required for conventional methanol catalyst.
- **Selective H₂S Removal** - For applications in which the CO₂ content of the syngas is high, co-absorption/removal of CO₂ can be costly, and undesirable. Lowering the treated syngas specification can simplify the design of the sulfur removal plant for selective H₂S removal and increase the quality of the feed gas to the sulfur recovery unit.
- **Expanded Technology Range** - Certain preferred solvents, which are noncompetitive at deep removal efficiencies, can now be added to the list of potential processes. Emerging

technologies, such as regenerable solid sorbents (hot-gas cleanup technology), can also be included on the list of potential processes for sulfur removal.

- **Single Sulfur Specification** - For a combined power generation/methanol production facility, relaxing the treated syngas sulfur specification to 20 ppmv would simplify the sulfur removal plant by producing a single treated gas stream instead of two streams, each with a different sulfur specification.

Study Objective

The objective of this study is to determine the cost savings for a coal-based methanol production facility operating with a sulfur-tolerant catalyst instead of a conventional catalyst. The cost saving, which is realized through design differences in the sulfur removal plant, is the metric by which the catalyst developers/manufacturers can determine whether or not there is sufficient incentive to develop a sulfur-tolerant catalyst.

Study Basis

Gasification Conditions	Oxygen-blown, 450-psig operating pressure
Syngas Composition	Determined for each gasifier/feedstock combination Syngas composition is not adjusted to methanol synthesis stoichiometry
Syngas Flow Rate	The flow rate of each clean syngas corresponds to a higher heating value of 515 MW
Syngas Sulfur Species	All organic sulfur in feedstock is assumed to be gasified and distributed between H ₂ S and COS
Treated Syngas Total Sulfur Specification	<0.1 ppmv - conventional methanol synthesis catalyst 20-30 ppmv - sulfur-tolerant methanol synthesis catalyst
Treated Syngas Delivery Pressure	1100 psig

Sulfur Removal Plant - Equipment Scope

- Regenerable solvent system plus its associated utilities
- Pre-solvent treating - if required to protect a particular solvent
- Post-solvent treating - if required to achieve the sulfur specification
- Syngas compression

Syngas compression is included because there is an increase in capital and operating costs as a result of pressure losses associated with post-solvent treating.

Sulfur Removal Technologies

Regenerable Solvents

The underlying principle of regenerable solvent sulfur removal is that a solute (sulfur species in the syngas) can be removed from the gas by dissolution on contacting a suitable solvent. The solvent has to be carefully selected such that, under a moderate change in operating conditions, the dissolution process can be reversed, releasing the solute in its original form and regenerating the solvent, which is then reused.

Chemical Solvents

Chemical solvents offer the advantage of being able to reduce the solute concentration in the treated gas to low levels at low operating pressure, but are limited in the amount of solute that can be absorbed by reaction stoichiometry and chemical equilibrium.

Physical Solvents

Physical solvents offer the advantage of high capacity for the solute, the capacity being directly proportional to the operating pressure. Lower solvent temperatures increase the solubility of the solute. In addition, the solvent is largely regenerated by pressure reduction alone compared to chemical solvents, which require significant heat input to regenerate the solvent.

Mixed Solvents

Mixed solvents are mixtures of chemical and physical solvents and exhibit features of both solvents.

Direct Oxidation

Wet oxidation has a major advantage over traditional solvents, as the need for a dry-oxidation sulfur recovery unit (Claus Plant) is eliminated. However, the state of the technology is such that wet oxidation is only competitive with the Solvent-Claus combinations at sulfur recoveries below 20 tons per day.

Pre-Solvent Purification

Depending on the particular sulfur removal technology, it is sometimes necessary to include upstream treating as part of the sulfur removal technology, to either protect the solvent from degradation, or to convert a sparingly soluble sulfur species to a more soluble form.

Post-Solvent Purification

For all regenerable solvents used in commercial sulfur removal operations, the cost of sulfur removal increases rapidly as the sulfur specification of the treated syngas approaches the gas phase equilibrium concentration of the sulfur species in the regenerated solvent. Therefore, it is often necessary to provide a final purification stage to reduce the sulfur content of the syngas to the < 0.1 ppmv requirement. Traditionally, the system-of-choice has been a fixed-bed of nonregenerable sorbent, such as zinc oxide. H₂S in the syngas reacts irreversibly with the sorbent, converting zinc oxide to zinc sulfide.

For a sulfur removal plant with post-solvent treating, one has to decide how much sulfur to remove with the regenerable solvent, and how much to remove with the nonregenerable sorbent. The cutoff point is determined when the cost of removing the next increment of sulfur from the syngas with solvent exceeds the cost of removing that increment with sorbent.

The cutoff point chosen for all solvents in the study is 5 ppmv total sulfur. Rectisol was evaluated at both 5 ppmv and < 0.1 ppmv.

Process Selection

Table 4.2.1 lists the four different combinations of feedstock, gasifier, and sulfur removal technology evaluated in the study.

Table 4.2.1 Evaluated Combinations of Feedstock, Gasifier, and Sulfur Removal Technology

Sulfur Removal Technology	Feedstock/Gasifier
MEA - aqueous alkanolamine (Chemical Solvent)	Petroleum Coke/Shell Coal Gasification Process (SCGP)
Rectisol - chilled methanol (Physical Solvent)	Illinois No. 6 Coal/Texaco Gasification Process (TGP)
Sulfinol - sulfolane/diisopropanolamine/water (Mixed Solvent)	Illinois No. 6 Coal/SCGP
SulFerox - Wet oxidation (Direct Oxidation)	Powder River Basin Coal/TGP

Costs Basis

The equipment costs were developed from in-house data for sulfur removal plants and from vendor quotations. Total project capital costs were developed from estimates for the total field costs, the home-office engineering costs, and a 20% contingency.

The annual operating costs for the sulfur removal plant were developed from utilities consumption (power, steam and cooling water), catalyst, chemical and solvent consumption, labor costs, maintenance costs, local taxes, insurance, and overheads.

Economic Analysis

Given the capital costs and annual operating costs for the sulfur removal plant, a discounted-cash-flow analysis was performed to determine the *annual revenue* (a positive cash flow) required to provide a 15% internal-rate-of-return (IRR) for the sulfur removal plant. The basis for the calculation is as follows:

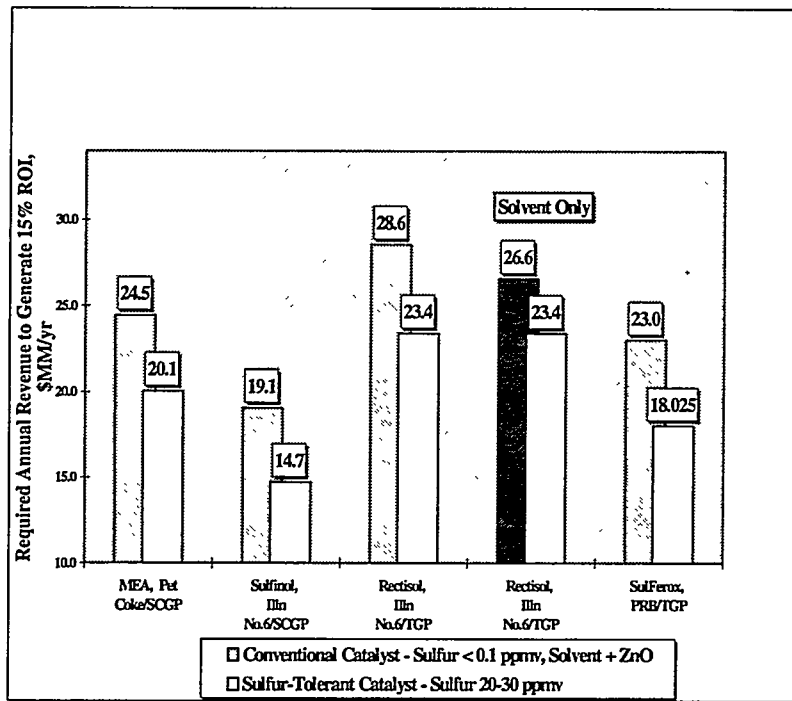
- Twenty year project life
- 100% equity financing

- After-tax basis for IRR
- Double-declining balance depreciation

Economic Incentive

The *economic incentive* is defined as the difference in the required *annual revenues* for a plant designed to achieve < 0.1 ppmv total sulfur in the treated syngas (conventional catalyst) and a plant designed to achieve 20 ppmv (sulfur-tolerant catalyst) using the same solvent.

Figure 4.2.1 Comparison of Sulfur Removal Systems - for Different 0.1 and 20 ppmv Sulfur Specifications



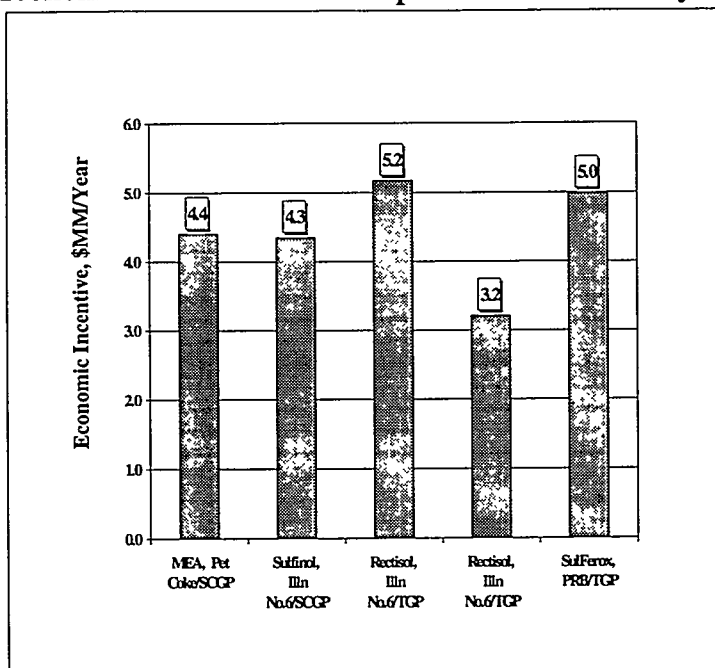
The *economic incentive* can be considered the net saving between the two different sulfur removal plant designs.

Study Results

The study results are the *economic incentives* for each of the four cases. Figure 4.2.1 shows the required *annual revenue* from product sales to provide a 15% IRR for the sulfur removal plant for all four solvents when designed to both sulfur specifications. Two sets of results are shown for Rectisol: the first set for solvent sulfur removal to 5 ppmv followed by zinc oxide final purification, and the second set for solvent-alone sulfur removal to < 0.1 ppmv (i.e., no final purification required).

Figure 4.2.2 shows the *economic incentive* - the difference in required *annual revenues* for each solvent/syngas combination.

Figure 4.2.2 Economic Incentive to Develop a Sulfur-Treated Synthesis Catalyst



To put the *economic incentive* in the producer's perspective, it is worth comparing this saving to the cash flows for the complete methanol production facility. If it can be accepted that the revenue from methanol sales exactly balances the negative cash flows, plus a 15% IRR, then the ratio of the *economic incentive to total revenues* provides an idea of the savings relative to the total project cash flows.

An 1,800 stpd Pet.Coke, SCGP, MEA facility can produce 1,660 stpd of methanol, in stoichiometric mode of operation. According to Figure 4.2.2, the *economic incentive* is 4.4 \$MM/yr. For a stable market price of 50 cents/gal of methanol, the annual sales revenue would be approximately 88 \$MM/yr. Therefore, if one assumes that the producer has sole access to the incentive and that the incentive is not discounted in any way, then the *economic incentive* would be $5\% \left(\frac{4.4 \times 100}{88} \right)$ of the total revenue needed to generate a 15% after-tax IRR. For a number of reasons, it is unlikely that the producer will receive the full incentive.

Conclusions

The *economic incentive* for sulfur-tolerant catalyst development is between \$3-5 million per year; assuming all other costs remain the same within a particular solvent case. The *economic incentive* is a maximum saving that, in practice, can never be fully realized by either the methanol producer or the catalyst developer/supplier. Several other economic factors discount its value to either party.

This study is a preliminary investigation. There are other syngas/solvent combinations that should be evaluated to complete the distribution curve of *economic incentives* needed to develop a sulfur-tolerant methanol synthesis catalyst.

TASK 5: PROJECT MANAGEMENT

5.1 Reports and Presentations

A draft of a topical report detailing the methanol/isobutanol campaign at LaPorte in the spring of 1994 was completed. The draft was first reviewed internally in February and then sent to DOE for review in March.

Monthlies for January, February and March were issued, and a draft quarterly for October through December 1995 was in preparation.

5.2 Management Activities

A meeting was held with Washington University personnel to discuss the results of the tracer study conducted during the LaPorte run in June 1995. Typically, an axial dispersion model, lumping different mixing mechanisms into a single dispersion coefficient, is used to model liquid mixing in bubble columns. The Washington University group has developed a two-dimensional model which accounts for convective as well as turbulence effects. Initial results indicate that the model is able to predict both the radial and axial movement of the tracer in the column. A Washington University/Air Products joint paper will be written based on this work.

A meeting was held with DOE personnel at PETC during January to discuss the F-T III run. The current plan as discussed between Air Products and Shell in mid December was presented. In general, the plan was well received, and DOE is looking forward to the run. Some issues raised by DOE need attention from Shell: DOE is going to need the LaPorte product analysis so that DOE and its contractors can study downstream processing. Shell should consider including the tracer study if Air Products/Washington University's current analysis of the 1995 hydrodynamic run shows significant understanding and the value of doing more under F-T III. ICI-Tracerco expenses can be covered under DOE's separate hydrodynamic program; however, operation time has to come out of the 30-day program. Data/results from the optical fiber probe (if obtained) need to be shared. Sparger information is needed to feed the data into DOE's Hydrodynamic program. The information will have to be shared with other subcontractors.

A meeting was held in March with personnel from Energy International (EI) to discuss a Fischer-Tropsch demonstration run at LaPorte for EI. Their overall process scheme and specific LaPorte objectives were discussed. Funding and timing for the run are key issues. The run would need to be fully funded by EI because all available DOE and Air Products funding is already committed. Furthermore, due to the existing schedule for F-T III and the Kingsport start-up, the next window for a LaPorte run is mid 1997, and that window may be used for an oxygenates run such as DME synthesis. EI prefers a demonstration at an earlier time.