

feed ratio used in this experiment. The H_2 co-feed does appear effect the hydrogenation/dehydrogenation equilibrium between alcohol and aldehyde and, therefore, is a factor in determining product selectivity within the C_4 oxygenates.

Table 33 also shows that co-feeding CO has a deleterious effect on catalyst performance. Alcohol conversions and isobutanol selectivities are decreased. A large increase in other oxygenates and unidentified heavy products suggests that side-reaction such as carbonylation may be occurring. Due to the unattractiveness of this result further characterization of the reaction products was not pursued.

The coupling of methanol and ethanol to isobutanol produces two equivalents of water as a co-product. At the conditions used for this process, the water gas shift equilibrium greatly favors the conversion of H_2O and CO to CO_2 , which a major product observed in the pilot plant tests. Therefore, this water co-product results in a substantial loss in carbon efficiency. One approach to overcome this loss is to recycle CO_2 to the process, thus forcing the production of H_2O . Two levels of CO_2 co-feed (1.5 and 2.8 $CO_2/MeOH$) have been evaluated in order to determine whether this approach has merit with the Pt on Zn/Mn/Zr catalyst system. Table 33 summarizes the results of this testing. CO_2 addition has a minimal effect on conversion levels, but results in lower selectivities to the desired iC_4 oxygenates due to higher CO formation. CO_2 selectivity is not substantially reduced. Therefore, it appears that the use of a CO_2 recycle is not effective for reducing the formation of carbon oxide products.

3.4 Pilot Plant Demonstrations (Task 3)

3.4.1 Methanol-Only Conversion over Pt on Zn/Mn/Zr Oxide Catalysts

The coupling of two C_1 oxygenates to a C_2 species is known to be the slow step in the production of isobutanol from either synthesis gas or methanol. In the case of C_2 - C_1 coupling,

an aldol condensation mechanism involving deprotonation from the resonance-stabilized a carbon of an acetaldehyde intermediate can be proposed. For C_1 - C_1 coupling, the deprotonation of a formaldehyde intermediate, which less acidic than acetaldehyde is required for an aldol-type condensation. Therefore, this mechanism appears less likely for the coupling of C_1 species. However, tests using a 10/1 methanol/ethanol blend at various space velocities have suggested that Pt on Zn/Mn/Zr oxide may be capable of promoting this reaction. In contrast, a Cu/Zn/Al oxide catalyst does not show any increase in higher oxygenates yield at high ethanol conversion and early screening indicated that it gives negligible methanol conversion in the absence of ethanol co-feed.

Three 2% Pt on Zn/Mn/Zr oxide catalyst formulations have been evaluated for the conversion of methanol only to higher branched oxygenates. Test conditions are identical to those employed with the 10/1 methanol/ethanol blend, except that a pure methanol feedstock has been used. Table 34 summarizes the overall results (conversions and selectivities) while Figures 19 and 20 show methanol conversions and isobutanol selectivities versus time on stream, respectively. For all of these catalysts, the products containing C-C bonds are virtually eliminated when a methanol only feed is used. Selectivities to total C_{4+} products are less than 3%. The major products arise from other reactions including methanol decomposition (CO , CO_2 , H_2), hydrogenation (methane), etherification (DME) and Cannizzaro condensation (methyl formate). These results clearly indicate the requirement for a C_2 intermediate for the aldol condensation to higher alcohols and the formation of such an intermediate from C_1 species is very slow over the Pt on Zn/Mn/Zr oxide catalyst system at the conditions used.

Higher temperature and pressure have been evaluated to try to push the conversion of methanol only to higher oxygenates with the reference 2% Pt on Zn/Mn/Zr oxide catalyst. A copper-lined reactor has been used in this testing to reduce methanol decomposition catalyzed by the stainless steel reactor walls at the elevated temperatures. Table 35 shows that increasing temperature to 400-450°C and pressure to 300 psig does not increase the formation of branched

C₄ oxygenates. Instead, CO and CO₂ remain the primary products. Therefore, the performance of this catalyst system for methanol only conversion is not improved by more severe operating conditions.

Based on the results obtained with Pt on Zn/Mn/Zr oxide catalysts using a methanol only feed, this catalyst system does not appear to be promising for the conversion of methanol by itself to higher alcohols. It appears that this catalyst is active only for the aldol condensation step, in which a C₂ aldehyde intermediate is condensed with C₁ species, in the overall mechanism. Therefore, the final pilot plant demonstration runs and the economic evaluation of this catalyst system have been directed at a process for the conversion of methanol with imported ethanol to higher alcohols.

3.4.2 Demonstration of Optimum Conditions for Methanol/Ethanol Conversion to Higher Alcohols with 2% Pt on Zn/Mn/Zr Oxide Catalyst

The process variables studies described in Task 4 have demonstrated the independent effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr oxide catalyst. The highest selectivities to the desired iC₄ oxygenates are obtained at the lowest temperature (325°C), highest pressure (300 psig) and moderate methanol/ethanol feed ratio (7/1 molar). In view of these results, an optimized run has been conducted using this combination of conditions. In addition, methanol space velocity was decreased from 2 hr⁻¹ to 1 hr⁻¹ by doubling the catalyst loading in order to obtain 50-60% methanol conversion at the lower temperature. The results of this test are summarized at the end of Table 32. The methanol conversion was within the targeted range and the isobutanol selectivity (22.2%) is the highest obtained in any testing in this program. While isobutyraldehyde is reduced (due to the use of higher pressure), the formation of methyl isobutyrate ester is higher than expected. Methyl acetate formation is also high, which is consistent with the earlier testing at 325°C. This suggests that the Cannizzaro reaction becomes more competitive as the aldol condensation step slows. The lower temperature also reduces the formation of light hydrocarbons, CO and CO₂ to the lowest levels observed with

this catalyst system.

In view of the superior selectivities, compared with other conditions, the results of this run have been used as a basis for the economic evaluation of a higher alcohols process using this catalyst. This work has been done as a part of Task 5 of the program.

3.4.3 Methanol/Ethanol Conversion with High H₂ Co-feed

One process concept for the integration of a high alcohols process with a conventional methanol synthesis plant is to place the process immediately after the methanol synthesis reactor using imported ethanol. One advantage of this configuration is that any CO and CO₂ formed in the higher alcohol synthesis reactor can be returned to the methanol synthesis reactor for conversion to additional methanol using the existing recycle loop. In addition, unconverted methanol can be recovered and used for the production of MTBE from the isobutanol in a separate step.

In order for this configuration to be feasible the higher alcohol condensation catalyst must be able to operate in the presence of high H₂ concentrations. The effluent from the methanol synthesis reactor typically contains about 70-80 mole% H₂ as well as some N₂, CO and CO₂. It is also desirable that this process operate at the high pressure of the methanol synthesis reactor (1000-1500 psig) so that the efficiency of the H₂/CO/CO₂ separation in the recycle loop is not reduced. Previous results have indicated that co-feeding H₂ at a low level (2/1 H₂/methanol molar feed ratio) has little effect on the performance of the Pt on Zn/Mn/Zr oxide catalyst. Methanol conversion is slightly increased and selectivity shifts from isobutyraldehyde to isobutanol with H₂ giving an overall slightly higher productivity for isobutanol. Table 36 summarizes the results of the pilot plant test of the 2% Pt on Zn/Mn/Zr oxide catalyst at high H₂ partial pressures comparable with those inside the methanol synthesis recycle loop. At the initial conditions (1200 psig total, 15/1 H₂/methanol) both methanol and ethanol conversion are very low with only small amount of isobutanol formed. Surprisingly, isobutyraldehyde selectivity was high which is inconsistent with the expected level of product hydrogenation that

should be occurring at these conditions. Decreasing pressure to 300 psig and then 50 psig (also with a decrease in space velocity) increased conversion and isobutanol selectivity, but it remained far below levels observed previously at lower H₂ levels. Again the isobutyraldehyde selectivity responded in an opposite manner from that expected, decreasing as H₂ content decreased. Elimination of the H₂ co-feed did not restore the performance of the catalyst to expected levels either at 50 psig or 300 psig. This suggests that the high H₂ partial pressure caused some degradation of the catalyst.

3.5 Economic Evaluation (Task 5)

3.5.1 Summary of Process Variable Studies/Optimum Conditions Obtained

Experimentally

With the 2% Pt on Zn/Mn/Zr oxide catalyst, the best performance was achieved experimentally in pilot plant run 325 using 325°C, 300 psig, 1 hr⁻¹ WHSV, and 7/1 methanol/ethanol molar feed ratio. The methanol conversion and carbon selectivity to isobutanol were 55.2% and 22.2%, respectively, the highest obtained in any testing performed to satisfy tasks 3 and 4 of the program. In view of the superior results of this test, these performance data were used as a basis for the economic evaluation of a commercial higher alcohols process according to Task 5 of the program.

3.5.2 Modeling of a Commercial Isobutanol Synthesis Plant

From the process optimization experimental results, a stand-alone isobutanol production plant operating at the "best-case" conditions (300 psig, 320°C, 1 hr⁻¹ WHSV) was the basis for economic evaluation. The single-pass methanol and ethanol conversions (55.2% and 97.0%), selectivity to isobutanol (22.2%) and product slate obtained in pilot plant work were used to model the commercial system with Hyprotech Hysim v2.50 process simulation software.

For process modeling, it was assumed that methanol alone contributed to the formation of all single-carbon species (CO, CO₂), all C₁-C₅ hydrocarbons, and the methyl groups of dimethyl ether, methyl formate, methyl acetate, methyl butyl ether, and methyl isobutyrate.

Furthermore, one carbon of the side products isopropanol and isopentanol was considered to originate from methanol. The smaller amounts of ethanol (12.5 mol-% of the liquid feed) charged were assumed to participate in producing all 2- and 4-carbon groups in the same ratios as shown in the yield data generated from pilot plant Run 325. The remaining carbon needed to generate the product slate (after conversion of 97% of the ethanol) was presumed to stem from the feed methanol. Generation of water and hydrogen was observed experimentally, and yields of these products were in accordance with 100% elemental O and H balances. The water gas shift reaction was also modeled and assumed to achieve equilibrium at reaction temperature. A comparison of actual measured and theoretical gas yields, as well as a summary of the conditions and reaction coefficients used in modeling, is provided in Table 37.

3.5.3 Basis for Capital Cost Estimate

A fresh feed rate of 672 MT/day (5300 BPSD) methanol and ethanol, supplied from a methanol synthesis plant (500 MT/day, 4000 BPSD) and purchased ethanol (172 MT/day, 1300 BPSD) was chosen for the commercial simulation. Because of the low selectivity to the desired isobutanol, the substantial liquid recycle of byproducts along with the unconverted feed gave a combined reactor feed rate of 20300 BPSD. The liquid recycle purge rate was chosen to prohibit > 1% loss of carbon contained in the feed and product streams. The equipment requirements for such a plant were similar to those for an isomerization technology (Penex) which UOP currently licenses extensively. Therefore, a capital cost estimate (+/- 30%) was prepared for the process based this well-established technology, excluding the costs of the makeup feed driers, makeup gas compressor, and product gas scrubber (Appendix I). The estimated erected cost was 5.9 MM dollars.

3.5.4 Process Simulation Results

Hyprotech Hysim v2.50 process simulation software was used with the NRTL activity property package (recommended for non-ideal components) to model the system. In the process flow diagram, shown in Figure 21, methanol and the ethanol co-feed are mixed and combined with recycle gas (CO, CO₂, and H₂) and then recycle liquid before being heated to the reactor inlet temperature. Although three reactors are illustrated to model methanol conversion, ethanol conversion and the water gas shift reaction, only one reactor would be used commercially. The reaction product is cooled and phase-separated. A significant portion of the separator gas is vented to prevent > 25 psia hydrogen partial pressure in the combined reactor feed, since this condition gave poorer selectivity experimentally.

The separator liquid, containing isobutanol, unconverted methanol and ethanol, as well as a number of byproducts, is charged to a distillation column. Excess of 99% of the isobutanol is recoverable in the bottoms product with negligible losses of methanol and ethanol. The byproduct isobutyraldehyde is recovered in the overhead product. The extent of buildup of this species in the liquid recycle loop is difficult to estimate from experimental data, since hydrogenation of this material to isobutanol might eventually occur, improving the alcohol yield. Nevertheless, a liquid purge is required to reject primarily alkane and ester side products, with some corresponding loss of methanol and ethanol. Heat integration between both the reactor and splitter column feeds and reactor effluent is considered for reduction of charge heater and column reboiler duties.

With liquid recycle, the overall carbon conversion is 98% with 22% selectivity to isobutanol. The expected production of isobutanol is 92 MT/day from 500 MT/day of methanol and 172 MT/day of ethanol feed. An additional 13 MT/day of isobutyraldehyde intermediate is recovered in the liquid product and vent streams. This material is considered to have the same value as isobutanol in one economic evaluation case, since it is conceivable that buildup of the C₄ aldehyde in the liquid and gas recycle loops would lead to its eventual conversion to isobutanol.

3.5.5 Vent Loss Study

The effect of varying separator temperature has been examined in detail, since increasing this temperature above 100°F (5°F approach to cooling water temperature) would reduce the amount of light byproducts in the liquid recycle stream and consequently the energy costs associated with product fractionation. Excessive separator temperatures, of course, give unacceptably large losses of feed and product in the recycle vent. One initial goal of the process simulation work, therefore, was to find the optimal separator temperature.

Several cases with separator temperatures ranging from 59-180°F were studied to evaluate trends in product losses through the recycle gas and liquid purge streams. The conditions used and results obtained are summarized in Table 38. In each simulation, fresh feed rates were adjusted to obtain the 20300 BPSD combined feed flow upon which the economic evaluation was based. For separator temperatures > 150°F, fresh feed rates substantially higher than the 5300 BPSD base case were possible since the liquid recycle stream was significantly reduced. In fact, the 150 and 180°F separator temperature cases assumed no liquid purge since all unwanted side products were vented and therefore did not accumulate appreciably in the liquid recycle loop. Losses of feed methanol out the recycle gas vent under these conditions, however, exceeded 3% of that charged to the reactor, as depicted in Figure 22. Other process parameters which were maintained constant in each simulation case were the molar methanol/ethanol ratio (7/1) and H₂ partial pressure (< 29 psia) in the combined feed. The importance of preserving these values was demonstrated experimentally in the process optimization work. When considering the effect of separator temperature on combined gas and liquid purge stream losses, the optimal value, giving a minimum of combined losses, was found to be approximately 120°F, as illustrated in Figure 23. Therefore, the material balance used for the economic analysis, given in Table 39, was based in this separator temperature.

3.5.6 Economic Analysis

3.5.6.1 Overview of Methodology

The combination of experimental performance data, the capital cost estimate, and the process simulation provided the basis needed to examine the economic viability of isobutanol synthesis from methanol and ethanol. The base case for economic analysis, therefore, used the best pilot plant results, the 5.9 million dollar initial capital estimate for a 20300 BPSD combined feed stand-alone unit, and the material balance given by the process simulation model at the optimal separator temperature. To complete the economic study, estimations of all operating costs (utilities, fixed costs, working capital, depreciation, and capital expenses) were required in addition to the current market feed and product costs. Isobutanol could be valued as a solvent or an MTBE precursor, the latter material having a significantly lower value but vastly broader market. Furthermore, a number of hypothetical cases were examined to quantify the benefit of improved selectivity to isobutanol. The most realistic of these was the incremental increase in isobutanol yield associated with complete hydrogenation of the intermediate isobutyraldehyde.

3.5.6.2 Utility and Other Operating Costs

In addition to the material balance, the Hysim software also provided an energy balance for the process model, allowing estimation of utility costs. A summary of major utility streams, with a description of where each utility is needed, the type of utility used, and the power required, is given in Table 40. The assumptions used in calculating these utility requirements, which include widely-accepted pump efficiencies, air cooler fan efficiencies, cooling water and air temperature approaches, and air cooler pressure drops, are given in Table 41. Electrical power was assumed for the feed pump, reactor effluent air cooler, recycle gas compressor, splitter column overhead (air cooled) condenser, and liquid recycle pump. The UOP cost basis for electricity is currently \$0.05 per kilowatt-hour. Fuel gas, valued at \$2.10 per million BTU, was considered for the feed preheater. Medium pressure (300 psig) steam, costing \$3.05 per thousand pounds, was assumed the heat transfer medium for the splitter charge

heater and reboiler. Of the three utilities used, the steam represented by far the largest cost. The standard UOP utility cost basis is presented in Table 42. Annual utility cost calculations for the base case isobutanol synthesis plant are shown in Table 43. In addition to utilities, the general economic assumptions used to estimate fixed costs, total plant investment, working capital, depreciation, and capital expenses, are given in Table 44.

3.5.6.3 Base Case Economic Study and Other Cases Considered

Using the fixed and variable production cost estimations outlined above, a complete economic summary for the base case (Case I) is presented in Table 45. In the section describing feed costs and product revenues, a fuel gas credit is taken for the large amounts of H₂, CO, and CO₂ byproducts generated. Also, isobutanol is valued as a solvent (\$903/MT), even though the expected 1998 U.S. consumption at this price is only 54,500 MT. Methanol and ethanol are both assumed to cost \$150/MT, which would take into account current levels of U.S. Government subsidies for ethanol. Even under these favorable circumstances, the total feed stock costs (\$33.63 MM/year) exceed product revenues (\$28.85 MM/year). When all fixed and operating costs are considered, a negative cash flow of \$16.5 MM/year is implied for the base case, due to the poor selectivity to isobutanol.

In an actual isobutanol synthesis plant, the intermediate isobutyraldehyde might be hydrogenated to the desired alcohol, giving a more favorable product yield. For this situation (Case II), isobutanol selectivity increases from 22.2 to 26.1%, based on feed carbon. The fuel gas credit, utility, and other costs remain comparable to the base case. If the catalyst and process parameters could eventually be improved to give 50% isobutanol selectivity (Case III), the expected fuel gas make would be reduced 30% and the utilities would be about 50% of the base case requirements. For comparative purposes, the final investigation (Case IV) assumes 100% selectivity to isobutanol, no fuel gas production, and a 75% reduction in utilities compared to the base case. A summary of the cases studied for economic purposes, along with the implications at each condition, is given in Table 46. Comparative product revenues, utility costs, and the isobutanol sale price needed to achieve 20% internal rate of return (IRR)

on the capital investment, are shown for each case in Table 47. A graphical representation of product price required for 20% IRR versus feed carbon selectivity to isobutanol, is given in Figure 24.

3.5.6.4 Conclusions of the Economic Analysis

Because of the low selectivity (22%) of the methanol conversion catalyst to isobutanol, the process is uneconomical, even if the isobutanol is valued as a solvent (\$903/MT) and not as isobutylene for MTBE production (\$352/MT). If the intermediate isobutyraldehyde is considered the same as isobutanol (valid if the aldehyde in liquid recycle of the commercial plant is hydrogenated), 26% selectivity to isobutanol can be achieved. Still, a selectivity of greater than 40% is needed for a 20% internal rate of return on the capital investment. The expected 1998 U.S. isobutanol consumption for solvent and other applications is 54,500 MT. A selectivity of at least 80% would be required for 20% IRR if isobutanol value is based on its gasoline (MTBE precursor) use. This market (10.6 million MT 1997 U.S. estimate) is substantially broader than the solvent market, and therefore a more reasonable basis for the economic analysis.

3.6 Direct Conversion of Synthesis Gas to Isobutylene (Isosynthesis)

The preliminary approach in this project was to identify an improved isosynthesis catalyst for the production of isobutylene from synthesis gas. Previous work has demonstrated a yield of about 4.0% using a modified ZrO_2 catalyst [46]. This is too low for an economic process. Several approaches to obtaining improved yields, including varying ZrO_2 catalyst preparation techniques, the use of catalyst additives, non- ZrO_2 catalysts, recycle of intermediates and alternative process conditions, have been investigated. The properties of the catalysts prepared in this portion of the project are summarized in Table 48. The results of laboratory plant tests to determine the yields of isobutylene afforded by these catalysts at 450°C, 1200 psig, 960 hr⁻¹

GHSV with a 1/1 H₂/CO feed are summarized in Table 49.

Testing of the ZrO₂ catalysts has shown only one variable, surface area, that reasonably correlates with performance. As shown in Table 50, surface area increases with reduced calcination temperature and isobutylene yield increases. However, the reaction must be carried out at temperatures lower than the calcination temperature to minimize sintering of the catalyst during operation. With catalysts calcined at temperatures below 450°C, operating conditions require very low space velocities for commercially relevant conversions, leading to uneconomic operating conditions. The benefits of increased surface area also appears to reach a limit at about 125 m²/g and 3.75% isobutylene yield. This is still considerably less than is needed for an economic process.

The highest reported yields of isobutylene have been obtained using ZrO₂ modified with the addition of various 'stabilizers', such as Y. A number of catalysts were prepared and the results summarized in Table 51. None of the additives tested produced a significant improvement in isobutylene yield compared with the unmodified ZrO₂.

Previous work has shown that various metal oxides produce levels of isobutylene comparable to ZrO₂. Table 52 summarizes the results for CeO₂ and Bi₂O₃. Bi₂O₃ was tested since it is a good oxide ion conductor, like many of the isosynthesis catalysts. None of the tests produced improvements over the unmodified ZrO₂.

The reaction produces ethylene and propylene as byproducts. If these materials could be recycled to the process and converted to isobutylene, the yield could be significantly increased. Similarly, if alcohols such as methanol or ethanol could be converted to isobutylene with high yield, the difficult first coupling step could be avoided. The results of adding possible intermediates to the feed to simulate recycle are summarized in Table 53. Unfortunately, none of the possibilities converts to isobutylene, rendering recycle ineffective.

The effect of process variables - pressure, temperature, space velocity and H₂/CO ratio - were examined to optimize the process. The comparisons are given in Tables 54-57. In general, increased pressure increases conversion, but increases the paraffin to olefin (P/O) ratio. Increased temperature increases conversion, increases methane formation and increases the P/O ratio. Decreased space velocity increases conversion and increases P/O ratio. Increased H₂/CO ratio increases the isobutylene yield and increases the conversion. It also improves the catalyst stability [7]. The overall conclusion is that operation at low to moderate temperatures and pressures with a high H₂/CO ratio produces the best isobutylene yield. Low space velocity tends to improve performance, but makes the process less economically attractive.

In summary, various approaches, including different catalysts, catalyst modifiers, optimized catalyst surface area, optimized process operating conditions and recycle of byproducts, have been evaluated to increase the production of isobutylene from synthesis gas. The best results achieved a maximum isobutylene yield of less than 4.0%, which is too low for an economic process. Attempts to recycle byproducts to increase the yield were unsuccessful. Overall, the isosynthesis approach does not appear to be a promising route to isobutylene production. The focus of this project was, therefore, shifted to the conversion of synthesis gas and light alcohols to higher branched alcohols that are intermediates .

4 CONCLUSIONS AND RECOMMENDATIONS

The conversion of synthesis gas to higher branched oxygenates, whether by an direct or indirect method, requires three catalytic steps. First, the CO must be hydrogenated to a C₁ alcohol or aldehyde intermediate. Next, a C-C bond must be formed by the condensation or carbonylation of the C₁ species to afford a C₂ intermediate. This species is then able to undergo an aldol-type condensation with additional C₁ intermediate to give the desired branched product. Most of the previous catalyst systems described in the literature have been applied to the overall synthesis gas to higher oxygenates process. However, it is possible to separate these steps into individual processes. In this way, catalyst formulations and process conditions can be used that are optimized for each reaction step. In this project work has focused on identifying a catalyst system and process for the second two steps of the overall reaction, the C₁ condensation and aldol condensation steps. This process could then be combined with a conventional methanol synthesis and synthesis gas production processes to provide an overall route from alternative fuel sources (coal or natural gas) to higher oxygenates.

In this project catalyst screening with a 10/1 methanol/ethanol feed has been used to identify potential catalysts for the aldol condensation step in overall synthesis gas to isobutanol process. A co-precipitated Cu/Zn/Al oxide catalyst, similar to a conventional methanol synthesis catalysts, was found to have activity for this reaction and was selected as a baseline material for comparison. Noble metal (Pt or Pd) on a co-precipitated Zn/Mn/Zr oxide support was found to be superior to the baseline catalyst in terms of activity as well as selectivity and yield of isobutanol and total C₃₊ oxygenates. Testing of this catalyst at high space times, where ethanol conversion was high, suggested that this type of catalyst might be able to convert methanol alone to higher oxygenates. In contrast, the Cu/Zn/Al baseline catalyst showed no evidence of such activity. However, subsequent testing of three Pt on Zn/Mn/Zr oxide catalysts with a methanol-only feed showed no formation of higher products, indicating that

considered to have the same value as isobutanol for economic purposes, since it is conceivable that buildup of the C₄ aldehyde in the liquid and gas recycle loops would lead to its eventual conversion to the desired product. The capital cost estimate for a 20300 BPSD combined feed commercial isobutanol synthesis plant was estimated to be 5.9 MM dollars based on an extensively-licensed UOP technology which is similar in design. The relationship between vent and purge stream losses and the separator temperature downstream of the reactor has been investigated, and the optimal separator temperature was found to be approximately 120°F. This information was used as well for the economic evaluation of the commercial process.

Because of the low selectivity (22%) of the methanol conversion catalyst to isobutanol, the process is uneconomical, even if the isobutanol is valued as a solvent (\$903/MT) and not as isobutylene for MTBE production (\$352/MT). If the intermediate isobutyraldehyde is considered the same as isobutanol (valid if the aldehyde in liquid recycle of the commercial plant is hydrogenated), 26% selectivity to isobutanol can be achieved. Still, a selectivity of greater than 40% is needed for a 20% internal rate of return on the capital investment. The expected 1998 U.S. isobutanol consumption for solvent and other applications is 54,500 MT. A selectivity of at least 80% would be required for 20% IRR if isobutanol value is based on its gasoline (MTBE precursor) use. This market (10.6 million MT 1997 U.S. estimate) is substantially broader than the solvent market, and therefore a more reasonable basis for the economic analysis. Considering the current performance limitations, this particular process for the conversion of lower alcohols to higher branched oxygenates cannot produce isobutanol at a price which would allow penetration into the gasoline market. Therefore, no competition to the current state-of-the-art TBA byproduct dehydration route to isobutylene is provided. UOP does not intend to continue pursuing this technology further.