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DEVELOPMENT OF A CATALYST FOR CONVERSION OF
SYNGAS-DERIVED MATERIALS TO ISOBUTYLENE

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EXECUTIVE SUMMARY

The initial objective of this program was to develop a catalyst and process for the conversion of synthesis gas to isobutylene via the isosynthesis process. Preliminary work directed at identifying potential catalysts for this reaction did not have promising results. Therefore, the objectives of this program were revised to the development of a catalyst and process for the conversion of synthesis gas to isobutanol. Two approaches have been investigated in this area: the direct conversion of synthesis gas to higher alcohols and indirect conversion via methanol produced using conventional methanol synthesis technology.

The isosynthesis reaction for the conversion of synthesis gas to branched hydrocarbons was pioneered by German workers during World War II. The primary products of this reaction are either isobutane or isobutylene depending on the catalyst system used. Thoria-based catalysts were found to give the highest yields, but virtually all of the products were alkanes. More recently, there have been several reports of olefin production using ZrO_2 -based. The preliminary work in this program focussed on the evaluation of ZrO_2 and modified ZrO_2 catalysts for the direct conversion of CO/H_2 to isobutylene via the isosynthesis reaction. All of the catalysts and conditions evaluated in this work gave isobutylene yields of less than 4% which is far below that required for an economically viable process. A summary of the key results from this portion of the project is given in Section 3.6. In view of the poor performance of these catalysts and the lack any encouraging results from other research groups working in the isosynthesis area, this approach was abandoned in favor of approaches related to higher alcohols synthesis.

Conventional methanol synthesis catalysts can be modified to increase the selectivity to higher alcohols, particularly isobutanol, from synthesis gas. It has been proposed that alcohol condensation is catalyzed by a basic function on the catalyst surface. For example, alkali-modified $\text{Cu}/\text{Zn}/\text{Al}$ catalysts have been commonly used. The isobutanol selectivities of the best catalysts to date remain below the level required for economic viability. Two problems

that need to be overcome are to increase the isobutanol/methanol product ratio to at least 1.0 and overcome the loss in synthesis gas conversion activity that typically occurs on alkali modification. The second approach investigated in this program has been to combine a conventional methanol synthesis catalyst with an alternative solid base catalyst. The use of Metal Oxide Solid Solutions (MOSSs) derived from hydrotalcites as the solid base component has been investigated. However, these materials have too much residual acidity to afford clean higher alcohols products. The results of this testing are described in Section 3.1.2.

The generally accepted mechanism for higher alcohol formation involves the formation of methanol followed by its condensation to higher alcohols. Therefore, it should be possible to combine a conventional methanol synthesis technology with a catalyst optimized for the condensation of alcohols to isoalcohols. In this process, the formation of the initial C-C bond is the most difficult step. The third approach for the production of higher alcohols pursued in this program has been to identify a catalyst and process for this reaction. Initial catalyst screening with a methanol-only feedstock gave very low conversions. Section 3.1.3 describes this work. In order to determine whether the lack of activity was due to poor catalysts or inappropriate selection of reaction conditions, a methanol/ethanol feedstock was employed. A promising catalyst formulation consisting of noble metal on a Zn/Mn/Zr mixed metal oxide support has been identified and mechanistic tests performed that suggest that this catalyst may be capable of methanol-only condensation. The effects of catalyst composition (Section 3.2) and process variables (Section 3.3) have been examined with this basic catalyst formulation. Finally, pilot plant demonstration runs with a methanol-only feed, at optimized conditions and with high H_2 co-feed have been completed (Section 3.4). The best performance has been obtained with a 2% Pt on co-precipitated Zn/Mn/Zr (60/20/20) oxide support at 325°C, 300 psig, 1 hr⁻¹ WHSV and 7/1 methanol/ethanol molar feed ratio. Conversions of methanol and ethanol are 55% and 97%, respectively, with 22% selectivity to isobutanol and 5% selectivity to isobutyraldehyde. A conceptual design of a combined methanol synthesis/higher alcohols synthesis process has been done and preliminary economic analysis completed (Section 3.5). Because of the low selectivity of the methanol conversion catalyst to isobutanol and the need to

imported ethanol, the process is uneconomical. 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.

1 OBJECTIVES

The original objective of this program was to develop a catalyst and process for the conversion of synthesis gas to isobutylene via the isosynthesis process. Preliminary work directed at identifying potential catalysts for this reaction did not have promising results. Therefore, the objectives of this program were revised to the development of a catalyst and process for the conversion of synthesis gas to isobutanol. Two approaches have been investigated in this area: the direct conversion of synthesis gas to higher alcohols and indirect conversion via methanol produced using conventional methanol synthesis technology.

The program has been divided into six tasks.

1. Catalyst identification and reaction mechanism
2. Catalyst development and optimization
3. Pilot plant demonstration runs
4. Process variable studies
5. Economic analysis
6. Reporting and administration

This report summarizes the technical results obtained in the first five tasks.

2 INTRODUCTION

2.1 Utilization of Higher Branched Alcohols (Isobutanol)

The development of alternative fuel sources is a national priority of the United States. One approach to achieve this end is the conversion of synthesis gas (CO/H_2) derived from coal or natural gas into compounds that can be blended into transportation fuels. The use of coal would take advantage of the United State's vast resources. Coal can be converted to synthesis gas by gasification although this has not been widely practiced to date due to high feed processing costs relative to other hydrocarbon sources. The majority of the world-wide production of synthesis gas by the steam reforming of natural gas or naphtha is widely practiced commercially.

The largest consumers of synthesis gas are methanol and ammonia synthesis. These are mature technologies that have been practiced commercially since the 1920's. Other petrochemical uses of synthesis gas include the Oxo process for the production of alcohols, detergents and solvents and the production of acetic acid and isocyanates. Synthesis gas can also be converted into gasoline-range paraffins with the Fischer-Tropsch process. This process uses a Fe or Co catalyst in a variety of processing schemes. However, after extensive research and development over the past two decades, F-T technology cannot compete with the production of gasoline from crude oil.

The introduction of reformulated gasoline into a large portion of the United State's gasoline market in the mid-1990's has created opportunities for new gasoline blending components. One of the key requirements of reformulated gasoline is that oxygenated compounds be added such that the O content of the final gasoline be 2.7 wt. % [1]. At the current time this oxygenate requirement is being filled principally by ethanol (mainly from fermentation) and methyl t-butylether (MTBE) produced by the etherification of isobutylene with methanol.

Other C₅-C₆ ethers, such as ethyl t-butylether (ETBE), t-amyl methylether (TAME) and diisopropylether (DIPE), are also attractive oxygenates for use in fuel blending. The production of MTBE and ETBE will ultimately be limited by the availability of isobutylene. The estimated U.S. capacity for MTBE in 1997 is about 70,000 thousand metric tons [2]. About 30% of the current MTBE market is supplied by isobutylene made by the dehydration of the t-butanol co-product of propylene oxide production. This market segment could also be supplied by isobutanol prepared from synthesis gas if an economically attractive process for the production of higher branched alcohols could be developed. The remaining portion of the isobutylene for MTBE production is derived from refinery streams (31 %), dehydrogenation of isobutane (31 %) and ethylene plants (11 %).

2.1.1 Current Production and Utilization of Isobutanol

Today isobutanol is obtained as a by-product of the Oxo process for the production of butyraldehyde. Its current market consists mostly of solvent, lube oil additive and speciality petrochemical uses. The demand for isobutanol can fluctuate since it can be readily interchanged with n-butanol in many solvent applications. The total U.S. consumption of isobutanol in 1993 was 118MM lb with an expected growth rate of 0.3 % for 1993-1998 [3]. The current (1996) price for isobutanol in the solvent applications is in the range of \$0.41/lb [4]. This market is not of sufficient size to warrant the production of isobutanol from alternative sources, such as synthesis gas. Therefore, the economics of isobutanol production must be attractive enough for it to penetrate the gasoline market. In order for this to occur isobutanol must be priced in the \$0.13/lb range in order to be an attractive feedstock for MTBE at \$0.128/lb (six month average) [5].

2.1.2 Isobutanol Dehydration to Isobutylene

Technology for the dehydration of branched C₄ alcohols is well established in the chemical industry. The separation of isobutylene from mixed butene streams by acid extraction, which is the most common method used, involves the selective hydration of isobutylene to t-butanol by aqueous HCl or H₂SO₄, followed by separation and decomposition of the alcohol back to

isobutylene [6]. Typical recoveries for this process are about 92 %. Dehydration of t-butanol, which is a by-product of propylene oxide plants, is the largest current domestic source of isobutylene for MTBE production. Commercial processes use t-butanol exclusively for this application due to its lower cost and greater supply relative to isobutanol. However, the dehydration technology is capable of using either feedstock. t-Butanol dehydration is typically done at about 200°C and 10 atmospheres using a TiO₂ supported catalyst [7]. The process operates at 100 % conversion and yields 93-95 % selectivity to isobutylene.

2.1.3 Isobutyraldehyde Hydrogenation to Isobutanol

In addition to isobutanol, a synthesis gas based process for higher branched oxygenates may also produce a substantial quantity of branched aldehydes. However, the hydrogenation of aldehydes to alcohols is a widely used process in the chemical industry. One of the major sources of n- and iso-butanols is the hydrogenation of the corresponding aldehydes made in the rhodium-catalyzed Oxo process [8]. The hydrogenation process is done in a single, gas-phase step using a temperature controlled reactor. Typical catalysts include supported Ni and Cu containing materials such as Cu/Zn oxide [9]. Process conditions are mild (140°C) with a high H₂ partial pressure to drive the hydrogenation equilibrium to very near completion. In higher alcohol synthesis, therefore, byproduct aldehydes, such as isobutyraldehyde, can be considered to have the same value as their homologous alcohols, since this conversion is well-known and straight-forward.

2.2 Formation of Higher Branched Alcohols from Synthesis Gas

The direct production of C₄₊ alcohols from synthesis gas has been of interest since the discovery of CO hydrogenation in the early 1900's. However, in contrast with methanol synthesis which can be accomplished with very high selectivity, the catalysts and conditions for producing higher alcohols generally gave complex product mixtures. Therefore, interest in this approach waned with the development of Oxo processes which afford better selectivity to

specific alcohols by the carbonylation of an olefin with CO and subsequent reduction of the aldehyde. Interest in higher alcohols for use as an alternative fuel (or additive) to gasoline was rekindled in the 1980's. Processes for the formation of higher alcohols from synthesis gas fall into two general categories: 1) methanol synthesis type processes which afford branched higher alcohols and 2) Fischer-Tropsch based processes which give normal alcohol products. Since this program is directed at the formation of isobutanol for further conversion to MTBE, the former catalyst systems are most pertinent. These processes have typically used alkali modified methanol synthesis catalysts. However, recently a new type of catalyst consisting of a noble metal on a basic metal oxide support has been reported to have high selectivity for isoalcohol formation.

2.2.1 Alkali Modified Methanol Synthesis Catalysts

The synthesis of higher alcohols from CO/H₂ using alkali modified methanol synthesis catalysts has been known since the 1920's [10]. In general, the function of the alkali promoters (K, Rb, Cs) is independent of the type of methanol synthesis catalyst used. Substantial work prior to 1957 was done using alkali modified Zn/Cr oxide catalysts which, although they require the use of high pressure and temperature, were the best methanol synthesis catalysts known at the time. Isobutanol is the primary C₄₊ product obtained with these catalysts, with highest yields reported for Rb or Cs on Zn/Cr oxide [10]. Other methanol synthesis catalysts that appear to be similar to Zn/Cr oxide by giving high isobutanol in the C₂₊ product when modified with alkali include ZnO alone [11], Cr/Mn oxide [12], Zn/Mn/Cr oxide [13], Cu/Zn/Cr oxide [14], V/Cu oxide [15] and Cd/Cr oxide [16]. In contrast with alkali-modified methanol synthesis catalysts, several Co containing catalysts, such as CoS on Cu/Mn oxide [17] and Co/Zn oxide [18], have been reported to give ethanol as the primary higher alcohol product.

In the early 1960's high activity Cu/Zn oxide-based catalysts were developed which allow the use of lower temperatures and pressures in the methanol synthesis reactor than earlier Zn/Cr oxide catalysts. Modification of these materials with alkali also affords higher alcohols.

Smith and Anderson found that the addition of K_2CO_3 to a commercial Cu/Zn/Al oxide catalyst increases higher alcohol selectivity giving an isobutanol-rich higher alcohol distribution [19]. This work also demonstrates that decreasing the $H_2:CO$ feed ratio from 2.0 to 0.5 and operating at a high $H_2 + CO$ conversion level increases selectivity to butanol. Klier and co-workers at Lehigh University have reported that Cs at 0.5 to 1.0 wt. % is the most effective modifying alkali metal for Cu/Zn oxide [20]. Workers at Air Products have evaluated this type of catalyst in the slurry phase pilot plant reactor at Laporte, Texas. This work has demonstrated per pass space time yields of 60 g isobutanol/kg catalyst/hr and 170 g C2-C6 alcohols/kg catalyst/hr [21].

2.2.2 Noble Metal on Zn/Mn/Zr Oxide Catalysts

The ability of supported noble metals, particularly Pd on SiO_2 , to catalyze the formation of methanol from synthesis gas was discovered in the late 1970's [22]. The proper selection of conditions was found to be critical to achieve high selectivity to methanol rather than methanation. Several other groups have investigated the reaction mechanism and kinetics of this system [23, 24]. Although this new class of methanol synthesis catalyst has not competed commercially with Cu/Zn/Al oxide catalysts, these findings do indicate that noble metal catalysts can have high selectivity for CO hydrogenation to alcohols.

In the late 1980's Keim and co-workers described that isobutanol could be formed with high selectivity from synthesis gas with the use of novel catalyst consisting of Pd and alkali on a mixed Zn/Mn/Zr oxide support [25]. Isobutanol yields as high as 740 g/l catalyst/hr have been reported at high temperature (420°C) and pressure (3700 psig). These catalysts have typically been prepared by the co-precipitation of the mixed metal oxide support using an alkali base solution followed by the addition of noble metal by impregnation. The effects of a wide variety of catalyst preparation variables and process conditions on the catalytic performance have been summarized [26].

2.2.3 Proposed Reaction Mechanisms

The formation of higher alcohols over alkali-modified methanol synthesis catalysts, such as Cu/Zn oxide, has been shown to occur by the condensation of lower alcohols. Smith and Anderson have proposed a growth scheme for the synthesis of higher alcohols from CO/H₂ involving distribution parameters for the addition of 1 and 2 carbon fragments to the α and β positions of adsorbed, oxygenated intermediates (Figure 1) [27]. Calculation of parameters from product selectivities over a K₂CO₃ modified Cu/Zn oxide catalyst indicates that α -addition is a slow step, while β -addition is fast. This results in selective formation of methanol and isobutanol, which can grow only by α -addition steps.

The reaction mechanism of the alcohol condensation steps have been investigated by several research groups using isotopic labeling. Elliot and Pennela have shown that when a small amount of ¹³C labeled methanol is added to the CO/H₂ feed over a Cu/Zn oxide catalyst the ethanol product obtained has all three combinations of ¹²C and ¹³C labeling in comparable amounts [28]. They interpreted this result as indicating that a C₁ species is a common intermediate in the formation of both methanol and ethanol. The Klier group at Lehigh has found that when unlabeled ethanol is added to this feed the light alcohols are very efficiently converted to higher alcohols over a Cs-modified Cu/Zn oxide catalyst affording 1-propanol and 1-butanol with ¹³C enrichment in the α and $\alpha + \beta$ carbons, respectively [29]. This result indicates that the C₁ intermediate involved in linear chain growth is formed preferentially from methanol rather than from CO. The identity of this C₁ intermediate as formyl has been suggested by chemical trapping experiments, spectroscopic observations and quantum chemical calculations.

Further ¹³C labeling studies on the Cs-modified Cu/Zn oxide catalyst system indicate that a second reaction pathway exists for the chain growth of C₄₊ oxygenates by the addition of C₁ or C₂ fragments to the β carbon of the growing chain [30]. Examples of this step include the formation of ¹³CH₃CH₂CH₂OH from CH₃¹³CH₂OH + CH₃OH and (¹³CH₃)₂CHCH₂OH from CH₃CH₂CH₂OH + ¹³CH₃OH. The experimental results indicate that the addition of alkali to

the Cu/ZnO methanol synthesis catalyst greatly promotes the β addition pathway over the α addition step to give higher selectivity to higher alcohols, in particular isobutanol. Based on these results, a mechanism has been presented by the Lehigh group for higher alcohol synthesis over alkali modified Cu/Zn oxide catalysts (Figure 2) [30]. Linear products are formed by the nucleophilic attack of a metal-bound formyl, arising from the insertion of CO into a metal hydride bond, on the α -carbon of a C_n alcohol or aldehyde to displace the oxygen (after hydrogenation in the case of aldehyde). This results in a linear C_{n+1} aldehyde which is hydrogenated to the alcohol. Branched products are proposed to arise from aldol coupling with oxygen retention reversal involving the condensation of a metal-coordinated C_n enolate species with methanol or formaldehyde to give a β -ketoalkoxide intermediate which rearranges via dehydration and hydrogenation to the C_{n+1} branched alcohol with retention of the oxygen of the C_1 starting fragment.

2.3 Formation of Higher Branched Alcohols from Light Alcohols

2.3.1 Condensation of Mixtures of Methanol, Ethanol and Propanol

A wide variety of catalysts have been reported over the last several years for the conversion of light alcohols (methanol, ethanol and propanol) to higher branched oxygenates, particularly isobutanol and isobutyraldehyde. Catalysts that have been described include single basic metal oxides (MgO, CaO) [31, 32], Rb/Ru/ Al_2O_3 [33], Cu/Zn/Al oxide [34, 35] and V/ TiO_2 [36, 37]. Typical conditions used in this work have been 350°C, 0 psig and about 1 hr⁻¹ methanol WHSV with a feed containing an excess of methanol.

The condensation of ethanol alone over a catalyst consisting of K_2CO_3 /MgO/Cu/Cr catalyst has been described by Farrar to afford only n-butanol [38]. This product is expected based on the aldol condensation pathway for a C_2 feed.

2.3.2 Condensation of Methanol Only

In contrast with the condensation of methanol with other light alcohols, there are few reports of the condensation of methanol alone to higher alcohols. Forzatti and co-workers have reported that C_{2+} oxygenates consisting mainly of isobutanol and isobutyraldehyde are produced in low selectivity when methanol is passed over a K modified Zn/Cr oxide catalyst at 300-400°C and 0 psig [39]. Most of the methanol feed is decomposed to CO and H_2 . Workers at Air products have recently claimed to have discovered a new process that affords 69% selectivity to isobutanol and 42% methanol conversion [40]. However, no details about the process have been provided.

2.4 Basic Metal Oxides

One of the initial approaches in this project to promote the formation of higher alcohols has been to combine novel strong base materials with conventional CO hydrogenation catalysts. The strong base materials used in this program have been prepared by the calcination of hydrotalcite precursors. These layered double hydroxide materials are based on brucite sheets, which are structurally similar to the octahedral layer of smectite clays (Figure 3). The substitution of Al^{+3} cations for the Mg^{+2} in the brucite layer generates residual positive charge. Because of this, layered double hydroxides are anion exchangers and base catalysts. These are the only known inorganic oxides that are anion exchangers. Calcination of layered double hydroxides affords materials with high surface areas ($> 200 \text{ m}^2/\text{g}$). The X-ray diffraction patterns of the calcined oxides are no longer consistent with layered double hydroxides, therefore, the term MOSS (Metal Oxide Solid Solution) has been used to describe them. The hydrothermal stability of these materials is excellent - the surface area is not affected by steaming at 600°C. The chemical composition of MOSSs can be varied over a wide range and catalytically interesting cations, such as Ni, Zn and Cr, can be incorporated into the framework. MOSSs have been shown to be active base catalysts. They have been used to catalyze aldol condensations and alcohol dehydrations [41].

2.5 Direct Conversion of Synthesis Gas to Isobutylene (Isosynthesis)

An alternative approach for the conversion of synthesis gas to branched hydrocarbons is the isosynthesis reaction that was pioneered by German workers during World War II. The primary products of this reaction are either isobutane or isobutylene depending on the catalyst system used. In general, the yields of the desired products, especially olefins, are very low.

The original German work focused on the use of thoria-based catalysts at high pressure conditions (30-300 atm). A survey of precipitated metal oxides (ThO_2 , Al_2O_3 , W_2O_3 , Cr_2O_3 , TiO_2 , BeO , ZrO_2 , UO_2 , ZnO , MnO , MgO , CeO_2) identified thoria as the most active material for the production of liquid hydrocarbons at 450°C and 150 atm [42]. Zirconia, alumina and ceria also give C_{4+} products, albeit less than ThO_2 . The highest yield of hydrocarbons reported in this work is 41 % of which 57% was isobutane, was obtained by modification of ThO_2 with 17 wt. % Al_2O_3 and 0.5 wt. % K_2CO_3 at 450°C and 300 atm using CO/H_2 with a 1:0.84 molar ratio.

Workers at Amoco have reported that cadmium on an acid support, such as zeolite, amorphous silica-alumina or clays affords isoparaffins, particularly isobutane and isopentane, from CO/H_2 [43]. The highest isobutane yields given in this report (10.7%) at 450°C, 1000 psig represent the best branched C_4 production reported in the literature, with the exception of the early German work.

In contrast with the above catalyst systems which afford isoparaffins, several groups have described the use of ZrO_2 -based catalysts for the production of isobutylene. Mayura, Onishi and co-workers obtained very low total hydrocarbon yield (0.4%) of which 77% was isobutylene in a conventional flow system at 370°C, 1 atm, 1:1 H_2/CO and 540 cc/g-hr CO [44]. Ekerdt's group at the University of Texas also has reported low CO conversion (<1%) and yields of total hydrocarbons (0.6%) and C_4 hydrocarbons (0.3%) with ZrO_2 [45]. In

contrast to these results, substantially higher conversions of CO to hydrocarbons have been claimed by workers at Shell [46]. This patent claims yields to isobutylene and total $C_4 + C_5$ are increased to 2.8-4.0% and 7.7-9.8%, respectively, by addition of Ca, Ba or Y to the ZrO_2 catalyst. These modifications also reduce the production of CH_4 . However, the loss of carbon to non-useable lights (CH_4 , CO_2) is remains substantial.

3 EXPERIMENTAL SUMMARY

Three approaches for the conversion of synthesis gas to isobutylene or products that can be used as precursor to isobutylene have been investigated in this project. The preliminary work focussed on the evaluation of ZrO_2 and modified ZrO_2 catalysts for the direct conversion of CO/H_2 to isobutylene via the isosynthesis reaction. All of the catalysts and conditions evaluated in this work gave isobutylene yields of less than 4% which is far below that required for an economically viable process. A summary of the key results from this portion of the project is given in Section 3.6. In view of the poor performance of these catalysts and the lack any encouraging results from other research groups working in the isosynthesis area, this approach was abandoned in favor of approaches related to higher alcohols synthesis.

Conventional methanol synthesis catalysts can be modified to increase the selectivity to higher alcohols, particularly isobutanol, from synthesis gas. It has been proposed that alcohol condensation is catalyzed by a basic function on the catalyst surface. For example, alkali-modified $\text{Cu}/\text{Zn}/\text{Al}$ catalysts have been commonly used. The isobutanol selectivities of the best catalysts to date remain below the level required for economic viability. Two problems that need to be overcome are to increase the isobutanol/methanol product ratio to at least 1.0 and overcome the loss in synthesis gas conversion activity that typically occurs on alkali modification. The second approach investigated in this program has been to combine a conventional methanol synthesis catalyst with an alternative solid base catalyst. The use of Metal Oxide Solid Solutions (MOSSs) derived from hydrotalcites as the solid base component has been investigated. However, these materials have too much residual acidity to afford clean higher alcohols products. The results of this testing are described in Section 3.1.2.

The generally accepted mechanism for higher alcohol formation involves the formation of methanol followed by its condensation to higher alcohols. Therefore, it should be possible to

combine a conventional methanol synthesis technology with a catalyst optimized for the condensation of alcohols to isoalcohols. In this process, the formation of the initial C-C bond is the most difficult step. The third approach for the production of higher alcohols pursued in this program has been to identify a catalyst and process for this reaction. Initial catalyst screening with a methanol-only feedstock gave very low conversions. Section 3.1.3 describes this work. In order to determine whether the lack of activity was due to poor catalysts or inappropriate selection of reaction conditions, a methanol/ethanol feedstock was employed. A promising catalyst formulation consisting of noble metal on a Zn/Mn/Zr mixed metal oxide support has been identified and mechanistic tests performed that suggest that this catalyst may be capable of methanol-only condensation. The effects of catalyst composition (Section 3.2) and process variables (Section 3.3) have been examined with this basic catalyst formulation. Finally, pilot plant demonstration runs with a methanol-only feed, at optimized conditions and with high H_2 co-feed have been completed (Section 3.4). A conceptual design of a combined methanol synthesis/higher alcohols synthesis process has been done and preliminary economic analysis completed (Section 3.5). Because of the low selectivity of the methanol conversion catalyst to isobutanol and the need to imported ethanol, the process is uneconomical. 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.

3.1 Catalyst Identification and Reaction Mechanism (Task 1)

The initial phase of this program has focussed on proof-of-principle testing to identify a catalyst for the conversion of synthesis gas to higher branched alcohols, particularly isobutanol. Due to poor results with a variety of catalyst for the direct conversion of CO/H_2 , the direction of this project was shifted to investigate the conversion of light alcohols (methanol and ethanol) to higher oxygenates. A secondary objective of this task has been to obtain key reaction mechanism information to help understand the performance of the best

catalysts found.

In this section, the pilot plants used for catalyst testing are described, as well as blank runs performed to measure background activity in the stainless steel reactors. The screening of catalysts for the direct conversion of CO/H_2 to higher alcohols is described. The shift to a light alcohol feed initially focussed on the conversion of methanol only to higher alcohols. However, poor results were obtained. Therefore, a 10/1 methanol/ethanol blend has been used to develop a standard catalyst screening test. Noble metal on Zn/Mn/Zr oxide catalysts have been found to give the highest selectivity and productivity of higher branched oxygenates. Space velocity testing also suggested that this catalyst system might be capable of converting methanol alone to higher oxygenates. Therefore, this catalyst type has been investigated further in the latter tasks of this program.

3.1.1 Pilot Plant Descriptions

Pilot Plant 700, an existing Fischer-Tropsch fixed bed pilot plant, has been modified for the screening of catalysts for the production of isoalcohols from synthesis gas. Tables 1 and 2 give a listing of the runs that have been conducted for the conversion of CO/H_2 and light alcohols, respectively, to higher branched oxygenates.

3.1.1.1 Pilot Plant for CO/H_2 Conversion to Higher Alcohols

A diagram of Plant 700 as used for testing catalysts for the conversion of CO/H_2 to higher alcohols is shown in Figure 4. Several modifications were required to the plant prior to use in this program. These included the addition of a new capillary to the CO/H_2 feed system to allow control of feed rates from 0.1 to 1.0 scf/hr, a separate pressure regulator after the reactor and a by-pass line around the hot traps used to collect wax during Fischer-Tropsch operation. A new 5/8" ID, 316 stainless steel differential reactor was dedicated to the isoalcohols project, to avoid cross-contamination with Fischer-Tropsch catalyst and products. The catalyst (sized to 20-40 mesh) was contained within the reactor using stainless steel screens.

A dual GC system has been used to obtain a complete product analysis. The entire reactor effluent is maintained at 100°C and passed to a Total Hydrocarbon GC to detect all hydrocarbons and oxygenates from C₁ through about C₁₅. The product is then passed through a cold (0°C) trap to condense the liquid product. The overhead gas is sent to a Total Gas GC to analyze for CO, CO₂, H₂, Ar, N₂ and C₁-C₃ hydrocarbons and a dry ice (-78 °C) trap to condense any residual liquid product. Initially, this GC system was shared with another Fischer-Tropsch pilot plant with samples alternated hourly when both plants were operating. However, the shake-down runs demonstrated that cross-contamination in the hydrocarbon GC was a serious problem. Therefore, a separate Total Hydrocarbons GC, for use during isoalcohols testing only, was added to the plant.

3.1.1.2 Blank Runs with CO/H₂ Feed

A blank reactor test using silica gel only has demonstrated that back-ground activity of the stainless steel reactor, particularly for CO₂ formation, is negligible at 310°C. Table 3 shows that product gas analysis is virtually identical to the feed analysis. The change-over time of the feed system at the rates used is about 4 hours.

Catalyst testing at 450°C has also been done in this program. However, blank tests in the stainless steel reactor loaded with SiO₂ gel or alpha-Al₂O₃ have shown high yields of CO and light hydrocarbons indicative of non-catalytic reactions occurring on the walls of the reactor. In an attempt to minimize these reactions, the use of a ceramic-lined reactor has been evaluated. When the reactor filled with either alpha-Al₂O₃ or quartz chips, light hydrocarbons and CO₂ yields were still greater than 2%. An empty ceramic-lined reactor gave about a 50% reduction in the by-product yields, indicating that some of the by-products are formed on the packing material.

3.1.1.3 Pilot Plant for Conversion of Methanol and Methanol/Ethanol to Higher Alcohols

A diagram of Plant 700 as used for testing catalysts for the conversion of methanol and

methanol/ethanol mixtures to higher alcohols is shown in Figure 5. A liquid feed system with flow rates maintained with a controlled pressure drop across a capillary was added to the plant.

3.1.1.4 Blank Runs with Methanol and Methanol/Ethanol Feeds

The results of blank reactor tests with the 10/1/20 methanol/ethanol/N₂ feed at 350°C are summarized in Table 4. A 316 stainless steel reactor has been used. Two packing materials have been used to fill the reactor volume above and below the catalyst bed. Borosilicate glass beads show significantly less activity for methanol decomposition than alpha-Al₂O₃. This packing material has been adopted for all subsequent testing.

In order to conduct catalytic tests at temperatures greater than 350°C, a copper-lined stainless steel reactor has been fabricated. Table 5 shows that a blank reactor test using a 1/2 methanol/N₂ feed in the original stainless steel reactor gave acceptable methanol loss at 250°C and 350°C (0.2% and 5.9%), but decomposition became excessive at 450°C (35%) and 500°C (68%). CO and H₂ are the primary products, although CH₄ was also observed at the highest temperatures. In contrast, the copper-lined reactor gave less than 10% methanol decomposition at 350, 400 and 450°C. At 350°C, C₂ oxygenates (DME and methyl formate) are the major products, while carbon oxides, particularly CO become more predominant at higher temperatures.

3.1.2 Catalyst Screening for CO/H₂ Conversion to Higher Alcohols

The initial phase of catalyst screening in this program focussed on the conversion of synthesis gas to higher branched alcohols. One of the ideas for an improved catalyst has been to combine a conventional methanol synthesis catalysts with a basic metal oxide which might promote the aldol condensation step of light alcohols to the desired isobutanol. Several Pd/K on Zn/Mn/Zr oxide catalysts, based on reports by Keim and co-workers, have also been tested. However, none of these catalysts has shown promise for the conversion of CO/H₂ to isobutanol at the conditions used.

3.1.2.1 Methanol Synthesis Catalysts

Shake-down testing of the pilot plant has been done using low temperature (Cu/Zn/Al) and high temperature (Zn/Cr) methanol synthesis catalysts. Both laboratory prepared and commercial samples of the former material have been tested.

3.1.2.1.1 Comparison of Commercial and Lab Prepared Cu/Zn/Al Oxide Catalysts

In order to establish the suitability of laboratory prepared Cu/Zn/Al oxide methanol synthesis catalysts for higher alcohol synthesis, they have been compared with two commercial Cu/Zn/Al oxide catalysts, a low temperature WGS catalyst (ICI 52-1) and a methanol synthesis catalyst (ICI 51-3). The results of reference runs of these materials at 310°C, 1100 psig, 2250 hr⁻¹ CO GHSV and 1/1 CO/H₂ molar feed ratio are given in Table 6. These materials show comparable performances for methanol synthesis at 310°C. The lab prepared catalysts give slightly higher CO conversions, but also more DME and CO₂, than the commercial samples. The presence of some residual acidity in the laboratory prepared materials may be the explanation of the slightly lower selectivity. These results were deemed similar enough for catalyst screening purposes.

3.1.2.1.2 Zn/Cr Oxide High Temperature Methanol Synthesis Catalyst

A Zn/Cr co-precipitated catalyst has been prepared and tested in the pilot plant at 450°C. This catalyst showed very poor performance. The results are summarized in Table 7 and compared with the performance of a Cu/Zn/Al oxide catalyst. Light hydrocarbons and CO₂ were the primary products observed, virtually no alcohols were produced. Subsequent blank reactor runs at 450°C (see above) demonstrated that these products are due to reactions occurring on the reactor walls.

3.1.2.2 Cu/Zn/Al Oxide Catalysts with Basic Metal Oxide Co-Catalysts

One of the approaches that has been investigated to increase the production of higher, branched alcohols from synthesis gas has been the combination of conventional methanol synthesis catalysts, such as Cu/Zn/Al oxide, with a basic co-catalyst. There is strong evidence

in the literature that a base-catalyzed aldol condensation type mechanism leads to the selective formation of isobutanol in these systems. While the metal oxide support of the methanol synthesis catalyst can provide the basic functionality, particularly when impregnated with alkali, one of the objectives of this program has been to determine whether the addition of a stronger base component to the catalyst formulation as a physical mixture might lead to improved performance. Pilot plant evaluations of 5 wt. % K (as KOH) on Al_2O_3 and SiO_2 as basic co-catalysts for the promotion of isoalcohol formation in combination with a Cu/Zn/Al oxide catalyst are summarized in Table 8. Conversions and selectivities with the K/ Al_2O_3 co-catalyst are nearly identical to those of the SiO_2 reference. Therefore, this material appears to be inert. Addition of K/ SiO_2 to the Cu/Zn/Al oxide resulted in a significant decrease in conversion and increase in DME selectivity. Potassium migration could be a possible explanation for this observation, but further investigation has not been pursued.

Three mixtures of the Cu/Zn/Al methanol synthesis catalyst and basic metal oxide co-catalysts have been evaluated. The basic co-catalysts have consisted of two Mg/Al MOSS samples (one lab prepared and one commercial sample obtained from Alcoa) and MgO. Table 9 shows the results of these pilot plant tests. All of the tests using the basic co-catalysts show an increase in CO and H_2 conversion. However, DME is the new product. This undesired by-product does not lie on the pathway from methanol to isobutanol. It is well known that even mild acid catalysts, such as gamma-alumina, can dehydrate methanol to DME. Therefore, this result suggests the presence of some acid sites on the Mg/Al MOSS and MgO materials. In an attempt to eliminate these sites, an Al/Mg MOSS sample has been impregnated with 0.2-0.3 wt. % alkali (Na, K, and Cs) and evaluated in combination with the Cu/Zn/Al oxide catalyst. Table 10 shows that the addition of this level of alkali to the Mg/Al MOSS is not effective for reducing the formation of DME.

The addition of alkali to Cu/Zn/Al oxide methanol synthesis catalysts has been used to increase selectivity to higher branched alcohols. Therefore, 1.3% Cs has been added to a laboratory prepared Cu/Zn/Al oxide sample by impregnation with an aqueous Cs formate solution. Table

11 shows that this catalyst was active for methanol synthesis, with reduced selectivity to CO₂ compared with the non-cesium catalyst. However, the production of the desired branched higher alcohols was negligible.

3.1.2.3 Zn/Mn/Zr Oxide Based Catalysts

Keim and co-workers have reported that very high selectivity to isobutanol from synthesis gas can be obtained with the use of Zn/Mn/Zr oxide based catalysts [25, 26]. The best isobutanol selectivities are obtained at very high pressures (250 bar) that are commercially unattractive. The literature preparations of these catalysts have been reproduced in order to evaluate their performance at more realistic conditions. A typical catalyst preparation consisted of co-precipitating the Zn/Mn/Zr support by simultaneously adding a 1M aqueous KOH solution and a 1M solution of the mixed zirconium, manganese and zinc nitrates to a stirred bucket over 20-30 minutes while maintaining the pH of the mixture at 10 and temperature at 50-60°C. The precipitate was aged in the solution for up to 5 hours then washed with water until the pH of the effluent was 7. The solid was recovered by filtration, dried at 155°C and calcined at 327°C under air for 3 hours. The noble metal component (Pd or Pt), and optionally alkali (K), were added by impregnation using an aqueous solution of either the metal chloride or the metal nitrate. The material was then calcined for a final time at 450°C in air for 6 hours to afford the finished catalyst.

Six pilot plant tests have been conducted using the Pd/K on Zr/Zn/Mn oxide catalysts. The results of these tests are summarized in Table 12. The temperature, feed rate and H₂/CO feed ratio used in these tests are comparable with those used by Keim, but the pressure (1100 psig) is substantially lower than that reported in the literature. All tests conducted at 450°C gave primarily light hydrocarbons and CO₂ rather than alcohols due to reactions catalyzed by the stainless steel reactor walls. A single test at 350°C showed higher selectivity to methanol, but low conversion. In contrast to the literature report, only traces of higher alcohol products were observed in these tests. It is suspected that the poor performance of these catalysts is due to the low pressure used. However, failure to precisely reproduce the catalyst formulation

from the limited description available in the literature cannot be ruled out.

3.1.3 Methanol and Methanol/Ethanol Conversion

The goals of this program were reassessed in light of the failure to identify any promising catalysts for the direct conversion of synthesis gas to higher alcohols. The problematic step in the conversion of either synthesis gas or methanol to higher alcohols is the coupling of two C_1 species to give a C_2 compound. Further condensation, ending with a branched C_4 oxygenate, is well preceded. Since the current commercial methanol synthesis process utilizing a Cu/Zn/Al oxide catalyst is more active for the conversion of CO/ H_2 than any of the modified higher alcohols catalysts tested in this program or described in the literature, it appears that an indirect two-step process might have advantages over the direct synthesis gas to higher alcohols process. First, an optimized methanol synthesis process can be used to maximize the activity and selectivity for CO hydrogenation. Secondly, a completely different catalyst composition, that does not need CO hydrogenation activity, can be utilized for the methanol condensation. Finally, the conditions of the condensation can be separated from those of methanol synthesis allowing the use of high temperatures and lower pressures. Therefore, catalyst screening in this program was re-directed to evaluate catalysts for the conversion of light alcohols to higher branched oxygenates. Initial testing was done using a methanol only feed, but very low conversions were obtained. The use of 10/1 methanol/ethanol feed mixture was adopted in order to screen catalysts. The reaction mechanism of the condensation reaction has been probed by conducting tests at varying space velocities.

3.1.3.1 Screening of Catalysts for the Conversion of Methanol to Isoalcohols

A variety of mixed metal oxide catalysts have been evaluated for the conversion of methanol to higher alcohols at a standardized set of conditions similar to those used for conventional methanol synthesis (250°C, 1100 psig, 2 hr⁻¹ methanol WHSV). Table 13 shows that all catalysts afforded very low conversions of methanol. DME, rather than higher alcohols, was the primary product in all cases. The initial runs employed a N_2 diluent. However, switching

to H_2 , to ensure catalyst reduction, did not result in any improvement in performance.

3.1.3.2 Screening of Catalysts for the Conversion of Methanol/Ethanol to Isoalcohols

It is well known that the reaction of methanol with ethanol to give isobutanol is significantly easier than that of methanol with itself. In fact, several recent literature reports have appeared describing the production of iso- C_4 oxygenates from methanol and ethanol [34, 36]. Since it was not clear whether the poor results obtained in the methanol only testing were due to inadequate catalysts or improper selection of conditions, testing with a methanol/ethanol feedstock has been used to identify suitable catalysts and conditions for the production of higher branched oxygenates.

3.1.3.2.1 Mg/Al Moss Catalysts - Establishment of a Catalyst Screening Test

The development of a catalyst screening test for the conversion of a mixed methanol/ethanol feed to higher oxygenates has been done using a Mg/Al MOSS catalyst. The effects of temperature, pressure and space velocity on performance with a 10/1 methanol/ethanol mixture are summarized in Table 14. At 250°C with an H_2 co-feed, methanol conversions were negligible. However, a small amount of aldehydes were observed in the product at 100 psig. At higher pressure (1100 psig) only DME was observed. Since the desired aldol condensation step for C-C bond formation may require the presence of aldehyde intermediates, the use of low pressure and elimination of the H_2 co-feed was pursued. Increasing temperature to 350°C gave a significant increase in conversion, while further reduction in pressure to 30 psig increased selectivity to C_{3+} alcohols. A final run at low space velocity afforded higher conversion, but selectivity to DME and C_{2+} hydrocarbons also increased suggesting that dehydration and hydrogenation reactions were becoming more dominant. Based on this work, conditions of 350°C, 30 psig, 2 hr^{-1} MeOH WHSV and 1/0.1/2 MeOH/EtOH/ N_2 molar feed ratio have been adopted for catalyst screening.

3.1.3.2.2 Methanol Synthesis Type Catalysts

A Cu/Zn/Al oxide low temperature methanol synthesis catalyst gives almost complete

conversion of both methanol and ethanol at the screening test conditions developed with the Mg/Al MOSS catalyst. CO, CO₂ and DME are the major products, but C₄ oxygenates are also observed including isobutanol, isobutyraldehyde and methylisobutylether (Table 15). The productivities for isobutanol and total C₃₊ oxygenates in this test are 25 and 76 g/kg catalyst/hr which remain below the targets for an higher alcohol production process.

The use of lower temperatures with the Cu/Zn/Al oxide catalyst has been evaluated. Higher C₃₊ oxygenates selectivity (31.8%) and productivity (121 g/kg cat/hr) are obtained at 300°C, but methanol conversion is substantially reduced. At 250°C, methanol and ethanol conversions are lowered further and selectivity and productivity to the desired oxygenate products are also reduced. The results are summarized in Table 15. In view of the performance of this catalyst it has been selected as a baseline material for comparison with new catalysts developed in this program.

Low Cu content Cu/Zn/Al oxide and Cu/Zn/Mn oxide catalysts are less active than the baseline catalyst, but have superior selectivity and productivity to the desired C₄ oxygenates (Table 16). However, comparison of the 350°C performances of these materials with that of the baseline catalyst at 300°C, where conversions are comparable, show similar productivities. It is also unlikely that these materials would be significantly more active for the C₁-C₁ coupling needed for methanol only conversion than the baseline catalyst. Zn/Cr and Zn/Al mixed metal oxide materials, based on high temperature methanol synthesis catalysts, have substantially lower activity and productivity of the desired higher oxygenate products.

3.1.3.2.3 Noble Metal/Zn/Mn/Zr Oxide Type Catalysts

Catalysts consisting of Pd impregnated on a Zn/Mn/Zr mixed metal oxide support prepared by co-precipitation of metal nitrates with KOH have been claimed to have high selectivity for isobutanol from synthesis gas [24, 25]. However, severe conditions (high temperatures and very high pressures) are required to achieve attractive conversion levels. One interpretation of these results is that this catalyst is active for the condensation of light alcohols to higher

alcohols with high selectivity to isobutanol, but requires severe conditions for CO hydrogenation. If this is the case, these materials would be promising catalysts for a methanol to higher alcohols process.

The ability of bifunctional materials to catalyze the conversion of light alcohols to higher branched alcohols can be rationalized in the following way. The aldol coupling reaction, which presumably is the C-C bond forming step in this system, likely requires the presence of aldehyde as a target for nucleophilic attack. This suggests that the rate of condensation might be increased if the concentration of aldehyde species in the feed can be raised. Noble metal catalysts are well known to catalyze the dehydrogenation of alcohols to aldehydes. For example, silver metal is used commercially for the conversion of methanol to formaldehyde. Therefore, the addition of a noble metal function to a catalyst support capable of promoting the aldol condensation reaction should lead to a superior catalyst.

Catalysts prepared by impregnating a representative Zn/Mn/Zr metal oxide support with 0, 0.2 and 2 wt. % Pd using a PdCl₂ solution have been evaluated using the methanol/ethanol screening test. These materials show lower activity than the baseline Cu/Zn/Al oxide catalyst, but significantly higher selectivity to isobutanol, isobutyraldehyde and total C₄₊ oxygenates (Table 19). In spite of the lower conversions, the Pd containing catalysts give higher productivities to the desired products than the baseline catalyst.

A variety of mixed metal oxide supports containing Zn, Mn, Cr, Cu, Ce, La and Al have been prepared by the co-precipitation of a mixed metal nitrate solution with KOH at constant pH. These supports, after drying and calcining, have been impregnated with both 2 wt. % Pd and 2 wt. % Pt and tested in the standard pilot plant screening test for the conversion of a 10/1 (molar) methanol/ethanol blend. Table 18 summarizes the testing results of the Pd containing catalysts, while Table 19 summarizes results with Pt containing materials. In the case of Pd, the Zn/Mn/Cr oxide support affords the highest isobutanol selectivity and productivity. The Zn/Mn/Zr oxide support gives comparable selectivity, but at a slightly lower activity level.

This material also shows lower CO_x selectivity due to reduced CO. The other supports tested all show lower selectivity to the desired isobutanol product than the best catalysts. The Zn/Mn/Zr oxide supports (1/1/1 and 1/1/0.2 molar ratio of metals) give the best Pt containing catalysts, with the Zn/Mn/Ce oxide a close second. In contrast with the Pd findings, Pt on the Zn/Mn/Cr support gives poor selectivity to isobutanol and total C_{4+} products and high selectivity to CO_x . The Zn/Mn/Cu and Zn/Mn/La oxide supports, as well as several bimetallic oxide supports, give lower isobutanol selectivity.

The effect of varying the noble metal has been investigated using the best two supports, Zn/Mn/Zr and Zn/Mn/Cr. The Pd or Pt addition clearly increases the activity of these catalysts for methanol/ethanol conversion (Table 20). Catalysts with either no noble metal or Ag (either impregnated or physically mixed), give much lower conversion levels. This suggests that the dehydrogenation of alcohol to aldehyde is an important, and perhaps rate limiting, step in the condensation process. On the other hand, isobutanol selectivity is relatively independent of the identity or presence of the noble metal in the case of Zn/Mn/Zr oxide. This suggests that oxygenate selectivity may be primarily a function of the basic metal oxide support. Therefore, variations of this support composition would be a reasonable approach for improving isobutanol selectivity. Table 21 shows an overall summary of the selectivities to all identified products observed with the Pt on Zn/Mn/Zr oxide and Pd on Zn/Mn/Zr oxide catalysts on a CO_x included basis. All of these catalysts show higher selectivity to isobutyraldehyde than to isobutanol. This is probably due to the low pressure (30 psig) used in this testing, where equilibrium favors the dehydrogenated product. The presence of substantial amounts of methyl isobutyrate, the ester derived from methanol and butyric acid, suggests that either further oxidation to the carboxylic acid or condensation of iC_4 aldehyde and methanol is also occurring. Acid catalyzed etherification of methanol to DME appears to be minimal, except for the Pd on Zn/Mn/Zr oxide catalyst, but light ester formation, presumably by the reaction of methanol with formaldehyde and acetaldehyde intermediates, occurs at about 3% selectivity. The Pd containing catalysts show twice as much CO formation as the Pt samples, which is highly undesirable since it represents the reverse of the mei.

synthesis process.

The reproducibility of the preparations of noble metal on mixed metal oxide catalysts has been evaluated by making new samples of Zn/Mn/Zr and Zn/Mn/Cr oxide supports following the same co-precipitation, washing and calcination procedures used previously. Table 22 summarizes the pilot plant results obtained with catalysts prepared by the impregnation of these supports with Pd and compares them with earlier catalyst samples. In the case of the Zn/Mn/Zr support, a first reproduction shows very comparable performance to the earlier sample. However, another sample prepared by a separate Pd impregnation on this second Zn/Mn/Zr oxide support showed substantially lower activity and selectivity to isobutanol. Differences in performance between two Pd impregnations on the same support are also seen with the original Zn/Mn/Cr oxide support. In this case, activities were similar but selectivities to isobutanol and total C₄₊ products were different. A second co-precipitation of the Zn/Mn/Cr oxide support afforded a very poor catalyst with low activity and selectivity to isobutanol.

Better catalyst preparation reproducibility has been obtained with two Pt containing catalysts made on Zn/Mn/Zr and Zn/Mn/Cr oxide supports. Table 22 compares the pilot plant results of these catalysts with earlier samples. The Pt on Zn/Mn/Zr oxide sample shows good reproducibility with the previous material, while the Pt on Zn/Mn/Cr catalyst shows lower activity and higher selectivity to total C₄₊ products than the original sample. It should be noted that the poor performances of these Zn/Mn/Cr catalysts is similar to that of the Pd catalyst prepared using the second Zn/Mn/Cr oxide support. In general, the reproducibility of noble metal on Zn/Mn/Zr oxide catalysts has been superior to that of the Zn/Mn/Cr formulations. A possible explanation for this observation may be that the co-precipitated supports may have differing amounts of isolated metals that can affect the noble metal function. Chromium is known to attenuate noble metal functions while zirconium usually does not.

3.1.3.2.4 Other Catalysts

The performances of catalysts consisting of Pt on several pure metal oxide supports is shown in Table 23. In the case of ZnO, the oxide powder was bound with 50% SiO₂ to obtain a material with a particle size sufficient for use in the pilot plant. While the ZnO sample shows some activity and selectivity for isobutanol formation, the MnO₂ and ZrO₂ samples have virtually no activity. Finally, Pt on MgO, TiO₂ and a Zn/Mg mixed oxide support (also bound with SiO₂) show high activity for methanol conversion, but low selectivity to isobutanol and total higher products. Instead, CO, CO₂, and light hydrocarbons are the major products observed.

A series of catalysts consisting of Cu and Mo on TiO₂, Mg/Al MOSS, and polyvinylpyridine polymer supports have been tested. The performances of these material are summarized in Table 24. The Cu on metal oxide samples give isobutanol and total C₄₊ product selectivities that are comparable with those obtained with the best Pt catalysts, but activity is substantially lower. The Mo containing catalysts have higher methanol and ethanol conversions, but poorer selectivities to the desired products. The polyvinylpyridine supported catalysts all show very low conversion and no production of either isobutanol or CO_x.

A variety of commercial and lab prepared MnO₂ catalysts have been evaluated in the standard methanol/ethanol pilot plant test. These catalysts all show very low activity and selectivity to isobutanol (Table 25). The negative ethanol conversions suggest that some methanol is being converted to ethanol over these catalysts, but the levels are very low. Two commercial MnO₂ samples have also been tested with 2% Pt and 2% Pd added by the standard aqueous metal chloride impregnation technique. These catalysts show substantially higher methanol and ethanol conversions, but also higher selectivity to CO_x (primarily CO). Selectivities to isobutanol are very low. Thus, alcohol decomposition appears to be the primary reaction over these materials.

3.1.3.3 Space Velocity Testing to Determine Reaction Pathways with Methanol/Ethanol

One of the primary mechanistic questions in the production of branched C_4 oxygenates from methanol is the relative rates of the C_1 - C_1 , C_1 - $C_{2,3}$ and C_2 - C_2 condensation steps. The latter condensations are sufficient for the production of higher alcohols from a methanol/ethanol feed blend. However, the C_1 - C_1 coupling step is necessary for the primary goal of this project, the condensation of methanol only to higher alcohols. In order to evaluate the extent of C_1 - C_1 coupling occurring over experimental catalysts, tests have been conducted to determine the dependence of product yields on space velocity. At conditions where ethanol conversion is high, an increase in the yields of isobutanol and other higher oxygenates as WHSV is decreased suggests that the desired products are being formed from methanol only.

The aldol condensation of two C_2 species is expected to yield straight chain C_4 products. However, the C_4 oxygenate products observed with the best catalysts identified in screening with a methanol/ethanol feed are highly branched. This suggests that their formation occurs by sequential C_1 aldol condensations to C_2 and C_3 intermediates and that C_1 - $C_{2,3}$ coupling is substantially favored over C_2 - C_2 condensation. In view of the dehydrogenation equilibrium constants at 327 °C of 0.03 for methanol to formaldehyde + H_2 and 1.12 for ethanol to acetaldehyde + H_2 , it appears that branched C_4 compounds are formed by the condensation of methanol with acetaldehyde and propionaldehyde intermediates.

Based on these findings, subsequent research has been focussed on the Zn/Mn/Zr support. Further tests with a methanol-only feedstock will be described in section 3.4.1 to characterize the ability of this catalyst system to affect the desired C_1 - C_1 condensation step.

3.1.3.3.1 Cu/Zn/Al Oxide Catalyst

The methanol, ethanol and total carbon conversions for the Cu/Zn/Al oxide baseline catalyst as a function of space time at 300°C and 30 psig are shown in Figure 6. At space times between 0.5 and 1.0 hr, ethanol conversion exceeds 90%, while methanol and total carbon conversions increase from about 70% to near 90%. However, isobutanol and total C_{4+} oxygenates yields

(on a % of total carbon basis) are essentially flat (Figure 7). Only CO yield shows an increase comparable with the total carbon conversion rise. This suggests that the additional conversion occurring in this portion of the catalyst bed is due to methanol reforming to CO rather than aldol condensation. Therefore, it appears that Cu/Zn/Al oxide material is a poor catalyst for the C_1 - C_1 condensation required for the production of higher oxygenates from methanol alone.

3.1.3.3.2 Pd on Zn/Mn/Zr Oxide

The 2% Pd on Zn/Mn/Zr oxide catalyst appears to be capable of condensing methanol alone to higher alcohols. Figure 8 shows methanol, ethanol and total carbon conversions as a function of space time. This data shows that ethanol conversion exceeds 80% at space times greater than 0.15 hr and reaches 95% at 0.50 hr. Figure 9 shows that over this range of space times the yields for the desired products, isobutanol and total C_{4+} oxygenates, increase 2-3 fold. The substantial rise in the yields of higher oxygenates after the near complete conversion of ethanol suggests that these products are formed by the reaction of methanol with itself or with another reaction intermediate.

3.1.3.3.3 Pt on Zn/Mn/Zr Oxide

The large scale 2% Pt on Zn/Mn/Zr oxide catalyst described in Task 2.2 has also been evaluated at varying space velocities. Figures 10-12 summarize the results of these runs. This data shows that the yields of C_{4+} oxygenates, particularly isobutanol and isobutyraldehyde, continue to increase as contact time is increased past the point of complete ethanol conversion (space times greater than 0.3 hr). Figure 11 shows that all three of the major C_4 oxygenate products (isobutanol, isobutyraldehyde and methyl isobutyrate) have increasing yields in this region. The major by-products that can be produced from methanol only (methyl formate and DME) are also increasing (Figure 12). These results suggest that the additional higher alcohol product may be arising from the conversion of methanol alone. However, other side-reactions involving methanol or formaldehyde only also appear to become more important at higher space times.

3.1.3.3.4 Pd on Zn/Mn/Cr Oxide

Similar testing with a 2% Pd on Zn/Mn/Cr oxide catalyst at low space velocities shows that at space times where ethanol conversion is complete (greater than 0.2 hr), the yield of isobutanol and total C₄₊ products is flat (Figure 13). This indicates that the additional methanol converted is going to other products, mainly CO and CO₂. Thus, the Zn/Mn/Cr support appears less active for methanol only conversion than the Zn/Mn/Zr oxide. In addition, comparison of the CO yields in Figures 9 and 13 shows that the Zn/Mn/Cr support is much more active for the decomposition of the light alcohols.

3.2 Catalyst Development and Optimization (Task 2)

Noble metal (Pt or Pd) on co-precipitated Zn/Mn/Zr oxide supports have been identified as promising catalysts for the synthesis of higher branched alcohols from a methanol/ethanol feed in the catalyst screening portion of Task 1 of this program. The highest selectivity and productivity for isobutanol and total C₄₊ products has been obtained with 2 wt. % Pt or Pd on a Zn/Mn/Zr oxide support. In Task 2 the effects of key compositional variables have been investigated. Metal oxide support composition and noble metal loading have been the variables examined. Table 26 summarizes analytical data on the Pt and Pd on Zn/Mn/Zr oxide catalysts that have been prepared in this task. Elemental compositions, apparent bulk densities (ABD) and surface areas, pore volumes and average pore diameters from N₂ BET porosimetry are included. Finally, a 300g batch of the best catalyst formulation, 2% Pt on Zn/Mn/Zr (60/20/20 mole ratio) oxide, has been prepared for use in process variable studies (Task 4) and demonstration runs (Task 3).

3.2.1 Support Composition

The mixed metal oxide support presumably provides the solid base functionality that catalyzes the condensation of lower aldehydes (formaldehyde and acetaldehyde) formed by alcohol dehydrogenation to higher oxygenates. The basicity of the support is expected to have a large

impact on the activity and selectivity the catalyst for this condensation. Varying the composition of the mixed metal support is one approach for modifying this catalyst property. The standard pilot plant test using a methanol/ethanol blend feed has been used to measure the effects of composition on performance for alcohol condensation.

A series of 2% Pt or 2% Pd on Zn/Mn/Zr oxide catalysts have been prepared using the co-precipitation and noble metal impregnation techniques. The ratios of the three major support components have been varied systematically between 10-60% to sample the composition space of the ternary mixed metal oxide. Table 27 summarizes the pilot plant testing results for the Pt containing catalysts. The key results are also shown in Figures 14 and 15 as a function of the metal oxide support composition. Figure 14 gives methanol and ethanol conversion as well as selectivities and productivities to the desired oxygenate products. Figure 15 shows the selectivities of some of the key by-products; methyl formate and methyl acetate which are presumably formed by the Cannizzaro reaction of the formaldehyde and acetaldehyde intermediates and CO_x . This data shows that a wide variation of the composition of the ternary metal oxide has only a small affect on catalyst performance. However, all three components appear to be important since single and dual oxide supports all have inferior performance to the ternary supports. A performance trend toward higher selectivity to isobutanol and isobutyraldehyde with increasing Zn and decreasing Zr contents can be seen in Figure 14. In addition, the support with the lowest Zn content gives the highest amount of Cannizzaro by-products and CO. Based on these results a support composition with >33% Zn and <33% Zr appears to most preferable for higher alcohol production.

The results for Pd containing catalysts prepared on the same ternary Zn/Mn/Zr oxide supports used above are summarized in Table 28 and Figure 16. All of these materials show lower selectivities to isobutanol and isobutyraldehyde products than the Pt catalysts. Overall selectivities and productivities to total higher products are comparable with the Pt containing catalysts, but selectivities to the desired C_4 oxygenates are substantially lower.

3.2.2 Nobel Metal Loading

The noble metal loading on the alcohol condensation catalyst will have a major impact on the cost of the catalyst and, therefore, the economic viability of the process. In addition, independence of the catalytic performance on the noble metal loading would suggest that alcohol condensation, rather than dehydrogenation to aldehydes, is the rate determining step in this process. If this is the case, the development of an improved catalyst needs to focus on the basic mixed metal support rather than the noble metal function.

Table 29 summarizes the pilot plant results obtained by impregnation of the Zn/Mn/Zr (60/20/20) oxide support from the support composition series with 0.5%, 1%, 2% and 5% Pt using the standard aqueous H_2PtCl_6 impregnation procedure. It can be seen that the highest selectivities to the desired C_4 oxygenates are obtained with the 2% Pt catalyst. However, all of the other catalysts gave higher alcohol conversion, as well as lower selectivities. Therefore, the selectivity differences could be due to catalyst activity rather than intrinsic catalytic performance. In order to properly compare these materials, a more thorough testing procedure, using varied space velocities to determine selectivity versus conversion relationships, is required. In contrast with the C_4 oxygenates, other by-products show clear trends with changing noble metal loadings. Increasing Pt decreases the levels of DME and CO, but increases the amount of Canizzarro products (methyl formate and methyl acetate). The latter observation suggests that more light aldehydes, particularly methyl formate, that can be condensed over the basic metal oxide via the Canizzarro reaction are produced with higher Pt catalysts.

In order to obtain a better comparison of catalysts with different noble metal loadings, a more thorough testing procedure has been utilized. Catalysts consisting of 0.5% and 2% Pt on Zn/Mn/Zr (60/20/20) oxide have been tested at methanol space velocities of 2, 3 and 4 hr^{-1} over 16 hour intervals to obtain data over a range of conversion levels. In contrast to the earlier results, these catalysts show little difference in activity. Figure 17 shows that the plots of methanol, ethanol and overall conversions versus space time are similar. Both samples

show lower activity on return to the initial conditions indicating that some catalyst deactivation occurred over the test. However, the loss in activity is less than that obtained with the space velocity changes. Figure 18 shows that the 2% Pt catalyst affords higher selectivity to the desired iC_4 oxygenated products (isobutanol, isobutyraldehyde and methyl isobutyrate).

Overall selectivities are summarized in Table 30 which indicates that the improved performance of the 2% Pt catalyst is due to a reduction in the amount of methyl formate, CO and other C_{4+} by-products. The C_1 - C_2 Cannizzaro reaction product, methyl acetate, increases with higher Pt.

The observed shift in oxygenate selectivity from methyl formate to methyl acetate and iso- C_4 oxygenates with increased Pt loading suggests that the extent of dehydrogenation affects the relative rates of C_1 - C_1 and C_1 - C_2 condensation. Aldol condensations (Reaction 1) are required for the production of the desired iso- C_4 oxygenates, while Cannizzaro condensations (Reactions 2 and 3) give rise to light ester products. In each of these reactions, aldehydes formed by alcohol dehydrogenation are key intermediates. At the high methanol/ethanol feed ratio used in the pilot plant testing, a high dehydrogenation activity catalyst (i.e. high Pt) would be expected to give a higher acetaldehyde concentration and, therefore, favor Reactions 1 and 2 over Reaction 3.

3.2.3 Catalyst Scale-up

The catalyst formulation studies have indicated that a catalyst composition of 2% Pt on a

60/20/20 (molar) Zn/Mn/Zr oxide support affords the best performance for higher oxygenate production. Therefore the preparation of this catalyst has been scaled-up from 30 g to 200 g. Pilot plant testing of the new material has shown that the methanol/ethanol conversion performance of this material is comparable with previous samples of the same nominal composition (Table 31). This large supply of catalyst has been used for all of the process variable studies of Task 4 and the demonstration runs of Task 3.

3.3 Process Variable Study (Task 4)

The effects of temperature, pressure and methanol/ethanol molar feed ratio on the performance of the 2% Pt on Zn/Mn/Zr Oxide catalyst has been evaluated in a series of pilot plant tests. The results of these runs are summarized in Table 32. Based on these findings a set of optimized conditions have been identified for the 2% Pt on Zn/Mn/Zr (60/20/20) oxide catalyst. A demonstration test at these conditions has been conducted under Task 3 of the program. The effects of co-feeding H₂, CO and CO₂ with the methanol/ethanol feed on catalyst performance have also been examined.

3.3.1 Temperature

Increasing temperature from 325°C to 375°C increases alcohol conversion, but reduces selectivity and productivity to the desired branched C₄ oxygenates. CO and light hydrocarbons production is substantially greater at the higher temperature, while CO₂ and methyl acetate (presumably from Cannizzaro condensation) formation is lower. Higher temperature also shifts the C₄ oxygenates product ratio toward isobutyraldehyde from isobutanol and methyl isobutyrate. Based on these results, it appears that lower temperature, with the use of lower space velocity to maintain conversion, is the preferred operating condition.

3.3.2 Pressure

The major effect of higher pressure operation is to shift the product ratio from isobutyraldehyde to isobutanol. CO selectivity is also increased, which is surprising considering that the thermodynamics of methanol decomposition to CO and H₂ should be disfavored by raising pressure. Operation at 300 psig affords the highest productivities of isobutanol and iC₄ oxygenates observed with a 10/1 methanol ethanol feed. The combination of higher pressure and lower temperature may allow these better oxygenate selectivities and productivities to be obtained while reducing the amount of CO produced.

3.3.3 Methanol/Ethanol Feed Ratio

Variation of the methanol/ethanol feed ratio has been used to gain a understanding of the mechanism of alcohol coupling. Decreasing the feed ratio from 10/1 to 7/1 increases methanol conversion as well as selectivity to each of the iC₄ oxygenates. CO_x selectivities are also slightly reduced. However, further reduction of the methanol/ethanol feed ratio to 4/1 does not give additional improvement as light esters, presumably arising from base-catalyzed Cannizzaro reactions, and unidentified heavy by-products increase. At a 1/1 feed ratio branched higher alcohol products are substantially reduced and light ester products dominant. The highest productivity of I-C₄ oxygenates has been obtained at a 7/1 methanol/ethanol feed ratio. This indicates that an excess of methanol is required to prevent other base catalyzed coupling reactions (such as the Cannizzaro reaction) from occurring over this catalyst.

3.3.4 H₂, CO and CO₂ Co-Feeds

Co-feeding H₂ at a 2/1 H₂/MeOH feed ratio had very little effect on the performance of the Pt on Zn/Mn/Zr oxide catalyst (Table 33). Methanol conversion is higher and selectivity shifts from isobutyraldehyde to isobutanol giving an slightly higher overall productivity for isobutanol. It has been speculated that the dehydrogenation of methanol and ethanol to the corresponding aldehydes is a key first step in the coupling mechanism. The presence of an H₂ co-feed might be expected to inhibit the formation of these intermediates and hinder the formation of higher alcohols. However, it appears that this is not a problem to the low H₂

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 H_2 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 CO_2 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 H_2 concentrations. The effluent from the methanol synthesis reactor typically contains about 70-80 mole% H_2 as well as some N_2 , CO and CO_2 . 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 H_2 /CO/ CO_2 separation in the recycle loop is not reduced. Previous results have indicated that co-feeding H_2 at a low level (2/1 H_2 /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 H_2 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 H_2 partial pressures comparable with those inside the methanol synthesis recycle loop. At the initial conditions (1200 psig total, 15/1 H_2 /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 H_2 levels. Again the isobutyraldehyde selectivity responded in an opposite manner from that expected, decreasing as H_2 content decreased. Elimination of the H_2 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 H_2 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 , CO_2), all C_1 - C_5 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 , CO_2 , and H_2) 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 C_4 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 H_2 , CO, and CO_2 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 H_2/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 H_2/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 H_2/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 C_1 alcohol or aldehyde intermediate. Next, a C-C bond must be formed by the condensation or carbonylation of the C_1 species to afford a C_2 intermediate. This species is then able to undergo an aldol-type condensation with additional C_1 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 C_1 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 C_{3+} 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 C_4 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.

5 TABLES

Table 1. Run List for CO/H₂ Conversion

RUN	CATALYST		CATALYST DESCRIPTION	LOADING	TEMP (C)	CONDITIONS		FEED RATIO
	A Book #	B Book #				TOTAL	CO	
			CATALYST A	CATALYST B	SIZE	g/g	INLET MAX PSIG	GHVS
106		7923-2	None	Silica Gel (Davison)	20-40M	0/6	310	1100 2250-675
107	7923-4	7923-2	Cu/Zn/Al (33/64/3) Oxides (LT WGS)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250-675
108	7923-4	7923-2	Cu/Zn/Al (33/64/3) Oxides (LT WGS)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250-675
109	7923-4	7923-6	Cu/Zn/Al (33/64/3) Oxides (LT WGS)	Mg/Al Clay (JSH)	Mg/Al=2	20-40M	310	1100 2250-675
112	7923-10A	7923-2	Cu/Zn/Al (30/45/25) Oxides (Lab. Na)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
113	7923-4	7923-2	Cu/Zn/Al (33/64/3) Oxides (LT WGS)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
114	7923-16A	7923-2	Zn/Cr (75/25) Oxides (Lab)	Silica Gel (Davison)	20-40M	3/3	450	1100 2250
115	7923-18	7923-2	Cu/Zn/Al (30/45/25) Oxides (Lab)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
116	7923-20	7923-6	Cu/Zn/Al (30/45/25) Oxides (Lab)	Mg/Al Clay (JSH)	Mg/Al=2	20-40M	310	1100 2250
117	7923-20	7923-22	Cu/Zn/Al (30/45/25) Oxides (Lab)	Mg/Al Clay (Alcoa)	Mg/Al=	20-40M	310	1100 2250
118	7923-20	7923-28	Cu/Zn/Al (30/45/25) Oxides (Lab)	MgO (JSH)		20-40M	310	1100 2250
119	7923-24	7923-2	Zr/Zn/Mn/K (33/33/33) Oxides (Lab)	Silica Gel (Davison)	20-40M	3/3	450	1100 2250
124	7923-38	7923-2	.14%Pd(NO ₃)/4.6%K/Zr/Zn/Mn Oxides	Silica Gel (Davison)	20-40M	3/3	450	1100 2250
125	7923-42A	7923-2	.15%Pd(NO ₃)/0.8%K/Zr/Zn/Mn Oxides	Silica Gel (Davison)	20-40M	3/3	450	1100 2250
126	7923-20	7923-22	Cu/Zn/Al (30/45/25) Oxides (Lab)	Mg/Al Clay (Alcoa)	20-40M	3/3	310	1100 2250
127	7923-20	7923-22	Cu/Zn/Al (30/45/25) Oxides (Lab)	Mg/Al Clay (Alcoa)	20-40M	3/3	230	1100 2250
128	7923-42A	7923-2	.15%Pd(NO ₃)/0.8%K/Zr/Zn/Mn Oxides	Silica Gel (Davison)	20-40M	3/3	350	1100 2250
129	7923-20	7923-22	Cu/Zn/Al (30/45/25) Oxides (Lab)	Mg/Al Clay (Alcoa)	20-40M	3/3	310	1100 2250
130	7923-44		.18%Pd(Cl)/1.6%K/Zr/Zn/Mn Oxides	None	20-40M	3/0	450	1100 2250
131	7923-46		.15%Pd(Cl)/SiO ₂	None	20-40M	3/0	450	1100 2250
132	7923-42A		.15%Pd(NO ₃)/0.8%K/Zr/Zn/Mn Oxides	None	20-40M	3/0	450	1100 2250
133		7923-2	None	Silica Gel (Davison)	20-40M	0/3	450	1100 2250
134			Ceramic-Lined Reactor	α-Alumina Filled			450	1100 2250
135			Ceramic-Lined Reactor	Empty			250-45	1100 2250
136			Ceramic-Lined Reactor	Quartz Chips Filled			250-45	1100 2250
137	7923-58A	7923-2	Cu/Zn/Al Oxide (ICI 51-3 catalyst)	Silica Gel (Davison)	20-40M	3/3	230-31	1100 2250
138	7923-20	7923-2	Cu/Zn/Al Oxide (Lab PPT)	Silica Gel (Davison)	20-40M	3/3	230-31	1100 2250
139	7923-20	7923-76	Cu/Zn/Al Oxide (Lab PPT)	5.0% K (KOH)/Al ₂ O ₃	20-40M	3/3	310	1100 2250
140	7923-20	7923-76	Cu/Zn/Al Oxide (Lab PPT)	5.3% K (KOH)/SiO ₂	20-40M	3/3	310	1100 2250
141	7923-20	7923-2	Cu/Zn/Al Oxide (Lab PPT)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
142	7923-85	7923-2	Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
143	7923-85	8074-10	Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	.32% Cs (J/Mg/Al MOSS (Alcoa)	20-40M	3/3	310	1100 2250
144	7923-85	8074-8	Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	.17% Na (J/Mg/Al MOSS (Alcoa)	20-40M	3/3	310	1100 2250
145	7923-85	7923-2	Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
146	7923-85	8074-9	Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	.15% K (J/Mg/Al MOSS (Alcoa)	20-40M	3/3	310	1100 2250
147	7923-98	7923-2	1.3% Cs (CsOOCH ₃)/Cu/Zn/Al Oxide	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
148	None		α-Alumina/Quartz Chips		20-40M	3/3	400	1100 2250
149	7923-97		Zn/Cr Oxide (2.8/1)		20-40M	3/3	400	1100 2250
150	7923-62		0.1%Pd/0.5%K/Zr/Zn/Mn Oxide		20-40M	3/3	400	1100 2250
151	None		α-Alumina/Quartz Chips		20-40M	3/3	310/400	1100 2250
152	7923-98	7923-2	% Cs (CsOOCH ₃)/Cu/Zn/Al Oxide	Silica Gel (Davison)	20-40M	3/3	310	1100 2250
153	7923-97		Zn/Cr Oxide (2.8/1)		20-40M	3/3	400	1100 2250

Table 2. Run List for Methanol and Methanol/Ethanol Conversion

RUN	CATALYST		CATALYST DESCRIPTION	LOADING	TEMP (C)	CONDITIONS			FEED RATIO
	A Book #	B Book #				TOTA	MeOH	MeOH/EtOH/N2(H2)	

154			None (Quartz Chips/a-Alumina)			250-31	1100	2	1/0/2 N2
155	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 N2
156	7887-11		Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 N2
157	7887-14		0.5%Cu / Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 N2
158	7887-18		0.5%Co / Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 N2
159	7923-81		Zn/Zr (50/50) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 N2
160	7923-81		Ce/Zn/Mn (33/33/33) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 N2
161	7887-14		0.5%Cu / Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 H2
162	7923-81		Zn/Zr (50/50) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 H2
163	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 H2
164	7923-98		1.3%Cs / Cu/Zn/Al (30/45/25) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 H2
165	7887-28		0.5%Ag / Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 H2
166	7923-55		Zr/Zn/Mn (33/33/33) Oxide (Lab PPT)	20-40M	5	250	1100	2	1/0/2 H2
167	7887-34		5.0%Cu / Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0/2 H2

RUN	CATALYST		CATALYST DESCRIPTION	LOADING	TEMP (C)	CONDITIONS			FEED RATIO
	A Book #	B Book #				TOTA	MeOH	MeOH/EtOH/N2(H2)	

168	7887-11		Mg/Al Clay (Alcoa)	20-40M	5	250	1100	2	1/0.1/2 H2
169	7887-11		Mg/Al Clay (Alcoa)	20-40M	5	250	100	2	1/0.1/2 H2
170	7887-11		Mg/Al Clay (Alcoa)	20-40M	5	350	100	2	1/0.1/2 N2
171	7923-28		MgO	20-40M	5	350	100	2	1/0.1/2 N2
172	7887-11		Mg/Al Clay (Alcoa)	20-40M	5	350	30	2	1/0.1/2 N2
173	7887-11		Mg/Al Clay (Alcoa)	20-40M	25	350	30	0.4	1/0.1/2 N2
174			None (Quartz Chips/a-Alumina)			350	30	2	1/0.1/2 N2
175	7923-8		Mg/Al Clay (Lab Prep??)	20-40M	5	350	30	2	1/0.1/2 N2
176	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
177	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	300	30	2	1/0.1/2 N2
178	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	250	30	2	1/0.1/2 N2
179	7923-16A		Zn/Cr (75/25) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
180	7923-69		Cu/Zn/Mn (34/33/33) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
181	7887-37		Zn/Al (74/26) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
182	7887-39		Cu/Zn/Al (11/63/26) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
183	7887-41		Zn/Al (63/37) Oxide (Lab PPT)	20-40M	5	350	30	2	1/0.1/2 N2
184	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	10	250	30	1	1/0.1/2 N2
185	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	5	250	75	2	1/0.1/2 N2
186	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	2.5	300	30	4	1/0.1/2 N2
187	7923-85		Cu/Zn/Al (31/42/27) Oxide (Lab PPT)	20-40M	10	300	30	1	1/0.1/2 N2
188	7923-55		Zr/Zn/Mn (34/34/32) Oxide	20-40M	5	350	30	2	1/0.1/2 N2
189	7923-62		0.2%Pd / Zn/Mn/Zr (34/34/32) Oxide	20-40M	5	350	30	2	1/0.1/2 N2
190	7923-64		2.1%Pd / Zn/Mn/Zr (34/34/32) Oxide	20-40M	5	350	30	2	1/0.1/2 N2

Table 2 (con't). Run List for Methanol and Methanol/Ethanol Conversion

RUN	A Book #	B Book #	CATALYST	CATALYST DESCRIPTION	LOADING g	SIZE	TEMP (C)	INLET MAX PSIG	CONDENS	FEED RATIO	MeOH/MeOH+EtOH+H ₂
191	7923-85			Cu/ZnAl (31/42/27) Oxide (Lab PPT)	1.75	20-40M	300	30	2	1/0.1/2 N ₂	
192	7923-85			Cu/ZnAl (31/42/27) Oxide (Lab PPT)		20-40M	300	30	5.7	1/0.1/2 N ₂	
193	7923-72			2.0%Pd / ZnMnCo (33/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
194	7923-88			2.0%Pd / ZnMnCo (33/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
195	7887-42			Cu/ZnAl (33/39/28) Oxide (Lab PPT)	5	20-40M	300	30	2	1/0.1/2 N ₂	
196	7923-84			2.1%Pd / ZnMnZr (34/34/32) Oxide	2.5	20-40M	350	30	4	1/0.1/2 N ₂	
197	7923-84			2.1%Pd / ZnMnZr (34/34/32) Oxide	1.75	20-40M	350	30	5.8	1/0.1/2 N ₂	
198	7923-84			2.1%Pd / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
199				None (Quartz Chips/a-Alumina)		20-40M	300	30	(2)	1/0.1/2 N ₂	
200	7923-84			None (Glass Beads)		20-40M	300	30	(2)	1/0.1/2 N ₂	
201	7923-84			2.1%Pd / ZnMnZr (34/34/32) Oxide	5	20-40M	300	30	2	1/0.1/2 N ₂	
202	7887-56			2.1%Ag metal / ZnMnZr (34/34/32) Oxide	5	20-40M	300	30	2	1/0.1/2 N ₂	
203	7887-50			2.0%Ag / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
204	7887-52			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
205	7887-48			2.0%Pd / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
206				None (Glass Beads)		20-40M	350	30	(2)	1/0.1/2 N ₂	
207				None (Quartz Chips/a-Alumina)		20-40M	350	30	(2)	1/0.1/2 N ₂	
208	7887-48			2.0%Pd / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
209	7887-50			2.0%Ag / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
210	7887-56			2.1%Ag metal / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
211	7887-48			2.0%Pd / ZnMnZr (34/34/32) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
212	7887-52			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
213	7887-58			2.0%Pd / Cu/ZnAl (33/39/28) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
214	7887-52			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
215	7923-95			ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
216	7887-62			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
217	7887-64			72.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
218	7887-68			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
219	7887-68			72.0%Pd / ZnMnCo (33/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
220	7887-72			2.0%Pd / ZnAl (74/26) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
221	7887-70			2.0%Pd / ZnCo (74/26) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
222	7887-80			2.0%Pd / Mn (100) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
223	7887-78			2.0%Pd / ZnMnCu (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
224	7887-82			2.0%Pd / ZnMnLa (34/32/34) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
225	7887-84			2.0%Pd / ZnMnZr (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
226	7887-82			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
227	7887-86			2.0%Pd / Zr (100) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
228	7887-90			2.0%Pd / ZnMnCo (34/33/33) Oxide	5	20-40M	350	30	2	1/0.1/2 N ₂	
229	7887-90			2.0%Pd / ZnMnCo (34/33/33) Oxide	4	20-40M	350	30	2.5	1/0.1/2 N ₂	
230	7887-80			2.0%Pd / ZnMnCo (34/33/33) Oxide	3	20-40M	350	30	3.3	1/0.1/2 N ₂	
231	7887-90			2.0%Pd / ZnMnCo (34/33/33) Oxide	2	20-40M	350	30	5	1/0.1/2 N ₂	
232	7887-90			2.0%Pd / ZnMnCo (34/33/33) Oxide	1	20-40M	350	30	10	1/0.1/2 N ₂	
233	7887-94			2.0%Pd / ZnO + SiO ₂ (1/1)	5	20-40M	300	30	2	1/0.1/2 N ₂	
234	7887-89			2.0%Pd / ZnMg (50/50) Oxide + SiO ₂ (1/1)	5	20-40M	300	30	2	1/0.1/2 N ₂	

Table 2 (con't). Run List for Methanol and Methanol/Ethanol Conversion

RUN	CATALYST		CATALYST DESCRIPTION	SIZE	LOADING g	TEMP (C)		TOTA PSIG	MeOH WHS	FEED RATIO MeOH/EtOH/N2(H2)
	A Book #	B Book #				INLET	MAX			
235	7887-96		2.0%Pt / MgO	20-40M	5	300	30	2	1/0.1/2 N2	
236	7887-96		2.0%Pt / MgO	20-40M	5	350	30	2	1/0.1/2 N2	
237	7887-96		2.0%Pd / MgO	20-40M	5	350	30	2	1/0.1/2 N2	
238	7887-94		2.0%Pt / ZnO + SiO2 (1/1)	20-40M	5	350	30	2	1/0.1/2 N2	
239	7887-89		2.0%Pt / Zn/Mg (50/50) Oxide + SiO2 (1/1)	20-40M	5	350	30	2	1/0.1/2 N2	
240	8125-8		2.0%Cu / TiO2	20-40M	5	350	30	2	1/0.1/2 N2	
241	8125-10		2.0%Mo / TiO2	20-40M	5	350	30	2	1/0.1/2 N2	
242	8265-12		2.0%Mo / Polyvinylpyridine (PVP425)	20-40M	5	350	30	2	1/0.1/2 N2	
243	8265-13		2.0%Cu / Polyvinylpyridine (PVP425)	20-40M	5	350	30	2	1/0.1/2 N2	
244	8265-16		2.0%Mo / Mg/Al MOSS (Alcoa)	20-40M	5	350	30	2	1/0.1/2 N2	
245	8265-18		2.0%Cu / Mg/Al MOSS (Alcoa)	20-40M	5	350	30	2	1/0.1/2 N2	
246	8265-14		2.0%Pd / Polyvinylpyridine (PVP425)	20-40M	5	350	30	2	1/0.1/2 N2	
247	8265-22		2.0%Pd / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
248	8265-24		2.0%Pd / Zn/Mn/Cr (33/33/33) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
249	8265-26		2.0%Pt / Zn/Mn/Cr (33/33/33) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
250	8265-32		2.0%Pd / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
251	8265-34		2.0%Pd / Zn/Mn/Zr (45/45/10) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
252	8265-36		2.0%Pt / Zn/Mn/Zr (45/45/10) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
253	8265-38		2.0%Pd / NH2-Terminated Polysiloxane	20-40M	5	350	30	2	1/0.1/2 N2	
254	8265-42		100% MnO2	20-40M	5	350	30	2	1/0.1/2 N2	
255	8265-44		100% MnO2	20-40M	5	350	30	2	1/0.1/2 N2	
256	8265-46		100% MnO2	20-40M	5	350	30	2	1/0.1/2 N2	
257	8265-48		100% MnO2	20-40M	5	350	30	2	1/0.1/2 N2	
258	8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
259	8265-52		250ppm Co / MnO2	20-40M	5	350	30	2	1/0.1/2 N2	
260	8265-36		2.0%Pt / Zn/Mn/Zr (45/45/10) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
261	NO RUN									
262	NO RUN									
263	8265-56		2.0%Pd / Zn/Mn/Zr (45/10/45) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
264	8265-60		2.0%Pd / MnO2 (Chemetals CIR 189)	20-40M	5	350	30	2	1/0.1/2 N2	
265	8265-61		2.0%Pt / MnO2 (Chemetals CIR 189)	20-40M	5	350	30	2	1/0.1/2 N2	
266	8265-64		2.0%Pd / Zn/Mn/Zr (10/45/45) Oxide (450C calc)	20-40M	5	350	30	2	1/0.1/2 N2	
267	8265-63		2.0%Pt / MnO2 (Chemetals ODC 924)	20-40M	5	350	30	2	1/0.1/2 N2	
268	8265-66		2.0%Pd / MnO2 (Chemetals ODC 924)	20-40M	5	350	30	2	1/0.1/2 N2	
269	8265-68		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide (450C calc)	20-40M	5	350	30	2	1/0.1/2 N2	
270	8265-69		2.0%Pd / Zn/Mn/Zr (20/60/20) Oxide (450C calc)	20-40M	5	350	30	2	1/0.1/2 N2	
271	8265-70		2.0%Pt / Zn/Mn/Zr (20/60/20) Oxide (450C calc)	20-40M	5	350	30	2	1/0.1/2 N2	
272	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
273	8265-77		2.0%Pt / Zn/Mn/Zr (45/10/45) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
274	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	4	350	30	2.5	1/0.1/2 N2	
275	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	3	350	30	3.3	1/0.1/2 N2	
276	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	2	350	30	5	1/0.1/2 N2	
277	8265-76		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	1	350	30	10	1/0.1/2 N2	
278	8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
279	8265-80		2.0%Pt / Zn/Mn/Zr (20/20/60) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
280	8265-83		2.0%Pd / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
281	8265-84		2.0%Pt / Zn/Mn/Zr (20/60/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	
282	8265-85		2.0%Pd / Zn/Mn/Zr (20/60/20) Oxide	20-40M	5	350	30	2	1/0.1/2 N2	

Table 2 (con't). Run List for Methanol and Methanol/Ethanol Conversion

RUN	CATALYST		CATALYST DESCRIPTION	LOADING	TEMP (C)	TOTAL	MeOH	FEED RATIO	
	A Book #	B Book #							INLET
CATALYST A									
CATALYST B									
SIZE									
283	8265-81		2.0%Pd / Zn/Mn/Zr (20/20/60) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
284	8265-86		0.5%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
285	8265-87		1.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
286	8265-88		5.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
287	8265-89		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide Calcined @ 450C before impregnation	20-40M	5	350	30	2 1/0.1/2 N ₂	
288	8265-90		2.0%Pt / Zn/Mn/Zr (20/20/60) Oxide Calcined @ 450C before impregnation	20-40M	5	350	30	2 1/0.1/2 N ₂	
289	8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide	HOS	5				
				0-16		350	30	2 1/0.1/2 N ₂	
				24-40		350	30	2 1/0.1/2 N ₂	
				48-64		350	30	1 1/0.1/2 N ₂	
				72-88		350	75	1 1/0.1/2 N ₂	
				96-112		350	30	2 1/0.1/2 N ₂	
290	8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
291	8265-78		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
292	8265-82		2.0%Pt / Zn/Mn/Zr (10/45/45) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
293	8265-50		2.0%Pt / Zn/Mn/Zr (33/33/33) Oxide	20-40M	5	350	30	2 1/0.1/2 N ₂	
294	8265-92		2.0%Pt / TiO ₂	20-40M	5	350	30	2 1/0.1/2 N ₂	
295	8265-94		0.5%Pt / Zn/Mn/Zr (60/20/20) Oxide	HOS	5				
				0-16		350	30	2 1/0.1/2 N ₂	
				16-32		350	30	3 1/0.1/2 N ₂	
				32-48		350	30	4 1/0.1/2 N ₂	
				48-64		350	30	2 1/0.1/2 N ₂	
296	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	0-16	5	350	30	2 1/0.1/2 N ₂	
				16-32		350	30	3 1/0.1/2 N ₂	
				32-48		350	30	4 1/0.1/2 N ₂	
				48-64		350	30	2 1/0.1/2 N ₂	
				0-16		350	30	2 1/0.1/2 N ₂	
297	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	16-32	5	350	30	2 1/0.1/2 N ₂	
				32-48		350	30	3 1/0.1/2 N ₂	
				48-64		350	30	4 1/0.1/2 N ₂	
				0-16		350	30	2 1/0.1/2 N ₂	
				16-32		350	30	3 1/0.1/2 N ₂	
298		None (Glass Beads)		32-40	5	250	30	2 1/0.1/2 N ₂	
				40-48		350	30	2 1/0.1/2 N ₂	
				48-56		450	30	2 1/0.1/2 N ₂	
				56-64		500	30	2 1/0.1/2 N ₂	
299	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	Dirty Feed	20-40M	5	350	30	2 1/0.1/2 N ₂
300	8265-95		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	Dirty Feed	20-40M	2.5	350	30	4 1/0.1/2 N ₂
301	8265-97		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	Dirty Feed	20-40M	5	350	30	2 1/0.1/2 N ₂
302	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	Dirty Feed	20-40M	5	350	30	2 1/0.1/2 N ₂
303	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	Dirty Feed	20-40M	5	350	30	2 1/0.1/2 N ₂
304	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.14/2 N ₂	
305	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.25/2 N ₂	
306	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/1.00/2 N ₂	
307	8265-98		2.0%Pt / Zn/Mn/Zr (60/20/20) Oxide	20-40M	5	350	30	2 1/0.25/2 N ₂	

Table 2 (con't). Run List for Methanol and Methanol/Ethanol Conversion

RUN	CATALYST		CATALYST DESCRIPTION	SIZE	LOADING g	CONDITIONS					FEED RATIO MeOH/EtOH/N ₂ /Others
	A Book #	B Book #				TEMP (C) INLET	TOTA PSIG	MeOH WHS	MAX		
308	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂
309	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	325	30	2			1/0.10/2 N ₂
310	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	375	30	2			1/0.10/2 N ₂
311	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	100	2			1/0.10/2 N ₂
312	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	300	2			1/0.10/2 N ₂
313	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /2 H ₂
314	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /2 CO
315	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /(CO ₂)
316	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0/2 N ₂ /2 C ₂ =
317	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /No CO
318	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /1.5 CO
319	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	350	30	2			1/0.10/2 N ₂ /2.8 CO
320	None	Glass Beads in Copper-Lined Reactor		HOS							
				0-12		500	30	2			1/0/2 N ₂
				12-24		450	30	2			1/0/2 N ₂
				24-36		400	30	2			1/0/2 N ₂
				36-48		350	30	2			1/0/2 N ₂
				48-60		300	30	2			1/0/2 N ₂
321	8265-98	2.0%Pt / ZnMnZr (60/20/20) Oxide		0-16	20-40M	5	450	30	2		1/0/2 N ₂
				16-32			350				1/0/2 N ₂
322	8265-98	2.0%Pt / ZnMnZr (60/20/20) Oxide		0-16	20-40M	5	350	30	2		1/0/2 N ₂
				16-32			400				1/0/2 N ₂
				32-48			450				1/0/2 N ₂
323	8265-98	2.0%Pt / ZnMnZr (60/20/20) Oxide		0-16	20-40M	5	350	300	2		1/0/2 N ₂
				16-32			400				1/0/2 N ₂
				32-48			450				1/0/2 N ₂
324	None	Glass Beads in Copper-Lined Reactor		0-16	20-40M	5	350	300	2		1/0/2 N ₂
				16-32			400				1/0/2 N ₂
				32-48			450				1/0/2 N ₂
325	8265-98		2.0%Pt / ZnMnZr (60/20/20) Oxide	20-40M	5	325	300	1			1/0.14/2 N ₂
326	8265-98	2.0%Pt / ZnMnZr (60/20/20) Oxide		HOS	20-40M	25					
				0-40			325	1200	1		1/0.14/3 N ₂ /15 H ₂
				41-56			325	300	1		1/0.14/3 N ₂ /15 H ₂
				57-88			325	50	0.5		1/0.14/3 N ₂ /15 H ₂
				89-112			325	50	0.5		1/0.14/3 N ₂
				113-160			325	300	1		1/0.14/3 N ₂

Table 3. High Temperature Blank Reactor Tests with CO/H₂ Feed

Conditions: 450°C, 1100 psig, 2250 hr⁻¹ CO GHSV, 1/1 CO/H₂ (molar)

	P700R133			P700R134			P700R135			P700R136		
	18 HOS SiO ₂ / 316SS Filler Blank	20 HOS	22 HOS	2 HOS a-Al ₂ O ₃ / Ceramic	8 HOS	14 HOS	23 HOS Empty Ceramic	25 HOS	27 HOS	23 HOS Quartz Chips / Ceramic	25 HOS	27 HOS
CONVERSION (% vs Ar)												
CO	9.41	8.70	8.37	6.51	5.52	6.69	2.45	2.70	3.38	7.29	6.26	4.47
H ₂	6.22	6.03	6.50	4.68	6.02	4.01	4.37	3.68	3.84	11.97	15.89	17.75
CO + H ₂	7.84	8.37	8.43	5.61	5.76	5.37	3.40	3.17	3.61	9.62	11.04	11.07
SELECTIVITY (mole %)												
C1OH	0.59	0.63	0.63	1.30	0.96	0.90	0.00	0.00	0.00	1.49	1.41	1.44
C2OH	0.40	0.39	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.28	0.29	0.33
nC3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
nC3OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
nC4OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
nC4OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.09	0.08
nC5OH	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.10	0.00
nC5OH	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C6+OH	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.00
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C1 Aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C2 Aldehyde	0.17	0.14	0.15	0.00	0.00	0.14	0.00	0.00	0.00	0.72	0.67	0.66
C3 Aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4 Aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5 Aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C6+ Aldehyde	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C1	24.00	24.13	24.31	31.88	31.65	32.36	34.98	61.67	47.12	37.77	38.36	38.24
C2	13.21	13.18	13.21	5.62	7.79	8.97	0.00	0.00	0.00	15.69	15.56	15.40
C3	5.75	5.75	5.77	3.99	4.57	5.05	0.00	0.00	0.00	9.81	9.31	8.99
C4	0.10	0.11	0.11	0.17	0.18	0.20	0.00	0.00	0.00	0.30	0.28	0.27
C5	0.21	0.20	0.20	0.24	0.24	0.22	0.00	0.00	0.00	0.52	0.46	0.41
C6+ + UNKs	2.00	1.60	1.62	0.87	0.99	1.31	0.00	0.00	0.00	3.67	3.45	3.27
CO ₂	52.76	53.64	53.59	55.94	53.64	50.85	85.02	36.33	52.88	29.23	29.99	30.91
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 4. Blank Reactor Tests with Methanol/Ethanol Feed

Blank Reactor Loading	Quartz/ α -Al ₂ O ₃	Glass Beads
Run Number	207	206
Conditions	350°C, 30 psig, 2 hr ⁻¹ MeOH WHSV, 10/1/2 MeOH/EtOH/N ₂ (molar)	
Conversion (%) MeOH EtOH	7.9 12.1	2.1 2.5
Selectivities (mole %)		
nC ₃ OH	0.0	0.0
nC ₄ OH	0.0	0.0
iC ₄ OH	0.3	0.4
iC ₄ Aldehyde	0.1	0.0
Me iButyrate	0.0	0.0
Other Oxygenates	0.5	3.8
Others (No ID)	1.0	0.8
C ₁ -C ₂ Oxygenates	93.8	76.9
C ₁ -C ₄ Hydrocarbons	3.6	13.3
CO	0.0	0.0
CO ₂	0.8	4.9

Table 5. Blank Reactor Tests at High Temperature with Copper-Lined Reactor

Blank Reactor Loading	Glass Beads in Stainless Steel Reactor				Glass Beads in Copper-Lined Reactor		
Run Number	298				324		
Hours on Stream	32-40	40-48	48-56	56-64	9-16	25-32	41-48
Conditions	30 psig, 2 hr ⁻¹ MeOH WHSV, 2/1 N ₂ /MeOH (molar)						
Temperature (°C)	250	350	450	500	350	400	450
Conversion (%) MeOH	0.2	5.9	35.2	68.1	0.2	2.1	8.8
Selectivities (mole %)							
nC ₃ OH	0.0	0.0	0.0	0.0	0.0	1.8	1.2
nC ₄ OH	0.0	0.0	0.0	0.0	0.0	0.7	0.0
iC ₄ OH	0.0	0.0	0.0	0.0	0.0	0.0	0.0
iC ₄ Aldehyde	0.0	0.0	0.0	0.0	0.0	0.6	0.0
Me iButyrate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Other Oxygenates	0.0	0.0	0.0	0.0	7.8	1.2	0.3
Others (No ID)	0.0	0.0	0.0	0.0	4.7	1.0	0.0
C ₁ -C ₂ Oxygenates	0.0	0.0	0.0	0.0	87.5	54.6	35.0
C ₁ -C ₄ Hydrocarbons	0.0	3.7	5.1	6.4	0.0	4.2	5.0
CO	100.0	92.6	91.2	88.3	0.0	30.9	51.7
CO ₂	0.0	2.0	2.1	4.2	0.0	5.0	6.8

Table 6. Comparison of Lab Prepared and Commercial Cu/Zn/Al Methanol Synthesis Catalysts

Conditions: 310 °C, 1100 psig, 2250 hr⁻¹ CO GHSV, 1/1 H₂/CO (molar)

Run	113	137	138	141	145
Catalyst	Commercial	Commercial	Lab Prepared		Lab Prepared
Mixed with SiO ₂ (1:1 wt.)	Cu/Zn/Al Oxide	Cu/Zn/Al Oxide	Cu/Zn/Al Oxide		Cu/Zn/Al Oxide
	ICI 52-1	ICI 51-3	7923-20		7923-85
Conversions (%)					
CO	28.1	25.4	25.4	29.7	31.2
H ₂	37.6	34.4	39.1	40.2	40.6
Selectivities (mole%)					
C ₁ OH	64.0	54.3	57.1	54.3	46.0
C ₂ OH	2.7	3.2	2.2	2.4	2.5
C ₃ OHs	1.1	1.0	0.7	0.9	1.1
n-C ₄ OH	0.6	0.5	0.3	0.3	0.5
i-C ₄ OH	1.0	1.0	0.6	0.9	0.6
C ₅₊ OH	1.2	1.7	0.4	0.3	0.9
DME	1.4	3.8	6.6	6.5	7.5
C ₁ HCBN	1.4	1.6	1.2	1.3	1.1
C ₂₋₄ HCBNs	1.8	2.5	1.2	1.8	1.7
Others	12.2	15.4	3.6	3.4	7.7
CO ₂	12.6	15.0	26.1	27.9	30.4

Table 7. Evaluation of Methanol Synthesis Catalysts

Run Hours on Stream	113 8-16	115 8-16	114 8-16
Catalyst	Cu/Zn/Al Oxide	Cu/Zn/Al Oxide	Zn/Cr Oxide
	Commercial	Lab Prepared	Lab Prepared
Conditions			
Temperature (C)	310	310	450
Pressure (psig)	1100	1100	1100
CO GHSV (hr ⁻¹)	2250	2250	2250
H ₂ /CO (molar)	1/1	1/1	1/1
Conversions (%)			
CO	28.1	28.7	27.1
H ₂	37.6	38.7	24.6
Selectivities (%)			
C ₁ OH	64.0	65.9	0.1
C ₂ OH	2.7	3.0	0.1
C ₃ OHs	1.1	1.4	0.1
n-C ₄ OH	0.6	0.7	0.1
i-C ₄ OH	1.0	1.3	0.1
C ₅₊ OH	1.2	1.8	0.1
DME	1.4	4.1	0.0
C ₁ HCBN	1.4	1.7	26.7
C ₂₋₄ HCBNs	1.8	2.3	24.8
Others	12.2	4.1	6.5
CO ₂	12.6	13.7	41.4

Table 8. Cu/Zn/Al Oxide with Supported Potassium Co-Catalysts

Run Hours on Stream	141 8-16	139 8-16	140 8-16
Catalyst	Cu/Zn/Al Oxide + SiO ₂ 1:1 (wt.)	Cu/Zn/Al Oxide + K/Al ₂ O ₃ 1:1 (wt.)	Cu/Zn/Al Oxide + K/SiO ₂ 1:1 (wt.)
Conditions Temperature (C) Pressure (psig) CO GHSV (hr ⁻¹) H ₂ /CO (molar)	310 1100 2250 1/1		
Conversions (%) CO H ₂	29.7 40.2	27.5 39.5	13.5 15.4
Selectivities (%) C ₁ OH C ₂ OH C ₃ OHs n-C ₄ OH i-C ₄ OH C ₅ +OH DME C ₁ HCBN C ₂₋₄ HCBNs Others CO ₂	54.3 2.4 0.9 0.3 0.9 0.3 6.5 1.3 1.4 3.4 27.9	61.9 1.4 0.6 0.2 0.7 0.6 7.2 1.5 1.3 2.5 22.1	44.9 0.6 0.3 0.1 0.2 1.1 19.1 2.9 2.8 2.9 25.1

Table 9. Evaluation of Methanol Synthesis Catalysts

Run	115	116	117	118
Catalyst	Cu/Zn/Al Oxide + SiO ₂	Cu/Zn/Al Oxide + Mg/Al MOSS (Lab Prep)	Cu/Zn/Al Oxide + Mg/Al MOSS (Commercial)	Cu/Zn/Al Oxide + MgO (Lab Prep)
Conditions	310°C, 1100 psig, 2250 hr ⁻¹ CO GHSV, 1/1 CO/H ₂ (molar)			
Conversions (%)				
CO	28.7	34.5	34.9	29.4
H ₂	38.7	45.5	43.6	43.4
Selectivities (mole%)				
C ₁ OH	65.9	51.5	47.1	72.6
C ₂ OH	3.0	1.2	0.8	1.4
C ₃ OHs	1.4	0.9	0.5	0.9
n-C ₄ OH	0.7	0.2	0.1	0.2
i-C ₄ OH	1.3	1.6	0.9	1.1
C ₅₊ OH	1.8	1.1	0.7	0.8
DME	4.1	20.4	26.3	7.0
C ₁ HCBN	1.7	1.0	0.8	1.8
C ₂₋₄ HCBNs	2.3	0.7	0.6	1.2
Others	4.1	4.4	2.7	2.6
CO ₂	13.7	17.0	19.5	10.4

Table 10. Cu/Zn/Al Oxide with Mg/Al MOSS Co-Catalysts

Run Hours on Stream	145 8-16	144 8-16	146 8-16	143 8-16
Catalyst	Cu/Zn/Al Oxide + SiO ₂ 1:1 (wt.)	Cu/Zn/Al Oxide + 0.2% Na Mg/Al MOSS 1:1 (wt.)	Cu/Zn/Al Oxide + 0.2% K/ Mg/Al MOSS 1:1 (wt.)	Cu/Zn/Al Oxide + 0.3% Cs/ Mg/Al MOSS 1:1 (wt.)
Conditions Temperature (C) Pressure (psig) CO GHSV (hr ⁻¹) H ₂ /CO (molar)	310 1100 2250 1/1			
Conversions (%) CO H ₂	31.2 40.6	30.2 43.1	29.4 39.5	32.2 41.5
Selectivities (%) C ₁ OH C ₂ OH C ₃ OHs n-C ₄ OH i-C ₄ OH C ₅ + OH DME C ₁ HCBN C ₂₋₄ HCBNs Others CO ₂	46.0 2.5 1.1 0.5 0.6 0.9 7.5 1.1 1.7 7.7 30.4	41.8 0.4 0.2 0.0 0.1 0.5 23.3 0.6 0.5 2.1 30.5	40.5 0.5 0.2 0.1 0.3 0.6 23.9 0.7 0.4 2.4 30.4	41.1 0.5 0.2 0.1 0.4 0.8 21.5 0.8 0.9 3.1 30.6

Table 11. Cs Addition to Cu/Zn/Al Oxide

Run Hours on Stream	145 8-16	147 8-16	152 8-16
Catalyst	Cu/Zn/Al Oxide + SiO ₂ 1:1 (wt.)	1.3% Cs on Cu/Zn/Al Oxide + SiO ₂ 1:1 (wt.)	
Conditions			
Temperature (C)	310		
Pressure (psig)	1100		
CO GHSV (hr ⁻¹)	2250		
H ₂ /CO (molar)	1/1		
Conversions (%)			
CO	31.2	23.8	23.1
H ₂	40.6	37.3	35.4
Selectivities (%)			
C ₁ OH	46.0	63.2	62.9
C ₂ OH	2.5	2.1	2.2
C ₃ OHs	1.1	0.8	0.9
n-C ₄ OH	0.5	0.3	0.3
i-C ₄ OH	0.6	0.6	0.9
C ₅₊ OH	0.9	0.4	0.5
DME	7.5	6.7	7.7
C ₁ HCBN	1.1	1.0	1.2
C ₂₋₄ HCBNs	1.7	1.3	1.0
Others	7.7	3.7	1.5
CO ₂	30.4	20.2	20.9

Table 12. Evaluations of Pd/K on Zr/Zn/Mn Oxide Catalysts

Conditions: 1100 psig, 2250 hr⁻¹ CO GHSV, 1/1 H₂/CO (molar)

Run	124	125	128	132	130	150	131
Catalyst	0.14% Pd (Pd(NO ₃) ₂) on K/Zr/Zn/Mn (4.6%/1/1/1)	0.15% Pd (Pd(NO ₃) ₂) on K/Zr/Zn/Mn (0.8%/1/1/1)			0.18% Pd (PdCl ₂) on K/Zr/Zn/Mn (1.6%/1/1/1)	0.23% Pd (PdCl ₂) on K/Zr/Zn/Mn (0.4%/1/1/1)	0.23% Pd (PdCl ₂) on SiO ₂
(Diluent)	SiO ₂	SiO ₂	SiO ₂	None	None	None	None
Temperature (°C)	450	450	350	450	450	400	450
Conversions (%)							
CO	14.3	8.5	6.2	17.9	8.5	9.3	8.5
H ₂	14.3	12.6	2.6	13.2	12.6	10.9	12.6
Selectivities (mole%)							
MeOH	1.5	7.7	39.4	10.9	7.7	6.4	7.7
C ₂₊ Alcohols	2.0	0.2	0.8	1.6	0.2	1.1	0.2
DME	0.0	0.0	33.4	0.0	0.0	19.6	0.0
C ₁₋₄ HCBNs	33.2	43.1	4.3	34.8	43.1	19.3	43.1
CO ₂	40.9	45.4	20.1	44.9	45.4	48.1	45.4

Table 13. Catalyst Screening for Methanol Condensation

Plant 700 Runs 154-167

Conditions: 250 °C, 1100 psig, 2 hr⁻¹ MeOH WHSV,
1/2 MeOH/N₂ or H₂ (molar)

CATALYST	N ₂ Co-Feed		H ₂ Co-Feed	
	MeOH Conv. (%)	DME Select. (mole%)	MeOH Conv. (%)	DME Select. (mole%)
Blank	3.2	87		
Cu/Zn/Al (30/45/25)	8.3	45.4	2.1	83.4
Cu/Zn/Al (30/25/45) + 1.3% Cs			1.9	92.2
Zr/Zn (50/50)	1.3	97.4	1.4	97.0
Zr/Zn/Mn (33/33/33)			1.4	89.3
Cs/Zn/Mn (33/33/33)	1.2	100.0		
Mg/Al MOSS	2.5	99.3		
Mg/Al MOSS + 0.5% Cu	1.6	90.4	1.5	93.7
Mg/Al MOSS + 5.0% Cu			1.9	89.3
Mg/Al MOSS + 0.5% Co	1.5	98.5		
Mg/Al MOSS + 0.5% Ag			1.7	96.4

Table 14. Evaluation of Mg/Al MOSS Catalyst for Methanol/Ethanol Condensation

Plant 700

Catalyst: Commercial Mg/Al MOSS (20-40 mesh)

Run	168	169	170	172	173
Conditions					
°C	250	250	350	350	350
psig	1100	100	100	30	30
hr ⁻¹ (MeOH)	2	2	2	2	0.4
EtOH/MeOH	0.1	0.1	0.1	0.1	0.1
Dil/MeOH	2 H ₂	2 H ₂	2 N ₂	2 N ₂	2 N ₂
Conversions (%)					
MeOH	-1.3	-0.1	7.9	6.5	21.6
EtOH	20.1	7.5	31.6	31.5	44.7
Selectivity (mole%, CO _x -free)					
C ₃ OH	0.0	7.6	7.2	10.1	4.8
n-C ₄ OH	4.1	1.4	0.2	0.8	0.6
i-C ₄ OHs	0.0	5.7	4.0	5.9	3.3
C ₅₊ OHs	0.0	0.6	0.7	1.2	0.5
DME	86.9	58.7	60.0	55.9	75.2
C ₁₋₃ ALD	0.0	11.3	9.3	9.6	0.8
C ₁ HCBN	4.3	1.6	1.5	1.9	1.2
C ₂₋₄ HCBN	4.7	3.8	1.4	1.3	9.6
Others	0.0	9.3	15.7	13.3	4.0

Table 15. Effect of Temperature on Performance of Cu/Zn/Al Oxide for Methanol/Ethanol Condensation

Plant 700

Catalyst: Cu/Zn/Al Oxide (30/45/25) 20-40 mesh

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

Run	176	177	178
Temperature (°C)	350	300	250
Conversion %			
C ₁ OH	92.3	50.7	17.0
C ₂ OH	96.9	89.5	11.4
Selectivity mole%			
nC ₃ OH	0.4	0.8	7.4
nC ₄ OH	0.1	0.1	0.3
iC ₄ OH	4.5	13.4	8.7
tC ₄ OH	0.2	0.0	0.0
Me ₂ O	8.3	7.0	5.4
Et ₂ O	0.9	0.7	0.6
MeOiC ₄	0.7	0.1	3.2
C ₂₋₃ ALD	1.1	1.3	13.0
iC ₄ ALD	6.6	6.9	2.2
ESTERS	3.3	10.5	12.5
C ₁₋₃ HCBN	3.2	2.5	1.3
CO	33.4	20.5	2.5
CO ₂	32.4	25.1	7.4
Others	4.9	11.1	35.5
Productivity g/kg cat/hr			
iC ₄ OH	26	56	21
C ₃₊ Oxygenates	76	121	43

Table 16. Evaluation of Methanol Synthesis Type Catalysts

Run	176	177	179	182	180	181	183
Catalyst	Cu/Zn/Al Oxide (31/42/27)		Zn/Cr Oxide (75/25)	Cu/Zn/Al Oxide (11/63/26)	Cu/Zn/Mn Oxide (34/33/33)	Zn/Al Oxide (74/26)	Zn/Al Oxide (63/37)
Temperature (°C)	350	300	350	350	350	350	350
Conversion (%)							
MeOH	97.6	67.3	14.9	62.3	50.8	15.5	17.7
EtOH	99.2	95.9	31.5	97.9	88.8	72.8	81.2
Selectivities (mole%)							
iC ₄ OH	2.0	5.8	2.8	7.5	5.5	1.1	2.0
iC ₄ Ald	2.2	2.3	0.4	6.0	7.2	0.2	0.2
Total C ₄₊ Oxy	5.9	12.7	6.2	21.4	14.6	9.8	8.9
CO	45.5	33.0	7.5	28.9	19.4	1.8	2.0
CO ₂	40.8	37.9	30.4	31.7	42.0	16.2	18.4
Productivities (g/kg cat/hr)							
iC ₄ OH	26	56	13	68	43	4	7
Total C ₄₊ Oxy	76	121	28	150	111	33	33

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 17. Evaluation of Pd on Zn/Mn/Zr Oxide Catalysts

Run	176	177	188	189	190
Catalyst	Cu/Zn/Al Oxide (31/42/27)		Zn/Mn/Zr Oxide (34/34/32)	0.2%Pd on Zn/Mn/Zr Oxide (34/34/32)	2.1%Pd on Zn/Mn/Zr Oxide (34/34/32)
Temperature (°C)	350	300	350	350	350
Conversion (%)					
MeOH	97.6	67.3	8.6	30.3	47.9
EtOH	99.2	95.9	49.5	87.5	97.4
Selectivities (mole%)					
iC ₄ OH	2.0	5.8	12.9	7.6	10.3
iC ₄ Ald	2.2	2.3	0.2	7.4	10.4
Total C ₄₊ Oxy	5.9	12.7	18.1	20.8	25.0
CO	45.5	33.0	0.0	9.1	14.7
CO ₂	40.8	37.9	14.3	26.0	28.2
Productivities (g/kg cat/hr)					
iC ₄ OH	26	56	13	41	80
Total C ₄₊ Oxy	76	121	28	111	192

Conditions: 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 18. Screening of 2% Pd on Mixed Metal Oxide Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
Zn/Mn/Zr (34/34/32)	7923-64	198	51 99	10	41	37	80	328
Zn/Mn/Cr (34/33/33)	7887-52	212	79 100	10	36	57	110	399
Zn/Mn/Ce (33/33/33)	7923-88	194	35 92	5	44	33	33	290
Cu/Zn/Al (33/39/28)	7887-58	213	89 100	7	28	56	87	348
Zn/Mn (50/50)	7923-72	193	42 95	7	21	40	50	150

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 19. Screening of 2% Pt on Mixed Metal Oxide Catalysts

Support Catalyst Number		Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
			MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
Zn/Mn/Zr (34/34/32)	7887-48	211	49	99	16	49	44	122	373
(45/45/10)	7887-36	252	56	100	12	42	48	100	350
Zn/Mn/Cr (34/33/33)	7887-62	216	51	90	2	12	75	17	102
Zn/Mn/Ce (33/33/33)	7887-68	219	50	100	12	46	48	91	349
Zn/Mn/La (34/32/34)	7887-82	224	58	99	8	33	64	68	281
Zn/Mn/Cu (34/33/33)	7887-76	223	32	95	7	37	37	37	196
Zn/Al (75/25)	7887-72	220	74	100	7	30	57	74	317
Zn/Cr (75/25)	7887-70	221	66	100	9	34	58	83	316
Zn/Zr (50/50)	7887-64	217	10	57	2	32	53	4	64
Mn/Zr (50/50)	7887-66	218	35	96	8	42	46	46	242

Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 20. Screening of Metals on Zr/Mn/Zr and Zn/Mn/Cr Oxides

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
Zn/Mn/Zr (34/33/32)								
7887-48 (2% Pt)	211	49	99	16	49	44	122	374
7923-64 (2% Pd)	198	51	99	10	41	37	80	328
7887-50 (2% Ag)	209	11	67	13	45	26	37	128
7887-56 (2% Ag metal)	210	6	63	14	47	16	30	101
7923-55 (no metal)	188	9	50	13	18	14	13	18
Zn/Mn/Cr (34/33/33)								
7887-62 (2% Pt)	216	51	90	2	12	75	17	102
7887-52 (2% Pd)	212	79	100	10	36	57	110	399
7923-95 (no metal)	215	5	43	1	36	31	2	72

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 21. Overall Selectivities (mole %) of Most Promising Catalysts

Run	198	212	211	216
Catalyst	7923-64 2%Pd on Zn/Mn/Zr Oxide	7887-52 2%Pd on Zn/Mn/Cr Oxide	7887-48 2%Pt on Zn/Mn/Zr Oxide	7887-62 2%Pt on Zn/Mn/Cr Oxide
nC ₃ OH	0.7	0.1	0.6	2.0
nC ₄ OHs	0.2	1.1	0.4	0.1
iC ₄ OH	9.9	10.2	16.4	2.1
C ₅ ⁺ OHs	0.8	1.1	0.9	0.5
iC ₄ Aldehyde	14.8	11.9	17.7	6.2
iC ₄ Methyl Ester	3.6	3.5	2.9	0.7
Other Oxygenates	2.2	3.3	1.0	1.1
C ₁₋₂ Aldehydes	0.0	0.0	0.6	0.0
C ₃ Aldehyde	0.8	0.3	0.7	6.6
DME	10.5	0.3	0.9	0.1
Methyl Formate	0.6	0.7	1.7	0.4
Methyl Acetate	2.4	2.0	1.3	2.7
C ₁₋₅ Hydrocarbons	6.0	3.5	1.6	1.6
CO	14.2	40.7	18.0	61.6
CO ₂	22.8	16.3	25.6	13.6
Others	10.5	5.0	9.7	0.7

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 22. Reproduction of 2% Pd and 2% Pt on Mixed Metal Oxide Catalyst Preparations

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
Pd/Zn/Mn/Zr (34/34/32)								
Precipitation 1 7923-64	198	51	99	8	41	37	62	328
Precipitation 2								
Impregnation 1 8265-22	247	45	97	7	38	48	52	273
Impregnation 2 8265-32	250	25	80	1	49	33	6	214
Pd/Zn/Mn/Cr (34/33/33)								
Precipitation 1								
Impregnation 1 7887-52	212	79	100	9	36	57	99	399
Impregnation 2 7887-90	228	87	100	5	26	67	65	305
Precipitation 2 8265-25	248	19	76	1	42	45	4	144
Pt/Zn/Mn/Zr (34/34/32)								
Precipitation 1 7887-48	211	47	99	14	49	44	102	373
Precipitation 2 8265-50	258	57	100	11	54	47	92	356
Pt/Zn/Mn/Cr (34/33/33)								
Precipitation 1 7887-62	216	51	90	2	18	75	17	102
Precipitation 2 8265-26	249	31	72	2	33	58	9	161

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 23. Screening of 2% Pt on Single/Double Metal Oxide Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
ZnO / 10% SiO ₂ Binder 7887-94	238	37	95	7	36	52	44	224
MnO ₂ 7887-80	222	36	83	2	14	77	9	63
ZrO ₂ 7887-86	227	46	53	0	2	85	0	13
MgO 7887-96	236	100	100	0	0	91	0	0
TiO ₂ 8265-92	294	100	99	0	1	83	0	0
Zn/Mg (50/50)/10% SiO ₂ 7887-89	239	71	100	6	25	70	65	250

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 24. Screening of Other Potential Higher Alcohols Catalysts

Support Catalyst Number	Run	Conversion (%)		Selectivity (mole%)			Productivity (g/kg cat/hr)	
		MeOH	EtOH	iC ₄ OH	Sum C ₄₊	CO _x	iC ₄ OH	Sum C ₄₊
TiO ₂								
2% Cu 8125-8	240	11	31	14	53	11	28	106
2% Mo 8125-10	241	38	77	2	27	11	9	121
Mg/Al MOSS								
2% Cu 8265-18	245	7	31	12	50	4	17	72
2% Mo 8265-16	244	14	34	8	24	11	19	56
Polyvinylpyridine								
2% Cu 8265-12	242	-1	11	0		0	0	
2% Mo 8254-13	243	3	-7	0		0	0	
2% Pd 8265-14	246	10	-3	0		0	0	

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 25. Screening of MnO₂ Based Catalysts for Higher Alcohols Synthesis

Catalyst Catalyst Number	Run	Conversion (%)		Selectivity (mole%)		Productivity (g/kg cat/hr)
		MeOH	EtOH	iC ₄ OH	CO _x	iC ₄ OH
Commercial MnO ₂						
Chemetals CIR-189						
None 8265-42	254	7	6	3	8	2
2% Pt 8265-61	265	49	80	4	64	28
2% Pd 8265-60	264	42	81	3	48	20
250ppm Co 8265-52	259	5	9	4	13	4
Chemetals ODC-924						
None 8265-44	255	7	-6	4	14	2
2% Pt 8265-65	267	57	79	1	78	11
2% Pd 8265-66	268	16	36	2	50	6
Laboratory MnO ₂						
Cryptomelane 8265-46	256	7	-7	3	21	2
Pharmacosiderite 8265-48	257	6	-15	0	4	0

Conditions: 350°C, 30 psig, 2 hr⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N₂

Table 26. Characterization of 2% Pt on Zn/Mn/Zr Oxide Supports and Catalysts

CATALYST NUMBER	DESCRIPTION OF CATALYST/SUPPORT (Targets)	ELEMENTAL ANALYSES (Wt.%)							ABD g/cc	N2 BET ANALYSIS			Plant 700 RUN NUMBERS
		Pt	Pd	Zn	Mn	Zr	Na, ppm	K, ppm		SA (m2/g)	PV (cc/g)	PD (Å)	
8265-72	60/20/20 Zn/Mn/Zr Oxide Support			42.2	10.2	19.9							272/274/275/276/277/291 284 285/288 285 296/297/299/300
8265-76	Impregnated with 2% Pt	1.9		41.2	10.0	19.5	90	2100	1.06	59	0.16	112	
8265-86	Impregnated with 0.5% Pt	0.6							1.11	68	0.15	68	
8265-87	Impregnated with 2% Pt	2.0								45	0.15	136	
8265-88	Impregnated with 5% Pt	6.4								48	0.16	134	
8265-94	Impregnated with 2% Pt	2.0								42	0.16	150	
8265-95	Impregnated with 0.5% Pt	0.5					125	2100	1.17	73	0.15	86	
8265-96	60/20/20 Zn/Mn/Zr Oxide Support			41.3	9.8	19.4				100	0.22	86	301 302-319/321-323
8265-97	Impregnated with 2% Pt	1.8					44	5300	1.00	79	0.20	102	
8265-98	Impregnated with 2% Pt	1.9		40.6	9.8	19.4	100	6800	0.98	56	0.17	118	
8265-28	45/45/10 Zn/Mn/Zr Oxide Support			18.1	13.1	5.7				44	0.15	134	252 251
8295-36	Impregnated with 2% Pt	1.9		33.7	26.2	11.1			0.73	36	0.13	144	
8265-34	Impregnated with 2% Pd		2.0						0.73	39	0.13	132	
8265-30	45/10/45 Zn/Mn/Zr Oxide Support			27.2	5.6	39.1				96	0.17	70	273 283
8265-77	Impregnated with 2% Pt	1.9		27.2	5.6	39.4			1.26	84	0.17	84	
8265-56	Impregnated with 2% Pd		1.9							65	0.14	86	
8265-20	33/33/33 Zn/Mn/Zr Oxide Support			21.8	18.2	26.7				129	0.20	62	266 247
8265-50	Impregnated with 2% Pt	2.0		21.3	17.6	28.5			0.71	84	0.21	98	
8265-22	Impregnated with 2% Pd		2.1						0.73	116	0.19	62	
8265-78	20/20/60 Zn/Mn/Zr Oxide Support									152	0.35	92	263
8265-80	Impregnated with 2% Pt	2.0		11.3	6.1	48.6				167	0.32	76	
8265-81	Impregnated with 2% Pd		2.1						1.10				
8265-62	20/60/20 Zn/Mn/Zr Oxide Support			17.1	29.1	24.0				107	0.25	96	268 262
8265-90	Impregnated with 2% Pt	1.9		16.6	28.4	23.2			1.23	87	0.25	114	
8265-85	Impregnated with 2% Pd		1.9						1.04	77	0.15	76	
8265-58B	10/45/45 Zn/Mn/Zr Oxide Support			6.2	16.2	43.3				185	0.37	80	278/279/290/292 280
8265-82	Impregnated with 2% Pt	1.8							0.63				
8265-83	Impregnated with 2% Pd		2.0						0.55	178	0.36	62	

**Table 27. Effect of Support Composition on Performance -
2% Pt on Zn/Mn/Zr Oxide Catalysts**

Catalyst Number	8265-76	8265-36	8265-77	8265-50	8265-80	8265-90	8265-82
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pt on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pt on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pt on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)
Run	272	260	273	258	279	288	278
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)						
Conversion (%)							
MeOH	58.7	63.6	68.3	57.3	59.0	69.9	73.3
EtOH	100.0	100.0	100.0	99.8	99.4	100.0	100.0
Selectivity (C%)							
nC3OH	0.0	0.0	0.0	0.2	0.3	0.0	0.0
nC4OH	0.0	0.0	0.0	0.0	0.1	0.1	0.0
iC4OH	11.1	10.4	8.0	10.8	8.9	8.2	8.9
iC4 Aldehyde	17.7	16.5	11.3	15.6	11.7	12.1	12.0
Me iButyrate	5.3	3.6	6.8	4.9	4.8	6.3	7.3
MeiBu Ether	0.0	0.1	0.3	0.0	0.0	0.0	0.1
C5+OH	0.9	0.9	0.9	1.1	1.5	1.3	1.0
Other Ald/Ketone	0.8	0.9	0.7	0.9	1.2	0.8	0.8
Other Esters	0.3	0.8	1.4	0.4	0.5	0.5	0.9
Others	5.3	7.6	5.2	9.8	18.8	13.1	4.9
DiME Ether	1.1	0.6	3.6	1.3	2.4	1.4	1.0
MeEt Ether	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Me Formate	2.5	4.2	3.3	2.7	1.5	1.7	0.6
Me Acetate	1.8	1.6	2.6	2.2	2.2	1.2	0.2
C1	0.8	1.4	2.2	0.9	0.8	1.3	0.6
C2+s	1.1	2.8	1.5	2.1	2.4	1.6	0.8
CO	25.4	22.5	24.2	21.0	15.5	24.5	38.6
CO ₂	26.0	27.4	26.4	26.2	27.0	25.9	22.3

**Table 28. Effect of Support Composition on Performance -
2% Pd on Zn/Mn/Zr Oxide Catalysts**

Catalyst Number	8265-34	8265-56	8265-22	8265-81	8265-85	8265-83
Description	2.0% Pd on Zn/Mn/Zr Oxide (45/45/10)	2.0% Pd on Zn/Mn/Zr Oxide (45/10/45)	2.0% Pd on Zn/Mn/Zr Oxide (33/33/33)	2.0% Pd on Zn/Mn/Zr Oxide (20/20/60)	2.0% Pd on Zn/Mn/Zr Oxide (20/60/20)	2.0% Pd on Zn/Mn/Zr Oxide (10/45/45)
Run	251	263	247	283	282	280
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)					
Conversion (%)						
MeOH	44.4	70.0	45.0	53.5	33.2	50.9
EtOH	96.4	98.7	97.3	97.0	66.5	96.4
Selectivity (C%)						
nC3OH	1.3	0.3	1.2	1.5	2.7	1.5
nC4OH	0.3	0.1	0.2	0.3	0.1	0.1
iC4OH	5.9	7.0	7.3	5.1	1.0	7.4
iC4 Aldehyde	12.1	8.7	11.8	7.3	4.1	9.6
Me iButyrate	1.8	3.5	2.2	1.5	1.3	2.9
MeiBu Ether	0.1	0.1	0.0	0.1	0.0	0.0
C5+OH	1.2	1.0	1.1	0.4	0.7	1.0
Other Ald/Ketone	4.1	1.2	3.2	3.8	11.7	4.0
Other Esters	0.3	1.2	0.4	0.5	0.2	0.3
Others	14.4	23.1	12.0	25.5	18.9	19.7
DiME Ether	0.5	2.2	1.6	2.6	0.4	0.7
MeEt Ether	0.0	0.1	0.0	0.1	0.0	0.0
Me Formate	7.0	3.6	2.1	2.0	0.3	0.9
Me Acetate	4.1	3.2	3.0	2.9	0.9	1.7
C1	1.1	0.9	1.2	1.1	0.7	0.5
C2+s	5.4	4.3	5.2	6.0	1.4	2.8
CO	13.6	13.5	21.7	14.4	40.4	21.7
CO ₂	27.0	25.9	26.0	24.8	15.1	25.2

**Table 29. Effect of Noble Metal Loading on Performance -
Pt on Zn/Mn/Zr Oxide Catalysts**

Catalyst Number	8265-86	8265-87	8265-76	8265-88
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)	1.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)	5.0% Pt on Zn/Mn/Zr Oxide (60/20/20)
Run	284	285	272	286
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)			
Conversion (%)				
MeOH	68.5	71.6	58.7	67.6
EtOH	100.0	100.0	100.0	99.8
Selectivity (C%)				
nC ₃ OH	0.0	0.0	0.0	0.1
nC ₄ OH	0.1	0.0	0.0	0.1
iC ₄ OH	8.5	9.2	11.1	8.2
iC ₄ Aldehyde	12.1	12.1	17.7	10.9
Me iButyrate	6.5	6.2	5.3	3.0
MeiBu Ether	0.1	0.1	0.0	0.1
C ₅ +OH	1.3	1.1	0.9	0.9
Other Ald/Ketone	0.8	0.7	0.8	0.8
Other Esters	0.6	0.4	0.3	0.7
Others	6.2	8.5	5.3	15.3
DiME Ether	2.1	1.3	1.1	0.6
MeEt Ether	0.0	0.0	0.0	0.1
Me Formate	1.0	1.2	2.5	3.3
Me Acetate	0.9	0.5	1.8	1.8
C ₁	1.0	1.2	0.8	1.3
C ₂ +s	1.0	1.1	1.5	3.2
CO	32.9	31.6	25.4	22.6
CO ₂	24.8	24.7	26.0	27.2

**Table 30. Effect of Noble Metal Loading on Performance -
0.5% and 2% Pt on Zn/Mn/Zr Oxide Catalysts**

Catalyst Number	8265-94			8265-95		
Description	0.5% Pt on Zn/Mn/Zr Oxide (60/20/20)			2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		
Run	295			297		
Conditions	350 C, 30 psig, 10/0.1/2/ MeOH/EtOH/N2					
MeOH WHSV (hr-1)	2	3	4	2	3	4
Conversion (%)						
MeOH	51.8	35.0	25.6	50.2	41.0	31.0
EtOH	99.9	93.7	86.6	99.0	94.3	90.7
Selectivity (C%)						
nC3OH	0.1	2.5	4.1	0.5	2.1	3.1
nC4OH	0.1	0.2	0.2	0.1	0.2	0.3
iC4OH	11.8	8.0	3.7	13.0	12.0	8.0
iC4 Aldehyde	17.8	16.5	11.1	16.2	18.6	18.1
Me iButyrate	4.8	1.6	0.9	5.4	3.9	2.9
MeiBu Ether	0.0	0.1	0.0	0.0	0.0	0.0
C5+OH	0.7	0.8	0.8	1.2	1.2	1.4
Other Ald/Ketone	0.7	6.0	11.4	1.8	5.0	7.5
Other Esters	0.3	0.1	0.1	0.1	0.0	0.0
Others	5.6	8.8	10.9	5.7	5.8	8.0
DiME Ether	0.9	0.4	0.4	1.2	0.8	0.6
MeEt Ether	0.0	0.0	0.0	0.1	0.1	0.1
Me Formate	2.6	2.3	3.7	0.8	0.7	0.7
Me Acetate	1.9	3.2	3.2	2.4	4.0	4.5
Hydrocarbons	1.7	1.1	1.1	2.2	1.9	1.7
CO	24.5	25.0	27.3	23.2	21.6	22.3
CO2	26.5	23.4	21.2	25.9	22.1	20.8

Table 31. Pilot Plant Performance of Large Scale Preparation of 2% Pt on Zn/Mn/Zr Oxide Catalyst

Catalyst	8265-76	8265-95	8265-98
	2% Pt on Zn/Mn/Zr (60/20/20) Oxide		
	Screening Preparation	Support Certification	Final 200 g Preparation
Plant 700 Run Number	272	297	308
Conditions	350°C, 30 psig, 2 hr ⁻¹ MeOH WHSV, 1/0.1/2 MeOH/EtOH/N ₂ (molar)		
Conversion (%)			
MeOH	58.7	50.2	53.4
EtOH	100.0	99.0	99.1
Selectivities (mole %)			
nC ₃ OH	0.0	0.5	0.4
nC ₄ OH	0.0	0.1	0.1
iC ₄ OH	11.1	13.0	11.6
iC ₄ Aldehyde	17.7	16.2	18.0
Me iButyrate	5.3	5.4	4.3
Other Oxygenates	2.0	3.2	1.5
Others (No ID)	5.3	5.7	7.3
C ₁ -C ₂ Oxygenates	5.4	4.5	4.1
C ₁ -C ₄ Hydrocarbons	1.9	2.2	1.4
CO	25.4	23.2	22.3
CO ₂	26.0	25.9	28.0
Productivities (g/kg/hr)			
iC ₄ OH	96	102	94
iC ₄₊ Oxygenates	360	340	348

Table 32. Effect of Process Variables on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide										
Run Number	309	308	310	308	311	312	308	304	307	306	325
Conditions	2 hr ⁻¹ MeOH WHSV, 2/1 N ₂ /MeOH (molar)										1 hr ⁻¹ WHSV
Temperature (°C)	325	350	375	350	350	350	350	350	350	350	325
Pressure (psig)	30	30	30	30	100	300	30	30	30	30	300
MeOH/EtOH (molar)	10/1	10/1	10/1	10/1	10/1	10/1	10/1	7/1	4/1	1/1	7/1
Conversion (%)											
MeOH	39.7	53.4	64.2	53.4	46.0	56.4	53.4	57.4	58.8	65.5	55.2
EtOH	96.6	99.1	98.1	99.1	95.7	97.6	99.1	97.4	93.4	82.8	97.0
Selectivities (mole %)											
nC ₃ OH	1.2	0.4	1.1	0.4	0.3	0.8	0.4	1.0	2.9	2.0	1.6
nC ₄ OH	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.5	1.2	0.1
iC ₄ OH	15.6	11.6	5.7	11.6	14.4	20.7	11.6	15.3	9.1	0.3	22.2
iC ₄ Aldehyde	16.6	18.0	13.4	18.0	11.2	7.2	18.0	19.0	12.9	1.0	4.8
Me iButyrate	4.9	4.3	2.1	4.3	5.1	5.6	4.3	5.4	4.9	0.2	9.1
Other Oxygenates	3.4	1.5	4.4	1.5	1.8	1.4	1.5	3.9	9.7	3.1	6.8
Others (No ID)	8.5	7.3	8.1	7.3	5.8	2.1	7.3	5.5	13.4	14.1	13.0
C ₁ -C ₂ Oxygenates	7.2	4.1	2.2	4.1	3.3	3.0	4.1	4.1	6.9	66.9	5.7
C ₁ -C ₄ Hydrocarbons	0.7	1.4	3.5	1.4	2.7	2.6	1.4	1.3	0.9	0.7	1.0
CO	14.5	22.3	33.9	22.3	26.2	31.2	22.3	18.1	13.0	5.1	14.6
CO ₂	27.5	28.0	25.5	28.0	29.2	25.2	28.0	26.2	25.8	5.6	21.1
Productivities (g/kg/hr)											
iC ₄ OH	102	94	54	94	104	176	94	150	109	7	105
iC ₄ Oxygenates	241	276	200	276	220	285	276	388	322	33	192

Table 33. Effect of H₂, CO and CO₂ Co-Feeds on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide				
Run Number	308	313	314	318	319
Conditions	325°C, 30 psig, 2 hr ⁻¹ MeOH WHSV				
MeOH/EtOH	10	10	10	10	10
N ₂ /MeOH	2	2	2	2	2
Other/MeOH	None	2 H ₂	2 CO	1.5 CO ₂	2.8 CO ₂
Conversion (%)					
MeOH	53.4	58.3	29.3	53.3	55.4
EtOH	99.1	99.5	90.5	99.6	98.9
Selectivities (mole %)					
nC ₃ OH	0.4	0.2	2.9	0.2	0.5
nC ₄ OH	0.1	0.0	0.2	0.0	0.0
iC ₄ OH	11.6	14.0	1.6	9.6	7.7
iC ₄ Aldehyde	18.0	11.6	7.5	18.0	15.9
Me iButyrate	4.3	7.3	0.9	6.5	4.9
Other Oxygenates	1.5	3.2	12.8	2.2	2.4
Others (No ID)	7.3	6.4	12.5	4.4	3.3
C ₁ -C ₂ Oxygenates	4.1	3.9	4.9	2.4	1.5
C ₁ -C ₄ Hydrocarbons	1.4	2.6	1.6	1.1	0.6
CO	22.3	24.4	28.1	32.6	36.1
CO ₂	28.0	26.4	27.2	23.0	27.3
Productivities (g/kg/hr)					
iC ₄ OH	94	122	9	78	63
iC ₄ Oxygenates	276	287	57	276	233

Table 34. Conversion of Methanol Only Using Pt on Zn/Mn/Zr Oxide Catalysts

Catalyst Number	8265-76		8265-50		8265-82	
Description	2.0% Pt on Zn/Mn/Zr Oxide (60/20/20)		2.0% Pt on Zn/Mn/Zr Oxide (33/33/33)		2.0% Pt on Zn/Mn/Zr Oxide (10/45/45)	
Run	272	291	258	293	278	292
Feed	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH	MeOH/EtOH	MeOH
Conditions	350 C, 30 psig, 2 hr-1 MeOH WHSV, N2 Inert					
Conversion (%)						
MeOH	58.7	49.6	57.3	49.1	73.3	60.1
EtOH	100.0	-	99.8	-	100.0	-
Selectivity (C%)						
nC3OH	0.0	0.0	0.2	0.0	0.4	0.0
nC4OH	0.0	0.0	0.0	0.0	0.0	0.0
iC4OH	11.1	0.2	10.8	0.2	8.9	0.2
iC4 Aldehyde	17.7	0.3	15.6	0.3	12.0	0.2
Me iButyrate	5.3	0.1	4.9	0.1	7.3	0.1
MeiBu Ether	0.0	0.0	0.0	0.0	0.1	0.0
C5+OH	0.9	0.2	1.1	0.3	1.0	0.1
Other Ald/Ketone	0.8	0.3	0.9	0.3	0.8	0.1
Other Esters	0.3	0.2	0.4	0.2	0.9	0.2
Others	5.3	0.9	9.8	0.8	4.9	0.8
DiME Ether	1.1	7.9	1.3	8.4	1.0	8.9
MeEt Ether	0.0	0.0	0.0	0.0	0.0	0.0
Me Formate	2.5	10.3	2.7	7.3	0.6	3.3
Me Acetate	1.8	0.0	2.2	0.0	0.2	0.0
C1	0.8	6.6	0.9	6.9	0.6	3.1
C2+s	1.1	0.7	2.1	1.2	0.8	0.4
CO	25.4	61.3	21.0	63.6	38.6	72.9
CO2	26.0	11.0	26.2	11.3	22.3	10.0

Table 35. Conversion of Methanol Only at High Temperature and Pressure

Catalyst	Glass Beads (Blank)				8265-98 2% Pt on Zn/Mn/Zr Oxide							
	324				322				323			
	9-16	25-32	41-48		9-16	25-32	41-48		9-16	25-32	41-48	
Run Number												
Hours on Stream												
Conditions	2 hr ⁻¹ MeOH WHSV, 2/1 N ₂ /MeOH (molar)											
Temperature (°C)	350	400	450		350	400	450		350	400	450	
Pressure (psig)	30	30	30		30	30	30		300	300	300	
Conversion (%)												
MeOH	0.2	2.1	8.8		45.9	95.6	95.7		46.7	95.4	96.3	
Selectivities (mole %)												
nC ₃ OH	0.0	1.8	1.2		0.0	0.0	0.0		0.0	0.0	0.0	
nC ₄ OH	0.0	0.7	0.0		0.0	0.0	0.0		0.0	0.0	0.0	
iC ₄ OH	0.0	0.0	0.0		0.1	0.1	0.0		0.2	0.2	0.1	
iC ₄ Aldehyde	0.0	0.6	0.0		0.2	0.3	0.2		0.1	0.1	0.1	
Me iButyrate	0.0	0.0	0.0		0.0	0.0	0.0		0.1	0.0	0.0	
Other Oxygenates	7.8	1.2	0.3		0.4	0.6	0.8		0.3	0.3	0.3	
Others (No ID)	4.7	1.0	0.0		0.2	1.3	0.7		0.2	0.9	0.2	
C ₁ -C ₂ Oxygenates	87.5	54.6	35.0		17.6	0.1	0.1		12.4	0.0	0.1	
C ₁ -C ₄ Hydrocarbons	0.0	4.2	5.0		5.2	6.9	7.6		2.4	2.6	3.4	
CO	0.0	30.9	51.7		67.3	81.2	80.6		76.5	90.9	90.7	
CO ₂	0.0	5.0	6.8		9.0	9.6	9.9		7.9	5.1	5.1	
Productivities (g/kg/hr)												
iC ₄ OH	0	0	0		0	2	0		2	2	0	

Table 36. Evaluation of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion at High H₂ Partial Pressures - Plant 700, Run 326

Catalyst	8265-98 2% Pt on Zn/Mn/Zr (60/20/20) Oxide				
Period HOS	5 33-40	7 49-56	10 73-80	13 97-104	18 137-144
Conditions	325°C, 7/1 MeOH/EtOH (molar), 3/1 N ₂ /MeOH (molar)				
Pressure (psig)	1200	300	50	50	300
MeOH WHSV (hr ⁻¹)	1.0	1.0	0.5	0.5	1.0
H ₂ /MeOH (molar)	15	15	15	0	0
Conversion (%)					
MeOH	15.3	26.3	53.3	61.6	43.9
EtOH	18.9	36.8	78.7	82.8	64.7
Selectivities (mole %)					
nC ₃ OH	0.2	0.2	0.1	2.0	0.0
nC ₄ OH	0.1	1.1	1.3	0.8	1.4
iC ₄ OH	1.1	1.3	3.4	1.9	2.6
iC ₄ Aldehyde	9.1	6.6	3.4	1.7	5.2
Me iButyrate	0.1	0.4	0.4	2.5	1.7
Other Oxygenates	13.2	16.8	13.5	6.6	9.2
Others (No ID)	0.3	2.4	11.9	16.2	12.7
C ₁ -C ₂ Oxygenates	4.1	5.1	1.5	9.2	12.4
C ₁ -C ₄ Hydrocarbons	1.4	0.5	0.4	0.5	0.4
CO	32.0	18.6	14.7	16.3	10.3
CO ₂	38.4	47.0	49.4	42.3	44.0
Productivities (g/kg/hr)					
iC ₄ OH	2	4	7	6	9
iC ₄ Oxygenates	13	19	15	13	35

Table 37. Modelling of Higher Alcohol Synthesis Process

Temperature, °C	325
Pressure, psig	300
MeOH LHSV, hr-1	1
MeOH/EtOH, molar	7
MeOH/N ₂ (H ₂), molar	0.5
Methanol Conv, %	55.18
Ethanol Conv, %	96.95

Assumptions:

1. C₅+ Alcohols are treated as C₅'s
2. "Other" Aldehydes and Ketones are treated as C₅'s
3. "Other" Esters are treated as C₆'s
4. "Other" Hydrocarbons are treated as C₆'s

	% Methanol Conversion	100% Conv Basis	% Ethanol Conversion	100% Conv Basis
Unconverted	44.82		3.05	
CO	12.09	21.91		
CO ₂	17.48	31.68		
n-C ₃ OH	0.44	0.80	3.07	3.17
n-C ₄ OH			0.40	0.41
i-C ₄ OH	7.29	13.21	38.96	40.19
C ₅ + OH	0.67	1.21	9.40	9.70
DME	0.87	1.58		
MeBuEther	0.01	0.02	0.16	0.17
i-C ₄ Aldehyde	1.55	2.81	8.47	8.74
"Other" Ald + Ketone	0.19	0.34	2.60	2.68
MeFormate	0.32	0.58		
MeAcetate	1.18	2.14	8.26	8.52
Me i-Butyrate	1.50	2.72	21.01	21.67
"Other" Esters			4.62	4.77
C ₂	0.61	1.11		
C ₃	0.20	0.36		
C ₅	0.01	0.02		
Other HC	10.77	19.52		
Total	100.00	100.00	100.00	100.00

	C	H	O	Reaction Coefficients for HYSIM Simulation:	
Methanol	1	4	1	Methanol	-100
Ethanol	2	6	1	Ethanol	-100
CO	1		1	CO	21.91
CO ₂	1		2	CO ₂	31.68
n-C ₃ OH	3	8	1	n-C ₃ OH	0.27
n-C ₄ OH	4	10	1	n-C ₄ OH	0.21
i-C ₄ OH	4	10	1	i-C ₄ OH	3.30
C ₅ + OH	5	12	1	C ₅ + OH	0.24
DME	2	6	1	DME	0.79
MeBuEther	5	12	1	MeBuEther	0.00
i-C ₄ Aldehyde	4	8	1	i-C ₄ Aldehyde	0.70
i-Pentanal	5	10	1	i-Pentanal	0.07
MeFormate	2	4	2	MeFormate	0.29
MeAcetate	3	6	2	MeAcetate	0.71
Me i-Butyrate	5	10	2	Me i-Butyrate	0.54
Et i-Butyrate	6	12	2	Et i-Butyrate	1.59
C ₂	2	6		C ₂	0.55
C ₃	3	8		C ₃	0.12
C ₅	5	12		C ₅	0.00
C ₆	6	14		C ₆	3.25
				H ₂	138.8
				H ₂ O	6.26
				C Balance:	100.00
				H Balance:	100.00
				O Balance:	100.00

Table 38. Isobutanol Process - Performance vs. Separator Temperature

Operating Conditions		"Best" Pilot Plant Results	Capital Cost Estimate Basis	Process Simulation				
					—————→			
Fresh Feed,	BPSD		5300	4980	5050	5090	5220	7120
Combined Feed,	BPSD		20300	20300	20300	20300	20300	20300
Fresh MeOH,	BPSD			3700	3750	3780	3870	5300
Combined MeOH,	BPSD			6430	6550	6640	6840	9140
Fresh MeOH,	KG-MOLES/HR			608	617	622	637	872
Combined MeOH,	KG-MOLES/HR			1057	1078	1092	1124	1504
Total Carbon In	KG-MOLES/HR			900	913	921	943	1290
HPS Temp,	°F			59	80	100	120	150
Recycle Gas/Comb Feed,	MOLAR			0.12	0.12	0.12	0.12	0.12
Recycle Gas/Fresh Feed,	MOLAR		1.0	0.33	0.33	0.33	0.33	0.28
Methanol/Ethanol,	MOLAR	7.0		7.0	7.1	7.1	7.1	7.0
H2 Partial Pressure,	PSIA	<29		26	28	25	25	25
Performance Data								
Carbon Conversion,	%			97.0	97.5	97.8	98.3	96.7
Isobutanol Selectivity,	%			22.1	22.2	22.1	22.1	22.2
Isobutanol Yield*,	%			21.5	21.8	21.8	21.5	21.2
Feed and Product Losses, Carbon % of Fresh Feed								
VENT LOSSES								
Methanol				0.3	0.5	0.8	1.3	3.2
Ethanol				0.0	0.0	0.0	0.0	0.1
Isobutanol				0.0	0.0	0.0	0.1	0.3
LIQUID PURGE LOSSES								
Methanol				2.6	1.9	1.3	0.4	0.0
Ethanol				0.0	0.0	0.0	0.0	0.0
Isobutanol				0.0	0.0	0.0	0.0	0.0
TOTAL			95	2.9	2.4	2.1	1.8	3.6

*NOTE: ISOBUTANOL LOST TO VENT IS SUBTRACTED FROM THE TOTAL YIELD

Weight Balance = Total MT Out/Total MT In = 100.08%

Table 39. Isobutanol Process - Material Balance

HYSIM (V2.50) - Generated Material Balance for 120 F Separator Case

	Feed Kg-Moles/hr			Product Kg-Moles/hr						
	Methanol	Ethanol		Recy Vent	Liq Purge	Ovd Vapor	Liq Product	Recy Lq	Recy Gas	
Methanol	650			12.4	4.0	0.2		494.7	2.3	
Ethanol		158		0.1				4.8		
Isobutanol				0.2			52.0	0.5		
C Conv:	98.3									
ICAOH Sol:	22.1									
TOTAL IN: PER DAY	Metric Tons Kg-Moles C Kg-Moles H Kg-Moles O	672 23095 84884 19347	TOTAL OUT: PER DAY	Metric Tons Kg-Moles C Kg-Moles H Kg-Moles O	673 23121 84935 19358					
MOLES C MOLES H MOLES O										
	C	H	O							
Methanol	1	4	1	9.55	3.08	0.17	0.00	400	1598	400
Ethanol	2	8	1	0.08	0.04	0.00	0.00	8	17	3
Hydrogen		2		49.49	0.00	0.12		0	49231	0
CO	1		1	32.81	0.00	0.10		1175	0	1175
CO ₂	1		2	304.09	0.18	2.05		6961	0	13922
n-C ₃ OH	3	8	1	0.92	0.82	0.02	5.89	382	1019	127
n-C ₄ OH	4	10	1	0.01			0.57	31	78	8
i-C ₄ OH	4	10	1	0.39	0.01	0.00	92.48	5015	12538	1254
C ₅ + OH	6	12	1	0.02			15.98	908	2180	182
DME	2	6	1	5.38	0.10	0.05		240	721	120
MeBuEther	5	12	1	0.24	0.05	0.00	0.01	17	41	3
i-C ₄ Aldehyde	4	8	1	12.50	3.67	0.18	2.58	1051	2101	283
i-Pentanal	5	10	1	0.01			4.35	253	507	51
MeFormate	2	4	2	2.48	0.15	0.03		89	177	89
MeAcetate	3	6	2	21.37	2.51	0.29	0.00	979	1958	853
Me i-Butyrate	5	10	2	1.08	0.18	0.01	40.81	2049	4099	820
Et i-Butyrate	6	12	2	0.08			6.84	357	714	119
C ₂	2	6		2.50	0.00	0.01		187	501	0
C ₃	3	8		0.79	0.00	0.01		55	148	0
C ₅	5	12		0.05	0.00	0.00		4	8	0
C ₆	6	14		39.59	2.85	0.58	0.00	2982	6958	0
Water	0	2	1	2.12	960.92	0.04		0	342	171
Total				485.49	14.33	3.84	169.34	23121	84935	19358

Table 40. Isobutanol Process - Summary of Utility Streams

<u>STREAM</u>	<u>DESCRIPTION</u>	<u>UTILITY</u>	<u>QUANTITY</u>
EN1	Feed Pump Power Delta P=325 psig	Electricity	42.3 KW
EN2	Feed Preheater Delta T=280 F End Temp=617 F	Fuel Gas	44.1 MMBtu/hr
EN3-EN5	Reaction Heat	(Assume Adiabatic)	0
EN6	Reactor Effluent Cooler Delta T=43 F End Temp=120 F	Electricity (Air Cooler)	67.1 KW
EN7	Compressor Delta P=40 psig	Electricity	57.1 KW
	Splitter Overhead Condenser Delta T= 144 F End Temp=170 F	Electricity (Air Cooler)	525 KW
EN9	Splitter Reboiler 398 F Bottoms 366 F Feed	MP Steam	199 Mlb/hr
EN10	Liquid Recycle Pump Delta P=115 psig	Electricity	41.8 KW
EN11	Splitter Charge Heater Delta T=175 F End Temp=366 F	MP Steam	74.6 Mlb/hr

Table 41. Calculation of Utility Requirements

#1	<u>Feed Pump</u>	Δ Enthalpy=29.4KW 80% motor eff. Factor for centrifugal pump=1.15	42.3 KW electric
#2	<u>Feed Preheater</u>		44.1 MM Btu/hr fuel gas
#3	<u>Reactor Effluent Cooler</u>	Δ Enthalpy=9.46 MM Btu/hr Cooling air $\Delta T=25^{\circ}\text{F}$ (95°F inlet, 120°F outlet) 0.453 Btu/ft ³ $\Delta P=5.4$ lb/ft ² , 70% fan eff., 90% motor eff.	67.1 KW electric
#4	<u>Recycle Gas Compressor</u>	Δ Enthalpy=39.7 KW 80% motor eff Factor for entrifugal pump=1.15	57.1 KW electric
#5	<u>Splitter Overhead Condenser</u>	Δ Enthalpy=221.2 MM Btu/hr Cooling air $\Delta T=75^{\circ}\text{F}$ (95°F inlet, 170°F outlet) 1.36 Btu/ft ³ $\Delta P=5.4$ lb/ft ² , 70% fan eff., 90% motor eff.	525 KW electric
#6	<u>Splitter Reboiler Bottoms</u>	Δ Enthalpy=161 MMBtu/hr	199 Mlb/hr medium pressure (300psig) steam
#7	<u>Liquid Recycle Pump</u>	Δ Enthalpy=29.1 KW 80% motor eff Factor for centrifugal pump = 1.15	41.8 KW electric
#8	<u>Splitter Charge Heater</u>	60.4 MMBtu/hr	74.6 Mlb/hr medium pressure (300psig) steam

Table 42. Utility Costs Basis

Fuel Oil Value \$0.28 per Gallon =====> \$79 per MT
 Fuel Oil Gravity 0.9500
 Fuel Oil Heat of Combustion 17,000 BTU/lb

HP Steam (Superheated) @600 psig and 700 deg F 1352 BTU/lb
 MP Steam (Saturated) @150 psig 1194 BTU/lb
 LP Steam (Saturated) @50 psig 1174 BTU/lb
 Boiler Feed Water @ 60 deg F 28 BTU/lb
 Boiler Feed Water @ 250 deg F 219 BTU/lb
 Boiler Efficiency 85%
 Boiler Heating Cost as Percent of Total 95%

Utility	Units	Calculated Value
Electrical Power	\$/KWH	\$0.04
High Pressure Steam	\$/MLB	\$3.45 *
Medium Pressure Steam	\$/MLB	\$3.03 *
Low Pressure Steam	\$/MLB	\$2.98 *
Boiler Feed Water	\$/MLB	\$0.42 *
Condensate (Credit)	\$/MLB	\$0.42 *
Cooling Water	\$/MGal	\$0.08
Fuel Fired	\$/MM BTU	\$2.10 *
Inert Gas	MSCF	\$1.32

Recommended Value
\$0.05
\$3.45
\$3.05
\$3.00
\$0.40
\$0.40
\$0.10
\$2.10
\$1.35

* Calculated from fuel oil value

Table 43. Calculation of Total Annual Utility Costs

Electric Power $(\#1 + \#4 + \#3 + \#5 + \#7) = 733.3 \text{ KW} \times 8000 \text{ hr} \times \$0.05/\text{KWH}$

= 0.293 MMS\$/yr

Fuel Gas $(\#2) = 44.1 \text{ MMBtu/hr} \times 8000 \text{ hr} \times \$2.10/\text{MMBtu}$

= 0.741 MMS\$/yr

Medium Pressure(300psig) Steam (#6 + #8)

$274 \text{ Mlb/hr} \times 8000 \text{ hr} \times \$3.05/\text{Mlb}$

= 6.68 MMS\$/yr

Total Utility Costs = 7.71MMS/year

Table 44. Basis for Economic Calculations

Fixed Costs	
Staffing	4.8 Operators/Position
Operator Salaries	\$33,000/yr
Supervision	37% Labor
Direct Overhead	45% Labor/Super
Maintenance	3% ISBL*
Plant Overhead	65% Labor/Maint.
Tax & Insurance	1.5% Fixed Inv*

Total Plant Investment	
ISBL Investment	Curve Costs
Offsites	30% ISBL*
Interest During Construction	10%/yr for 3 years
Royalties	Full UOP Rates
Catalyst/Adsorbent Inventory	Capitalized

Working Capital	
Raw Materials Storage	15 days at Delivered Value
Total Products in Storage	15 Days Cost of Production
Accounts Receivable	30 Days Production (Key Products)
Accounts Payable (Credit)	30 Days Production (Raw Materials)
Cash Kept on Hand	7 Days Gross Profit
Noble Metal Inventory	Full Inventory at Market Value (Pt @ \$376/tr oz)
Warehouse Inventory	2% ISBL Investment*
Chemicals Inventory	Full Inventory at Market Value (Solvent, Desorbent, ect...)

Depreciation	
ISBL Depreciation	10%/yr
Offsite Depreciation	10%/yr
Royalty Depreciation	10%/yr
Inventory Depreciation	10%/yr (Composite Account)
Depreciation Schedule	Straight Line

Capital Expenses	
Interest on Capital	None
Interest on Working Capital	10%/yr

Utility	Units	Value
Electrical Power	\$/KWH	\$0.05
High Pressure Steam	\$/MLB	\$3.45
Medium Pressure Steam	\$/MLB	\$3.05
Low Pressure Steam	\$/MLB	\$3.00
Boiler Feed Water	\$/MLB	\$0.40
Condensate (Credit)	\$/MLB	\$0.40
Cooling Water	\$/MGal	\$0.10
Fuel Fired	\$/MM BTU	\$2.10
Inert Gas	MSCF	\$1.35

* Parameters designated by an asterisk should not be considered in economic evaluations where two or more cases are compared to each other.

Table 45. Base Case Economics for Methanol to Isobutanol

Basis		333.33 8 000	60 days/yr hour/yr	Daily production		95.1 MT/day
VARIABLE COSTS AND REVENUES						
Mass Balance						
	Units	Units/yr	Units	\$MM/yr		
Main products						
Methanol	MT	31,687	903	28.61		
Fuel Gas	MMBtu	120 000	2.00	0.24		
Total products	MT	31,687		28.85		
Feedstocks						
Methanol	MT	186667	150	25.00		
Ethanol	MT	57500	150	8.63		
Total feedstocks		244167		33.63		
Consumables, catalysts, adsorbents, and chemicals						
Catalysts and chemicals			SMT	\$MM/yr		
			15.77	0.50		
Total consumables				0.50		
Utilities						
	Btu/MT	Units/MT	SMT	\$MM/yr		
Power, kWh	0.055	185.1	8 255	0.29		
Steam (HP), Mlb	3.45		0 000	0.00		
Steam (MP), Mlb	3.05	69.16	210 995	6.69		
Steam (LP), Mlb	3.00		0 000	0.00		
Boiler feed water, Mlb	0.40		0 000	0.00		
Condensate, Mlb	0.40		0 000	0.00		
Cooling water, MGal	0.1		0 000	0.00		
Fuel-fired, MMBtu	2.10	11.13	23 373	0.74		
Hot gas, Mlb	0.045		0 000	0.00		
Total utilities			243.63	7.72		
FIXED OPERATING COSTS						
				\$MM/yr		
Labor						
Operators per shift	4.8	333 000	per year	0.76		
Supervisors	37%	of operating labor		0.28		
Direct overhead	45%	of labor & superv.		0.47		
				1.51		
Maintenance						
Materials and labor	3%	of ISBL investment		0.18		
Overhead expenses						
Plant overhead	65%	of labor & maintenance		1.10		
Taxes and insurance	1.5%	of fixed investment		0.14		
				1.23		
Other expenses						
Waste of catalyst (debt)	0%	per year (100% equity)		0.21		
Waste of working capital	10%	per year		0.21		
Product shipping	\$10	per MT		0.32		
Sales and admin.	0.2%	of sales		0.06		
				0.59		
CAPITAL CHARGES						
Depreciation and amortization						
ISBL	10%	per year		0.68		
OSBL	10%	per year		0.24		
Royalties	10%	per year		0.00		
Capitalized inventories	10%	per year		0.00		
				0.92		
CAPITAL ITEMS						
Plant investment				\$MM		
M & L				4.4		
DE & CE				1.5		
ISBL				5.9		
OSBL @ 35% ISBL				2.07		
Interest @ 10% 2 year				1.23		
Total fixed investment				15.20		
Working capital				\$MM		
Feedstock storage	15 days			1.51		
Main product storage	15 days			1.29		
By-product storage	15 days			0.00		
Accts. receivable	30 days			2.60		
Accts. payable	30 days			(3.03)		
Cash in hand	7 days			(0.35)		
Spares	2% ISBL			0.12		
Total working capital				2.14		
Catalysts, adsorbents, and chemicals inventory						
Catalysts						
Chemicals						
Total inventory				0.50		
ECONOMIC ANALYSIS						
				\$MM/yr	\$MT	\$/lb
					%	cents/lb
Gross margin						
Main product sales				28.85	910.57	0.41
By-product sales						
Minus feedstock cost				33.63	1 061.16	0.48
						72.7
Gross margin				(4.77)	(160.59)	(0.67)
						(43.82)
Variable costs						
Consumables				0.50	15.77	0.01
Utilities				7.72	243.63	0.11
						4.56
Total variable costs				8.22	259.40	0.12
						17.8
						75.48
Fixed costs						
Labor				1.51	47.67	0.02
Maintenance				0.18	5.59	0.00
Overhead expenses				1.23	38.67	0.02
Other expenses				0.59	18.56	0.01
						5.41
Total fixed costs				3.51	110.50	0.06
						7.6
						32.24
Cash cost of production						
				48.36	1 431.36	0.65
						416.53
Cash cost of production for main product						
				48.36	1 431.36	0.65
						416.53
Cash flow						
				(16.50)	(520.79)	(0.34)
						(151.55)
Capital charges						
Plant depreciation				0.92	28.03	0.01
Royalty amortization				0.00	0.00	0.00
Inventory amortization				0.00	0.00	0.00
						0.00
Total capital charges				0.92	28.03	0.01
						2.0
						8.45
Net cost of production						
				46.28	1 460.39	0.66
						100.0
						424.97
Net cost of production for main product						
				46.28	1 460.39	0.66
						424.97
Pre-tax income						
				(17.42)	(549.82)	(0.26)
						(160.00)
Simple pre-tax ROI, %						
				(189.38)		
Simple payback, years						
				(0.56)		
DCF IRR, %						
				ERR @ 10 years	ERR @ 20 years	
DCF payback, years						
				(0.58) @ 20%	(0.57) @ 10%	
Main product						
20% IRR	1 483.04	@ 10 years		1 483.41	@ 20 years	
30% IRR	1 517.70	@ 10 years		1 511.35	@ 20 years	
40% IRR	1 544.06	@ 10 years		1 540.06	@ 20 years	

Table 46. Summary of Economic Cases

(\$9.2 MM Capital Investment is Assumed for 500 MT/day Methanol Consumption in Each Case)

CASE I. BASE CASE

Assume: Best Results from UOP Research Pilot Plant Work are Obtained Commercially, Isobutanal in the Product Stream has the Same Value as Isobutanol

This Implies:

- 22.2% Carbon Selectivity to Isobutanol + Isobutanal Gives 31687 MT/yr Product**
- H₂, CO, and CO₂ Byproducts Give 120,000 MMBtu/yr Fuel Gas Credit**
- Utilities Costs to Fractionate Liquid Byproducts from Main Product are 7.72 MMS/yr**

CASE II

Assume: All Isobutanal Produced is a Reaction Intermediate and Therefore Eventually Converted to the Desired Isobutanol Product

This Implies:

- 26.1% Carbon Selectivity to Isobutanol Gives 37137 MT/yr Product**
- Same Fuel Gas Credit as the Base Case**
- Same Utilities Costs as the Base Case**

CASE III

Assume: 50% Selectivity to Isobutanol is Achievable Commercially

This Implies:

- 50% Carbon Selectivity to Isobutanol Gives 71264 MT/yr Product**
- Fuel Gas Credit is Reduced 30% from the Base Case**
- Utilities Costs are Reduced 50% from the Base Case**

CASE IV

Assume: 100% Selectivity to Isobutanol is Achievable Commercially

This Implies:

- 100% Carbon Selectivity to Isobutanol Gives 142528 MT/yr Product**
- No Fuel Gas Credit**
- Utilities Costs are Reduced 75% from the Base Case**

Table 47. Basis for Economic Analysis

(500 MT per Day Methanol Feed)

CASE NUMBER

I II III IV

Carbon % Selectivity to Isobutanol	22	26	50	100
Feed (Methanol + Ethanol) Requirement MT/yr	224000	224000	224000	224000
Product (Isobutanol + Isobutanol) Generation MT/yr	31700	37100	71300	142500
Feed Cost (\$150 per MT for both MeOH and EtOH) MM\$/yr	33.63	33.63	33.63	33.63
Utilities Cost MM\$/yr	7.72	7.72	3.86	1.93
Fixed Capital Investment MMS	9.20	9.20	9.20	9.20
Product Sale Price Needed for 20% IRR \$/MT	1490	1270	620	310

Table 48. Isosynthesis Catalyst List

Catalyst	Description	Surface Area, m ² /g	Calcination Temp, °C
IS-1	ZrO ₂ ^b	63	500
IS-2	ZrO ₂ ^b	74	450
IS-3	ZrO ₂ ^b	28	600
IS-4	ZrO ₂ ^b	35	550
IS-5	ZrO ₂	45	600
IS-6	1% Y-ZrO ₂	71	600
IS-7	3% Si-ZrO ₂	120	600
IS-8	Commercial-CeO ₂	2.3	-
IS-9	CeO ₂ ^b	69.9	500
IS-10	1% Ba-ZrO ₂	71.4	550
IS-11	ZrO ₂	81.0	500
IS-12	2% Ba-ZrO ₂	95.6	500
IS-13	ZrO ₂	60	550
IS-14	1% Cs-ZrO ₂	64.6	500
IS-16	ZrO ₂	73.6	500
IS-17	2% Cs-ZrO ₂	110	500
IS-18	50% IS-16 + 50% Clay	-	-
IS-19	1% Cu-ZrO ₂ ^c	71.9	450
IS-20	1% Co-ZrO ₂ ^c	71.9	450
IS-21	ZrO ₂	88.0	500
IS-22	5% Y-ZrO ₂	123.0	500
IS-23	8% La-ZrO ₂	119.0	500
IS-24	15% Zr-SiO ₂	514.0	650
IS-25	Bi ₂ O ₃ ^b	-	500
IS-26	ZrO ₂	91.0	475
IS-27	10% Zr-SiO ₂	253	450
IS-28	10% Zr-SiO ₂ -Al ₂ O ₃	299	450
IS-29	1% Y-ZrO ₂ /n-C ₇ ^a	-	450
IS-30	1% Cs-ZrO ₂ /EtOH ^a	-	450
IS-31	1% Cs-ZrO ₂ /Me ₂ CO ^a	-	450
IS-32	ZrO ₂	95	475
IS-33	ZrO ₂	107	450
IS-34	ZrO ₂	122	425

^a Solvent Extracted^b Precipitated^c Prepared by spray-impregnating nitrate salt onto IS-16

Table 49. Isosynthesis Run Summary

Run	Cat.	Description	Feed H ₂ :CO Ratio	Feed Additive	CO Conv., %	iC4= Yield, %
1	IS-1	ZrO ₂	1:1	None	16.7	1.50
5	-	Blank	1:1	None	0.4	0.00
6	IS-3	ZrO ₂	1:1	None	4.9	0.79
7	IS-4	ZrO ₂	1:1	None	15.3	1.56
8	IS-1	ZrO ₂	1:1	None	17.5	1.54
9	IS-5	ZrO ₂ , sol-gel	1:1	None	23.9	2.21
10	IS-6	1% Y-ZrO ₂ , sol-gel	1:1	None	26.4	1.69
11	IS-7	3% Si-ZrO ₂ , sol-gel	1:1	None	18.7	0.77
12	IS-5	ZrO ₂ , sol-gel	1:1	None	34.9	1.51
13	IS-8	CeO ₂	1:1	None	4.6	0.00
14	IS-9	CeO ₂	1:1	None	43.2	0.75
15	IS-10	1% Ba-ZrO ₂ , sol-gel	1:1	None	24.6	1.54
16	IS-11	ZrO ₂ , sol-gel	1:1	None	30.2	2.23
17	IS-12	2% Ba-ZrO ₂ , sol-gel	1:1	None	23.0	2.24
18	IS-11	ZrO ₂ , sol-gel	0.7:1	None	25.2	1.89
19	IS-14	1% Cs-ZrO ₂ , sol-gel	1:1	None	25.0	2.27
20	IS-15	2% Ba on IS-11	1:1	None	24.4	2.18
21	IS-16	ZrO ₂ , sol-gel	1:1	None	21.9	2.26
22	IS-17	2% Cs-ZrO ₂ , sol-gel	1:1	None	23.1	1.76
23	IS-18	50% IS-16 + clay	1:1	None	25.8	2.23
24	IS-17	2% Cs-ZrO ₂ , sol-gel	0.5:1	None	15.7	1.14
25	IS-17	2% Cs-ZrO ₂ , sol-gel	0.5:1	None	17.5	1.13
26	IS-17	2% Cs-ZrO ₂ , sol-gel	0.5:1	None	12.6	1.17
27	IS-14	1% Cs-ZrO ₂ , sol-gel	0.5:1	None	17.8	1.71
28	IS-17	2% Cs-ZrO ₂ , sol-gel	0.5:1	None	13.1	0.57
29	IS-19	1% Cu-ZrO ₂ , sol-gel	1:1	None	27.9	2.17
30	IS-20	1% Co-ZrO ₂ , sol-gel	1:1	None	28.7	1.43
31	IS-17	2% Cs-ZrO ₂ , sol-gel	0.5:1	None	17.1	1.16
32	IS-21	ZrO ₂ , sol-gel	1:1	None	23.9	2.28
33	IS-21	ZrO ₂ , sol-gel	1:1	None	21.8	1.53

Table 49. (con't.) Isosynthesis Run Summary

Run	Cat.	Description	Feed H ₂ :CO Ratio	Feed Additive	CO Conv., %	iC4= Yield, %
34	IS-21	ZrO ₂ , sol-gel	2:1	None	21.3	2.33
35	IS-23	8% La-ZrO ₂ , sol-gel	2:1	None	24.4	1.13
36	IS-22	5% Y-ZrO ₂ , sol-gel	2:1	None	23.7	1.14
37	IS-24	15% Zr-SiO ₂ , sol-gel	2:1	None	1.5	0.00
38	IS-25	Bi ₂ O ₃ , precip.	2:1	None	2.2	0.00
39	IS-21	ZrO ₂ , sol-gel	2:1	Ethylene	-	1.39
40	IS-21	ZrO ₂ , sol-gel	2:1	Propylene	-	1.16
41	IS-21	ZrO ₂ , sol-gel	2:1	Propylene	-	1.50
42	IS-26	ZrO ₂ , sol-gel	2:1	Propylene	-	2.14
43	IS-26	ZrO ₂ , sol-gel	2:1	None	20.99	2.10
44	IS-26	ZrO ₂ , sol-gel	2:1	None	27.17	2.76
45	IS-27	10% Zr-SiO ₂ , sol-gel	2:1	None	2.12	0.00
46	IS-28	10% Zr-SiO ₂ -Al ₂ O ₃ , sol-gel	2:1	None	2.35	0.00
47	IS-26	ZrO ₂ , sol-gel	2:1	Ethanol	19.48	1.72
48	IS-29	1% Y-ZrO ₂ , extracted	2:1	None	27.0	1.86
49	IS-30	1% Cs-ZrO ₂ , extracted	2:1	None	29.7	1.76
50	IS-31	1% Cs-ZrO ₂ , extracted	2:1	None	28.3	1.53
51	IS-13	ZrO ₂ , sol-gel	2:1	None	19.6	1.70
52	IS-13	ZrO ₂ , sol-gel	2:1	None	20.5	2.00
53	IS-32	ZrO ₂ , sol-gel	2:1	None	16.4	2.41
54	IS-33	ZrO ₂ , sol-gel	2:1	None	28.9	3.70
55	IS-34	ZrO ₂ , sol-gel	2:1	None	31.7	3.75
56	IS-33	ZrO ₂ , sol-gel	1:1	None	23.0	2.32
57	IS-21	ZrO ₂ , sol-gel	2:1	None	33.8	1.24
58	IS-32	ZrO ₂ , sol-gel	2:1	None	27.8	3.57
59	IS-33	ZrO ₂ , sol-gel	2:1	None	25.5	3.17

Table 50. Effect of Catalyst Calcination Temperature and Surface Area

Calcination Temperature, °C	Surface Area, m ² /g	Isobutylene Yield, %
550	60	2.00
500	88	2.33
475	95	2.41
450	107	3.70
425	122	3.75

Table 51. Effect of Additives to Zirconia Catalysts on Isobutylene Selectivity

Additive	Isobutene Yield, %
None	2.26
1% Y	1.69
3% Si	0.77
1% Ba	1.54
2% Ba	2.24
1% Cs	2.27
2% Cs	1.76
1% Cu	2.17
1% Co	2.14

Table 52. Non-Zirconia Catalysts

Catalyst	Isobutylene Yield, %
ZrO ₂	3.75
CeO ₂ - Commercial	0.00
CeO ₂ - Precipitated	0.75
Bi ₂ O ₃	0.00

Table 53. Effect of Intermediate Recycle

Intermediate	Major Products
Ethylene	Ethane, <i>n</i> -Butene, Heavies
Propylene	Propane, Heavies, Ethylene
Ethanol	Ethylene, Ethane, Propylene, <i>n</i> -Butene, Heavies
Methanol	Methane, Dimethyl Ether

Table 54. Effect of Pressure
(450°C, 960 hr⁻¹ GHSV, 1/1 H₂/CO)

Pressure (psig)	300	600	1200
CO conversion (%)	6.3	13.6	20.9
Selectivity (%C)			
CO ₂	67.7	53.6	54.5
C ₁	19.4	17.4	19.1
I-C ₄	0	5.8	7.3
I-C ₄ ⁺	0	5.8	3.6

Table 55. Effect of Temperature
(1200 psig, 960 hr⁻¹ GHSV, 1/1 H₂/CO)

Temperature (°C)	353	450	500
CO conversion (%)	1.7	20.9	42.3
Selectivity (%C)			
CO ₂	87.5	54.5	45.3
C ₁	12.5	19.1	21.3
I-C ₄	0	7.3	10.5
I-C ₄ ⁺	0	3.6	0

Table 56. Effect of Space Velocity
(450°C, 1200 psig, 1/1 H₂/CO)

CO GHSV (cc/cc cat/hr)	540	960	2100
CO conversion (%)	36.8	20.9	16.7
Selectivity (%C)			
CO ₂	48.8	54.5	49.4
C ₁	17.5	19.1	15.7
I-C ₄	11.1	7.3	9.0
I-C ₄ ⁺	3.7	3.6	9.0

Table 57. Effect of H₂/CO Feed Ratio
(450°C, 1200 psig, 960 hr⁻¹ GHSV)

H ₂ /CO Ratio	Catalyst	CO Conversion, %	Isobutylene Yield, %
0.5	IS-17	15.7	1.14
1.0	IS-17	23.1	1.76
1.0	IS-21	21.8	1.53
2.0	IS-21	21.3	2.33

6 FIGURES

Figure 1.

a = C_1 chain growth at α -carbon
b = C_1 chain growth at β -carbon
c = C_2 chain growth at β -carbon

Figure 2.

LINEAR GROWTH

BRANCHED GROWTH

Figure 3.

COMPARISON OF BRUCITE AND HYDROTALCITE

BRUCITE

HYDROTALCITE

UOP 1866A-6

Figure 4.

Figure 5.

Figure 6.

Cu/Zn/Al Performance vs. Space Time Methanol/Ethanol to Higher Alcohols

Figure 7.

Cu/Zn/Al Performance vs. Space Time Methanol/Ethanol to Higher Alcohols

Figure 8.

Figure 9.

Figure 10.

Pt on Zn/Mn/Zr Oxide Performance vs. Space Time
Methanol/Ethanol to Higher Alcohols

Figure 11.

Figure 12.

Pt on Zn/Mn/Zr Oxide Performance vs. Space Time Methanol/Ethanol to Higher Alcohols

Figure 13.

Figure 14.

2% Pt on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

Run Number
MeOH/EtOH Conversions (%)
iC₄OH/iC₄ Ald/Sum C₄+ Selectivities (mole %)
iC₄OH/Sum C₄+ Productivities (g/kg cat/hr)

Figure 15.

2% Pt on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

Run Number
Me Formate/Me Acetate Selectivities (mole %)
CO/CO₂ Selectivities (mole %)

Figure 16.

2% Pd on Zn/Mn/Zr Oxide Catalysts Effect of Support Composition

Testing Conditions: 350 °C, 30 psig, 2 hr⁻¹ MeOH WHSV,
1/0.1/2 MeOH/EtOH/N₂ (molar)

Figure 17.

Figure 18.

Figure 19.

Comparison of MeOH/EtOH and MeOH-only Feeds
 Conditions: 350 C. 30 psig. 2 hr-1 MeOH WHSV. 1/0.1/2 or 1/0/2 MeOH/EtOH/N₂ (molar)

Figure 20.

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NOE120#H.SIM

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Figure 22.

VENT LOSSES vs SEPARATOR TEMPERATURE

DOE ISOBUTANOL SYNTHESIS SIMULATION

250 psig separator pressure, 7/1 MeOH/EtOH and ¹³⁵25 psia H₂ partial pressure in combined feed

Figure 23.

LIQUID PURGE, VENT, AND TOTAL FEED & PROD LOSSES vs SEPARATOR TEMPERATURE
DOE ISOBUTANOL SYNTHESIS SIMULATION

250 psig separator pressure, 7/1 MeOH/EtOH and 25 psia H₂ partial pressure in combined feed

Figure 24.

PRODUCT PRICE NEEDED FOR 20% INTERNAL RATE OF RETURN vs SELECTIVITY
DOE ISOBUTANOL SYNTHESIS ECONOMICS

Base Case = 22.1% Carbon Selectivity to Isobutanol from Pilot Plant Studies

7 APPENDIX

UOP Memorandum

Date: November 20, 1995

To: Ben Spehlmann

From: Cost Engineering

Subject:

DOE PROJECT

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**Proposed Isobutanol Synthesis
Approximate Capital Cost No. 95125
Re: Your Memo Dated October 25, 1995
728008-15**

We are noting the preliminary curve-type Capital Costs (based on U.S.A. Gulf Coast erection to UOP Standards) for the units as described below, exclusive of offsites. The estimated costs given below are on an open shop (non-union) labor basis.

Unit

Penex Unit

Fresh Feed, BPSD	5300
Combined Feed, BPSD	20,300
Sep. Press. PSIG	450
H ₂ /Hr	1.0
Makeup Gas Compressor	Not Included
Makeup Gas Driers	Not Included
Feed Driers	Not Included
Stabilizer	Included
Off Gas Scrubber	Not Included

Approximate Capital Cost - Class C ($\pm 30\%$)

Penex Unit, M+L - \$MM	\$4.4
DE+CE \$MM	<u>1.5</u>
Estimated Erected Cost	\$5.9MM

D.L. Oak

Date: November 20, 1995
To: Ben Spehlmann
Subject: DOE Project
Page 2 of 3

Please find below a list of items not included in our curve cost estimates along with a list of our assumptions regarding economic conditions. It is important that these lists be given to the recipient of this estimate. The recipient could then understand UOP's scope and basis, as well as those project specific costs not addressed by our curves. This knowledge enables the recipient to select from, and make allowances for, those additional items that are applicable to this specific project. Cost Estimating is available to provide support for both the cost numbers and the estimate's scope and basis.

ITEMS NOT INCLUDED IN UOP COST ESTIMATES OF BATTERY LIMIT COSTS, UNLESS SPECIFIED AS INCLUDED:

1. Cost of land, site preparation, and soil investigation
2. Piling or any unusual foundation requirements
3. Docks, marine terminals, or jetties
4. Access roads to site
5. Home Office Administration Building
6. Worker's transportation allowance, employee housing, worker's barracks, canteens, and recreation facilities
7. Overtime pay during construction
8. Know-how fees and royalties on licensed processes
9. Owner's expenses in developing the project
10. Local permits, taxes and fees, or specific costs of doing business in the area
11. Items concerned with export shipments, such as ocean freight, export crating, marine insurances, import taxes and customs
12. Operating capital and investment in goods in the process
13. Escalation on materials and labor due to price fluctuation or economic conditions
14. Contingencies
15. Cost of startup including testing, manpower, utilities, operating manuals and training programs
16. Spare parts, special tools or maintenance equipment
17. Catalyst, chemicals and raw materials including initial fills or inventories
18. Customer or national standards or codes
19. Special pollution or noise control facilities
20. Electrical main substations
21. Power generation
22. Water or hydrocarbon pipelines
23. Additions or extension to utilities systems or offsites
24. Laboratory facilities or supplies
25. Special communications or computer systems

Date: November 20, 1995
To: Ben Spehlmann
Subject: DOE Project
Page 3 of 3

**THE FOLLOWING ASSUMPTIONS ARE NORMALLY MADE REGARDING
ECONOMIC CONDITIONS AT THE TIME THE JOB IS BID:**

1. There will be an adequate supply of skilled labor available for construction.
2. There will be a reimbursable contract with a fixed cost for Home Office services.
3. The plant will be constructed in the U.S. Gulf Coast.
4. There is no lost time due to climatic conditions.
5. Material and labor prices are based on the date of the estimate.

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