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 Cu/Zn/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 sold 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 methnaol/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 C_5-C_6 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 C_4 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 H_2SO_4, 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 TiO_2 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 H_2 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 C_{4+} 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/H_2 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 C_{4+} 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 C_{2+} 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 the 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/H_2 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 K_2CO_3 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 ^{13}C labeled methanol is added to the CO/H_2 feed over a Cu/Zn oxide catalyst the ethanol product obtained has all three combinations of ^{12}C and ^{13}C labeling in comparable amounts [28]. They interpreted this result as indicating that a C_1 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 ^{13}C enrichment in the α and $\alpha+\beta$ carbons, respectively [29]. This result indicates that the C_1 intermediate involved in linear chain growth is formed preferentially from methanol rather than from CO. The identity of this C_1 intermediate as formyl has been suggested by chemical trapping experiments, spectroscopic observations and quantum chemical calculations.

Further ^{13}C labeling studies on the Cs-modified Cu/Zn oxide catalyst system indicate that a second reaction pathway exists for the chain growth of C_{4+} oxygenates by the addition of C_1 or C_2 fragments to the β carbon of the growing chain [30]. Examples of this step include the formation of $^{13}CH_3CH_2CH_2OH$ from $CH_3{}^{13}CH_2OH + CH_3OH$ and $(^{13}CH_3)_2CHCH_2OH$ from $CH_3CH_2CH_2OH + {}^{13}CH_3OH$. 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 m^2/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 described 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.