THE THERMODYNAMICS OF HIGHER ALCOHOL SYNTHESIS

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Liquefaction Contractor's Review Meeting
U. S. Department of Energy
Pittsburgh Energy Technology Center
September 3-5, 1991
Pittsburgh, PA

ABSTRACT

The thermodynamics of the formation of mixed alcohols from synthesis gas was investigated by calculating the equilibrium composition of a system containing CO, H_2, CO_2, H_2O and all of the possible isomers of the C_1 through C_4 alcohols. These calculations were performed using the Gibbs free energy minimization module in the ASPEN PLUS process simulation package.

The calculations that have been performed to date are based on the assumption that all of the reactants and products are ideal gases. Parametric studies were carried out to define the effects of temperature, total pressure, CO/H_2 ratio and the presence or absence of the water-gas shift reaction on the conversion of reactants and on the product distribution. The feed was assumed to consist of a mixture of H_2 and CO, with no other components present. The major conclusions from the work to date are: 1) the apparent stoichiometry of alcohol formation depends on the extent to which the shift reaction takes place; 2) the equilibrium conversion of the limiting reactant is above 90% at all temperatures up to 773 °K; 3) the C_4 alcohols are the dominant product at all temperatures up to 773 °K; at equilibrium, only minor amounts of the C_1 through C_3 alcohols are formed; 4) tertiary butanol is the preferred C_4 alcohol isomer below about 473 °K; between about 473 and 773 °K, isobutanol is the preferred species, and; 5) total pressure has very little effect on reactant conversion and product distribution.

INTRODUCTION

North Carolina State University is in the first year of a three-year contract with the Department of Energy entitled *Novel Approaches to the Production of Higher Alcohols from Synthesis Gas* (DE-AC22-90PC90043). The structure of the contract is shown in Table 1.

Table 1
Contract Structure

Task Number	Title
1	Program Management
2	Liquid-Phase, Higher Alcohol Process With Recycle Of Lower Alcohols
3	Novel Catalysts For Synthesis Of Higher Alcohols
4	Synthesis Of Higher Alcohols Via Acid-Base Catalysis
5	Technology Evaluation

The experimental equipment required for Tasks 2, 3 and 4 is currently in various stages of procurement, installation and debugging. The experimental data that have been obtained to date are not sufficient to form the basis for a paper. The major objective of Task 5 is to develop process designs and perform economic evaluations based on the results of Tasks 2, 3 and 4; this task will not produce substantive results until comprehensive experimental data are available.

In many of the existing experimental studies of the synthesis of higher alcohols from mixtures of H_2 and CO (synthesis gas), methanol has been the primary product and the yields of C_2 and higher alcohols have been disappointingly low. A good deal of research has gone into developing catalysts with greater selectivity towards C_2^+ alcohols. Some additional research on improved catalysts for the production of higher alcohols will be carried out under Task 3 of this contract. Special emphasis will be placed on

catalysts that can be employed in a liquid-phase, i.e., slurry-reactor, process.

It may also be possible to modify the process design, using the principles of chemical equilibrium, to increase the production of higher alcohols. One of the concepts that will be tested in Task 2 is the recycle of lower-molecular-weight alcohols, such as methanol and perhaps ethanol, in order to shift the net product distribution towards the more valuable higher alcohols. By recycling a sufficient amount of the undesired species, e.g., methanol, to satisfy the equilibrium relationship for the methanol synthesis reaction, it should be possible to prevent any *net* formation of that species. Under that circumstance, all of the synthesis gas that was converted to alcohol would go into the desired species.

In order to provide a theoretical basis for testing this process concept, a detailed study of the chemical equilibria that apply to the production of higher alcohols from synthesis gas was initiated. The results that have been obtained to date are reported in the following sections of this paper. These results will help to guide experimental studies aimed at testing the utility of the alcohol recycle concept. They will also be useful in understanding the boundaries and constraints that thermodynamics imposes on process and catalyst development.

SCOPE OF STUDY

The reactions considered in this study were:

Alcohol Synthesis:

$$n\,CO + 2n\,H_2 \leftrightarrow C_nH_{(2n+1)}OH + (n-1)\,H_2O \qquad (I)$$

$$n = 1, 2, 3, 4$$

Water-Gas Shift:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (II)$$

In these chemical equations, the symbol "↔" indicates that the reaction is thermodynamically reversible.

Only the reactions that produce the C_1 through C_4 alcohols were considered in the following calculations; it was assumed that the C_5^+ alcohols would not form. All of the possible isomers of propanol and butanol were considered, i.e., normal propanol, isopropanol, normal butanol, secondary butanol, isobutanol and tertiary butanol. Isobutanol and tertiary butanol have branched hydrocarbon backbones. As gasoline additives, these two alcohols have higher octane ratings than their unbranched counterparts, whether they are used directly or are used as building blocks to form ethers for use as additives.

When the formation of the C_3 and C_4 alcohol isomers is considered, there are nine reactions that are in simultaneous chemical equilibrium, Reaction II plus eight reactions of the form of Reaction I. For each of these reactions, an equilibrium expression can be written that relates the concentrations of the reactants and products to an equilibrium constant, K_i, which is a function only of temperature. Assuming that all of the species are gases, the equilibrium expression has the form:

$$K_i = \Pi_j(f_j^{\nu j,i}) = \Pi_j(\phi_j p_j^{\nu j,i}) \qquad (1)$$

In Equation 1, the subscript j denotes a chemical species, the subscript i denotes a reaction, Π_j denotes the product over all j, $\nu_{j,i}$ is the stoichiometric coefficient of species j in reaction i, f is the fugacity, ϕ is the fugacity coefficient and p is the partial pressure. The stoichiometric coefficient, $\nu_{j,i}$, is positive if j is a product in Reaction i and is negative if j is a reactant. In all of the following calculations, ideal gas behavior has been assumed, so that $\phi_j = 1.0$.

There are twelve different chemical compounds in the system, whose partial pressures at equilibrium are unknown. In concept, the equilibrium composition of the system can be determined by simultaneously solving nine equilibrium expressions, one for each of

the nine reactions, together with the three elemental balances for C, H and O. However, when multiple equilibria are involved, it is frequently easier to solve for the equilibrium composition of the system by using mathematical techniques that minimize the total Gibbs free energy of the system, subject to the constraints of the elemental balances.

The compositions that follow were calculated using the Gibbs free energy minimization module in the ASPEN PLUS process simulation package. The temperature and total pressure of the system were specified as part of the input to the program, as were the number of moles of each component in the feed. The other required input to the program was the species present, i.e., all of the chemical compounds that were either reactants or products in any of the chemical reactions. Each of the twelve chemical compounds involved in the present study is included in the ASPEN PLUS Pure Component Data Base. This data base contains the atomic formula for each compound and the thermochemical data, i.e., standard Gibbs free energy of formation, standard enthalpy of formation, and heat capacity as a function of temperature, that is required to minimize the total Gibbs free energy of the system.

In some of the calculations described below, it was assumed that the water-gas shift, Reaction II, did not take place. Calculations for this case were performed as described above, except that CO_2 was not listed in the input to the program as an allowable species.

As noted previously, the calculations described in this paper are based on the assumption that each of the reactants and products behaves as as ideal gas. This assumption is an idealization in two respects: 1) some of the gaseous species, e.g., the alcohols, are non-ideal at some of the conditions of temperature and total pressure that are covered by the calculations, and; 2) at the high product concentrations that result from the assumption that chemical equilibrium is attained, the partial pressures of certain species, e.g., the branched butanols and water, can exceed their equilibrium vapor pressure. Nevertheless, the results obtained under the ideal gas assumption provide a "baseline" for evaluating the overall thermodynamic constraints on system behavior and for evaluating

the potential utility of process concepts such as product recycle.

RESULTS

Stoichiometric Impact of the Shift Reaction

An examination of Reaction I shows that the number of atoms of oxygen in the carbon monoxide that reacts is greater than the number of atoms of oxygen in the alcohol that is formed, except for n = 1, where the atoms of oxygen in the reacted CO exactly equal those in the product methanol. According to Reaction I, this excess oxygen is "rejected" via the formation of water. When alcohols are formed according to Reaction I, the stoichiometric CO/H_2 ratio is 0.50 for all values of n.

Reaction II, the water-gas shift reaction, may be multiplied by (n-1) and added to Reaction I to give:

$$(2n-1)\ CO + (n+1)\ H_2 \leftrightarrow C_nH_{(2n+1)}OH + (n-1)\ CO_2 \qquad (III)$$

Equation III describes a situation where oxygen is rejected via CO_2 instead of H_2O. In this case, the stoichiometry of alcohol formation depends on the molecular weight of the alcohol, as shown in Table 2.

Table 2

Stoichiometry Of Alcohol Formation From Synthesis Gas When Oxygen Is Rejected Via CO_2

n	Stoichiometric Ratio CO/H_2	CO_2/CO
1	0.5	0
2	1.0	0.33
3	1.25	0.40
4	1.40	0.43

Alcohol formation from synthesis gas is similar to Fischer-Tropsch

chemistry in some respects. In both reactions, oxygen can be rejected via either CO_2 or H_2O, depending on the shift activity of the catalyst and the operating conditions of the process. Moreover, in both cases, the apparent stoichiometry of the reaction depends on the molecular weight of the products, at least for low carbon numbers.

The Effect of Temperature on Reaction Behavior

A series of calculations was carried out to define the effect of temperature on the thermodynamics of alcohol synthesis. The total pressure, P, was 70 atmospheres absolute and the feed consisted only of CO and H_2 in a 1/2 molar ratio for all of the calculations in this series. The shift reaction was permitted to come to equilibrium.

For the reactants, CO and H_2, the results are expressed in terms of the percentage conversion, x_j, defined as:

$$x_j = 100(\text{moles j in} - \text{moles j out})/\text{moles j in}$$

For the products, the results are expressed as the fractional yield of product j based on CO, Y(j/CO), defined as:

$$Y(j/CO) = (\text{atoms of C/molecule of j})(\text{moles j out-moles j in}) \div (\text{moles CO in-moles CO out})$$

The fractional yield of any species, j, is equal to the fraction of the carbon atoms in the CO that actually reacts that are found in the "j" that leaves the system.

The calculated conversions of H_2 and CO are shown in Figure 1 as a function of temperature over the range from 300°K to 800°K. Most experimental research on the formation of higher alcohols has been conducted in the temperature range of 500 to 700°K. Calculations were carried out at lower temperatures in order to understand the impact of using thermodynamic data at 298°K, without any temperature correction, to evaluate the behavior of the system at reaction conditions.

Figure 1
Conversion As A Function Of Temperature

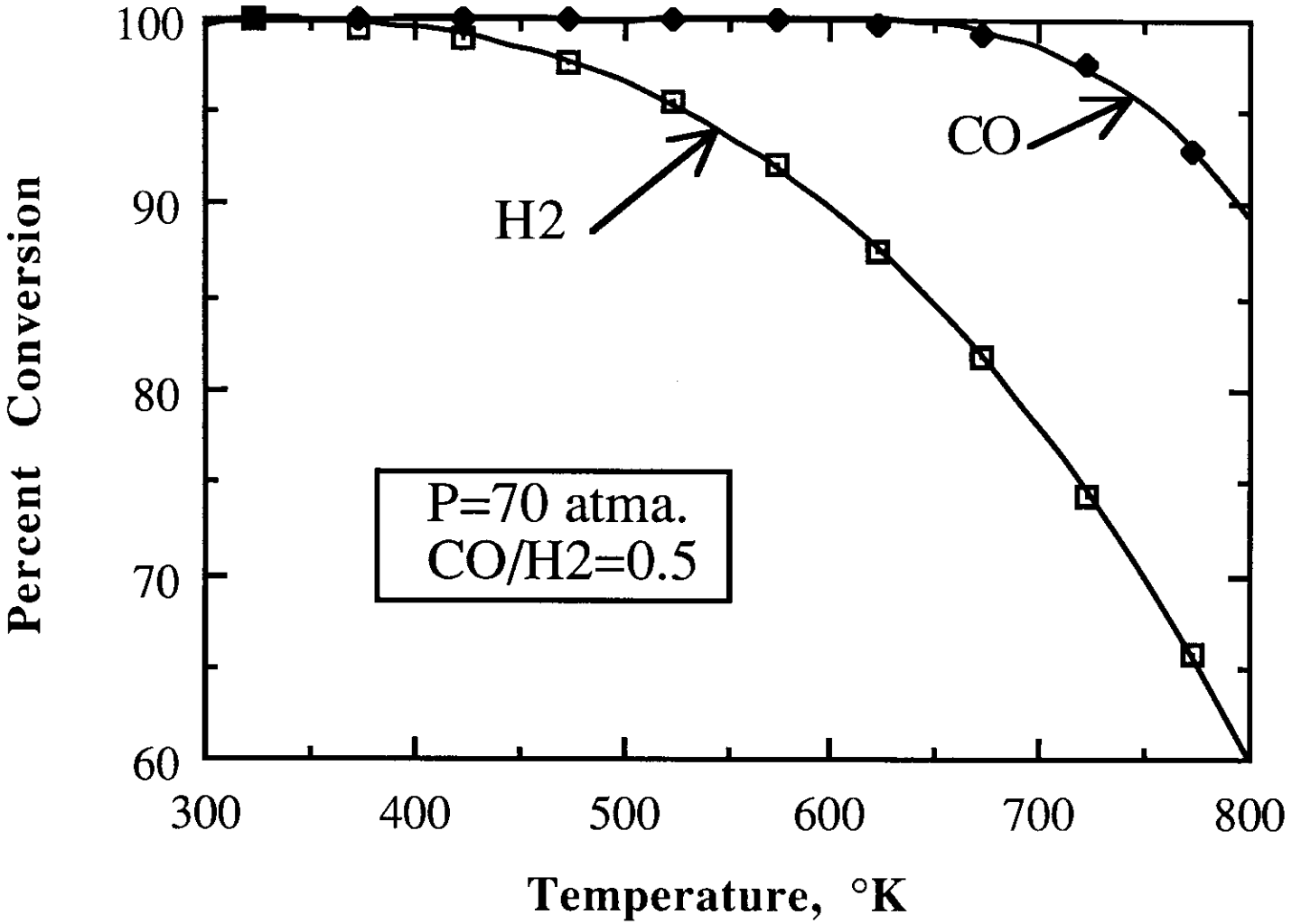


Figure 1 shows that the equilibrium conversion of CO is very high over the whole range of temperature considered. Below about 700°K, the equilibrium CO conversion is essentially 100%. Between 700 and 773°K, it is still above 90%. The calculated conversion of H_2 is lower than the conversion of CO because these two species are affected differently by the shift reaction. Carbon monoxide is a reactant in both alcohol formation, Reaction I, and water-gas shift, Reaction II. Hydrogen is a reactant in alcohol formation, but is produced by the shift reaction. The difference between the conversion curves for these two species is a measure of the importance of water-gas shift. If this reaction did not take place, the H_2 and CO conversion curves would be identical at a CO/H_2 ratio of 0.5.

The fractional yield of CO_2 based on CO is shown as a function of temperature in Figure 2. This figure illustrates the competition for CO between the alcohols and CO_2. At low temperatures, very few of the carbon atoms in the CO that reacts appear in CO_2. However, the yield of CO_2 increases with temperature until it reaches a value of about 0.3 at about 800°K. This value is only slightly below the range of stoichiometric yields shown in Table 2 for the case where oxygen rejection is exclusively by means of CO_2. If the shift reaction occurs, it can play an important role in oxygen rejection at temperatures above about 500°K.

Figure 3 shows the yield of methanol as a function of temperature. Two points are worthy of note. First, this yield is very small over the whole range of temperature. Methanol is not favored thermodynamically in the competition for the available CO between the possible products. Second, the yield of methanol *increases* with temperature. This increase seems counterintuitive, since the formation of methanol from synthesis gas is exothermic. However, methanol formation is less exothermic than the formation of the higher alcohols. Consequently, the equilibrium constant for methanol formation does not decrease as rapidly with temperature as the equilibrium constants for most of the competing reactions. This accounts for the increase in methanol yield with temperature.

Figure 2
Carbon Dioxide Yield As A Function Of Temperature

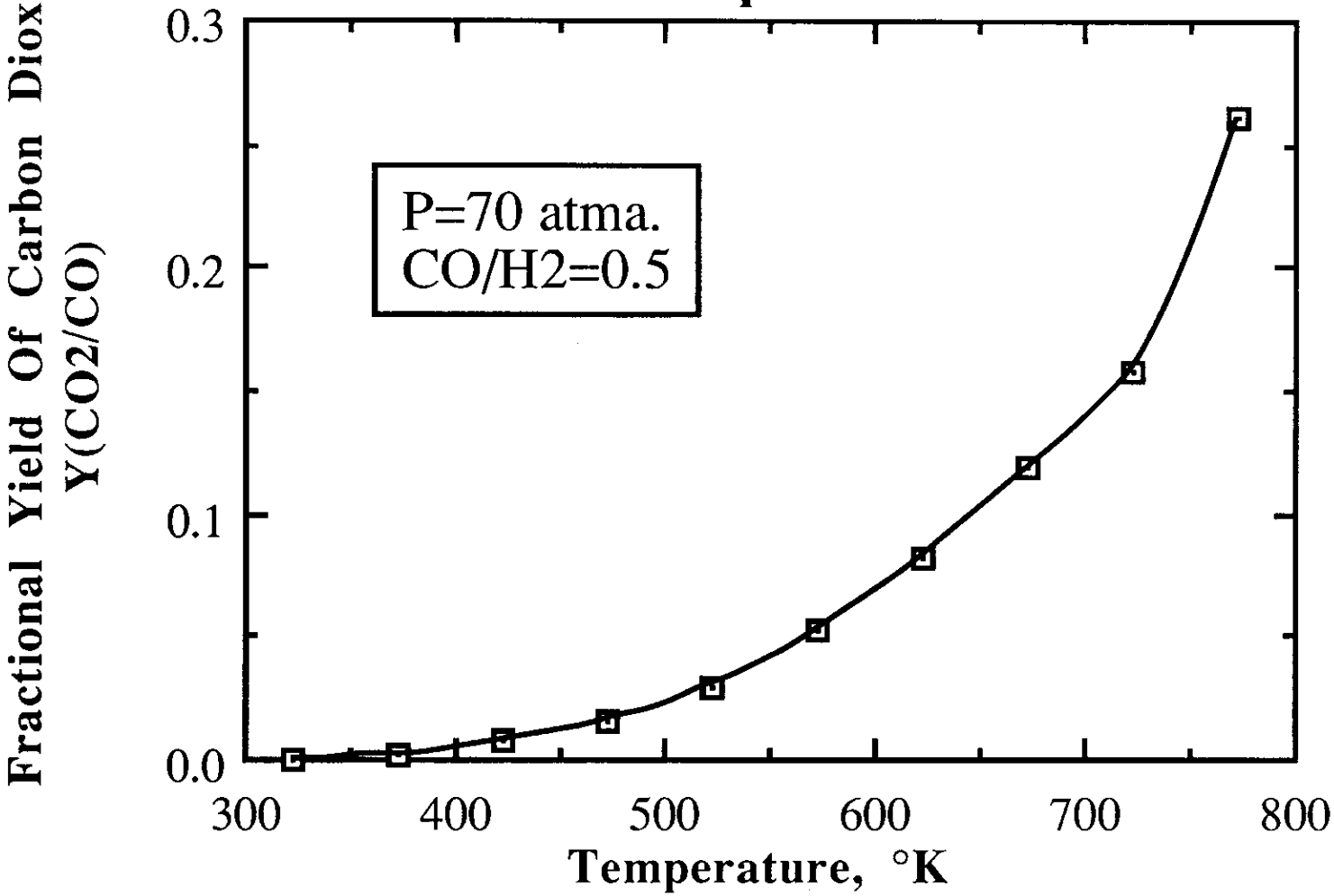
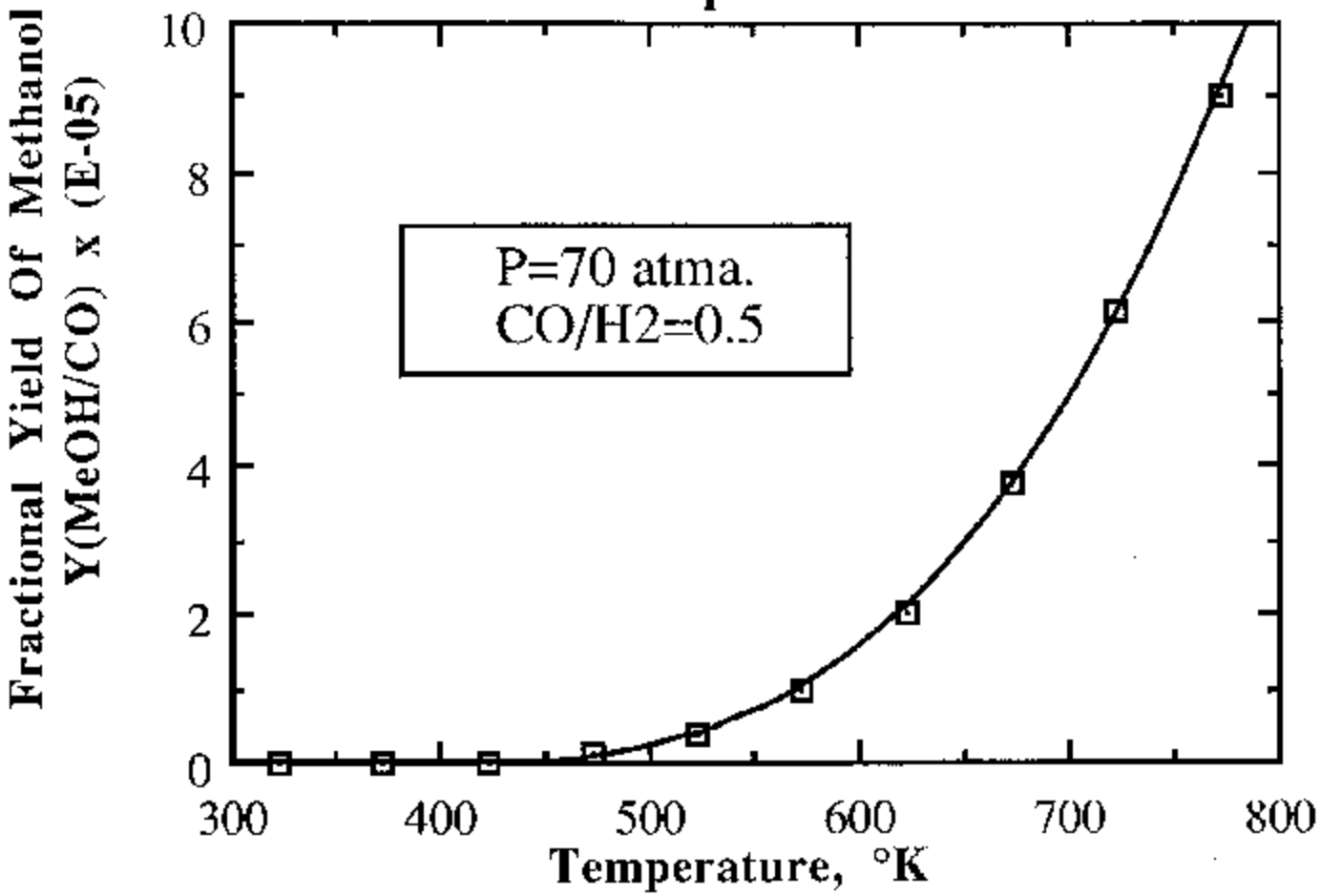


Figure 3
Methanol Yield As A Function Of Temperature



The yields of the C_2 and C_3 alcohols are presented in Figure 4. At the conditions of this study, the individual yields of these three alcohols are not significant if thermodynamic equilibrium is attained.

Figure 5 shows that the C_4 alcohols are the dominant alcohol fraction at chemical equilibrium. At the low end of the temperature range, the yield of the four C_4 alcohols taken as a group is very close to unity, indicating that essentially all of the carbon atoms in the CO that is reacted are in the C_4 alcohols. The total yield of the C_4 alcohols decreases with temperature, largely due to the increasing importance of the shift reaction, as discussed in connection with Figure 2.

The distribution of C_4 alcohol isomers is shown in Figure 6. At ambient temperature, tertiary butanol is the dominant species thermodynamically; the yields of the other three isomers are all negligible. However, as temperature increases, the amount of t-butanol declines rapidly and isobutanol becomes the predominant species at about 450°K. Secondary butanol also increases with temperature; its equilibrium concentration becomes comparable to that of t-butanol at about 600°K. Figure 6 illustrates the error that could result from drawing conclusions based only on calculations at ambient temperature. Such a practice could lead to the erroneous conclusion that t-butanol was thermodynamically preferred, whereas at representative reaction temperatures of 550 to 700°K, the equilibrium yield of t-butanol is quite low and i-butanol is the dominant species thermodynamically.

The issue of which butanol isomer is thermodynamically favored is potentially important. Tertiary butanol could have value as a raw material for producing methyl tertiary butyl ether, a valuable gasoline additive. The utility of the methyl ether of isobutanol as a blending component for motor gasoline has not been established.

The Effect of Pressure on Reaction Behavior

Figure 4
C2 & C3 Alcohol Yields As A Function Of Temperature

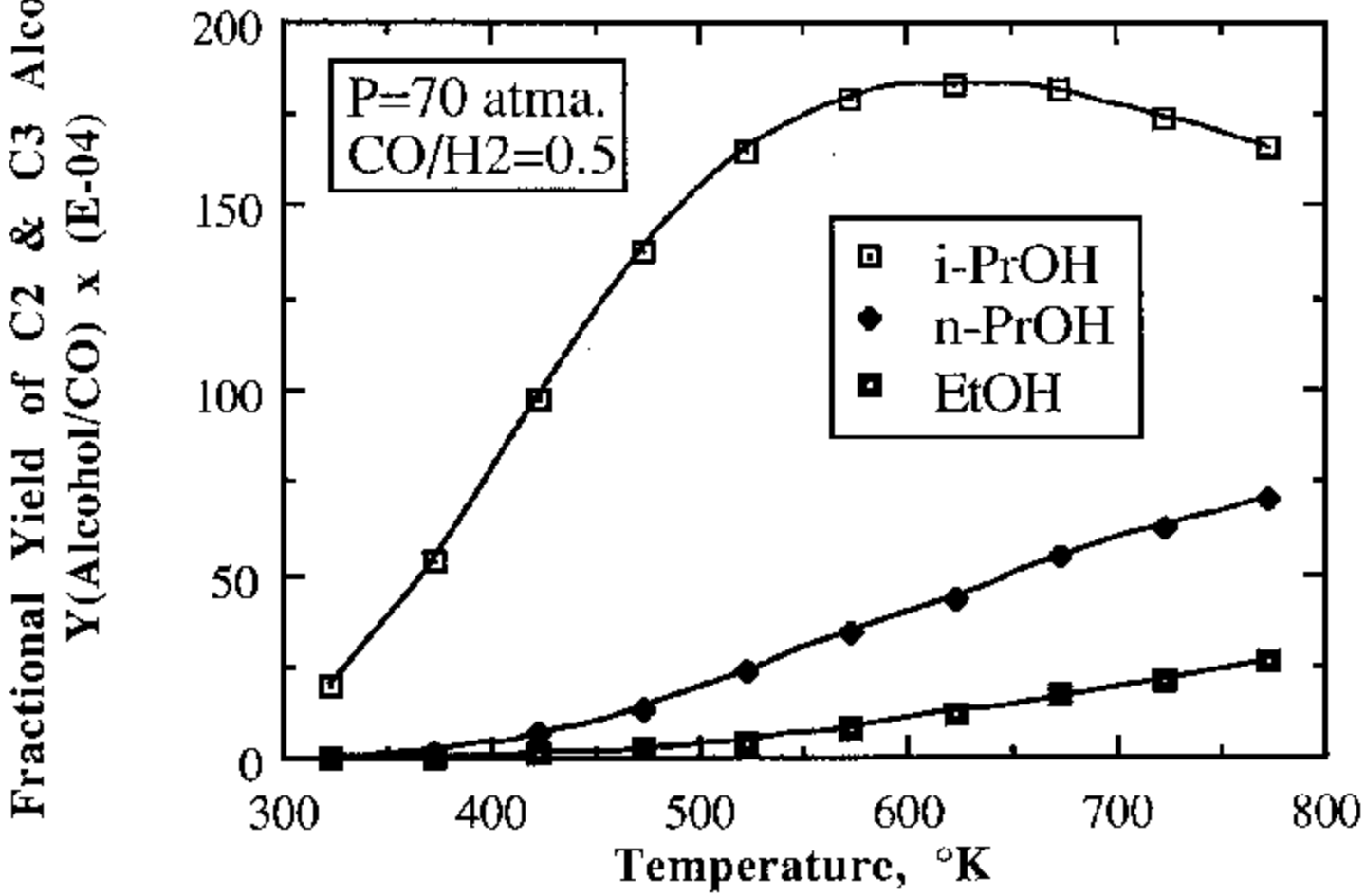


Figure 5
Total C4 Alcohol Yield As A Function Of Temperature

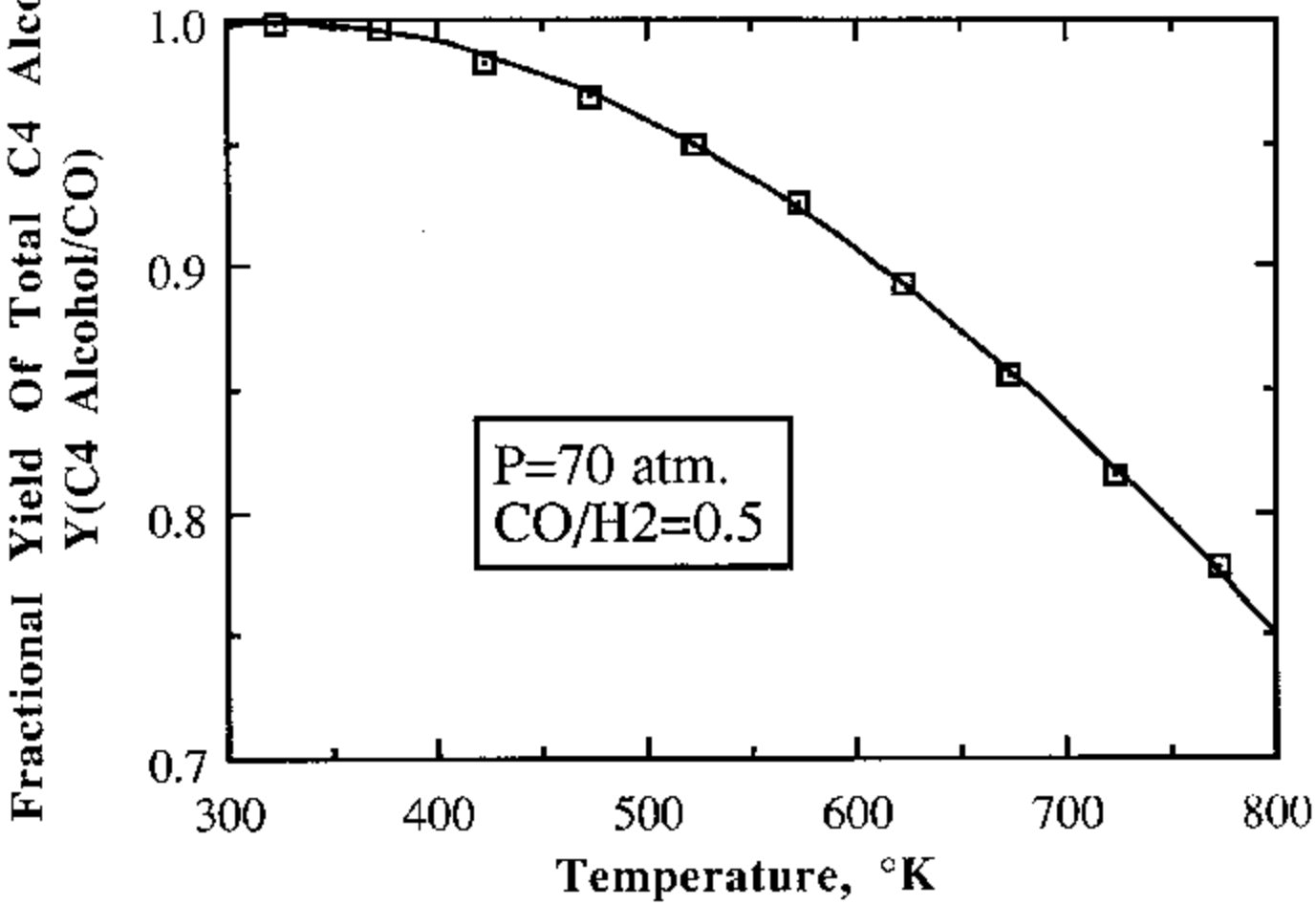
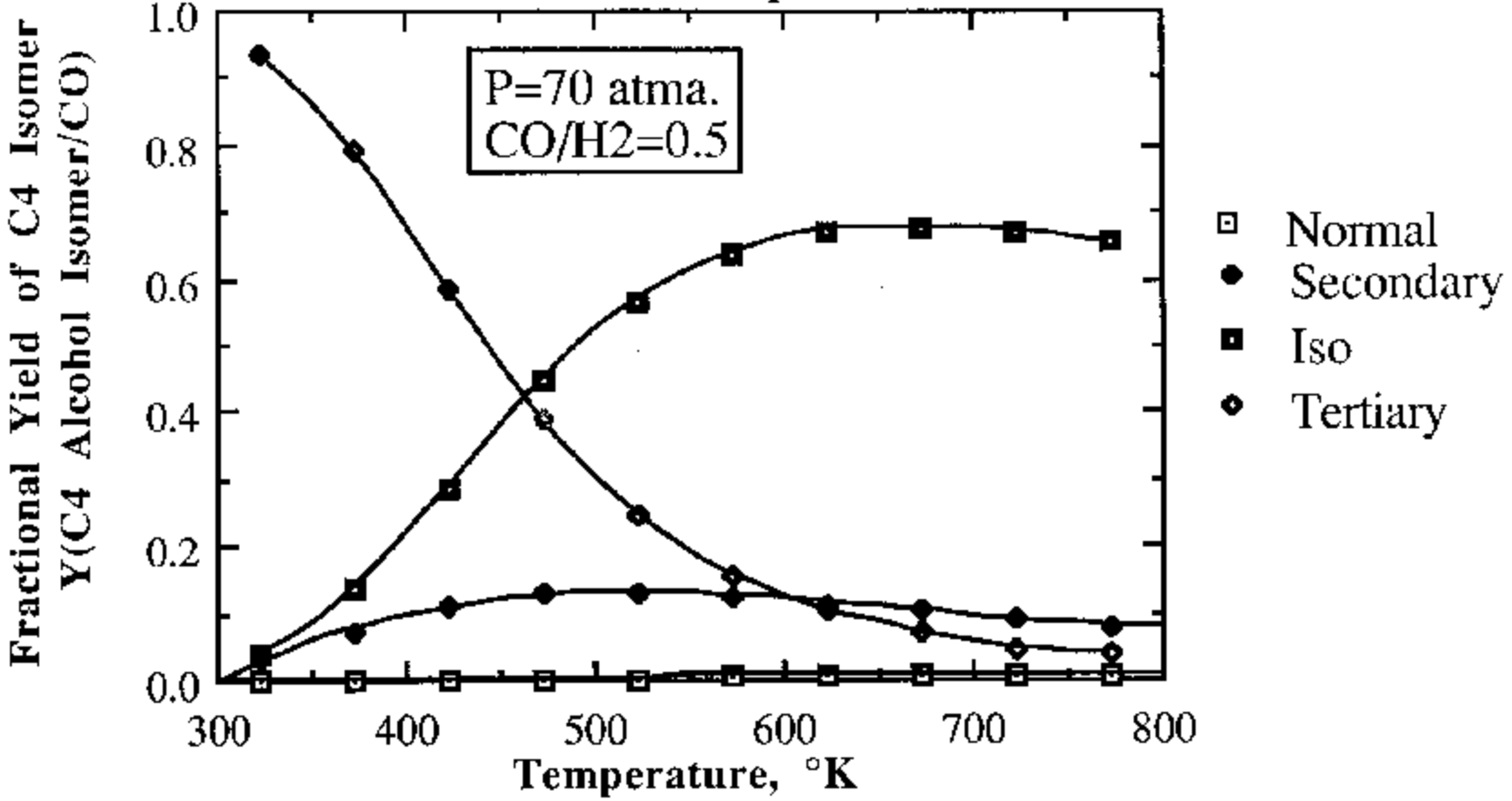


Figure 6
C4 Alcohol Isomer Distribution As A Function Of Temperature



A second series of calculations was carried out to define the effect of total pressure on the thermodynamics of alcohol synthesis. For these calculations, the temperature, T, was 523°K and the feed consisted of CO and H_2 in a 1/2 molar ratio. Once again, the shift reaction was allowed to come to equilibrium. The calculations covered a range of pressure from 1 atmosphere absolute to 170 atmospheres absolute. Experimental studies have typically been conducted in the range of about 70 to 200 atma.

The results of these calculations showed that total pressure has very little effect on the thermodynamics of the present system, except at very low pressures. Therefore, only a few results will be presented to illustrate this lack of sensitivity.

Figure 7 shows the effect of pressure on the conversion of carbon monoxide. Although conversion declines in the low end of the pressure range, it is above 99.5% even at atmospheric pressure. Figure 8 shows the effect of pressure on the fractional yield of CO_2. Of all of the parameters calculated, $Y(CO_2/CO)$ is the most sensitive to pressure. Carbon dioxide is formed via the shift reaction, whose equilibrium is not sensitive to pressure when all species involved are ideal gases. However, the alcohol synthesis reactions, which compete for CO with the shift reaction, are favored by higher pressure. This accounts for the decreasing yield of CO_2 as the total pressure is raised.

Figure 9 shows the distribution of C_4 alcohol isomers. The yield of all four isomers increases somewhat as the pressure is raised from 1 atmosphere. For any increment of pressure, this increase is very nearly equal to the decrease in the yield of CO_2. The yields of methanol, ethanol and propanol increase only slightly with pressure. Changes in pressure do not cause a change in the C_4 alcohol isomer distribution.

The Effect of CO/H_2 Ratio on Reaction Behavior

A third set of calculations was carried out to explore the effect of CO/H_2 ratio on the thermodynamics of the mixed alcohol system.

Figure 7
Carbon Monoxide Conversion As A Function Of Pressure

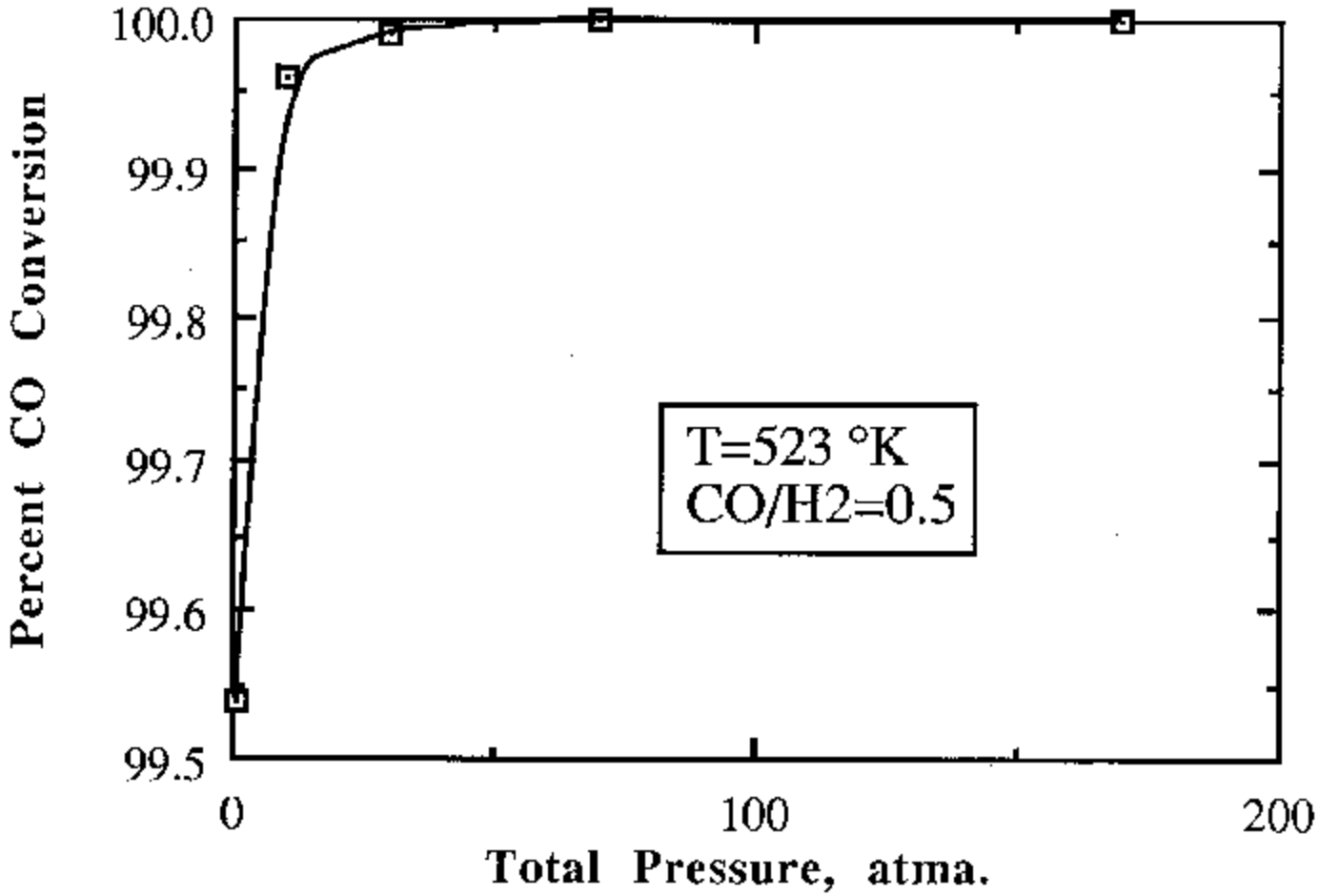


Figure 8
Carbon Dioxide Yield As A Function Of Pressure

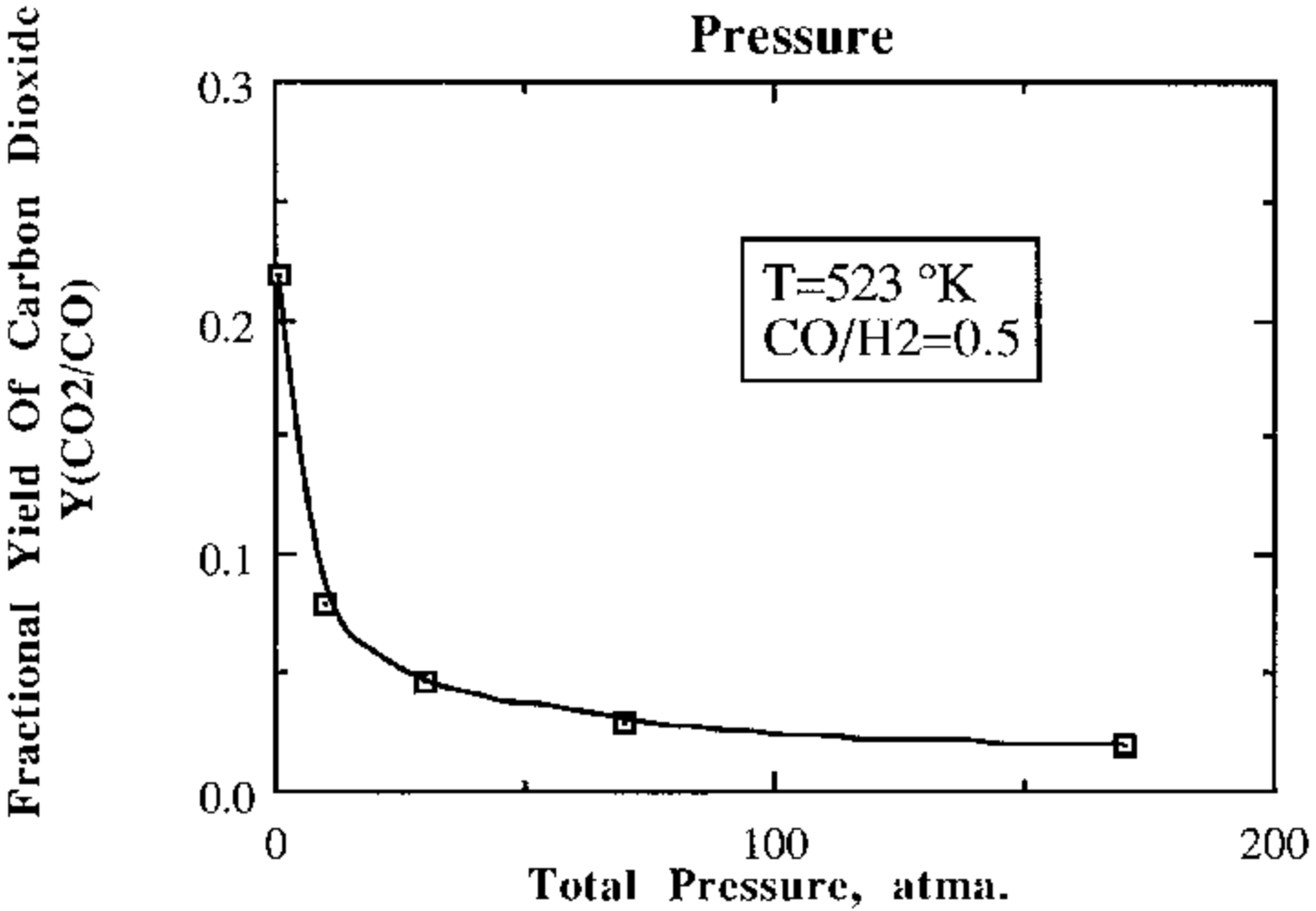
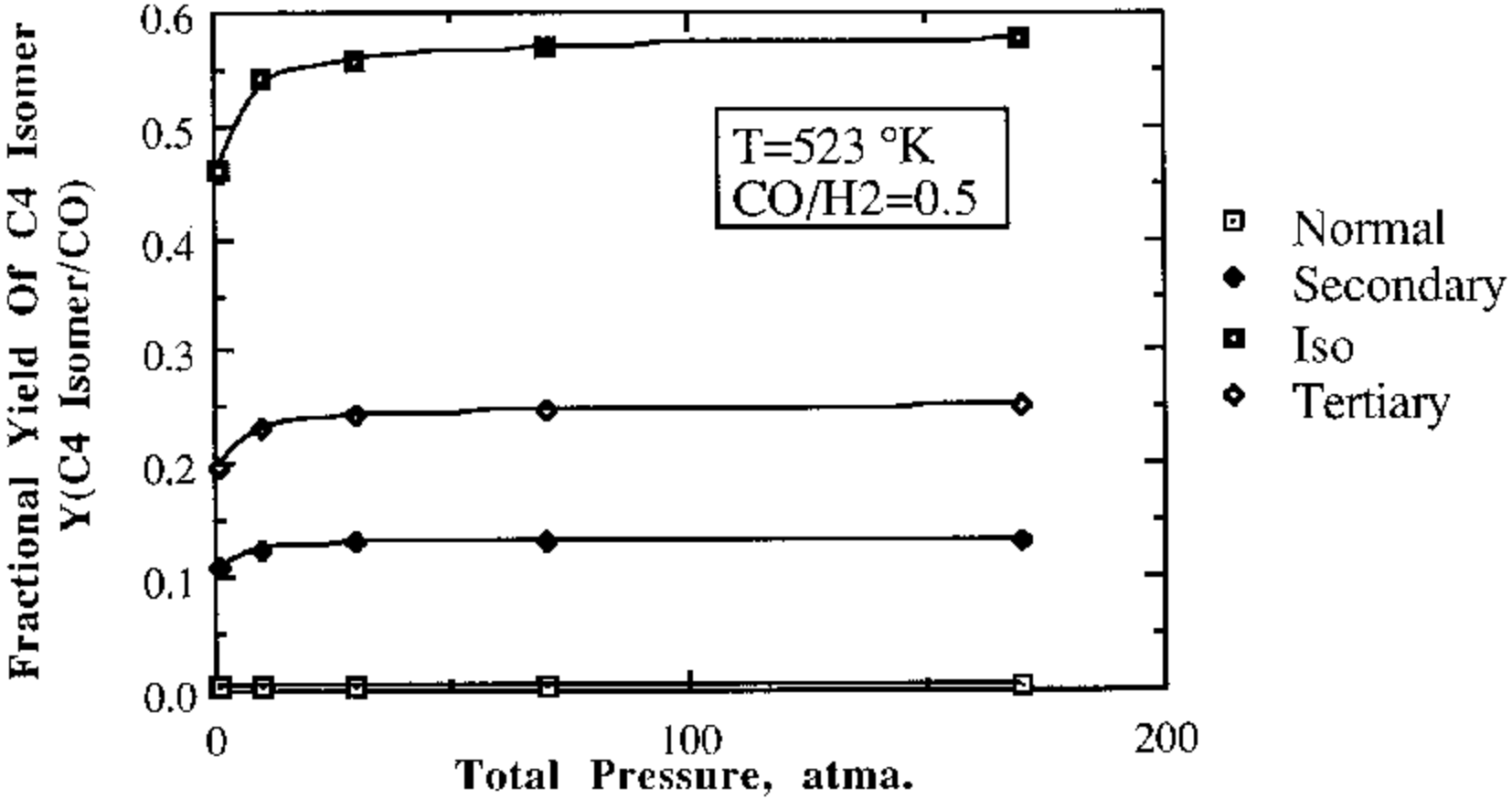


Figure 9
C4 Alcohol Isomer Distribution As A Function Of Pressure



The temperature, T, was 523 °K and the total pressure, P, was 70 atmospheres absolute for all of these calculations. As with previous studies, the water-gas shift reaction was allowed to equilibrate.

The CO/H_2 ratio is an important variable in a number of applications, such as the coproduction of alcohols and electric power in a coal gasification combined cycle (CGCC) plant. In these plants, synthesis gas is produced by reacting coal, oxygen and steam in a coal gasifier. Some older gasifiers, such as the so-called "dry bottom" Lurgi, produce synthesis gas with a CO/H_2 ratio of about 0.5. Modern, high-temperature, entrained-flow, slagging gasifiers, such as the Texaco, Shell and Dow gasifiers, produce synthesis gas with a CO/H_2 ratio in the range of 1 to 2. Synthesis gas leaving the gasifier is cleaned to remove impurities and some or all of it is fed directly to the alcohol synthesis process, without shifting to adjust the CO/H_2 ratio. Gas that bypasses alcohol synthesis is combined with unconverted gas leaving the alcohol synthesis section and the mixture is fed to a combined-cycle power generation unit.

Figure 10 shows that the equilibrium CO conversion is essentially 100% when the CO/H_2 ratio is below about 1.4. Conversion decreases as the CO/H_2 ratio increases above this value. The behavior of the CO conversion with CO/H_2 ratio illustrates the points that were made earlier concerning the stoichiometric impact of the shift reaction. At the temperature and total pressure of Figure 10, butanols are the dominant product thermodynamically. In this case, Table 2 shows that the stoichiometric CO/H_2 ratio is 1.4 when the water-gas shift reaction is important. Below a ratio of 1.4, CO is the limiting reactant and its equilibrium conversion is essentially 100%. When the CO/H_2 ratio exceeds 1.4, CO is no longer the limiting reactant. The decline in conversion at ratios above 1.4 is the result of an increasing stoichiometric excess of CO.

Figure 11 shows that the behavior of the CO_2 yield is consistent with the above stoichiometric arguments. At values of the CO/H_2

Figure 10
Carbon Monoxide Conversion As A Function Of CO/H2 Ratio

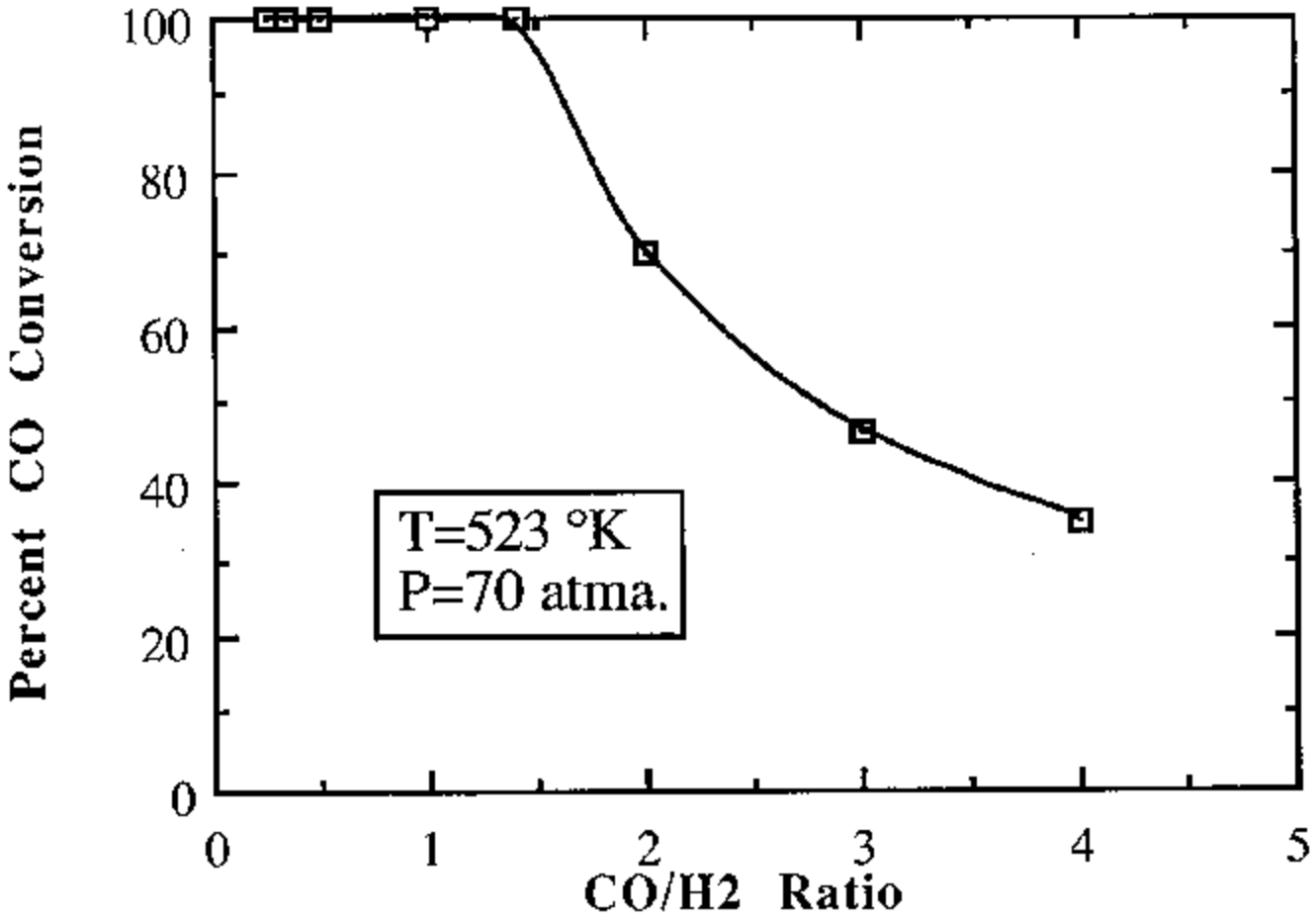
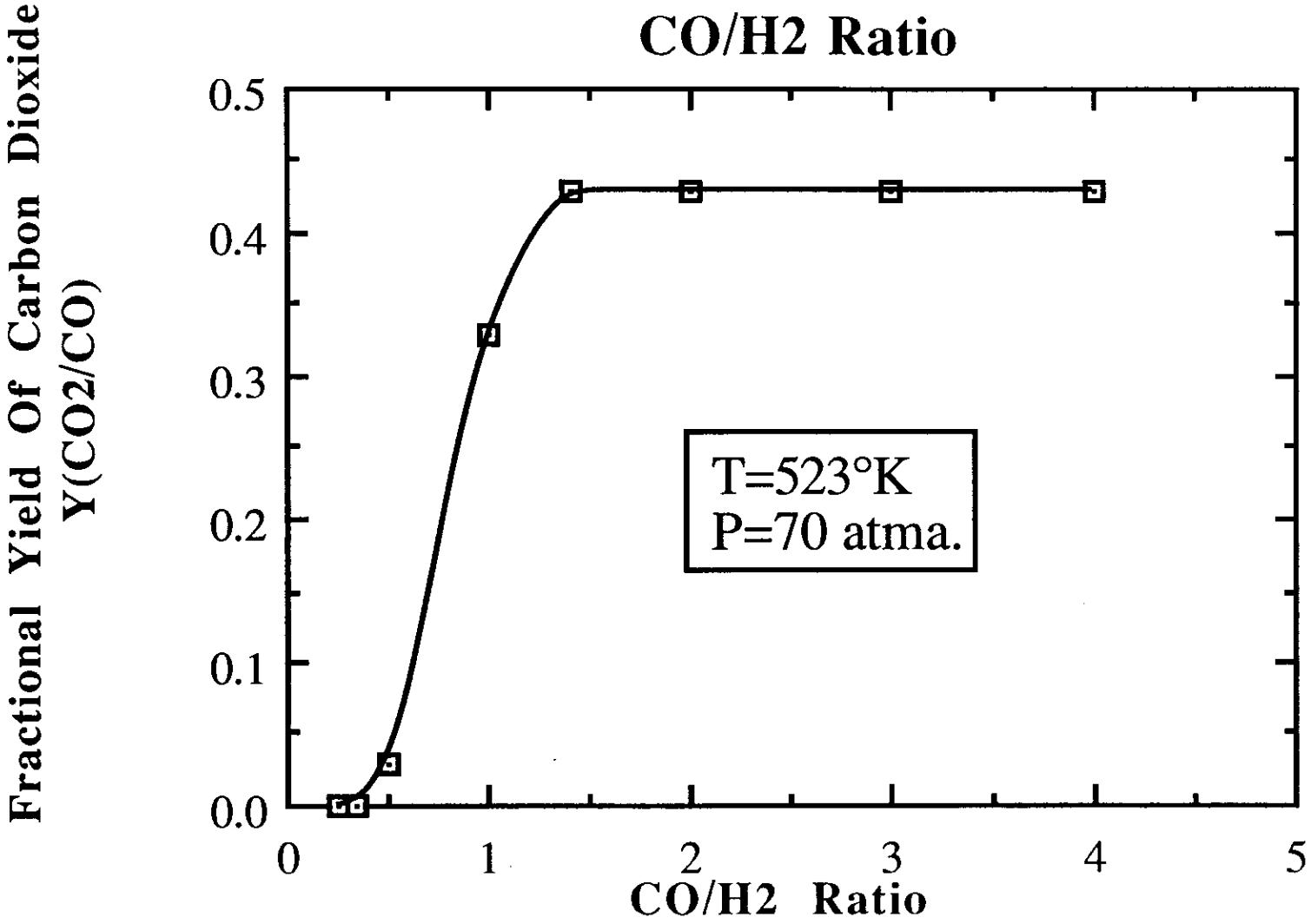


Figure 11
Carbon Dioxide Yield As A Function Of CO/H2 Ratio



ratio above 1.4, the CO_2 yield is 0.43. This is the value shown in Table 2 for the case of butanol formation under conditions where all oxygen rejection is via CO_2.

Figure 12 shows an interesting characteristic of system behavior that occurs when the water-gas shift reaction is allowed to come to equilibrium. The yield of isopropanol decreases as the CO/H_2 ratio increases until, at a ratio of about 2, there is essentially no isopropanol remaining in the system at equilibrium. Plots of the yields of n-propanol, ethanol and methanol show the same behavior, i.e., the yield of the alcohol declines to a negligible level as the CO/H_2 ratio is increased above a value of about 2.

Figure 13 shows the effect of CO/H_2 ratio on the distribution of C_4 alcohol isomers. As this ratio increases from its lowest value, the yields of all four isomers decrease as a result of the increasing importance of the shift reaction. In other words, the increasing yield of CO_2 shown in Figure 11 comes largely at the expense of the yields of the C_4 alcohol isomers. The distribution of isomers is independent of CO/H_2 ratio above a ratio of about 1.4, which corresponds to the ratio at which all of the oxygen rejection is via CO_2. This independence of isomer distribution shows that the disappearance of the C_1 through C_3 alcohols at high CO/H_2 ratios, as noted in the discussion of Figure 12, is not simply a matter of a limited quantity of hydrogen being allocated to the thermodynamically most favored compound. Note that no redistribution of hydrogen occurs between the C_4 alcohol isomers. The behavior of the yields of the C_1 through C_3 alcohols with CO/H_2 ratio appears to be connected, at least in part, to the stoichiometry of the reactions by which they are formed.

The Effect of the Water-Gas Shift Reaction

Figures 14, 15 and 16 show the effect of the presence or absence of the water-gas shift reaction on the equilibrium behavior of the higher alcohol system. When the water-gas shift reaction does not take place, the CO conversion, as shown in Figure 14, reflects the

Figure 12
Isopropanol Yield As A Function Of CO/H2 Ratio

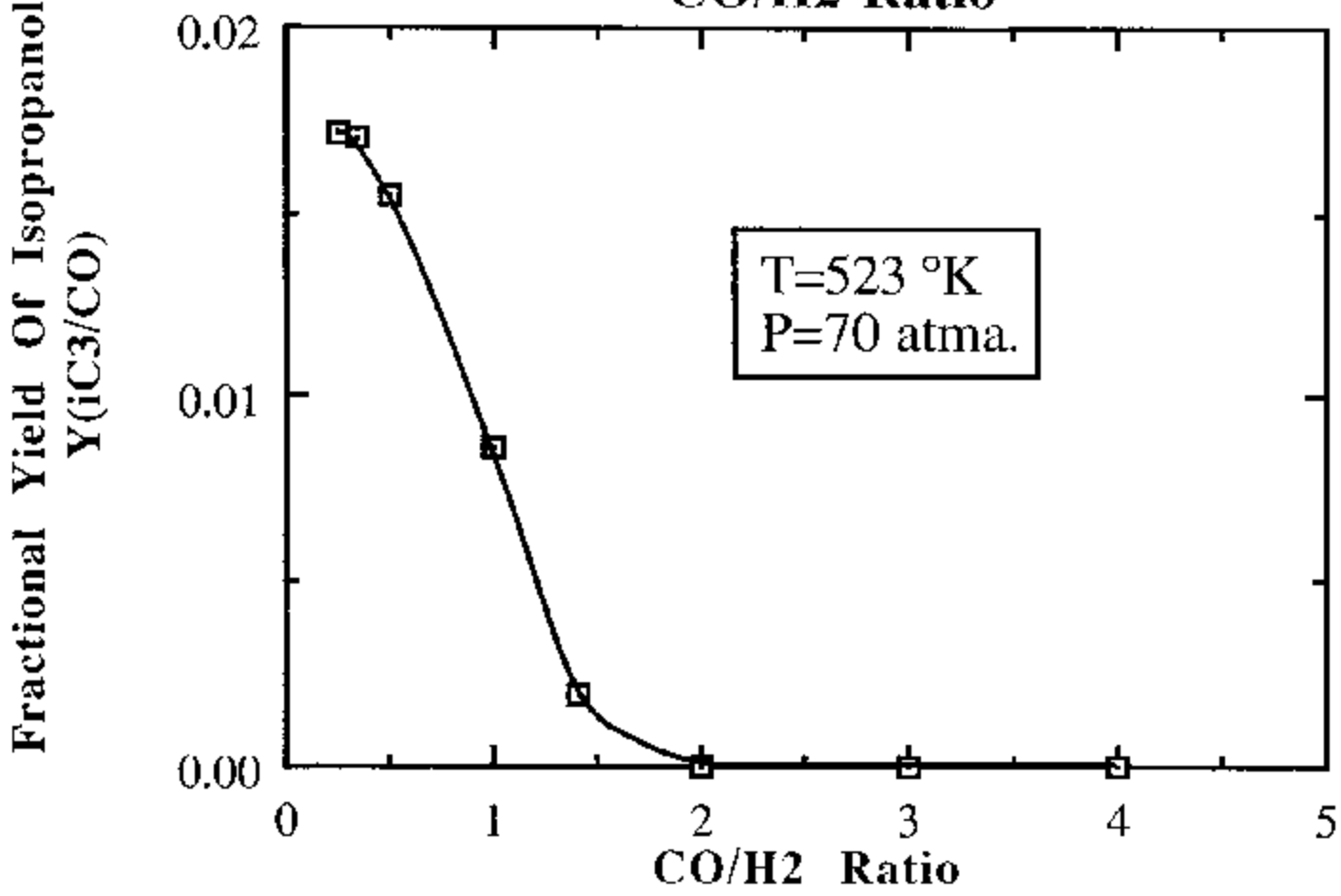


Figure 13
C4 Alcohol Isomer Distribution As A Function Of CO/H2 Ratio

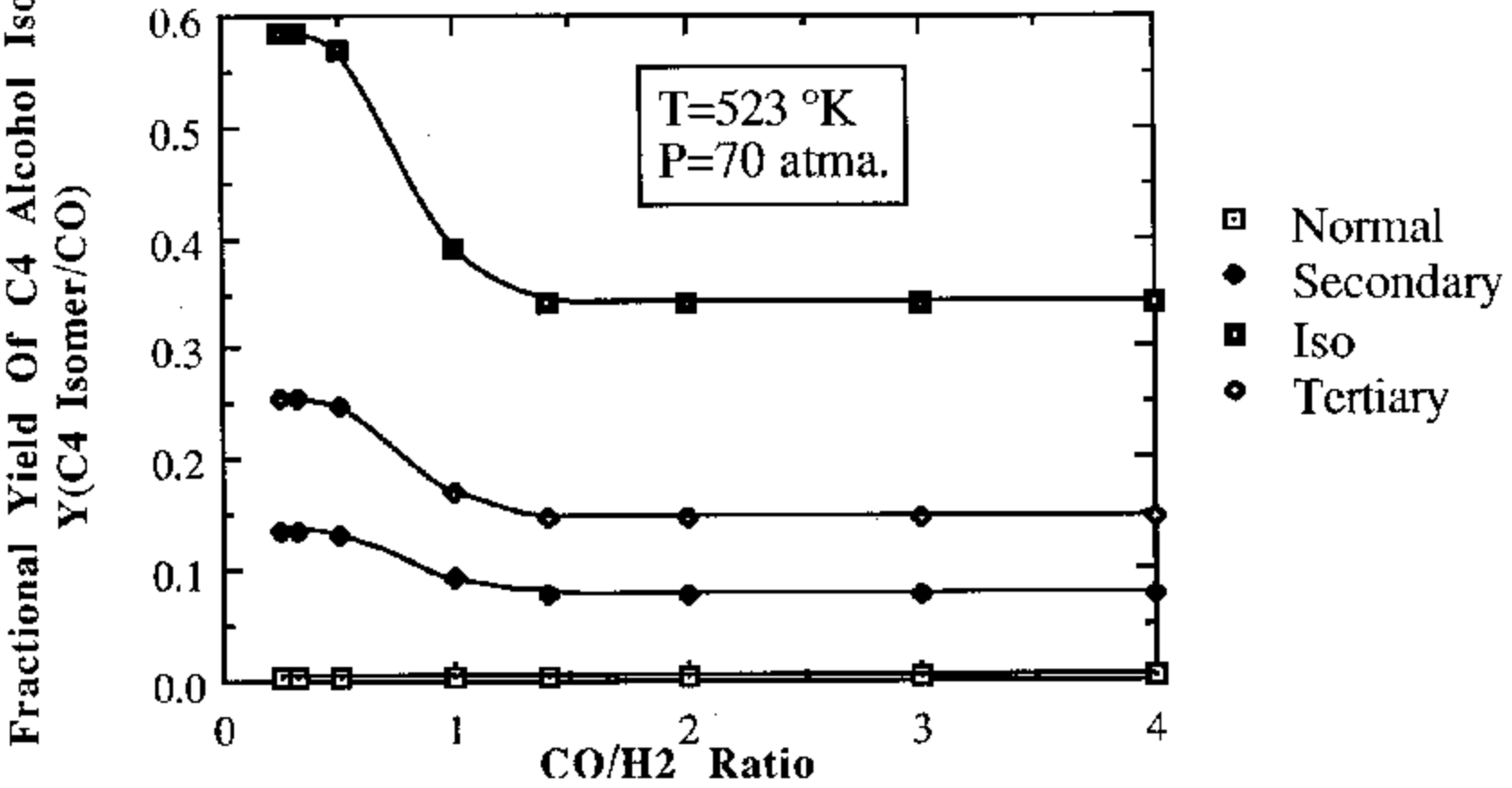
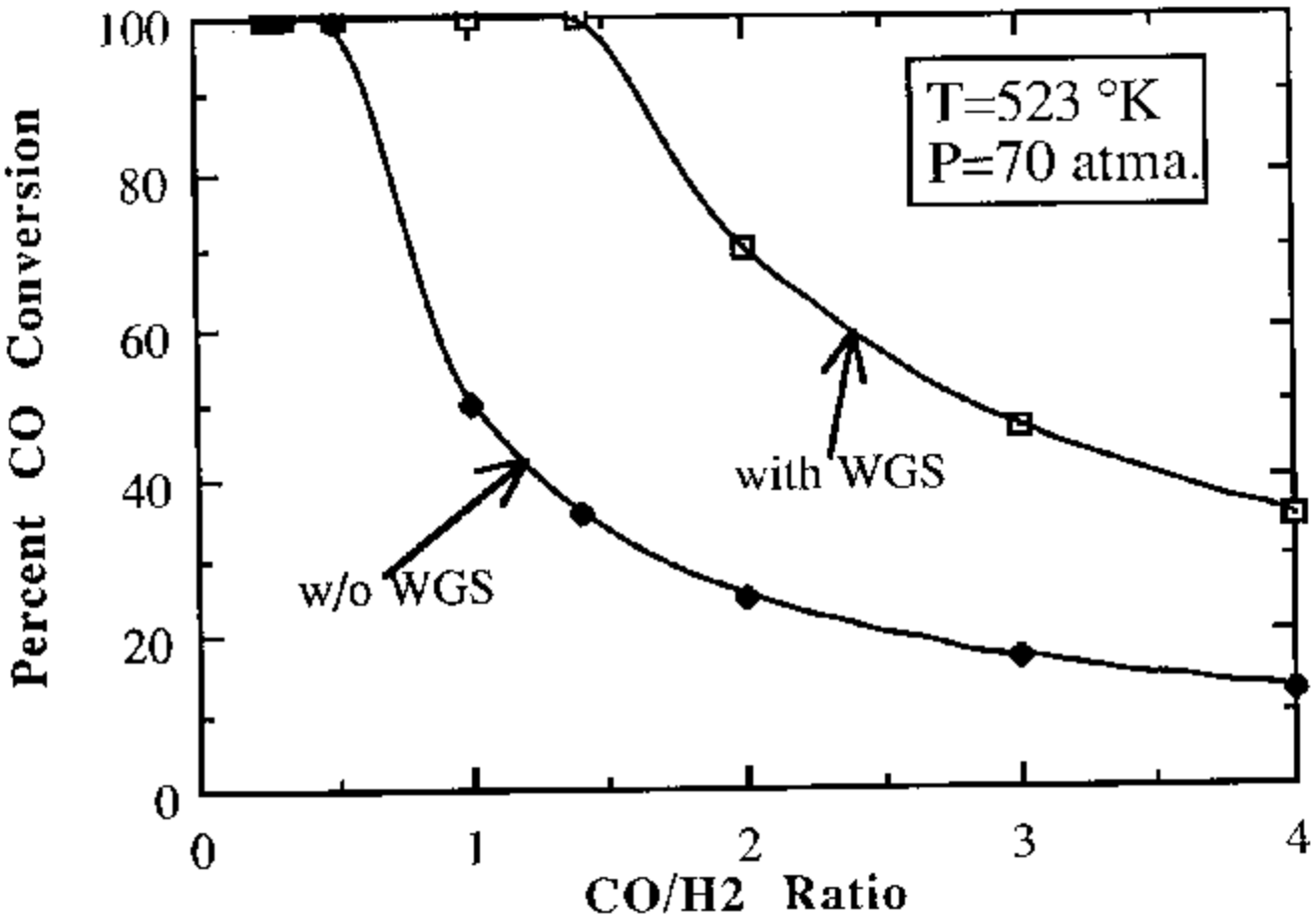


Figure 14
The Effect of Water-Gas Shift On CO Conversion



stoichiometry of Reaction I, where all oxygen rejection is via water. Without the shift reaction, CO is the limiting reactant at CO/H_2 ratios below 1. The equilibrium conversion in this region is essentially 100%. At CO/H_2 ratios above 1, H_2 is the limiting reactant and the CO conversion declines as the CO/H_2 ratio increases. At any CO/H_2 ratio greater than 1, the equilibrium CO conversion is greater when the shift reaction takes place than when it does not.

Figure 15 shows the contrast between the behavior of the isopropanol yield with and without the shift reaction. Without water-gas shift, this yield is not dependent on the CO/H_2 ratio. In contrast, as pointed out in the discussion of Figure 12, the isopropanol yield decreases with increasing CO/H_2 ratio when the shift reaction does take place, and reaches a value of essentially zero at a ratio of about 2.

Figure 16 contrasts the behavior of isobutanol, the thermodynamically-dominant species, in the presence and absence of the shift reaction. As with isopropanol, the yield of isobutanol does not depend on CO/H_2 ratio if the shift reaction does not take place. When the shift reaction does occur, as noted in the discussion of Figure 13, the yield of isobutanol declines with increasing CO/H_2 ratio up to a ratio of about 1.4, where the yield becomes invariant to further increases of this ratio.

CONCLUSIONS

The ASPEN PLUS process simulation package is a very useful tool in defining the thermodynamic behavior of the reactions by which higher alcohols are synthesized from CO/H_2 mixtures. The present studies are currently being extended to include the possibility of forming more than one phase and to explore the effect of removing the assumption of ideal gas behavior. The ASPEN PLUS package is also being used to study the behavior of the system when various alcohols are included in the feed. These calculations are designed to simulate recycle of undesired alcohol components so as to inhibit their further formation and/or to convert them to more valuable

Figure 15
The Effect of Water-Gas Shift On Isopropanol Yield

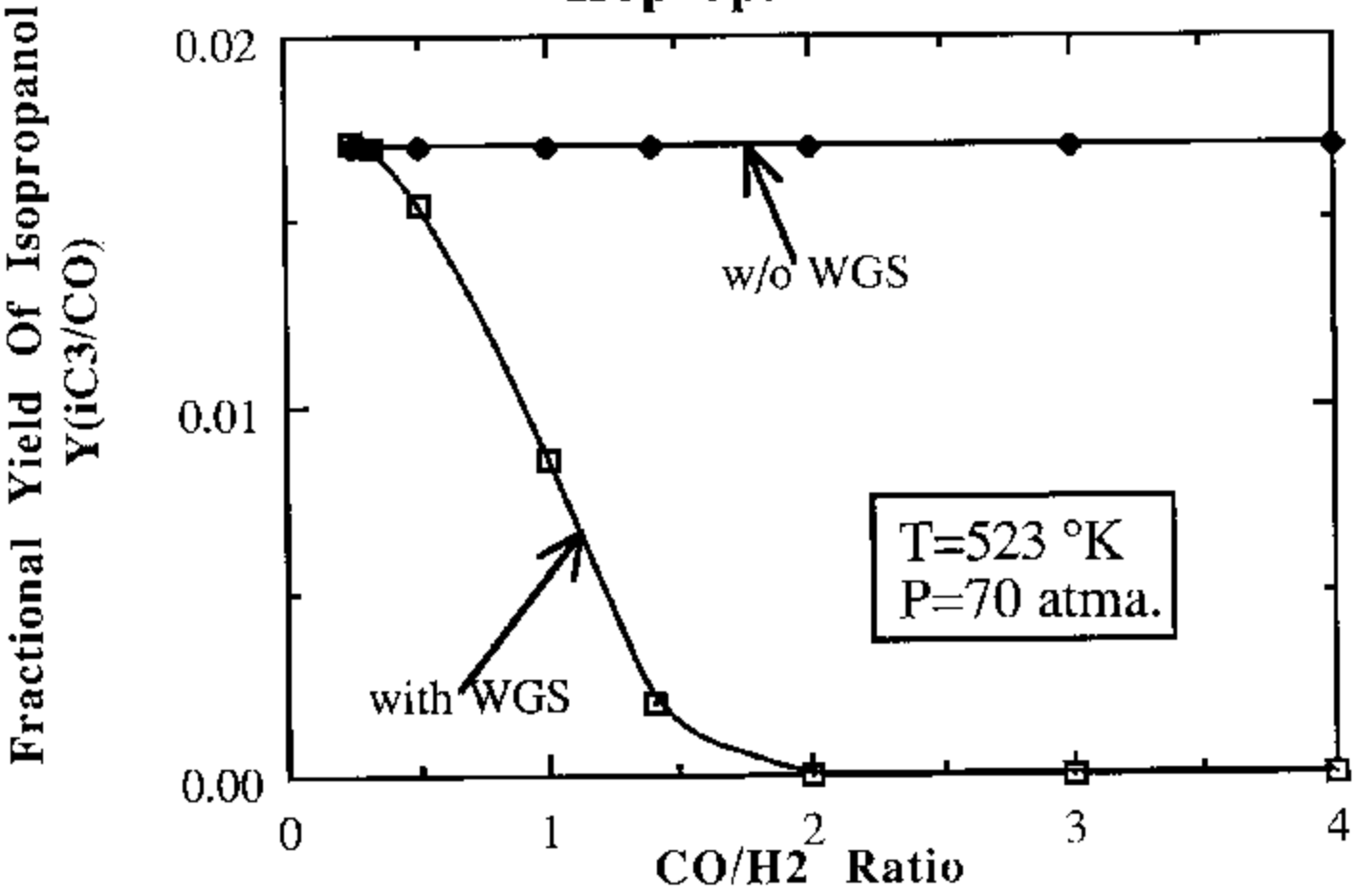
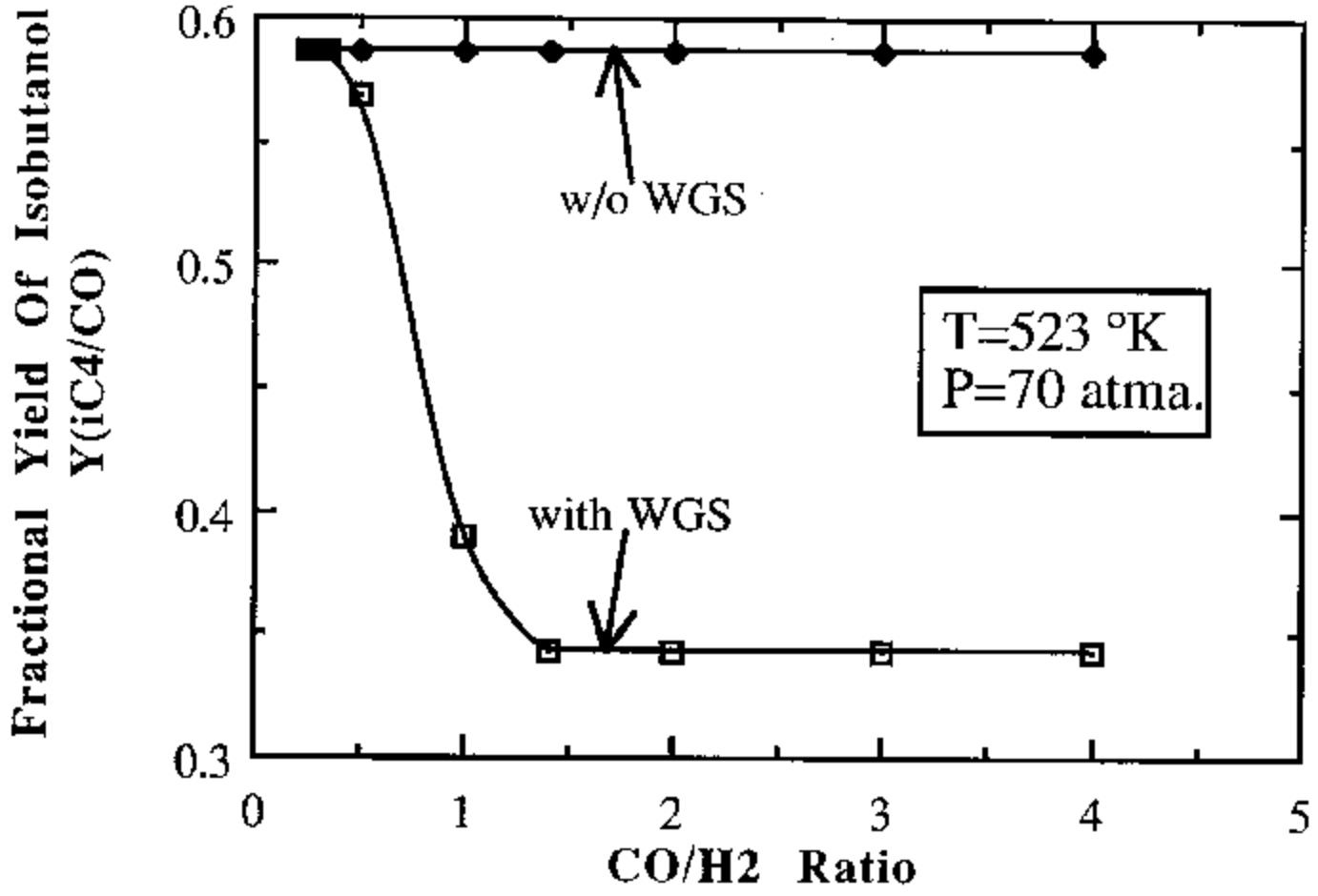


Figure 16
The Effect Of Water-Gas Shift On Isobutanol Yield



The most important conclusions resulting from the work done to date are:

1) The apparent reaction stoichiometry depends on the extent of the shift reaction, i.e., on the extent to which oxygen molecules in the CO are rejected by either H_2O or CO_2. When oxygen rejection is largely via CO_2, the apparent stoichiometry also depends on the relative amounts of the various alcohols that are formed.

2) The equilibrium conversion of the limiting reactant is above 90% at all temperatures up to 773 °K.

3) The C_4 alcohols are the predominant product at all temperatures up to 773 °K.

4) Tertiary butanol is the predominant C_4 alcohol isomer at temperatures below about 473 °K; at higher temperatures up to 773 °K, isobutanol is the thermodynamically-preferred species.

5) Oxygen rejection is largely via CO_2 at higher temperatures and CO/H_2 ratios.