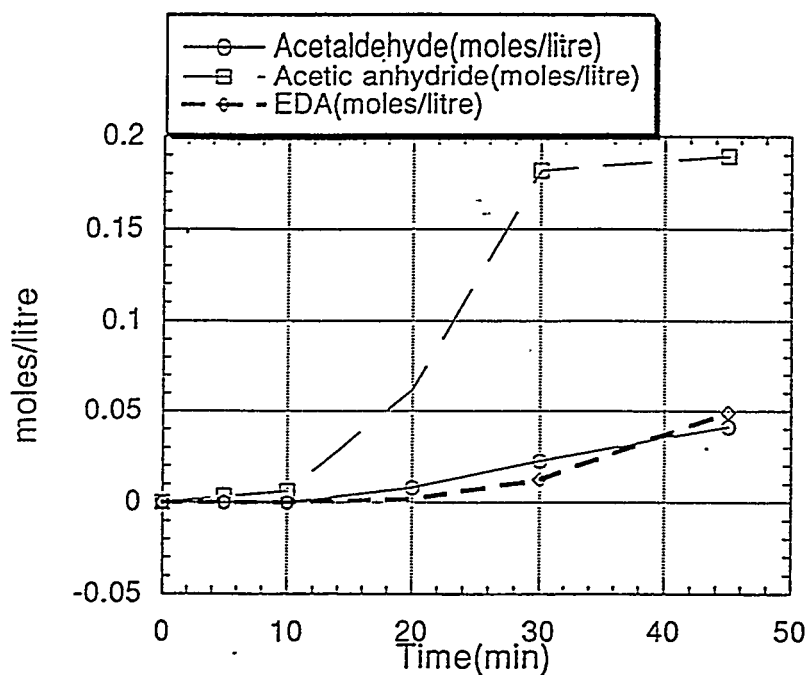


In contrast to these results, the earlier homogeneous catalytic reaction in the 300 cc reactor showed a different product profile. Figure 3.2.6 shows this different product profile over a period of 45 minutes. These results indicate that to get an adequate concentration of EDA in the reaction, the carbonylation reaction to form acetic anhydride must work well. For unknown reasons the 100 cc reactor experiment gives a different reaction pathway. Therefore, experiments in the 300cc reactor are planned.

Figure 3.2.6 300 cc Autoclave Run



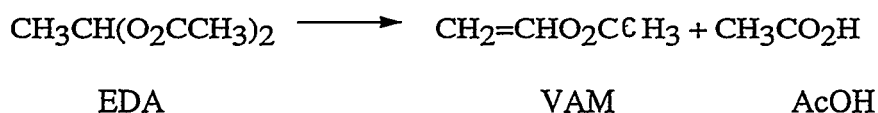
Ethylidene Diacetate to Vinyl Acetate

Background for EDA Cracking

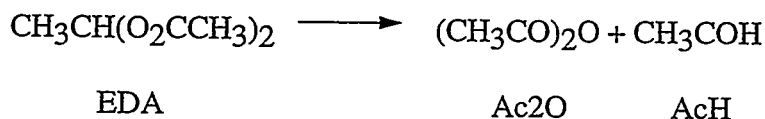
The cracking of ethylidene diacetate (EDA) $[\text{CH}_3\text{CH}(\text{O}_2\text{CCH}_3)_2]$ to vinyl acetate (VAM) $[\text{CH}_2=\text{CHO}_2\text{CCH}_3]$ and acetic acid has been shown to proceed at about 170°C via benzenesulfonic acid catalysts in the liquid phase. Efforts to extend this catalysis to the gas phase are underway.

Temperature Effects

The desired cracking chemistry is as follows:



One potential unwanted reaction is the reverse synthesis reaction of EDA from acetic anhydride and acetaldehyde, as follows:



In order to determine how much back reaction existed, a blank tube was loaded in the reactor oven. A 0.2 ml/hr liquid feed of EDA with 10 cc/min of N₂ was fed to the reactor tube. This feed, once vaporized, was approximately 5 mol% EDA in N₂. At 180°C, the predominate peak observed was ethylidene diacetate. However, approximately 1% acetic anhydride and acetaldehyde from the reverse synthesis reaction was observed. These levels are sufficiently low as to pose no major problems with interpretation of results. As an alternative, the addition of acetic anhydride to the liquid feed should prevent this reaction.

At 200°C, the reactor system quickly plugged. It is presumed that at temperatures above 180°C, the ethylidene diacetate decomposes to VAM, which quickly polymerizes to polyvinyl acetate. This result sets temperature limits for the catalysis to under 200°C.

Catalytic Runs

Several catalysts were tested for the cracking of EDA to VAM and acetic acid. Unfortunately, these were examined at too high a temperature. Qualitative results are discussed below.

Sulfated Zirconia

Two grams of sulfated zirconia catalyst were loaded in a reactor tube and placed in the lab reactor system. A flow of 0.35 ml/hr EDA and 10 cc/min N₂ was initiated. The reactor was heated to 250°C. The reactor system plugged within several hours. However, several injections were obtained before plugging. In addition to unreacted EDA, the following materials were detected:

- VAM and Acetic Acid - from cracking
- Acetic anhydride and Acetaldehyde - from reverse synthesis
- C₂ and C₃ gases (ethylene/ethane/propylene/propane)
- Trace amounts of CO₂

Activity appeared to start high and drop off quickly. This may indicate deactivation of the catalyst or may be caused by the plugging.

C Coated w/NR50

Several carbons coated with NR50 (Nafion®) were examined. As mentioned previously, these were evaluated at temperatures above 200°C and were prematurely ended by plugging of sample lines.

Initial conversion of EDA was in excess of 90%, although selectivity to VAM and acetic acid was less than 25%. The predominant peak was acetic anhydride, suggesting that the same catalyst may effect not only the cracking, but also the dissociation of EDA. As mentioned previously, acetic anhydride may need to be added to the feed to suppress this reaction.

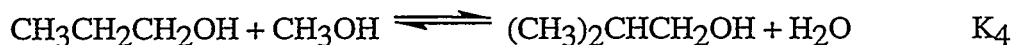
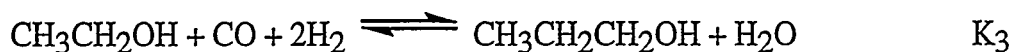
The product slate was very similar to that reported above for sulfated zirconia.

Syngas to Higher Alcohols

Equilibrium Concentration of Alcohols in Syngas to Higher Alcohols

A mol fraction vs temperature plot of the equilibrium concentrations of methanol, ethanol, n-propanol and isobutanol based on experimental (or estimated) thermodynamic values is needed to understand the conversion of syngas to higher alcohols. The existing thermodynamic parameters for all compounds involved are from Air Products' thermo database, CAPP.

The reactions to be considered are in Scheme 1 using H₂O rejection for oxygen removal. The temperature coordinate is 275, 325, 375, and 425°C. Mol fraction vs temperature plots were done at 1, 50 and 100 bar.



Scheme 1. Higher alcohol synthesis with H₂O rejection

The first-pass results obtained are shown below by computing the equilibrium concentrations of alcohols obtained from converting 70 mol% CO and 30 mol% H₂. Plots for 1 and 100 bar are represented in Figures 3.2.7 and 3.2.8, respectively.

Figure 3.2.7 Plot of Mol Fraction of Alcohols vs Temperature at 1 Bar with H₂O Rejection

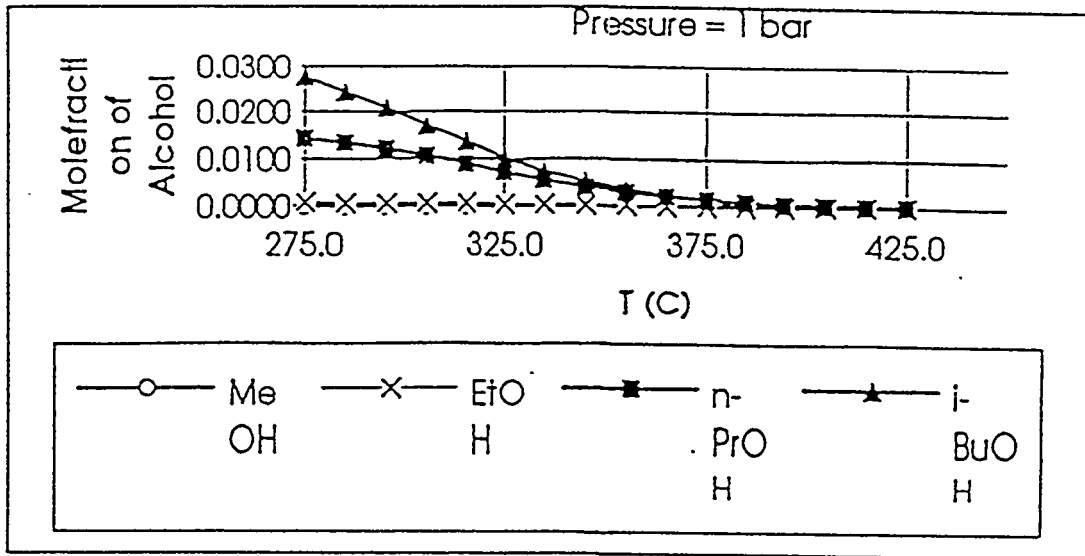
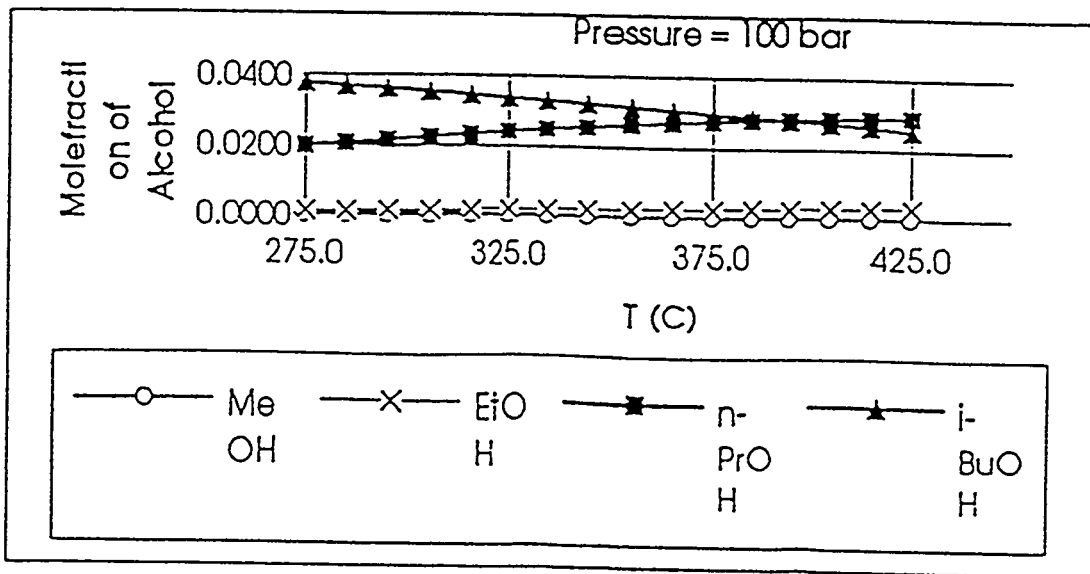
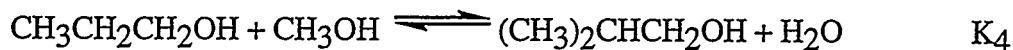
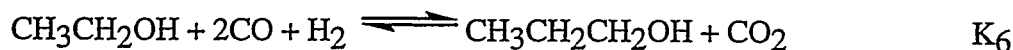
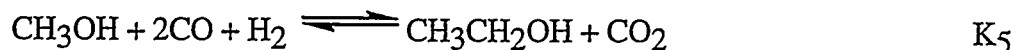


Figure 3.2.8 Plot of Mol Fraction of Alcohols vs Temperature at 100 Bar With H₂O Rejection



The same approach was applied toward the reactions in Scheme 2. Here, however, CO₂ is rejected instead of H₂O for oxygen removal.



Scheme 2. Higher alcohol synthesis with CO₂ rejection

Plots for 1 and 100 bar are represented in Figures 3.2.9 and 3.2.10, respectively.

Figure 3.2.9 Plot of Mol Fraction of Alcohols vs Temperature at 1 Bar With CO₂ Rejection

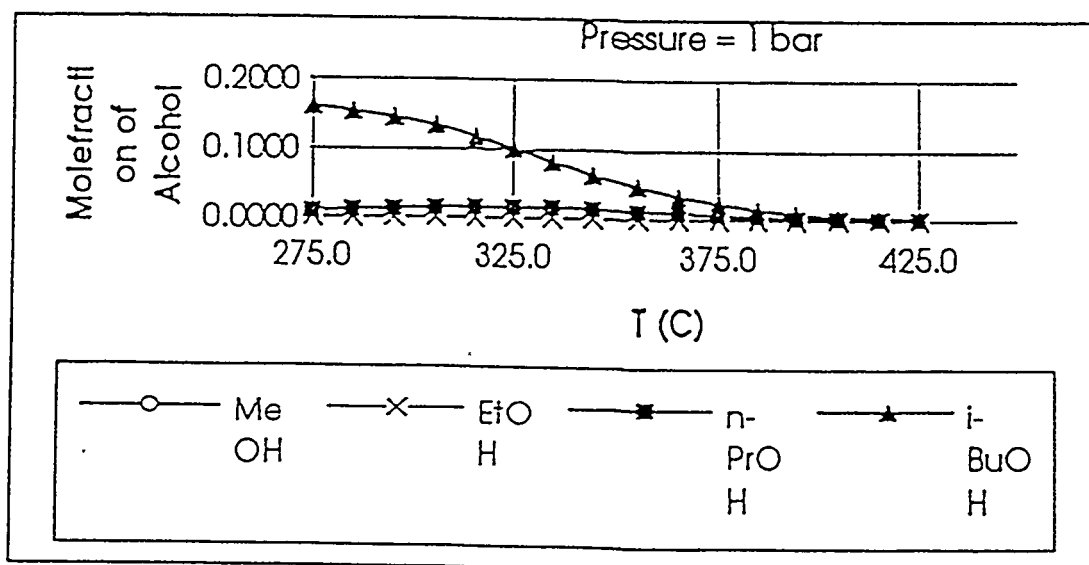
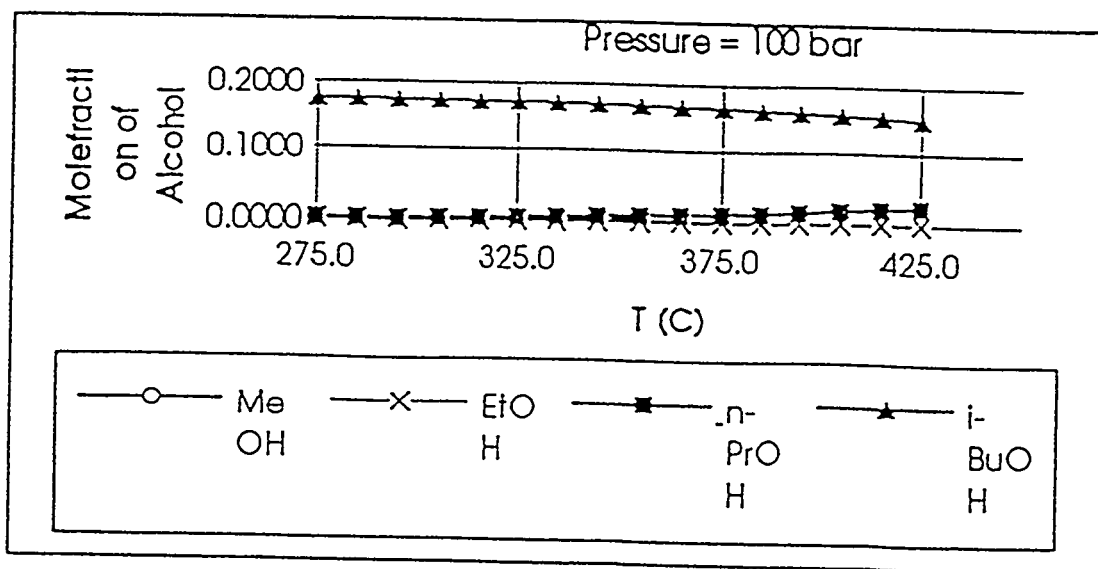


Figure 3.2.10 Plot of Mol Fraction of Alcohols vs Temperature at 100 Bar with CO₂ Rejection



The plots are revealing, especially the difference between H₂O and CO₂ rejection. No methanol is observed in all cases, even at the higher pressures. The chemical pathways were fixed (see Scheme 1 and 2). In all the plots the remaining mol fractions are CO and H₂. In general it can be seen that the higher pressure favors a higher mol fraction of alcohols. Comparison of the 100 bar plot for H₂O and CO₂ rejections reveals a marked difference, that is, isobutanol is dramatically favored.

If these calculations resemble any approximation to the true thermodynamic picture, does this suggest that any catalyst for HAS should also have built in shift activity.

3.2.3 4Q FY95 Objectives

Future plans for Task 3.2 will focus on the following areas:

- continue to screen immobilized catalyst candidates for hydrocarbonylation of dimethyl ether to ethylidene diacetate.
- continue catalyst development work on the cracking of ethylidene diacetate to vinyl acetate and acetic acid.

Task 3.3 New Processes for Alcohols and Oxygenated Fuel Additives

3.3.1 Isobutanol Synthesis in a Three Phase System (RWTH Aachen)

Fixed Bed Reactor Design and Runs

The problem of methanization was solved. The activity toward methane was in the same low range W. Falter mentioned. His STY to isobutanol could be reproduced with an additional amount of methanol (Table 3.3.1).

Table 3.3.1 Comparison of Catalytic Results

Run	WF 77 /thesis p. 143	CH 51-10	CH 51-11
Temperature [°C]	423	415	400
Pressure [MPa]	25	25	25
GHSV [h ⁻¹]	20000	20000	20000
Conversion CO [%]	22	33	31
Selectivity CO ₂ [%]	46	24	20
STY [g l ⁻¹ h ⁻¹]			
Methane	40	45	< 30*
Methanol	340	1095	1390
Isobutanol	355	414	360

* below the minimum registration value
Catalyst: ZrO₂/ZnO/MnO/K₂O (pH 9)

To obtain these results it was necessary to enlarge the volume of the filter filled with activated carbon and to change the arrangement of the catalyst in the fixed bed. It was optimal to mix the catalyst particles with only a few glass particles and to fill the remaining five centimeters of the tubular reactor with pure glass particles. This arrangement seemed to make catalyst poisons adsorb onto the surface of the glass particles instead of onto the active site of the catalysts.

Slurry Reactor Design and Runs

The results obtained in the slurry reactor clearly showed external parameter effects. The only intrinsic effect was observed by changing the temperature. The influence of reaction temperature on selectivity in slurry and fixed bed reactors was comparable in a qualitative way.

Decalin was used because of its resistance to hydrogenation and cracking, rendering it suitable for slurry runs. It does not hamper analytical measurements and will be used as inert oil until further notice. A disadvantage of decalin is the very high volatility, which could be compensated through refilling by a high pressure pump. If alternatives are found that show better properties relative to solubility and rate of diffusion of feedstock and products, they will be investigated further.

A temperature of about 160°C for the reflux condenser seems to be a useful compromise. At lower temperatures, the removal of products is hindered, and above 180°C, loss of decalin increases rapidly.

The slurry runs had a catalyst content of about 4 wt%. Two indications for mass transfer limitation were obtained as follows:

1. By increasing stirring speed, the STY to methanol and isobutanol increases remarkably. For example, doubling the stirring speed from 1000 to 2000 rpm increases the STY to methanol by 30%, while isobutanol is also synthesized in notable amounts.
2. STY to methanol and isobutanol is directly proportional to the applied mass flow of feed stock. Doubling GHSV doubles yield products as well. Selectivity and conversion are not affected. Catalyst capacity seems to be under-utilized. By increasing the mass flow, the concentration gradient across the boundary layer is increased, thereby increasing the diffusion rate.

The influence of reaction temperature mentioned earlier for the fixed bed reactor also holds qualitatively for the slurry reactor. In the range of 400°C, the STY of isobutanol and methane increase and decrease, respectively. Quantitatively, the activity for the slurry reactor is less than that for the fixed bed reactor (Table 3.3.2):

Table 3.3.2 Comparison of STY in Two Different Reactors

STY [g/(l*h)]	slurry reactor	fixed bed reactor
isobutanol	130	540
methanol	800	1500
isobutanol/methanol	0.16	0.36

At the same measured temperature in both reactors, the selectivity to isobutanol by the slurry reactor is lower. The following reasons for this behavior can be assumed:

1. By reducing the size of the catalyst particles as well as back mixing in the slurry reactor, heat transport is improved. The temperature rise at the active sites of the catalyst in the slurry is lower compared with the fixed bed. Thus, the temperature necessary for the synthesis of isobutanol is not reached.
2. The mass transfer limitation mentioned above may cause a shift of activity towards the different products.

Catalyst Preparation and Screening

Besides transferring the syngas conversion to isobutanol from a fixed bed into a slurry bed system--the main objective--the search for suitable catalysts under reproducible preparation conditions is ongoing. The latest results with alkaline promoted ZrO₂/ZnO/MnO- catalysts showed significant activity towards isobutanol and methanol. In the fixed bed as well as in the

slurry bed system, the optimum reaction conditions for these catalysts are $p > 200$ bar, $T > 400^\circ\text{C}$. Therefore the main objective of current research has to be understanding and optimizing this catalyst type and related ones in order to achieve milder reaction conditions.

Alkali Impregnation of Coprecipitated Catalysts

First results of this work have been presented in the last quarterly report. So far as the $\text{ZrO}_2/\text{ZnO}/\text{MnO}$ - type catalysts precipitated at different pH- values have been investigated, the major difference is in the alkali content. As described in the last report, a large number of alkali free coprecipitated catalysts have been prepared and impregnated with defined amounts of potassium compounds. The following set of catalysts (Table 3.3.3) will be tested:

Table 3.3.3 Coprecipitated Catalysts of the $\text{ZrO}_2/\text{ZnO}/\text{MnO}$ - Type

	Precipitation pH = 9	Precipitation pH = 11	Precipitation pH = 11 + 0.25 wt. % Pd
Potassium / wt. %	0.0	0.0	0.0
		0.5	0.5
	1.0	1.0	1.0
		2.0	2.0
	3.0	3.0	3.0
		4.0	4.0

calcination temperature = 450°C

This set of catalysts will clarify the influence of the pH of precipitation, the alkali content and the palladium impregnation. If these runs are successful, further catalysts will be prepared in order to investigate effects of different first and second main group bases and different transition metals like copper, platinum or rhodium.

Sol-Gel Based Catalysts

To elucidate the scope and limits of the $\text{ZrO}_2/\text{ZnO}/\text{MnO}$ system for isobutanol synthesis, different synthesis procedures are being investigated. Among others a relatively new and promising route is formed by the sol-gel method as was already pointed out in the last quarterly report. Sol-gel preparation initially involves the formation of a sol (ideally consisting of a viscous clear solution) followed by formation of a gel. Generally metal alkoxides are used as starting materials that form gels in which an oxide network is progressively built via inorganic polymerization reactions. Using this procedure one can obtain mesoporous zirconium oxide with high surface areas and narrow pore size distributions. The objective of the present work is the introduction of zinc and manganese precursors without sacrificing the beneficial properties of the zirconium oxide network.

Depending on the reaction conditions, the product of a sol-gel reaction may be a precipitate, a colloid, a sol or a gel. For clarity, a gel can be defined as a clear, three dimensional oxide network in which the solvent fills the pores.

Control of hydrolysis and condensation reaction rates can be influenced by the addition of complexing agents such as acetic acid or acetylacetone. In addition one can differentiate between acid and base catalyzed sol-gel reactions. Under acidic conditions, hydrolysis occurs at a faster rate than condensation, and the resulting gel is weakly branched. Condensation is accelerated relative to hydrolysis with increasing pH. Thus, a base-catalyzed gel is highly branched and contains colloidal aggregates. In this way the pore structure (surface area, pore volume and pore size distribution) can be tuned. The influence of the above described parameters on the formation of a multicomponent gel has been investigated. The wet gels were transformed into so-called aerogels via supercritical drying in an autoclave. These materials will be impregnated with defined amounts of potassium compounds, and tests will be performed in the near future. Future work will also include the preparation of different zirconia supports impregnated with zinc and manganese precursors.

Catalyst Screening

For catalyst screening a large number of test runs under reproducible reaction conditions are necessary. However, attempts to do this in a discontinuous way by using batch autoclaves failed. Catalysts that showed significant differences towards activity and selectivity in a continuous system behave nearly identically to each other in discontinuous runs.

In order to screen catalysts parallel to the comparison of the fixed bed and slurry reactions, a second isobutanol unit has been built. This unit is simpler than the existing one. An on-line analysis and process control system have been excluded, but the unit is capable of nearly the same reaction conditions as the first one, that is:

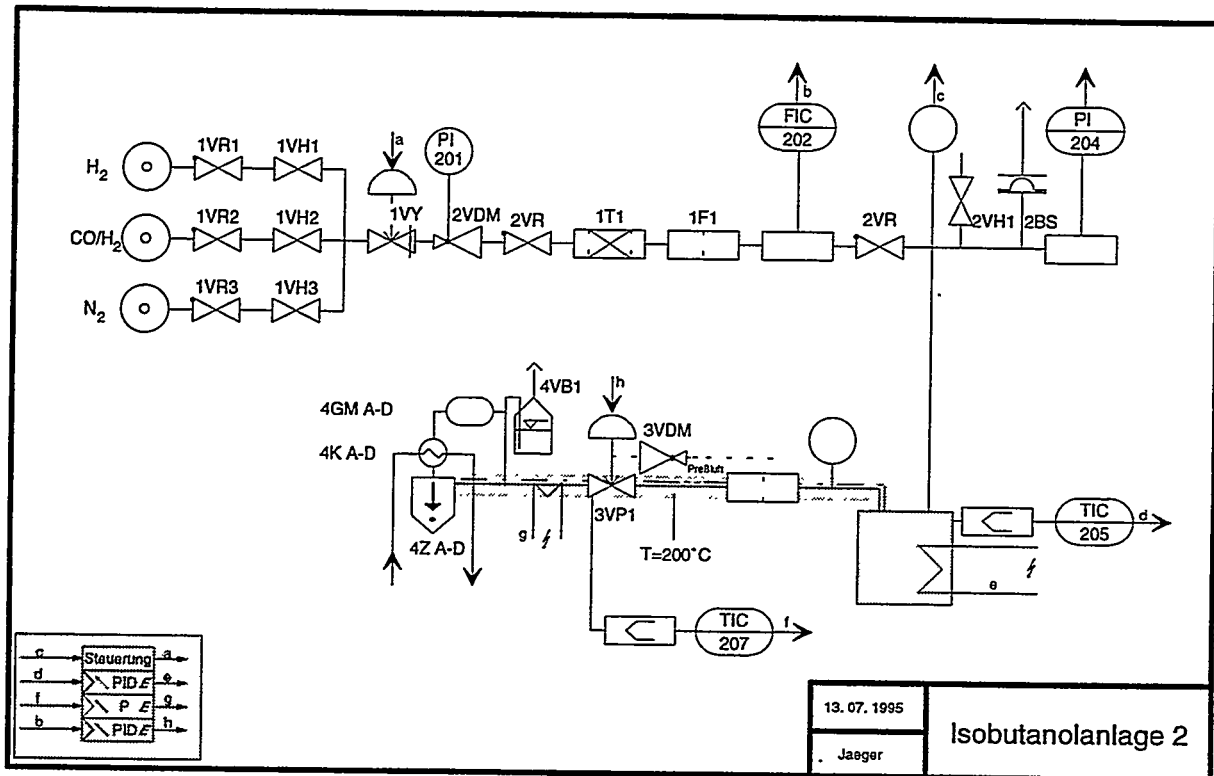
- pressure: 300 bar
- temperature: 500°C
- mass flow: 60 NI/h.

The fixed bed reactor used in this unit is a U-tube with an outer diameter of 8 mm and an inner diameter of 5 mm. The length of each tube leg is less than 15 cm. The reactor is placed in an oven with a height of 20 cm and an inner diameter of 8 cm. This type of reactor has a very smooth inner surface and is, as well as the rest of the unit, built from stainless steel. The unit has been completed, and first calibration runs are estimated for the middle of July.

Appendix 3.3 Legend to the Flow Scheme

- VR back pressure valve
- VH stop valve
- T drier filled with activated carbon
- F sintered metal filter
- VDM pressure regulator
- FIC thermal mass flow meter
- PI manometer
- BS rupture disc
- TIC jacket thermocouples
- Z cyclone
- VB bubbler
- KA-D multiple coil condenser
- GMA-D gas probe

Flow scheme of the Second Continuous Isobutanol Unit



3.3.2 Oxygenates via Synthesis Gas (Lehigh University)

Overall 3QFY95 Objectives

- (i) Continue studies of increasing the conversion of H_2/CO to higher alcohols by promotion of the $C_1 \rightarrow C_2$ carbon chain growth step over Cs-promoted $Cu/ZnO/Cr_2O_3$ and MoS_2 catalysts,
- (ii) Enhance the $C_2 \rightarrow C_3 \rightarrow C_4$ carbon chain growth steps over $Cs/Cu/ZnO/Cr_2O_3$ catalysts, and
- (iii) Prepare and test high surface area Cu/ZrO_2 catalysts, both Cs-doped and undoped, that are candidates for the synthesis of C_1 - C_5 alcohols, in particular branched products such as isobutanol.

Results and Discussion

Double Bed Catalyst Studies

As documented in previous reports, the Cs-promoted ternary Cu-based catalyst has been the center of recent kinetic studies of higher alcohol synthesis (HAS), and it is characterized, under optimized HAS operating conditions, by high productivities toward the intermediate species (ethanol (EtOH) and propanol (PrOH)) that lead to isobutanol (2m-PrOH) formation. The $C_1 \rightarrow C_2$ step is the slow synthesis step, and the EtOH is rapidly converted to PrOH and subsequently to 2m-PrOH. With an increase in the reaction temperature to at least $340^\circ C$, enhanced levels of ethanol and propanol are converted to isobutanol (and other terminal branched products). However, at this high temperature, the Cu-based catalyst tends to deactivate within a short period (150 hr).

An alternative approach to the enhancement of ethanol and propanol conversion to isobutanol is represented by the coupling of the low temperature Cu-based catalyst to a high-temperature catalyst, that is, the commercial Cu-free ZnO/Cr_2O_3 catalyst. During this quarter, double-bed experiments were designed and performed using a series configurations in which the Cs-doped $Cu/ZnO/Cr_2O_3$ catalyst occupied the top layer in the downflow reactor and was kept at a temperature of $\leq 325^\circ C$, and a Cs-doped ZnO/Cr_2O_3 catalyst occupied the lower layer where the temperature was kept at $\geq 400^\circ C$. The reactor is described in greater detail later in this report.

Preparation of the Catalysts. A single sample of the commercial ZnO/Cr_2O_3 catalyst (Harshaw Zn-0311 T 1/4") was broken, sieved to 0.85-2.0 mm particles that were calcined under N_2 at $400^\circ C$ for 4 hr, and doped with $CsOOCH$. The calcined catalyst was added to a N_2 -purged aqueous solution of $CsOOCH$, which was then slowly evaporated under flowing N_2 at $50^\circ C$. The dried catalyst was recalined at $350^\circ C$ for 3 hr. The composition of the catalyst corresponded to 4 mol% $CsOOCH/ZnO/Cr_2O_3$, which was not determined to be an optimized level of the promoter. By X-ray powder diffraction (XRD), it was shown that the catalyst consisted of crystalline $ZnCr_2O_3$ with spinel-like structure and microcrystalline ZnO . Reduction of the catalyst was carried out at $450^\circ C$ under a flowing $H_2/N_2 = 2/98$ vol% mixture (60 ml/min) at ambient pressure. The temperature was decreased and the reduction terminated when the quantity of

water generated by reduction of the catalyst, as monitored by gas chromatography (GC), decreased significantly.

The Cs/Cu/ZnO/Cr₂O₃ was prepared by using the same doping procedure with a CuO/ZnO/Cr₂O₃ = 30/45/25 mol% catalyst that was prepared by coprecipitation of a hydrotalcite-like precursor calcined using a step-wise procedure to 350°C, which was maintained for 3 hr. The composition of the doped catalyst corresponded to 3 mol% CSOOCH/CuO/ZnO/Cr₂O₃. Reduction was carried out at 250°C using the procedure described above.

Catalyst Testing. Catalyst testing was carried out in a tubular down-flow fixed-bed reactor. A schematic description of the catalyst testing system is provided in Figure 3.3.1. Special arrangements were made to minimize the formation of iron carbonyl formed by contact of CO with iron-containing surfaces. The deposition of iron from Fe(CO)₅ over the Cu-based catalyst sites is in fact known to cause irreversible deactivation. Charcoal and molecular sieve traps were employed for filtering the CO stream fed from high-pressure stainless steel tanks, an internally copper-lined stainless steel reactor and copper thermocouple wells for the reading of the catalyst temperature were adopted, and a water cooling system was used to keep the temperature of the stainless steel tubing upstream from the reactor below 65°C. Indeed, elemental analysis of tested catalysts (500 hr on stream) indicated iron content <60 ppm.

In the case of the single-bed experiments, 2.0 g of each catalyst was diluted with 0.5 mm Pyrex beads to a total volume of about 7.0 ml. The bed (about 7 cm long) was placed in the center of the reactor tube (1.9 cm I.D. and 55 cm long), using 3.0 mm Pyrex beads as packing material upstream and downstream. In the case of the double-bed experiments, 1.0 g of each catalyst was diluted with the Pyrex beads up to a 4.0 ml volume. As indicated in Figure 3.3.2, the Cs/Cu/ZnO/Cr₂O₃ bed was loaded in the top portion of the reactor, about 15 cm downstream from the reactor inlet section. The Cs/Zn/Cr₂O₃ bed was loaded in the bottom portion of the reactor at a distance of about 20 cm below the first bed. The temperatures of the beds were monitored by use of two independent thermocouples, a copper-thermocouple well being connected to each reactor end.

The catalyst pretreatments in the double-bed reactor required a step-wise procedure. Initially, the Cu-based catalyst was reduced by heating the top portion of the reactor at 250°C under flowing H₂/N₂ mixture, while the bottom portion of the reactor was kept unheated. When the reduction was completed, the first bed was cooled to room temperature under flowing N₂. Subsequently, the treatment of the zinc chromite catalyst was carried out by heating the bottom portion of the reactor to 450°C under a flowing H₂/N₂ mixture. During this phase, in order to "protect" the Cu-based catalyst from possible Cu sintering or over-reduction, the temperature of the first bed was kept below 70°C by means of an external water circulating system.

The gas stream fed to the synthesis reactor consisted of a mixture of H₂, CO, and N₂, where separate lines for H₂ and CO allowed for easily varying the H₂/CO molar ratio (N₂/CO = 5/95 mol% in each experiment). Nitrogen behaved as an inert in the reacting system and provided an

Figure 3.3.1 Schematic of the Catalyst Testing Unit

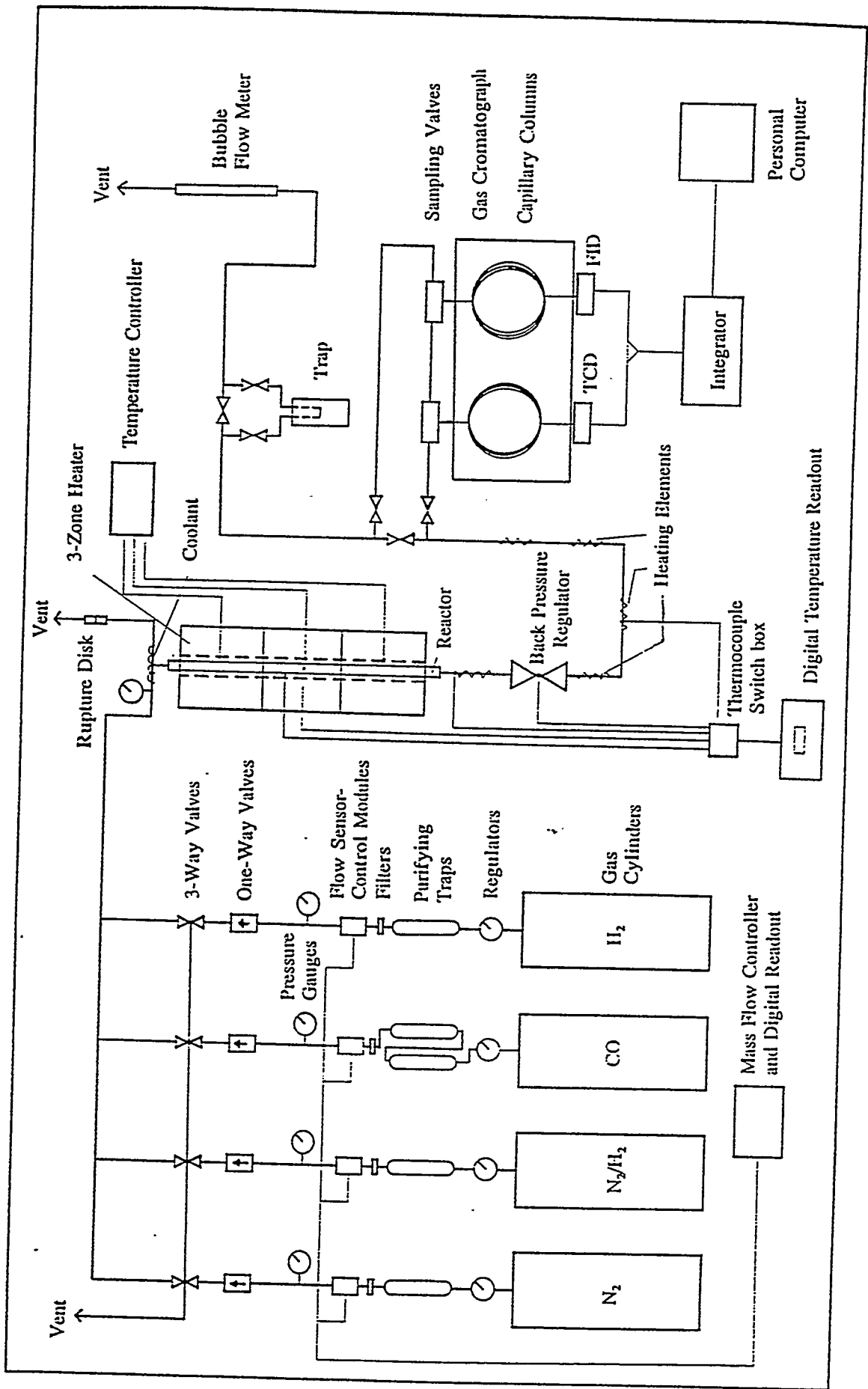
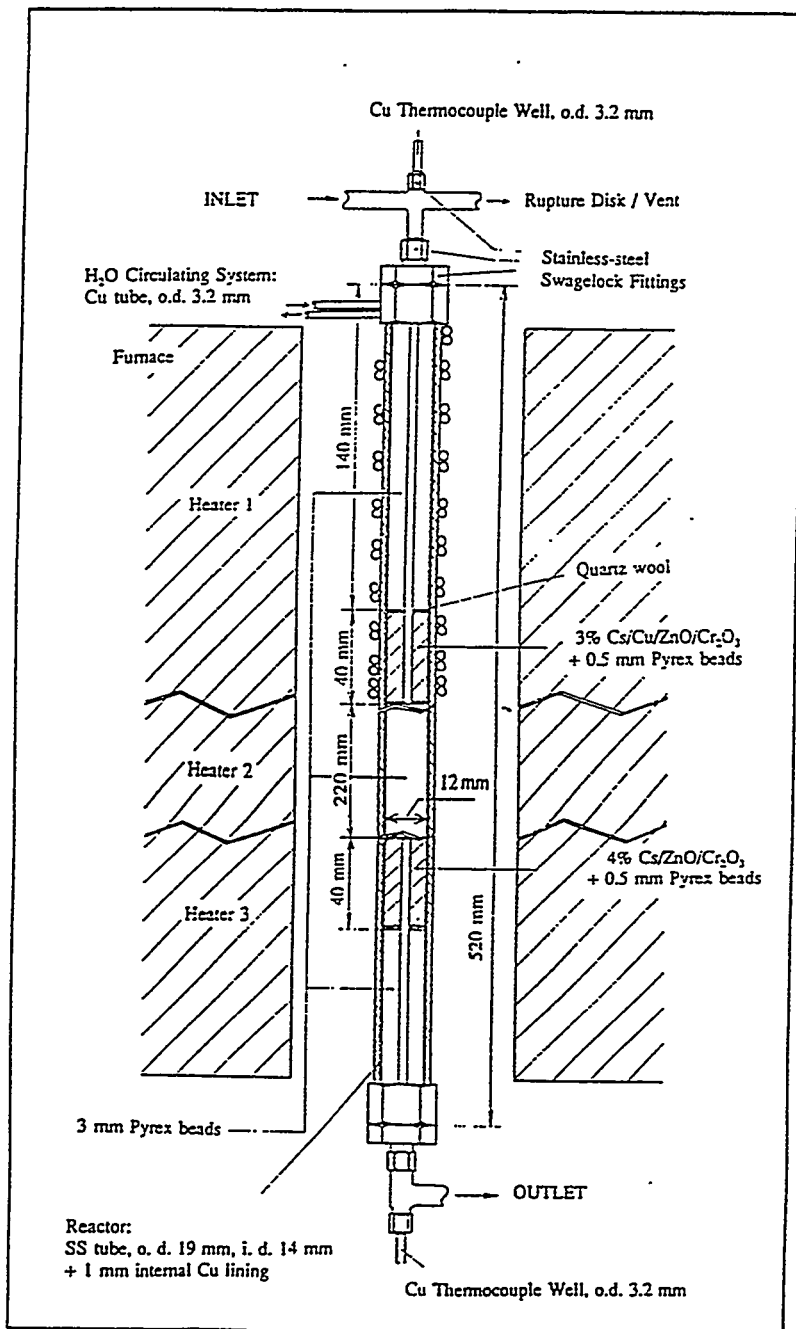


Figure 3.3.2 Scaled Drawing of the Copper-Lined Synthesis Reactor used in the Double-Bed Experiments. Note that the water circulating system was employed during the catalyst reduction treatments, but it was removed during the activity testing experiments. The same cooling system was used during the testing of the single bed 3 mol % Cs/Cu/ZnO/Cr₂O₃ catalyst to maintain the temperature of the stainless steel tubing upstream from the reactor below 65°C.



internal standard for the evaluation of the product yields. The kinetic runs carried out over the Cs/Cu/ZnO/Cr₂O₃ catalyst ranged over the following windows of operating variables: T = 310-340°C, P = 6.5-7.6 MPa, H₂/CO = 0.45-3.5, gas hourly space velocity (GHSV) = 3,300-18,375 l(STP)/kg cat/hr. The activity tests over the Cs/ZnO/Cr₂O₃ catalyst and the double-bed experiments were carried out at constant pressure (7.6 MPa) and synthesis gas composition (H₂/CO = 0.75), while the GHSV was varied in the range of 5,450-18,375 l(STP)/kg cat/hr. Over the zinc chromite catalyst, a constant temperature of 405°C was maintained. In the double-bed experiments, the first and second beds were kept at 325 and 405°C, respectively. In each experiment, the set of conditions was maintained for a period of 24 hr.

Quantitative Product Analysis. The reactor outlet stream was sampled every 20-60 min using an on-line automated heated sampling valve and analyzed by a Hewlett-Packard 5390 gas chromatograph. The analyses were quantified and averaged for evaluation of product yields and selectivities after a steady-state activity was reached (about 6 hr from the initial setting of the operating conditions). A Molsieve capillary column was used to separate N₂, CH₄ and CO. The column was connected to a thermal conductivity detector (TCD). The CO/N₂ and CH₄/N₂ molar ratios were applied as follows to evaluate CO conversion and methane production:

$$\begin{aligned} \% \text{CO conversion} &= 1 - (\text{CO}/\text{N}_2)_{\text{outlet}} / (\text{CO}/\text{N}_2)_{\text{inlet}} \\ \text{CH}_4 \text{ productivity} &= \text{CH}_4/\text{N}_2 * \text{N}_2 \text{ Molar Flow} * \text{MW}_{\text{CH}_4} \quad (\text{g}/\text{kg cat}/\text{h}) \end{aligned}$$

Knowledge of methane productivity provided for the quantification of the oxygenates and hydrocarbons separated in a capillary CP13 column and analyzed by a flame ionization detector (FID). The same column was temporarily connected to the TCD to determine CO₂ and H₂O yields. The FID response factors were determined by a thorough calibration of the instrument, resulting in significant deviations from the literature data. The identification of products was based on comparison of the retention times with those of known standards and on fragmentation patterns obtained from analyses of liquid samples by a Hewlett-Packard gas chromatograph/mass spectrometer. Carbon balances were calculated in each experiment by comparing the overall amount of carbon detected in the outlet product mixture with the measure of CO conversion; relative errors were always lower than 10%.

Experimental Results. The catalysts were systematically tested at three different GHSV conditions while the other reaction parameters were maintained constant. Comparisons of the CO conversions and product space time yields of the double bed catalyst system with the single bed catalysts are given in Tables 3.3.4 and 3.3.5 for GHSV = 5450 and 18,375 l/kg cat/hr, respectively. The mol% CO conversion is expressed as the total quantity of CO converted to products, including CO₂.

Comparisons of the data in Table 3.3.4 (GHSV = 5450 l/kg cat/hr) show that:

- While the 3 mol% Cs-promoted Cu/ZnO/Cr₂O₃ catalyst provided high productivities to methanol, ethanol, and propanol, the 4 mol% Cs-doped commercial high-temperature ZnO/Cr₂O₃ catalyst exhibited a low selectivity to methanol (due to the chemical equilibrium

of methanol synthesis) and very low productivities to ethanol and propanol, which are efficiently converted to isobutanol (due to the higher reaction temperature).

- In the coupled double-bed configuration, a synergism between the two catalysts was obtained. This synergism resulted in enhanced productivities to isobutanol (47% incremental increase with respect to the single low temperature Cu-based catalyst and 94% incremental increase with respect to the single high-temperature catalyst). As expected, the coupling allowed the efficient conversion of ethanol and propanol "intermediates" formed over the top Cu-based catalyst to form the terminal isobutanol over the bottom layer of Cu-free high temperature catalyst.
- Due to the increased reactor exit temperature, the productivity of methanol over the double-bed catalyst system was much lower than that over the single Cu-based catalyst. This consequently resulted in a much improved isobutanol/methanol molar ratio (1.0/11.8 for the single Cs/Cu/ZnO/Cr₂O₃ catalyst and 1.0/1.7 for the double-bed catalyst configuration). The lower quantity of methanol produced in the double-bed system resulted from partial decomposition of the methanol formed over the first bed to CO + H₂ over the second high temperature bed.

The experimental results shown in Table 3.3.5 (GHSV = 18,375 l/kg cat/hr) confirm the concept of using a double-bed catalyst system, with each of the catalyst beds at different temperatures to optimize the chemical syntheses occurring over each. It was noted that at high space velocity, very high productivities to isobutanol can be obtained. In fact, the overall productivity of the C₄-C₆ 2-methyl iso-alcohols is nearly 200 g/kg cat/hr. It was also noted that some 20% of the C₇ oxygenates formed over the double-bed catalysts at both gas velocities consisted of 2-methyl-1-hexanol.

The double-bed catalysts were also tested at GHSV = 12,000 l/kg cat/hr, and it was observed that the CO conversion levels and the product space time yields fell between those obtained at the lower and higher GHSV results shown in Tables 3.3.4 and 3.3.5. A comparison of the results obtained over the double-bed catalysts at the three reactant flow rates is shown in Table 3.3.6, where the CO conversion is expressed on the basis of CO₂-free products.

In these experiments, quantities of ketones and aldehydes were observable. In Tables 3.3.4-3.3.6, these products are grouped with the corresponding alcohol products. Methyl esters are also formed but are not included in the tables. Of particular interest is the observation that no significant increase in the formation of methane was observed over the double-bed configuration with respect to the single-bed Cu-based catalyst, although some increase in the formation of higher hydrocarbons was evident. However, at the lower H₂/CO molar ratio of 0.45, Table 3.3.7 gives an indication of the side products formed during alcohol synthesis over the single bed low temperature catalyst.

The 3 mol% Cs/Cu/ZnO/Cr₂O₃ catalyst was retested at 310°C and 7.6 MPa with H₂/CO = 0.45. The GHSV utilized was 5500 l/kg cat/hr instead of 5450 l/kg cat/hr. Nearly identical results were obtained, except the methanol space time yield was 250 g/kg catal/hr (compare with Table 3.3.7).

Table 3.3.4 Kinetic Runs over a 3% Cs Cu/ZnO/Cr₂O₃ Catalyst and a 4% Cs Zn/Cr₂O₃ Catalyst (first and second column, respectively). The results are compared with the performances obtained by coupling the two catalysts (third column) in a double-bed experiment (top bed = 3% Cs Cu/ZnO/Cr₂O₃, bottom bed = 4% Cs Zn/Cr₂O₃).

Operating conditions:

3% Cs Cu/ZnO/Cr₂O₃: T = 325°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 5450 l/kg cat/hr

4% Cs Zn/Cr₂O₃: T = 405°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 5450 l/kg cat/hr

Double-bed run: T_{TOP BED} = 325°C, T_{BOTTOM BED} = 405°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 5450 l/kg cat tot/hr

	Cs/Cu/ZnO/Cr ₂ O ₃ (g/Kg cat/hr)	Cs/Zn/Cr ₂ O ₃ (g/Kg cat/hr)	Cs/Cu/ZnO/Cr ₂ O ₃ + Cs/Zn/Cr ₂ O ₃ (g/Kg cat/hr)
MeOH	268.0	52.8	56.5
EtOH	20.0	0.77	1.07
PrOH	38.8	3.82	6.52
BuOH	6.55	0.29	1.36
PentOH	2.8	0.17	1.15
2m-PrOH	52.08	39.54	76.79
2m-BuOH	10.93	4.26	16.22
2m-PentOH	4.816	2.44	8.88
2-BuOH	4.50	1.84	1.02
3m-2-BuOH	5.00	0.46	2.77
3-PentOH	4.18	0.38	2.33
2m-3-PentOH	7.40	2.93	10.5
C ₇₊ oxygenates	47.80	51.8	55.4
CH ₄	11.05	2.82	10.56
C ₂₊ hydrocarbons	8.17	10.89	13.23
% CO conversion	30.64%	12.03%	18.70%

Table 3.3.5 Kinetic Runs over a 3% Cs Cu/ZnO/Cr₂O₃ Catalyst and a 4% Cs Zn/Cr₂O₃ Catalyst (first and second column, respectively). The results are compared with the performances obtained by coupling the two catalysts (third column) in a double-bed experiment (top bed = 3% Cs Cu/ZnO/Cr₂O₃, bottom bed = 4% Cs Zn/Cr₂O₃).

Operating conditions:

3% Cs Cu/ZnO/Cr₂O₃: T = 325°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 18375 l/kg cat/hr

4% Cs Zn/Cr₂O₃: T = 405°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 18375 l/kg cat/hr

Double-bed run: T_{TOP BED} = 325°C, T_{BOTTOM BED} = 405°C, P = 7.6 MPa, H₂/CO = 0.75,
GHSV = 18375 l/kg cat tot/hr

	Cs/Cu/ZnO/Cr ₂ O ₃ (g/Kg cat/hr)	Cs/Zn/Cr ₂ O ₃ (g/Kg cat/hr)	Cs/Cu/ZnO/Cr ₂ O ₃ + Cs/Zn/Cr ₂ O ₃ (g/Kg cat/hr)
MeOH	1200.0	173.4	178.80
EtOH	68.70	2.75	7.05
PrOH	83.20	11.49	23.54
BuOH	15.23	0.95	4.18
PentOH	9.61	0.62	3.09
2m-PrOH	65.60	74.13	138.82
2m-BuOH	21.04	8.35	32.96
2m-PentOH	14.4	5.28	21.71
2-BuOH	9.68	2.5	5.17
3m-2-BuOH	10.17	0.94	7.22
3-PentOH	10.24	1.21	7.71
2m-3-PentOH	16.02	5.54	23.14
C ₇₊ oxygenates	67.50	78.0	105.5
CH ₄	10.4	4.14	12.06
C2+ hydrocarbons	6.00	15.79	24.02
% CO conversion	14.65%	6.30%	11.71%

Table 3.3.6 Productivities and CO Conversions Observed for High Alcohol Synthesis with $H_2CO = 0.75$ Synthesis Gas at 7.6 MPa over the Double Bed 3 mol% Cs/Cu/ZnO/Cr₂O₃ and 4 mol% Cs/ZnO/Cr₂O₃ Catalysts under the Following Operating Conditions:

Top Bed: 3 mol% Cs/Cu/ZnO/Cr₂O₃ (1 g), 325°C

Bottom Bed: 4 mol% Cs/ZnO/Cr₂O₃ (1 g), 405°C.

The productivities of aldehydes and ketones have been added to those of the primary and secondary alcohols, respectively.

	GHSV = 5,450 l(STP)/kg cat/h (g/kg cat/h)	GHSV = 12,000 l(STP)/kg cat/h (g/kg cat/h)	GHSV = 18,375 l(STP)/kg cat/h (g/kg cat/h)
MeOH	56.5	114.3	178.8
EtOH	1.1	3.9	7.0
PrOH	6.5	18.7	23.5
BuOH	1.3	3.3	4.2
PentOH	1.1	2.3	3.1
HexOH	1.3	1.9	2.3
2m-PrOH	76.8	114.6	138.8
2m-BuOH	16.2	27.1	32.9
2m-PentOH	8.9	16.0	21.7
2m-HexOH	7.5	17.4	24.0
2-BuOH	1.0	4.4	5.2
3m-2-BuOH	2.8	6.9	7.2
3-PentOH	2.3	6.8	7.7
2m-3-PentOH	10.5	19.7	23.1
MF	6.1	8.9	11.3
MAC	2.1	2.0	1.7
DME	2.9	4.4	4.8
C ₇₊ oxygenates	46.9	135.5	81.5
CH ₄	10.5	12.4	12.0
C ₂ -C ₄ hydrocarbons	17.0	25.6	28.0
% CO conv. (CO ₂ free)	12.0%	9.4%	6.6%