Impregnation Techniques

The observed synergistic effect of zinc and manganese oxide on isobutanol production prompted an investigation of the influence of different impregnation sequences on catalytic behavior. For this purpose, two different zirconia supports were prepared according to a precipitation and a sol-gel method, as shown in Table 3.3.7.

Table 3.3.7 Analytical Data of Zirconia Supports[1]

	BET (m2/g)	Mean pore size (Å)
Precipitation (LiOH, 80°C, pH 9)	275	35
Sol-Gel (HOAc/Zr 1.75; H2O/Zr 4)	159	65

[1] Both supports were calcined at 400°C.

These supports were impregnated in three different modes. The first method involved a primary impregnation with zinc acetate followed by a secondary impregnation with manganese acetate. The second method followed the reverse route—impregnating first with manganese and then with zinc. In the third method, mixtures of zinc- and manganese-acetate were used. All impregnations were conducted so as to obtain final loadings of 10 mol%, respectively, of zinc and manganese. Between subsequent impregnations, the samples were calcined at 400°C.

The use of deposition-precipitation techniques (selective precipitation of precursors on supports) is also being examined.

3.3.2 Oxygenates via Synthesis Gas (Lehigh University)

Overall 4QFY95 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

Cu/ZrO_2 Catalysts

Zirconia-based catalysts are being investigated for their potential as alcohol synthesis catalysts, and a series of CuO/ZrO_2 catalysts having different Cu/Zr molar ratios were previously prepared by aqueous coprecipitation at constant pH and temperature as described in quarterly progress report no. 2.

A fresh sample of the CuO/ZrO_2 = 10/90 mol% catalyst (2 g mixed with Pyrex beads for dilution) was loaded into the reactor after being calcined in air at 350°C. It was then reduced at 250°C using a constant flow of 2 vol% H_2/N_2 gas mixture at atmospheric pressure; the formation of H_2O during the reduction process was monitored by gas chromatography. After the reduction was complete, the reactor was cooled to ambient temperature, the gas flow was changed to H_2/CO = 70/30 mol% synthesis gas, and the reactor was pressurized to 7.6 MPa. After the gas hourly space velocity (GHSV) was verified as 6120 l/kg cat/hr, the temperature was increased to 250°C, and steady-state testing was carried out. The 70/30 composition satisfies the stoichiometric condition for product formation.

After the above experiment, the quantity of CO_2 in the $H_2/(CO + CO_2)$ = 70/30 mol% synthesis gas was systematically varied from 0% to 30% by using the following gas mixtures:

$H_2/CO/CO_2$ = 70/30/0
70/28/2
70/25/5
70/20/10
70/15/15
70/10/20
70/5/25
70/2/28
70/0/30

The gas mixtures were changed while the reaction temperature and pressure were maintinaed at the constant preset values. Preliminary results showed that the presence of CO_2 in the synthesis gas steadily promoted the formation of methanol while inhibiting the formation of dimethylether (DME), as shown in Figures 3.3.5 and 3.3.6.

After testing with the sequence of increasing CO_2 concentration was completed, the reactant mixture was changed to the original CO_2-free H_2/CO = 2.33, and a slightly lower catalytic activity was noted. The productivities of both methanol and dimethylether (DME) were somewhat lower than the initially observed space time yields. However, with an increase in the CO_2 content of the reactant again, reproducible catalyst behavior was observed, as shown in Figures 3.3.5 and 3.3.6. Therefore, no significant deactivation was observed during this testing with CO_2 in the synthesis gas reactant mixture.

Figure 3.3.5 Space Time Yields (g/kg catal/hr) of Methanol *vs* CO_2 Content in the $H_2/(CO + CO_2) = 70/30$ mol% Synthesis Gas at 250°C and 7.6 MPa with GHSV = 6,120 l/kg catal/hr

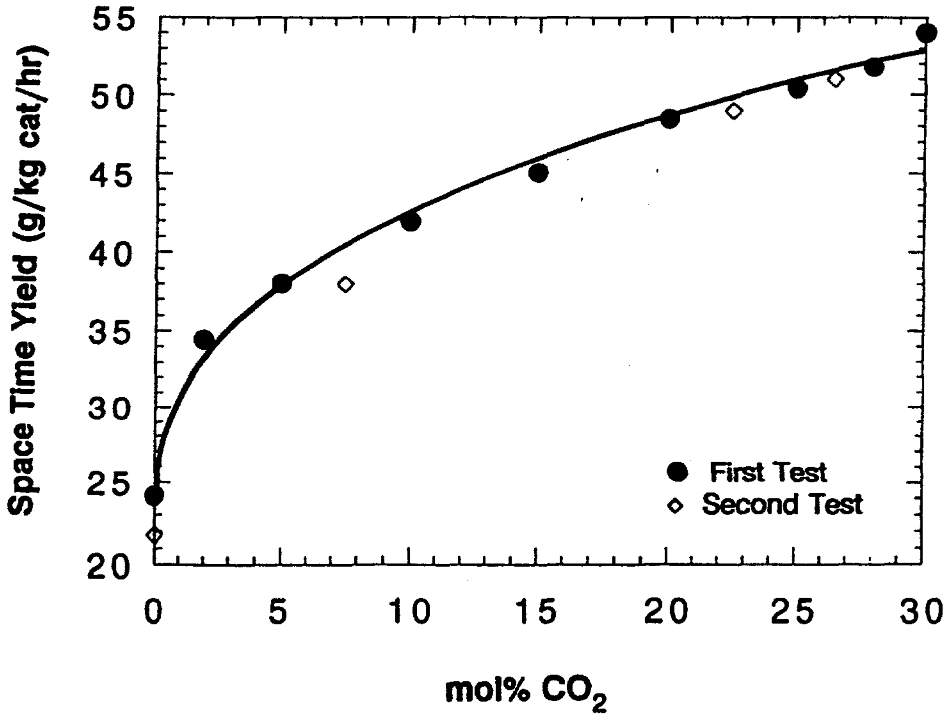
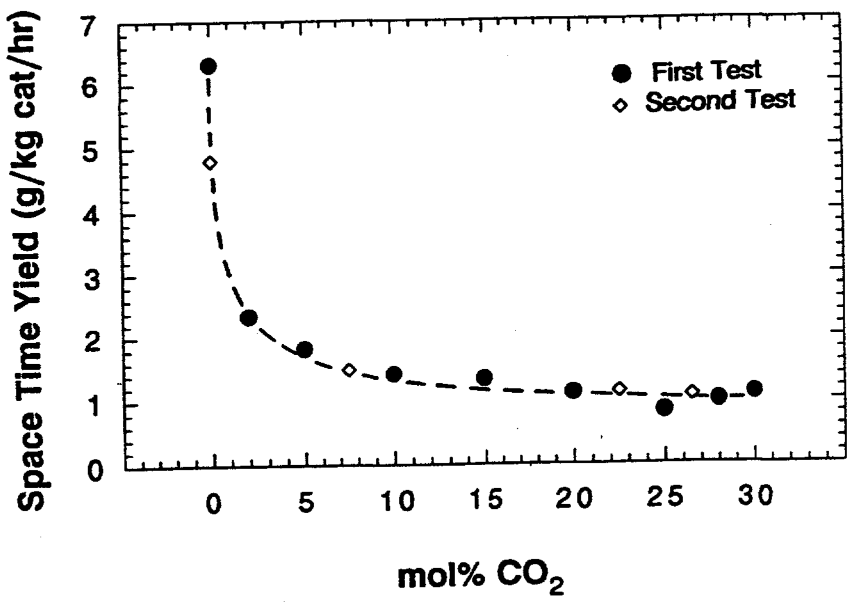


Figure 3.3.6 Space Time Yields (g/kg catal/hr) of Dimethylether *vs* the CO_2 Content in the $H_2/(CO + CO_2) = 70/30$ mol% Synthesis Gas at 250°C and 7.6 MPa with GHSV = 6,120 l/kg catal/hr



This continuous testing to determine the effect of CO_2 on the catalytic behavior of the Cu/ZrO_2 = 10/90 catalyst was carried out over two weeks. This same catalyst sample was tested further in studying the effect of reaction temperature and H_2/CO synthesis gas ratio on the activity and productivity of the catalyst. The reaction temperature was varied from 250 to 330°C while a H_2/CO = 0.45 synthesis gas was maintained at 7.6 MPa with GHSV = 5500 l/kg cat/hr. The space time yields (STY) of methanol and dimethylether are shown in Figure 3.3.7. A significant increase in the space time yield of dimethylether (DME) was observed with increasing reaction temperature. The DME productivity ranged from 5 g/kg cat/hr at 250°C to 105 g/kg cat/hr at 330°C. However, methanol space time yield remained approximately constant at »20 g/kg cat/hr, after a small initial increase from 16.5 g/kg cat/hr.

While the other reaction conditions were maintained, the H_2/CO ratio was varied from 0.45 to 2.33 at a constant reaction temperature of 310°C. Increasing the H_2/CO ratio had a gradual effect on the space time yields of the products, as shown in Figure 3.3.8. The DME productivity slowly decreased from 60 to 44 g/kg cat/hr as the H_2/CO ratio was increased. Methanol productivity exhibited a small increase from 22 g/kg cat/hr (H_2/CO = 0.45) to 30 g/kg cat/hr (H_2/CO = 1.50), but a further increase in the H_2/CO ratio did not have an effect on the methanol space time yield.

A Cu/ZrO_2 = 30/70 mol% catalyst was tested to determine if its catalytic behavior was similar to that of the Cu/ZrO_2 = 10/90 mol% catalyst. As with the 10/90 mol% sample, the DME productivity showed a marked increase with temperature, as shown in Figure 3.3.9; the STY increased from 5 g/kg cat/hr at 250°C to 86 g/kg cat/hr at 330°C. The space time yield for methanol was observed to increase from 17 g/kg cat/hr at 250°C to 34 g/kg cat/hr at 290°C, but it then decreased slowly to 21 g/kg cat/hr at 330°C. The trends observed in STY of the products with increasing H_2/CO ratio were similar to those of the 10/90 mol% catalyst, as indicated by comparing Figure 3.3.10 with Figure 3.3.8. The DME STY decreased slowly from 58 g/kg cat/hr (H_2/CO = 0.45) to 44 g/kg cat/hr (H_2/CO = 2.33). The STY of methanol increased from 24 g/kg cat/hr (H_2/CO = 0.45) to 38 g/kg cat/hr (H_2/CO = 2.33). The increased Cu content of the Cu/ZrO_2 = 30/70 catalyst did not appear to significantly affect the observed catalytic behavior of the catalyst compared with the Cu/ZrO_2 = 10/90 catalyst.

BET surface areas of the tested catalysts were 72 m^2/g for the 10/90 mol% sample (after »1 month of testing at 7.6 MPa and various temperatures extending up to 330°C) and 55 m^2/g for the 30/70 mol% sample. The corresponding values for the fresh, calcined catalysts were 148 and 78 m^2/g, respectively.

X-Ray diffraction (XRD) powder patterns of both 10/90 and 30/70 mol% tested catalysts did not show any peaks corresponding to crystalline copper. However, the tested 30/70 mol% sample exhibited a sharp pattern assignable to crystalline zirconia. The fresh, calcined catalysts of both compositions were observed to be X-ray amorphous.

Figure 3.3.7 Effect of Reaction Temperature on the Productivity of Methanol and Dimethylether from $H_2/CO = 0.45$ Synthesis Gas at 7.6 MPa and GHSV = 5500 l/kg cat/hr over the $Cu/ZrO_2 = 10/90$ mol% Catalyst

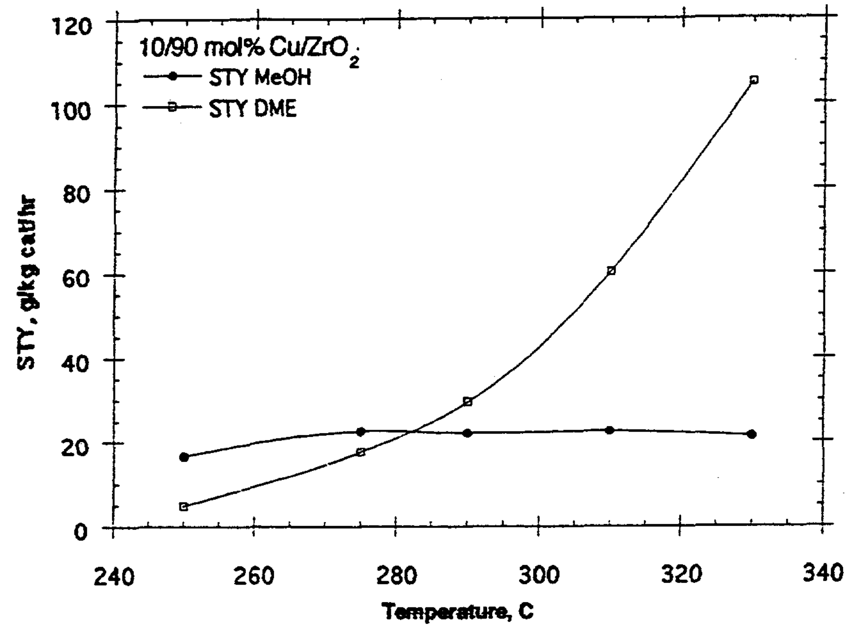


Figure 3.3.8 Effect of the H_2/CO Synthesis Gas Ratio on the Productivity of Methanol and Dimethylether at 310°C, 7.6 MPa, and GHSV = 5500 l/kg cat/hr over the $Cu/ZrO_2 = 10/90$ mol% Catalyst

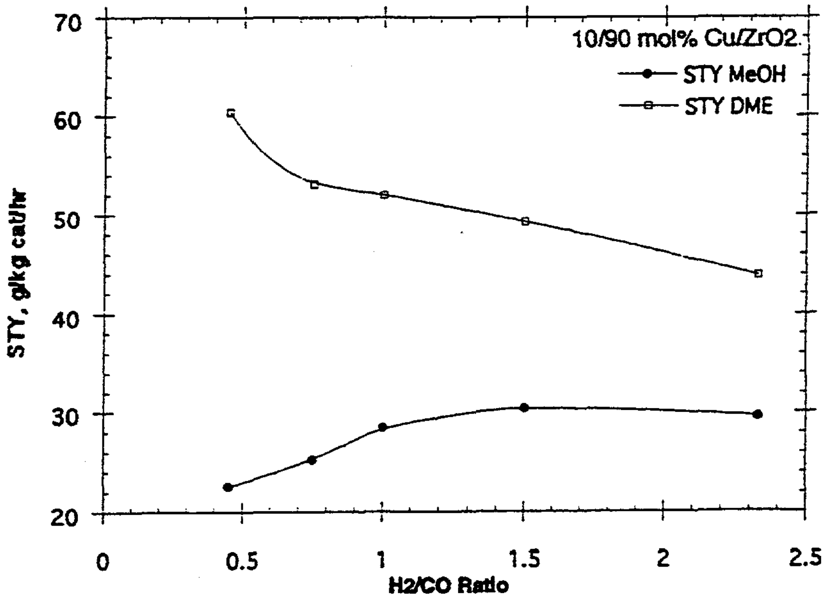


Figure 3.3.9 Effect of Reaction Temperature on the Productivity of Methanol and Dimethylether from $H_2/CO = 0.45$ Synthesis Gas at 7.6 MPa and GHSV = 5500 l/kg cat/hr over the $Cu/ZrO_2 = 30/70$ mol% Catalyst

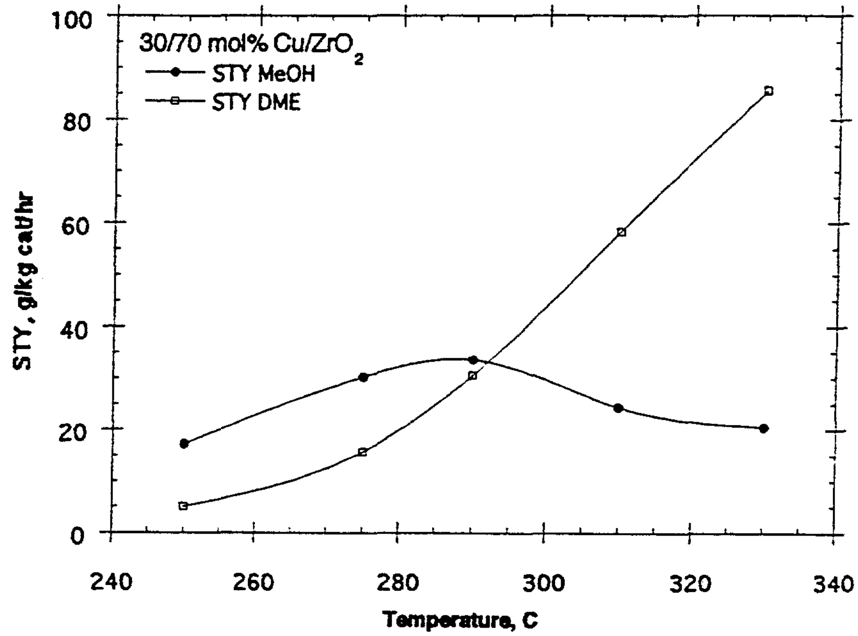
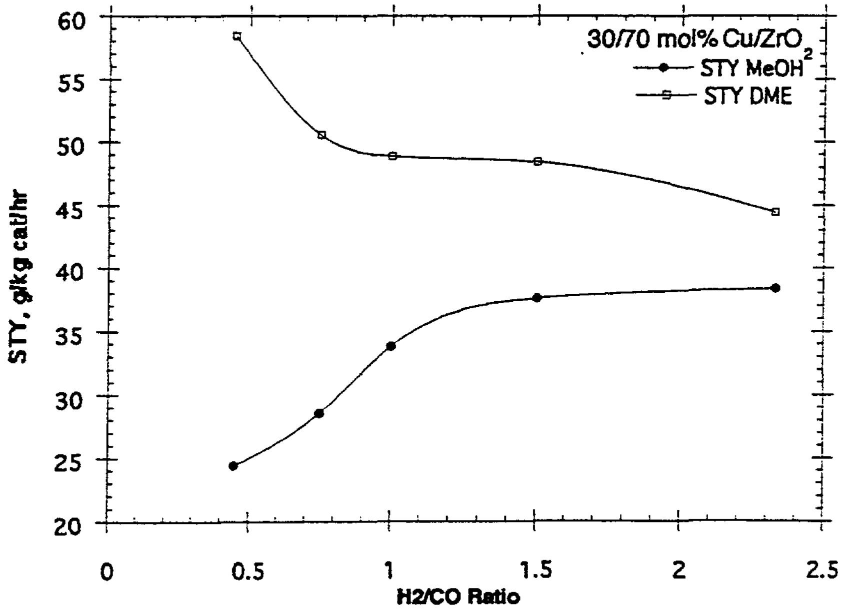


Figure 3.3.10 Effect of the H_2/CO Synthesis Gas Ratio on the Productivity of Methanol and Dimethylether at 310°C, 7.6 MPa, and GHSV = 5500 l/kg cat/hr over the $Cu/ZrO_2 = 30/70$ mol% Catalyst



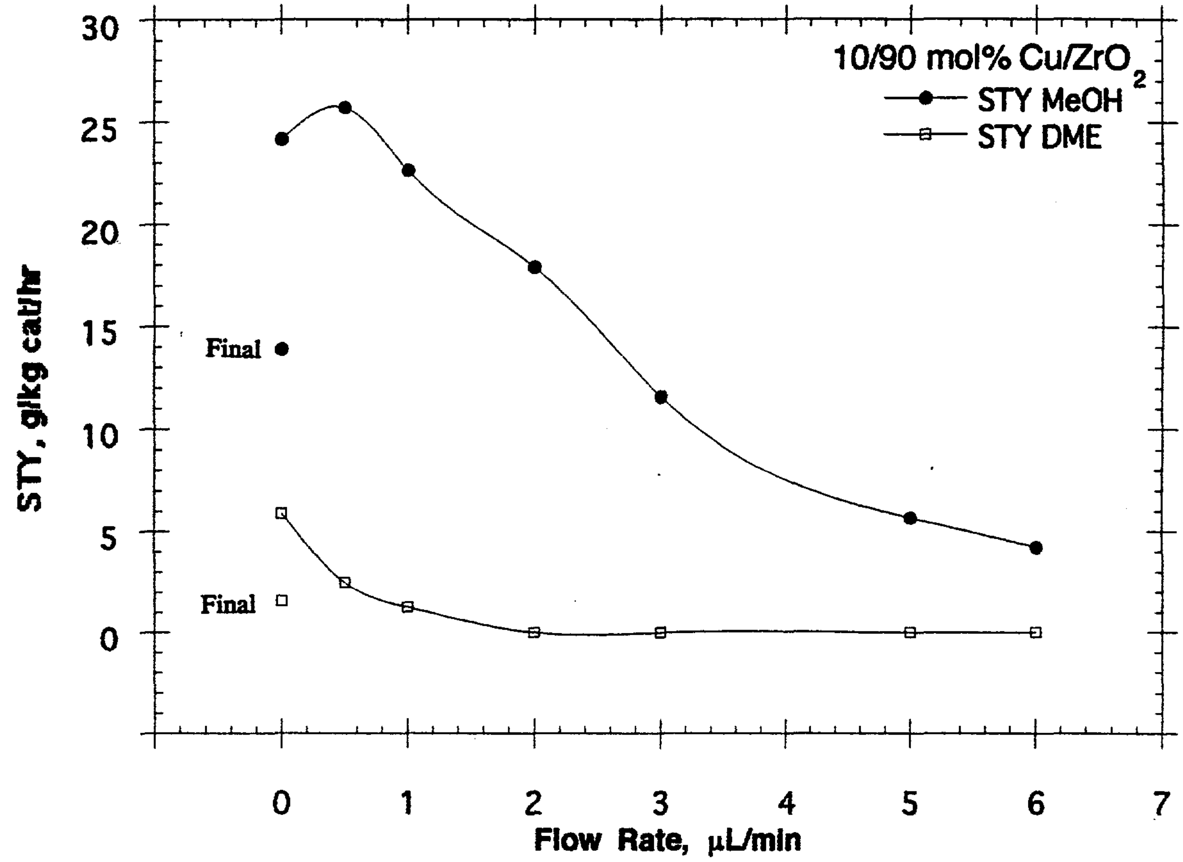
Since a significant effect on the catalytic behavior of the Cu/ZrO_2 catalysts was observed with addition of CO_2 to the synthesis gas, the effect of the presence of water in the synthesis gas was investigated. A fresh portion of the Cu/ZrO_2 10/90 mol% catalyst was freshly calcined and reduced using the procedure described previously. The catalyst was then tested with H_2/CO = 2.33 synthesis gas at 250°C, 7.6 MPa, and with GHSV = 6120 l/kg cat/hr. Once steady-state conversion was attained, water was injected at the top of the preheater section of the reactor into the H_2/CO reactant mixture with a Gilson liquid pump. The inlet of the reactor was heated to 125-130°C to ensure that the water was vaporized as it entered the reactor. Water injection rates of 0.5, 1.0, 2.0, 3.0, 5.0, and 6.0 ml/min were utilized, and this also increased the total GHSV slightly. For every injection experiment, the catalytic data were collected for at least 10 hr in order to confirm the steady-state condition.

The main products observed were methanol and dimethylether. As expected, CO_2 was also produced as a result of the water gas shift reaction (WGSR). Methanol productivity (STY) showed a gradual decrease from »25 g/kg cat/hr when no water was injected to »4 g/kg cat/hr for a water injection rate of 6.0 ml/min, as indicated in Table 3.3.8 and Figure 3.3.11. Likewise, DME productivity also decreased upon water injection, and the DME STY was nearly zero for the higher water injection rates, as shown in Figure 3.3.11. In contrast, the formation of CO_2 *via* the WGSR showed a continuous increase with the amount of water injected, wherein the CO_2 STY increased from 30 g/kg cat/hr with no water injection to 131 g/kg cat/hr at the highest water injection rate of 6.0 ml/min. Although the experimental procedures were different, it is interesting to note that the WGSR-generated CO_2 did not promote methanol synthesis, as was the case when the CO reactant was progressively replaced by CO_2.

Table 3.3.8 Water Injection Rate into the H_2/CO = 2.33 Synthesis Gas Mixture and the Influence on the Reactant Composition, GHSV and Product Productivities at 250°C and 7.6 MPa

Water Injection Rate (ml/min)	H_2/CO/H_2O (mol%)	GHSV (l/kg/hr)	CO Conv. (mol%)	CH_3OH STY (g/kg/hr)	DME STY (g/kg/hr)	CO_2 STY (g/kg/hr)
0.5	69.8/29.9/0.3	6140	3.0	25.7	2.5	29.5
1.0	69.5/29.8/0.7	6160	4.3	22.6	1.3	49.5
2.0	69.1/29.6/1.3	6200	6.6	17.9	»0	83.9
3.0	68.6/29.4/2.0	6240	8.8	11.6	»0	107.0
5.0	67.7/29.0/3.2	6325	11.5	5.7	»0	123.6
6.0	67.3/28.8/3.8	6365	12.6	4.2	»0	131.0

Figure 3.3.11 Effect of Water Injection on the Productivities, Expressed as Space Time Yields, of Methanol and Dimethylether from $H_2/CO = 2.33$ Synthesis Gas at 250°C and 7.6 MPa with GHSV = 6120 l/kg cat/hr



After completion of the water injection experiments, testing was carried out under the initial reference conditions to compare the final activity of the catalyst with the initial activity. The catalyst showed deactivation, and the methanol and DME productivities were 14 and 1.6 g/kg cat/hr, respectively, as shown by the data points in Figure 3.3.11. Chemical analysis of the catalyst showed that no significant iron deposition *via* iron carbonyl occurred during the testing (i.e., it was below the detection limit of <79 ppm for the size of the sample submitted for analysis).

Double Bed Catalyst Studies

In a continuation of alcohol synthesis over ZnO/Cr_2O_3-based catalysts, both alone and in tandem in the two catalyst bed configuration (see quarterly technical progress report 3QFY95), testing at higher reactor pressure was initiated using a high GHSV of 18,375 l/kg cat/hr. In the double bed experiment, the top bed consisted of 3 mol% $Cs/Cu/ZnO/Cr_2O_3$ while the lower bed was composed of a 4 mol% $Cs/ZnO/Cr_2O_3$ catalyst. Doping of both catalysts after calcination in N_2 was carried out using a N_2-purged aqueous solution of CsOOCH solution with a $CuO/ZnO/Cr_2O_3$

catalyst prepared *via* a hydrotalcite precursor and a commercial ZnO/Cr_2O_3 catalyst (Harshaw Zn-0311 T 1/4"). The two catalyst beds were reduced separately with a 2 vol% H_2/N_2 gas mixture at 250°C (top bed) and 400°C (bottom bed). The inital testing of the catalyst was carried out at 7.6 MPa with $H_2/CO = 0.75$ synthesis gas with GHSV = 18,375 l/kg cat/hr, and the temperatures of the top and bottom beds were maintained at 325 and 405°C, respectively.

After steady-state testing under these conditions, the pressure of the reactor was increased to 10.5 MPa (1500 psig) and then to 12.6 MPa (1800 psig). The experiment will be continued by reducing the reaction pressure back to 10.5 MPa and then to 7.6 MPa. Both TCD and FID GC detectors were used for exit stream analysis, and condensible products were collected in a cold trap for subsequent GC/MS analyses. Confirmation of all reaction products is being carried out, and the results of this testing will be presented in the next quarterly report when the data analysis will be complete.

Overall 1QFY96 Objectives

Future plans for Task 3 will focus on the following areas:

(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 $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ dual bed 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.

3.3.3 Study of Reaction Conditions and Promotion of Group VIII Metals for Isobutanol Synthesis (University of Delaware)

Introduction

Different precipitation procedures for mixed-oxide catalyst preparations are thought to be important for altering structures and compositions, since the precipitation sequence of each compound formed, its crystallinity and homogeneity, can be varied in this way. However, the effects of these variables are not very significant based on experimental observations. This is consistent with previous results on precipitation methods, from which it was observed that the catalysts made by the normal, reverse, and pH-swing precipitation methods display basically the same catalytic behavior in higher alcohol synthesis. One likely explanation of the results is that the solid structures of the catalysts prepared by the different methods each transformed to the same final structure during calcination, reduction, and reaction. This notion is supported by the identical XRD patterns of the used catalysts in the previous study. These results also imply that the solid structure, especially the structure of the active state of the catalysts, is not thermally stable enough to withstand pretreatment and reaction conditions. To solve this problem, identification of the active structure or active phase (i.e., the structure and how to identify it) will be a crucial aspect of future study. Once this structure is established, we can be more specific on how to stabilize the site rather than the mixture as a whole and therefore be closer to our target.

The washing process plays a role in establishing the performance of these catalysts. Catalysts washed with water prove to have better isobutanol selectivity than either the unwashed or water-acetone washed catalysts. Although generally this might be attributed to differences in porosity or accessible surface area, in this case it seems more likely that residues on the surface poison or cover active sites. Furthermore, removal of excess alkali is probably most important, since alkali doping does not improve these catalysts, but rather tends to render them *less active and selective.*

Finally, an effort has been made to reduce the copper level of the best catalyst composition uncovered from earlier studies. However, no significant difference between the catalytic performance of the new low-copper catalysts and the earlier high-copper catalysts was observed. This was hinted at and can be explained in terms of the previous findings of the factorially designed catalyst preparation experiments.

Experimental

The catalysts discussed in this quarterly report, together with their compositions and preparation methods, are summarized in the Table 3.3.9.

Catalyst CF6KOHN was made at constant pH (=12) by adding both the mixed-nitrate and KOH solutions at the same time to the mixing tank (adjusting dropping rate to keep pH constant). It has the same composition as our best catalyst, F6KOHN (see Table 3.3.9). Three catalysts derived from this catalyst precursor were unwashed CF6KOHN (calcined without washing of the precipitate), washed CF6KOHN (calcined after thoroughly washing the precipitate), and washed, Li doped CF6KOHN (washed CF6KOHN, calcined and doped with $LiNO_3$).

Catalyst 62895 was made by instant mixing of nitrates and KOH solutions. This catalyst had exactly the same composition as F6KOHN except that *no copper* was included.

Catalyst 71195 was prepared in order to examine the effects of higher, final precipitation pH and longer aging time on performance.

Catalysts made to evaluate the effects of the lowered copper level and the water or water-acetone washing process were 72095W, 72095A (F6KOHN made with water wash or water-acetone wash), 72195A (half the copper level of 72095A, acetone washed), 72195W (half the copper of level 72095W, water washed), and 72495A (1/4 copper level of 70295A, acetone washed).

The standard reaction test procedures used in this study were as follows: each catalyst was reduced at 260°C with $5\%H_2/N_2$ for 24 hours, and tested at 350-425°C, $CO/H_2 = 1$, 950 psi and GHSV = 2900/h.

Table 3.3.9 Catalyst Compositions

Catalyst	Composition	Preparation Method
F6KOHN	MnO/CuO=0.5, ZnO/CuO=0.5, ZrO_2/CuO=2, CoO=0.2 wt%	Coprecipitation by dropping KOH to nitrate solution (pH <0 to 12), wash twice. Aging for 3 hours. Calcine at 400°C/N_2/3h
unwashed -CF6KOHN	Same as above	Constant pH=12 coprecipitation, no washing triple times
CF6KOHN	Same as above	Constant pH=12 coprecipitation, no washing triple times
CF6KOHNLi	Same as above except 4 wt% $LiNO_3$ doping	Same as above
71195	Same as F6KOHN, $LiNO_3$=4 wt%	Same as above except final pH=13.5 and aging for 8 hours
72095W	MnO/CuO=0.5, ZnO/CuO=0.5, ZrO_2/CuO=2, CoO=0.2 wt% (mole ratios)	Coprecipitation by dropping KOH to nitrate solution (pH <0 to 12). Aging for 3 hours. Washing three times with H_2O. Drying at 100°C/18h. Calcine at 400°C/N_2/3h.
72095A	Same as above	Same as above except that the precipitate was further washed with acetone before drying and calcination
72195W	MnO/CuO=1, ZnO/CuO=1, ZrO_2/CuO=4, CoO=0.2 wt% (mole ratios, 1/2 Cu level of 72095)	Same as 72095W
72195A	Same as above	Same as above except that the precipitate was further washed with acetone before drying and calcination
72495A	MnO/CuO=2, ZnO/CuO=2, ZrO_2/CuO=8, CoO=0.2 wt% (mole ratios, 1/4 Cu level of 72095)	same as above

Results and Discussion

Effects of Catalyst Preparation Methods

The constant pH precipitation method of preparation did not lead to any significant change in catalyst performance. CF6KOHN displayed very similar behavior to catalyst F6KOHN, which was reported on earlier. At a very early stage in this project, we also reported that different precipitation methods, namely, normal, reverse, and pH swing precipitations, showed little effect on catalytic performance. Based on that work, the activity of catalyst 62895, made by instant mixing of nitrate and KOH solutions, was attributed to the absence of copper. The catalyst exhibited lower CO conversion and liquid yield, higher hydrocarbon selectivity, and lower isobutanol selectivity when compared with washed CF6KOHN. Therefore, it seemed necessary to include the copper component in the catalyst to achieve both high activity and isobutanol selectivity. To avoid copper agglomeration, maintain high activity and produce high isobutanol selectivity, lowering the copper content while simultaneously increasing its stability and dispersion would be a useful goal. Catalyst 71195 was prepared to examine the effects of higher, final precipitation pH and longer aging time on catalytic performance. Neither of these variables showed a significant effect on performance under our standard reaction test conditions. This can be seen from the very similar activity of 71195 and that of the previously studied F6KOHNLi.

The Effects of Washing Procedures on Catalytic Performance

From the results on the unwashed and washed CF6KOHN, it can be seen that washing of the precipitate or hydrogel plays an important role in achieving high activity and isobutanol selectivity. The washed CF6KOHN not only showed significantly higher CO conversion and liquid yield, but it also showed better isobutanol selectivity than did unwashed-CF6KOHN. This result may be accounted for if the washed CF6KOHN has a higher porosity and surface area or less residue covering the active sites. The washing step may also modify the surface composition of the catalyst prior to calcining. Removing excess alkali ions and other soluble components by washing the precipitate may result in better exposure of and access to the active sites on the surface.

Interestingly, lithium doping on the washed CF6KOHN did not improve the catalyst. Instead, it slightly reduced CO conversion, liquid productivity and isobutanol selectivity. This result is consistent with our previous report on alkali doping having a negative effect, but it is not what is expected based on the literature. This suggests that these catalysts operate by a different mechanism than the retro-aldol condensation proposed by Klier, but they are quite similar to the catalysts prepared by Keim. This result is logical since, given the catalyst's low surface area, the simple incipient-wetness alkali doping method may actually cover active sites, thereby acting as a textural poison and not as a promoter (see Table 3.3.10). Residual alkali, not removed after precipitation, would presumably function in the same fashion.

Table 3.3.10 Performance of the Catalysts

Catalysts	T°C	CO conv.%	CH selec.%	CO2 selec.%	MeOH wt%	nPrOH wt%	iBuOH wt%	Other wt%	Yield g/g/h
Unwashed	350	3	12	65	50.4	6.5	7.6	35.4	0.013
CF6KOHN	400	8	14	55	30.0	9.5	4.8	55.7	0.039
	425	11	18	60	17.4	10.3	7.8	64.4	0.050
CF6KOHN	350	12	7	30	69.0	1.9	15.7	13.4	0.050
	400	22	12	37	25.9	3.1	24.2	46.7	0.080
	425	27	22	42	15.9	9.3	15.6	59.1	0.085
CF6KOHNLi	350	5	14	52	66.8	3.3	14.8	15.0	0.038
	400	17	19	47	29.6	10.5	17.6	42.3	0.078
	425	22	26	46	19.6	13.8	11.0	55.5	0.067
62895	350	7	9	30	85.0		10.9	4.1	0.033
	400	12	20	44	44.4	3.3	10.0	42.4	0.038
	425	18	32	47	16.8	5.1	10.0	68.1	0.050
71195	350	8.7	8.9	29.9	76.8	2.7	16.5	4.0	0.045
	400	22.9	16.3	39.5	34.9	9.5	21.6	34.1	0.076
	425	27.6	26.1	46.8	22.1	11.3	12.8	53.8	0.078

In conjunction with this result, we note that the washing process did show an effect on the liquid product distributions of the catalysts. Comparisons of 72095A, 72095W, 72195A, and 72195W indicate that the water-only washing procedure is better than the water-acetone procedure for enhancing the isobutanol selectivity and productivity, as shown in Table 3.3.11. This implies that water, with its high solubility, more effectively removes excess alkali and other solubles that may inhibit activity.

Table 3.3.11 Liquid Distributions (wt%) and Yields (g/g/h)

	MeOH	EtOH	nPrOH	iBuOH	Other	Yield
72095A						
350°C	81.5	0.0	1.1	14.3	3.1	0.064
400°C	31.2	0.7	1.0	20.4	46.6	0.070
425°C	20.0	0.6	1.6	18.7	59.0	0.052
72095W						
350°C	74.1	0.0	1.0	16.1	8.9	0.060
400°C	37.1	0.0	1.3	26.6	35.0	0.073
425°C	21.3	0.4	1.6	21.8	54.9	0.060
72195A						
350°C	69.2	0.6	0.7	12.7	16.9	0.075
400°C	28.7	0.0	0.8	17.7	52.8	0.059
425°C	15.1	0.3	1.0	16.8	66.8	0.061
72195W						
350°C	72.20	0.0	0.7	14.7	12.7	0.064
400°C	33.2	0.5	0.9	25.9	39.5	0.073
425°C	16.0	0.7	1.1	18.4	63.7	0.059
72495A						
350°C	71.1	0.0	0.4	11.1	17.3	0.073
400°C	28.2	0.6	0.9	20.7	49.6	0.061
425°C	21.1	1.1	0.9	18.7	58.2	0.059

Reaction conditions: 950 psi, 2900 h^{-1}

The water-acetone washing procedure did not improve the surface area of the catalysts; (see 70295A vs. 72095W, 72195A vs. 72195W in Table 3.3.12) taken together with the fact that the procedure worsened isobutanol selectivity, it is clear that any anticipated benefit of the acetone-water washing procedure on physical properties, and, hence, selectivity is nonexistent. The results, on the other hand, do indicate that different washing procedures can have an impact on the performance of the catalysts, probably through removal or lack of removal of excess base. The observation that more than 50% of the surface area of the catalysts collapses after prolonged on-stream use indicates that the most active structures of the catalysts were probably destroyed in the early stages of treatment and reaction.

Table 3.3.12 Surface Area of the Catalysts (m^2/g)

	Fresh	Used
720925A	108.2	47.5
72095W	107.9	49.3
72195A	114.8	50.1
72195W	128.1	55.8
72495A	116.9	56.9

Effects of Copper Level of the Catalysts

Based on previous results and discussions at the Annual Review in Pittsburgh, the copper level of the catalysts was an important factor to be examined. Initially, one might have expected major modifications in catalyst performance with a decrease in copper levels, since we had seen from previous experiments that a catalyst without copper showed poor performance. However, in this set of experiments, when the copper level was decreased by half in 72195A and by one fourth in 72495A from the copper level of 72095A, no significant changes in catalyst activity, selectivity, and productivity were noted (see Tables 3.3.11 and 3.3.13).

Table 3.3.13 Performance of the Catalysts (@ 950 psi, 2900 h^{-1})

	CO_2 Selectivity (%)	CxHy Selectivity (%)	CO Conversion (%)	H_2 Conversion (%)
72095A				
350°C	25.5	8.3	11.4	12.6
400°C	38.0	17.2	23.2	18.3
425°C	44.5	28.4	26.0	21.7
72095W				
350°C	21.0	6.1	13.5	13.4
400°C	34.2	14.9	25.3	18.5
425°C	36.5	24.9	30.1	22.9
72195A				
350°C	26.3	8.5	12.7	14.4
400°C	42.1	21.6	24.1	18.7
425°C	46.7	33.7	28.2	22.8
72195W				
350°C	33.37	11.4	10.0	12.2
400°C	46.8	24.0	21.5	18.1
425°C	42.6	33.9	31.5	26.5
72495A				
350°C	34.0	11.9	11.3	14.0
400°C	43.1	22.1	22.8	18.4
425°C	44.4	31.2	26.3	21.6

Another interesting result observed was that surface area increased slightly with the decrease in copper level for both the fresh and used catalysts (see Table 3.3.12).

Taken together and with earlier work, these results indicate that the copper contents of catalysts can be significantly lowered. This could be important for preventing copper agglomeration. The decrease in the catalysts' copper content also increases the other metal oxide/CuO ratios of the catalysts. According to our factorially designed experiment, the metal oxide/CuO ratios play an important role in alcohol selectivities. Yet, we did not observed any significant changes in alcohol selectivities with the increase in oxide/CuO ratios for this set of catalysts. Two aspects need to be considered for rationalizing the two sets of results: (1) while MnO/CuO, ZnO/CuO, and ZrO_2/CuO ratios increased in the order of 72095A → 72195 → 72495, the ratios among MnO, ZnO, and ZrO_2 remained unchanged. The beneficial effect of increased ZrO_2/CuO ratio on isobutanol selectivity might be offset by the negative effect of the increased MnO/CuO ratio on isobutanol selectivity. Thus the factorially designed experiments left open the question of the effect of absolute CuO level. Presumably, if we had probed a range of copper levels between zero and ~10 wt%, the level in 72495A, then a significant effect would have been noted. Instead our experiments were conducted at copper levels above this critical content, and the effect of variation in copper seems minimal. (2) As seen from previous reports, most of our catalysts have behaved similarly, giving high $C0_2$ selectivity, moderate CO conversion and hydrocarbon selectivity, moderate liquid productivity, and consistent liquid product distribution patterns. This might imply that our catalysts may be working close to equilibrium, that is., at reaction conditions (low pressure and relatively high reaction temperature) where reactions progress to their thermodynamic limits and are not under kinetic control. Therefore, further work needs to be done to optimize the reaction conditions while continuing the exploration of catalysts for enhanced isobutanol production. Also, thermodynamic computations will be done to examine this possible equilibrium effect.

Conclusions

The different precipitation methods of the mixed oxide catalysts discussed in this report do not show any significant effects on catalyst performance. However, thorough washing of the precipitates with water was proven to be a better procedure compared with the other methods tested. This agrees well with our earlier observation that the excess alkali doping does not improve these catalysts; thus pointing away from the retro-aldol condensation mechanism. Decreasing the copper level of the catalysts did not significantly change catalytic performance. This implies that the levels of the other components, such as MnO and ZnO, need to be adjusted.

3.5 Poison Resistant Catalysts Development and Testing

The initial effort under this task is to build a mobile facility that will test feed gas and various feed gas cleanup methods at customer locations, as well as at Air Products. A secondary goal is to provide a laboratory that can be used for testing poison resistant catalysts, if such a program is warranted. The need for such a program will be evaluated after the costs of sulfur removal are analyzed. This latter effort is part of Bechtel's tasks, and it will be reported on separately by Bechtel. This report describes the design of the AF^2DU (Alternate Fuels Field Development Unit).

3.5.1 Design

Schematic drawings of the AF^{2}DU are presented in Figures 3.5.1-3.5.8. Since the system must be movable to a customer's location, it is mounted on a trailer, depicted in Figure 3.5.1. The trailer comprises laboratory and office areas, both of which will have adequate ventilation and alarm systems to protect occupants. Safety will be covered in Air Products' normal hazards review procedure. The trailer will meet all relevant OSHA and BOCA codes. This aspect along with a complete set of schematics and operating plans will be documented after the hazard review is completed.

The air conditioned and heated office area (Figure 3.5.2) contains an Allen-Bradley control system modeled after the Air Products standard system used in remote locations and not our laboratory systems. Its main advantage over Windows-based PC systems is that its robustness enables proper operation and data saving after a power failure. It can, of course, communicate electronically with Air Products' normal PC-based data analysis routines. Electronic data transmission over phone lines is provided for; two phone lines have been installed so that data can be transmitted as necessary. The office area also contains a desk, as well as work benches and chemical cabinets necessary for sample preparation and operation of the reactor. Under normal operating conditions, the entire AF^{2}DU will be operated by a single person covering a 24 hour period.

The gas feed system, shown in Figure 3.5.3, allows the feed of selected poisons as well as syngas to the reactor system. Poison removal techniques can be tested in the adsorber system shown in Figure 3.5.4. The section contains five beds that can be filled with various materials. The beds can be regenerated automatically with temperature programming provided by the automatic control system. This system is also capable of blending feed gases from a second source. This feature could be used in testing at a location having recycle gas flow as well as in blending selected poisons into the feed.

The reactor system shown in Figure 3.5.5 contains a 300 cc reactor. The system is essentially a duplicate of that in the laboratory so that results between the field and the laboratory will be directly comparable.

The analytical system is shown in Figures 3.5.5-3.5.8. Since we will be testing for unknown materials as well as known poisons, the system is extensive and flexible. The actual analysis will be done in two Hewlet-Packard 6890 gas chromatographs. These are modern systems fitted with a variety of detectors that enable flexible analysis. The capability of the detectors is summarized in Table 3.5.1. Details of the system are given below.

Figure 3.5.1 Trailer

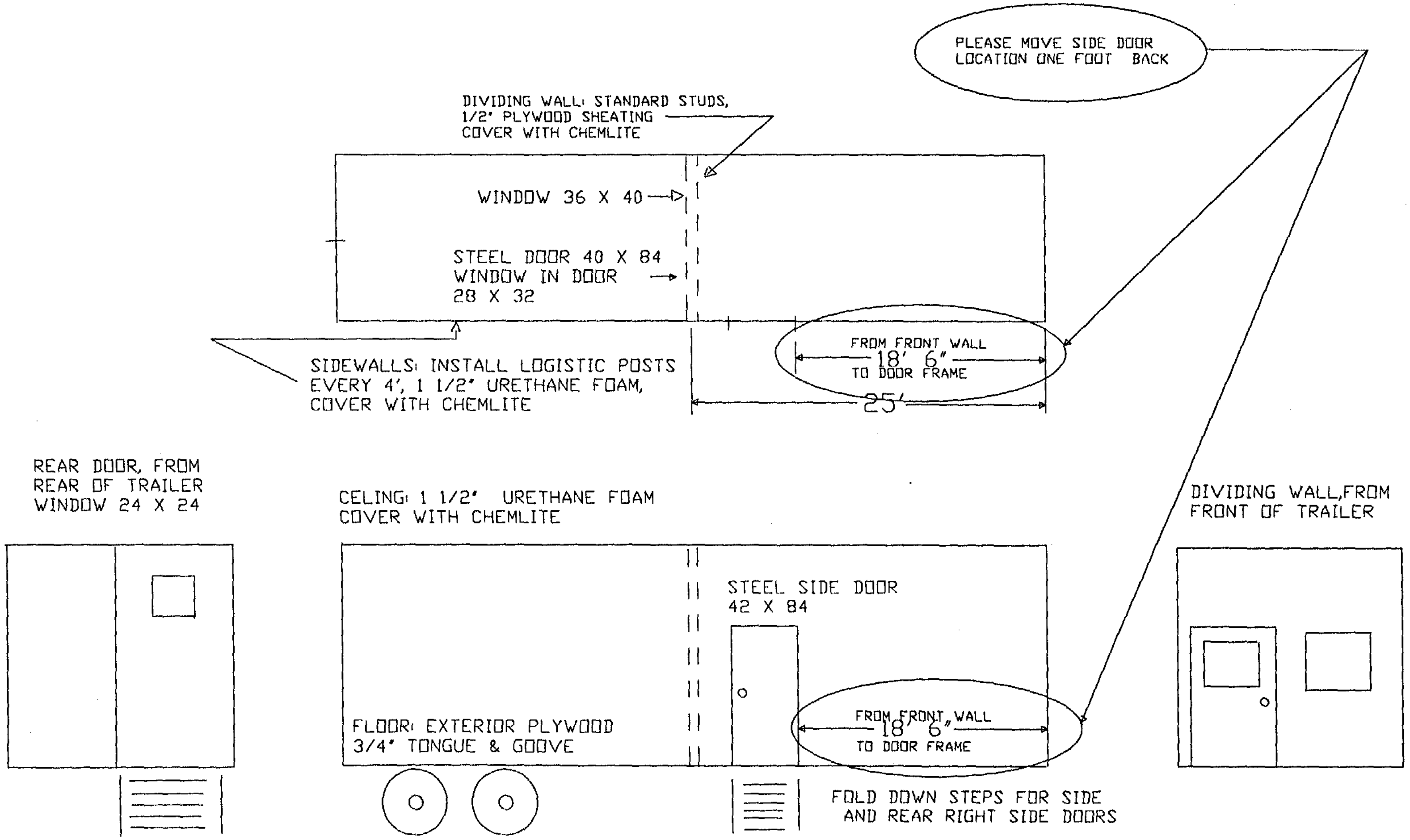


Figure 3.5.2 Layout

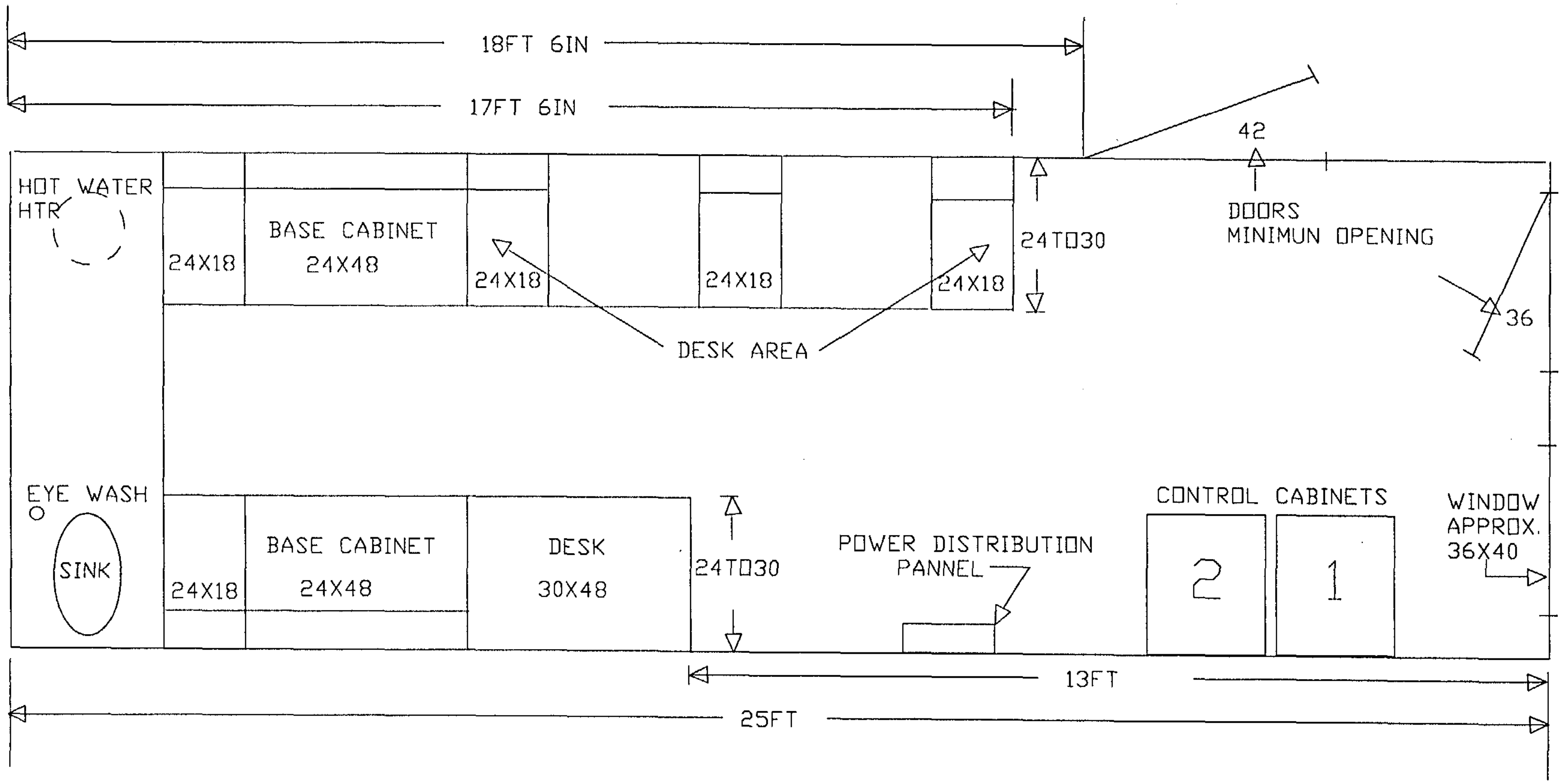


Figure 3.5.3 Field Test Unit
Gas Feed System

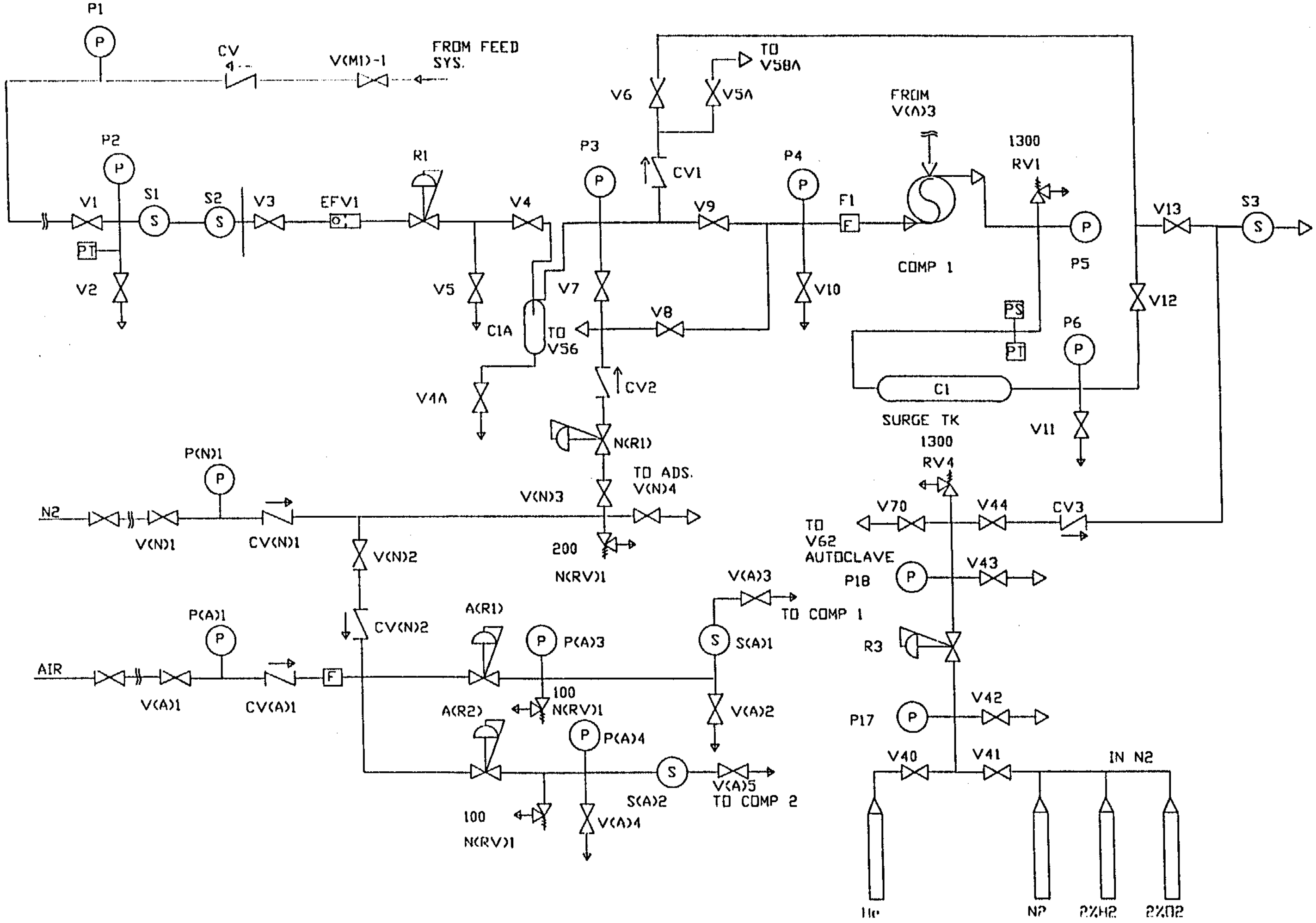


Figure 3.5.4 Field Test Unit Adsorber System

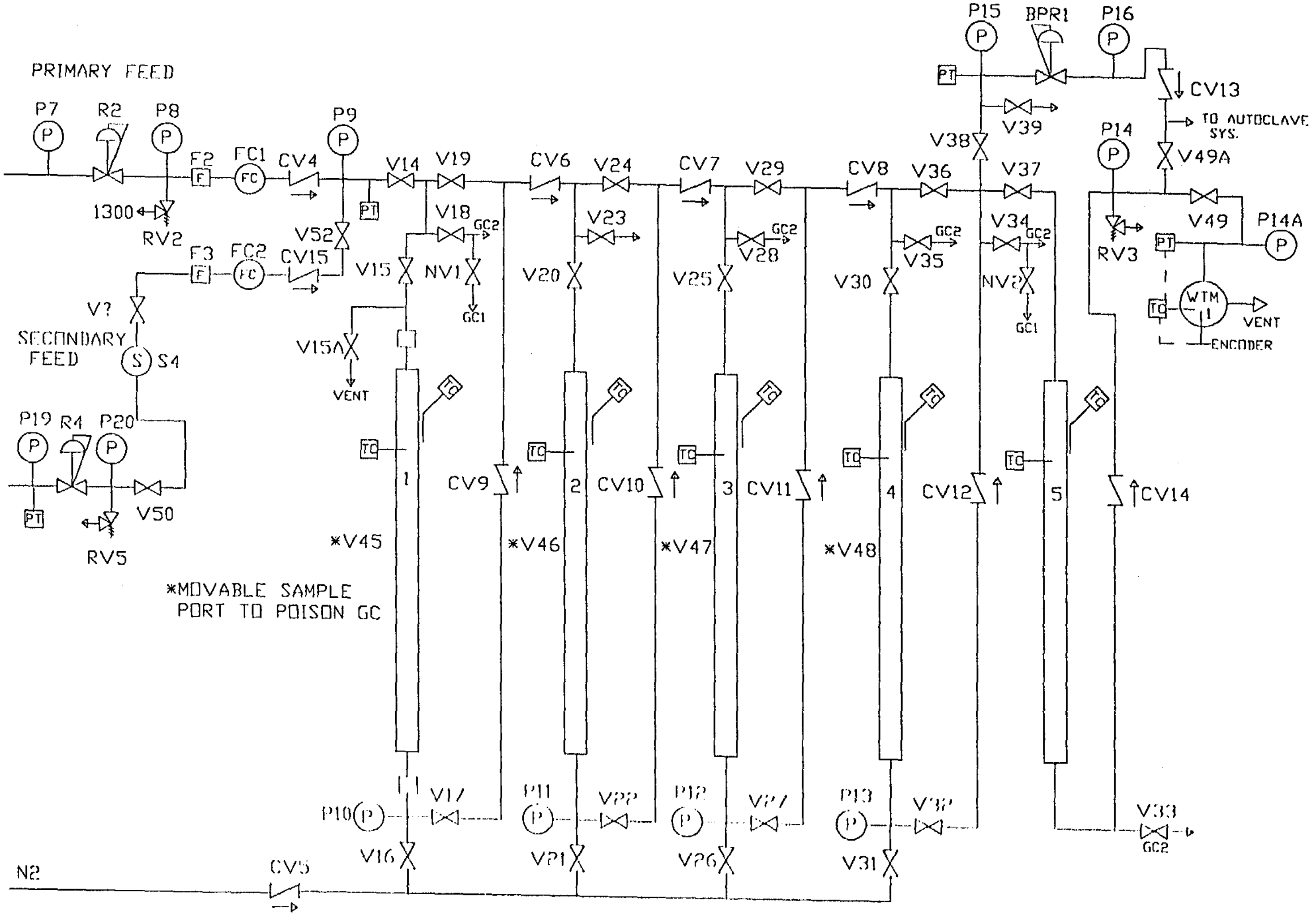


Figure 3.5.5 Field Test Unit
Autoclave System

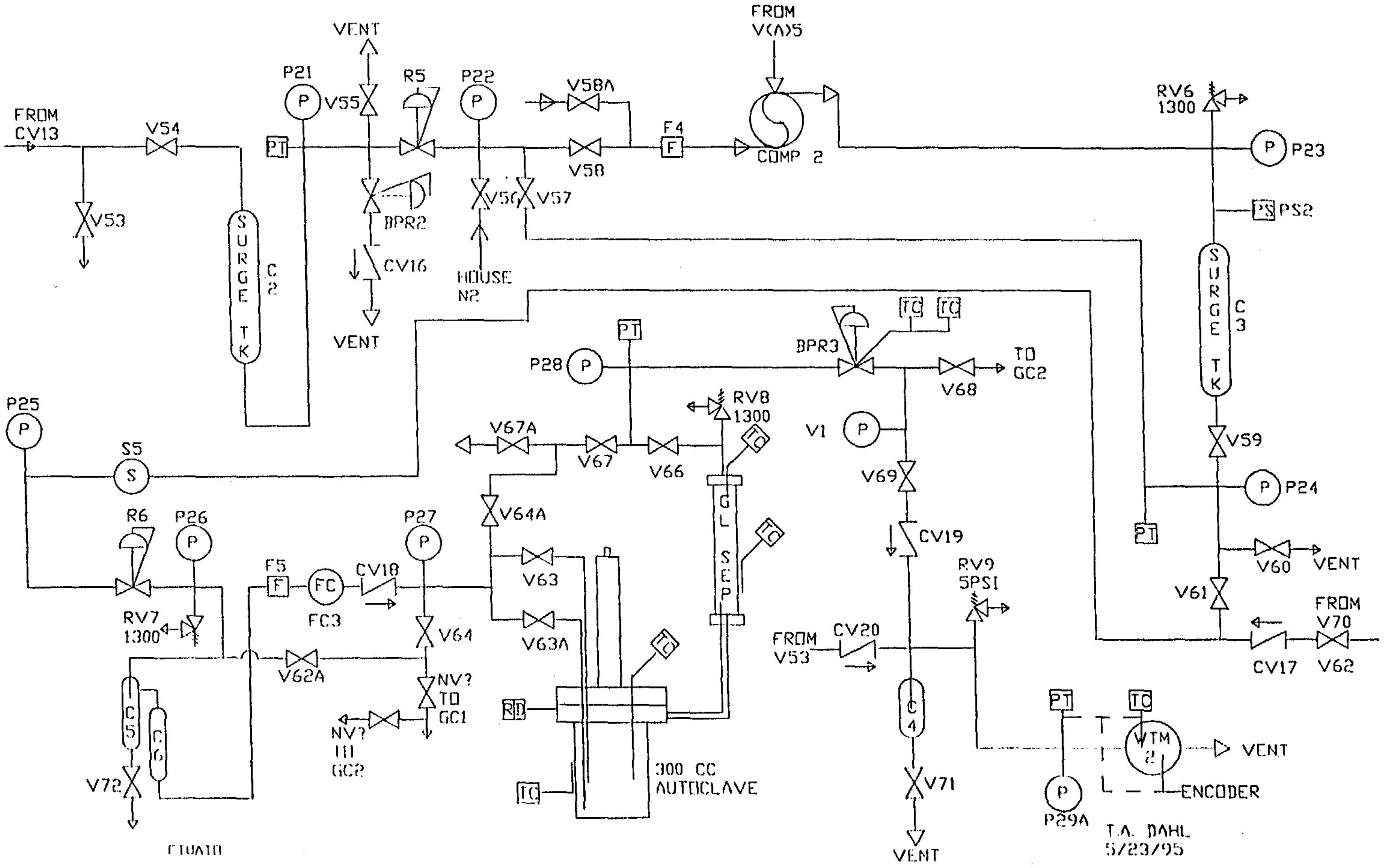


Figure 3.5.6 Field Test Unit GC Gas System

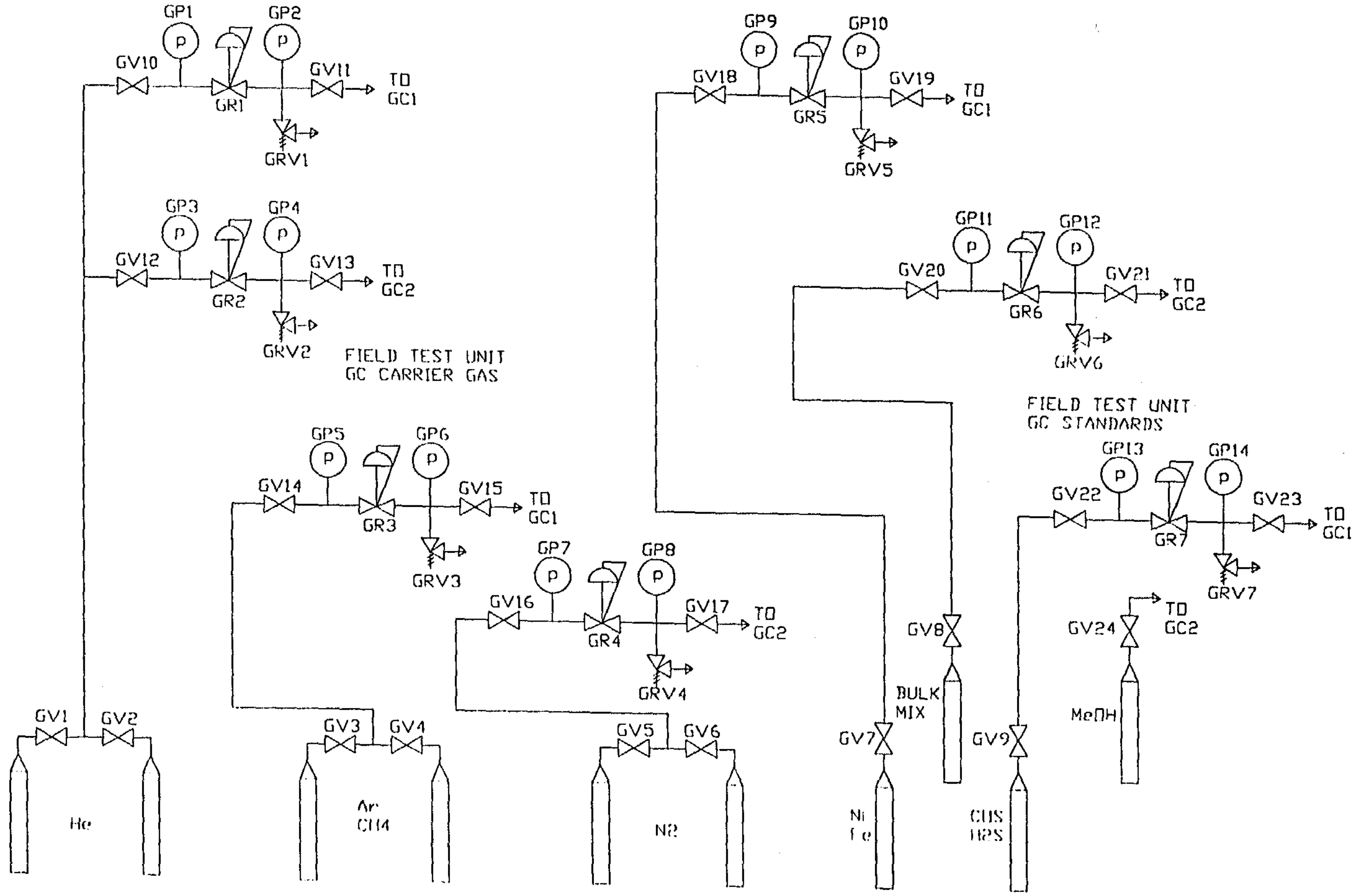


Figure 3.5.7 Sampling System for Poison GC

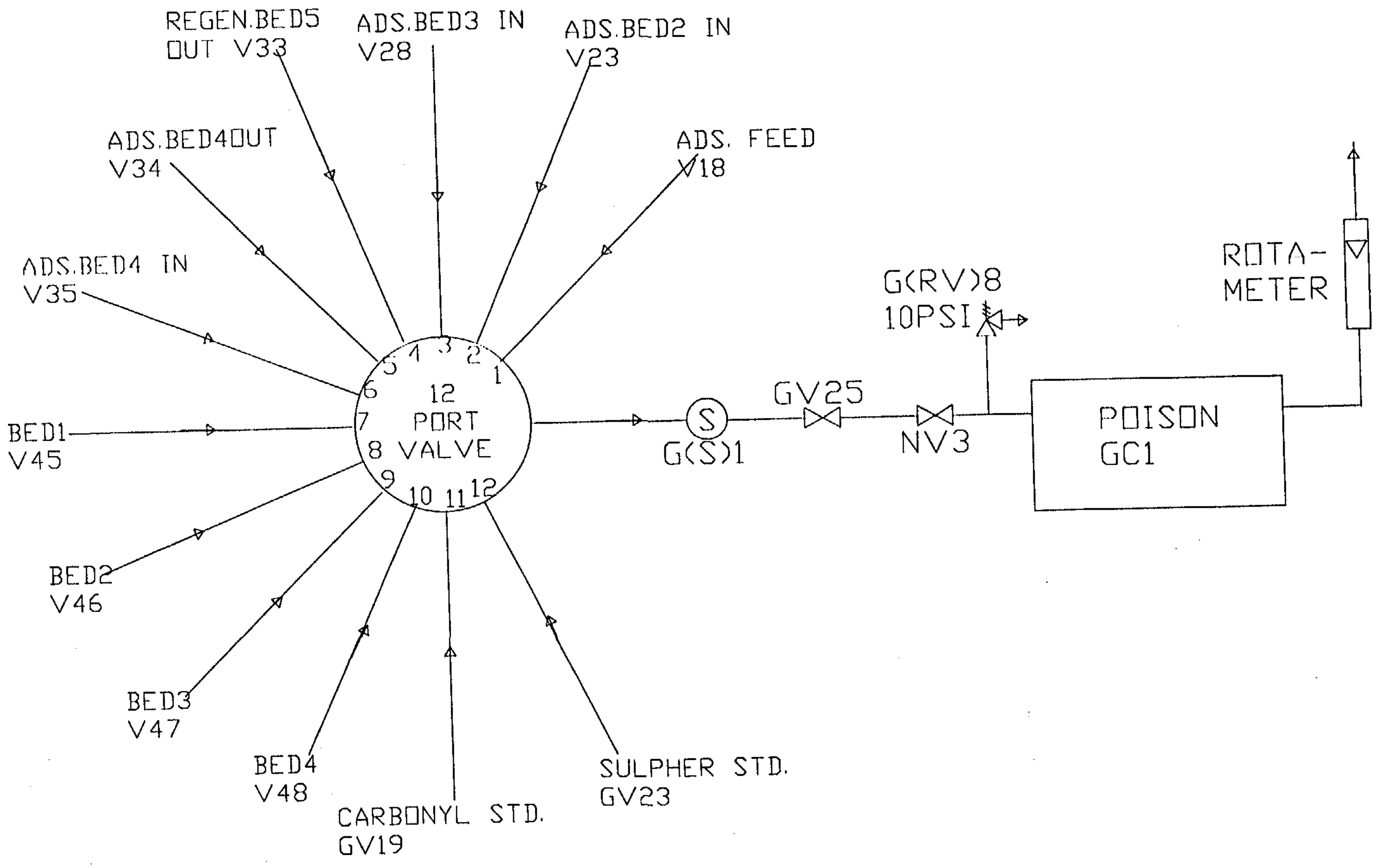


Figure 3.5.8 Sampling System for Bulk GC

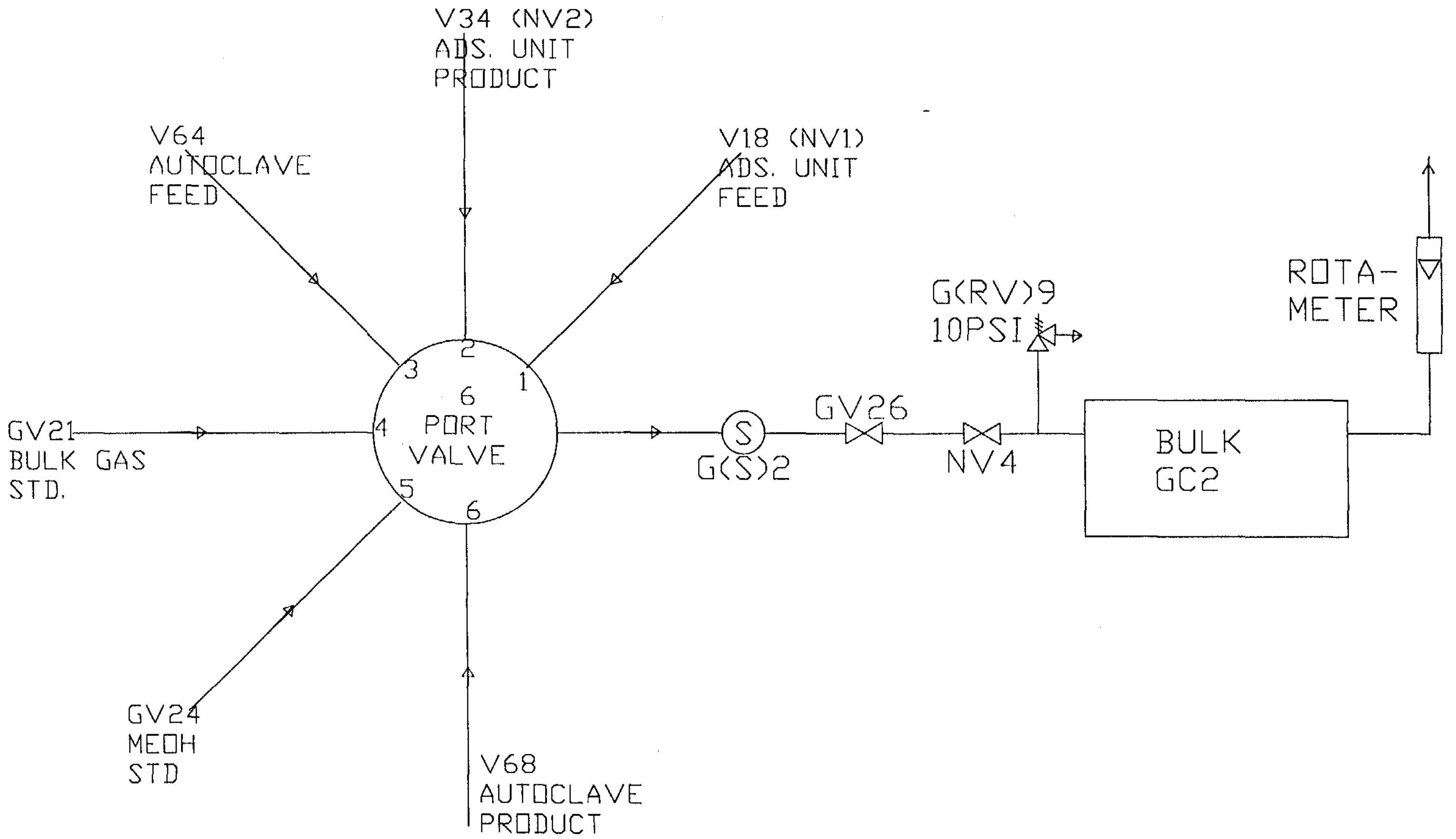


Table 3.5.1 GC Detector Capabilities

Detector	Substance(s) Measured
TCD(thermal conductivity)	CO, CO_2,N_2, H_2
FID(flame ionization)	Organics(alcohols, etc.)
SCD(sulfur chemiluminescence)	S
ECD(electron capture)	Ni, Fe

The "Poisons GC" will be an HP-6890 GC with one electronic pressure controlled (EPC) packed injector and the appropriate valving to do simultaneous injections of the sample into two columns. One column will be interfaced to an Hewlett-Packard Electron Capture Detector (ECD) to analyze nickel and iron carbonyls, and the other column will be interfaced to a Sievers Sulfur Chemiluminescence Detector (SCD) to conduct trace sulfur analysis. The SCD will monitor carbonyl sulfide, hydrogen sulfide and sulfur dioxide to 0.03 mg/L.

The second "Bulk Gas GC" will be another HP-6890 GC with two thermal conductivity detectors (TCDs) and one flame ionization detector (FID) with full EPC. The FID will be configured to do hydrocarbon or alcohols analysis. The first TCD analyzes for carbon dioxide, oxygen, nitrogen, methane and carbon monoxide. The lower limit for all components is 200 ppm except for carbon monoxide, which is 400 ppm. The second TCD detects hydrogen to a lower detection limit of 100 ppm. The TCD signals are electronically summed to provide a single signal output.

These GCs will be configured by Wasson ECE, a certified Hewlett-Packard channel supplier. The base HP-6890 instrument will be purchased from Hewlett-Packard and shipped to Wasson along with the Sievers SCD. Wasson will install the Sievers detector, the necessary valves and columns to perform the analyses stated above. Upon completing the configuration, Wasson will test and install the equipment, train personnel in the use of the equipment and guarantee the performance of the GCs to meet all the detection limits specified above. The Nelson Turbochrom equipment and computer work station will have to be ordered separately and installed in the trailer when the GCs arrive. Because Turbochrom cannot as yet fully control the new HP-6890 GC, Turbochrom 900 series A/D interfaces will have to be used.

The stream selection system will be automated by Chatham Instruments. Since integrators will not be used, the Nelson Turbochrom system will have to be able to control the stream select valves. This will require that some external computer code be written for Turbochrom to fully control and read the sample stream number from the stream select valves into the computer. The old stream select valves will be refurbished and used again in the new system to help control cost.

Careful selection of the detector, sampling ports and columns allows the capability of measuring poisons with only two Gcs, which is the number necessary to do normal laboratory analysis of reaction and feed products.

3.5.2 Schedule

Since they are long lead time items, the trailer and the analytical systems were ordered in May 1995. A summary of the detailed schedule is provided in Table 3.5.2.

Construction of the trailer will be completed by the end of April when the shakedown run is completed. The project is on time and within budget for this quarter. The trailer has been purchased and the interior modified. The electrical hookups to the trailer have been completed, and utility hookup is underway.

TASK 4: PROGRAM SUPPORT

Bechtel's project personnel attended the DOE Contractors' Review Meeting on 28 through 31 August and a kick-off meeting at Air Products' Allentown office on 1 and 2 August. They reported the following:

- *Task 1.3, Fischer-Tropsch Support (Catalyst/Wax Separation)* - Due to reassignment of personnel, no work was performed on this task during the reporting period.

- *Task 4.2, Commercial Applications (Mixed Alcohol Synthesis)* - Additional modifications to the economic analysis spreadsheet models for the two scenarios of gasification coupled with mixed alcohol synthesis have been implemented, and the models are being tested. Development of a model for the third scenario of a stand-alone mixed alcohol synthesis plant was started. Work on the second scenario, a refinery plant, was continued with the use of a linear programming model to analyze product slates and revenue.

- *Task 4.5, Syngas Generation and Cleanup* - Detailed material balances for the coal and coke feedstocks to predict the expected composition of the cleaned syngas discharging from several sulfur removal processes were developed and submitted to gasification vendors and acid gas removal equipment vendors for their comments. Various designs of a natural gas, partial oxidation gasifier to produce syngas were evaluated and, for two of these, estimates of capital and operating costs were made.

TASK 5: PROJECT MANAGEMENT

5.1 Reports and Presentations

A two-day meeting was held with DOE and subcontractors to kick off the Alternative-Fuels II and Slurry Bubble Column Reactor (Hydrodynamics) programs. Preliminary results from the June hydrodynamic run were presented at the meeting. Interesting discussions followed the presentations. DOE was quite impressed with the large number of objectives achieved in a single campaign.

A final topical report on the results of the Fischer-Tropsch II demonstration was completed. Comments and suggestions received from DOE personnel on the draft report were incorporated into the final report.

5.2 Management Activities

A meeting was held with Reema International (now REMTECH) and DOE on August 29 to discuss Reema's interest in demonstrating their F-T process at LaPorte. Reema is a small, privately owned oil and gas company based in Denver, Colorado. Significant business and technical discussions are required before the project can be kicked off. An operating window of April-June 1996 was given, assuming we do not need significant modifications and the project can be kicked off in the October - November time frame.

Table 3.5.2 Schedule Summary
Field Test Unit
Revised August 22 1995

Month			Completion Date	Vendor
May :				
	Purchase Trailer		Complete	
	Power To Trailer		Complete	
		Order Analytical Equipment	Complete	
Jun./Jul./Aug.:				
	Prepare Trailer		Complete	
	In Place At Iron Run		Complete	
		Floor, Walls, Ceiling,	Complete	
		Outside Door	Complete	
		Rear Door	Complete	
		Office Equipment		
		Work Bench /Storage Cabinets		
		Determine Lab Automation	Complete	
		Order Automation Components	1 Sept. 95	Dahl
	Electrical			
		Transformer in Place	Complete	
		Distribution Panel	Complete	
		Heating	1 Sept. 95	Fac.Svcs.
		Lighting	1 Sept. 95	Fac.Svcs.
Sept./Oct./Nov.:				
	Utilities			
		Ventilation	25 Aug. 95	HT Lyons.
		Cooling	25 Aug. 95	HT Lyons.
		Phone Lines	15 Sept. 95	Fac.Svcs. Water
		15 Dec. 95	HT Lyons.	
		Air/Nitrogen	15 Dec. 95	HT Lyons.
		Syn. Gas Feed Lines	15 Dec. 95	HT Lyons

Table 3.5.2 Schedule Summary (continued)

Month			Completion Date	Vendor
Dec./Jan./Feb.96:				
	Install Lab Equipment			
		Allen Bradley Programming	15 Dec. 95	MIS
		Excel Spread Sheet/PE Nelson Interface		15 Dec. 95 MIS
		Unit Electrical Connection	15 Dec. 95	IET
		Unit Mechanical Connection, Rebuild as		HT Lyons
		Necessary.	15 Dec. 95	Dahl
		Analytical Equipment Delivery	5 Oct. 95	Wasson
		Installation & Test	15 Dec. 95	Wasson / CRSD/MIS
Mar.:				
	Hazards Review Complete		1 Mar. 96	Dahl
	Leak Check / Operational Test		29 Mar.96	Dahl
Apr.:				
	Shake Down Run		3 May 96	Dahl