CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION

In this review, we will use transition metal as a promoter at various ratio. The name of catalyst and compositions are shown in table 5A below.

Table 5A Names of base metal copper catalyst

Name	Composition of catalysts
CU	2%Cu
SM1	2%Cu 1%Sm
SM4	2%Cu 4%Sm
ZR0.25	2%Cu 0.25%Zr
ZR0.75	2%Cu 0.75%Zr
ZR1.2	2%Cu 1.2%Zr
SZ1	2%Cu 0.25%Sm 1.2%Zr
SZ2	2%Cu 0.25%Sm 0.75%Zr
SZ3	2%Cu 0.8%Sm 1.2%Zr
ND0.25	2%Cu 0.25%Nd
ND1	2%Cu 1%Nd
ND4	2%Cu 4%Nd

Name	Composition of catalysts
PR0.25	2%Cu 0.25%Pr
PR1	2%Cu 1%Pr
PR4	2%Cu 4%Pr
CE1	2%Cu 0.25%Ce
CE2	2%Cu 1%Ce
CE3	2%Cu 4%Ce
CE4	1%Ce 0.45%Cu
CE5	1%Ce 1.31%Cu
CE6	1%Ce 2.12%Cu
CE7	1%Ce 2.72%Cu
CE8	1%Ce 3.21%Cu
ZN1	2%Cu 12%Zn
ZN2	2%Cu 8%Zn
ZN3	2%Cu 4%Zn
ZN4	3%Cu 4%Zn
ZN5	4%Cu 4%Zn
ZN6	5%Cu 4%Zn
COM	Commercial Catalyst MK-101 VNR.22803

5.1 Copper base catalysts

In this research, we selected 2% Cu as base catalyst [7]. Experimental results are shown in figures 5.1.1-5.1.3

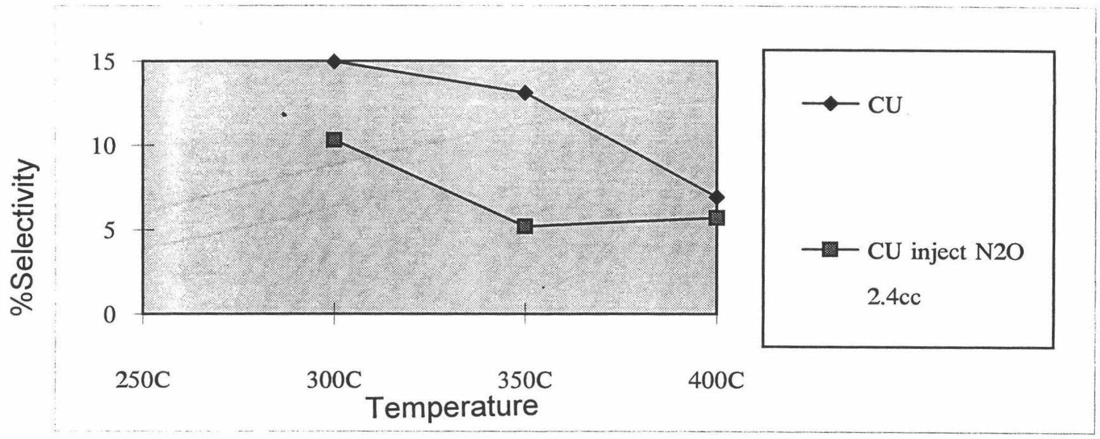

Figure 5.1.1 Effect of reaction temperature on %selectivity of CU

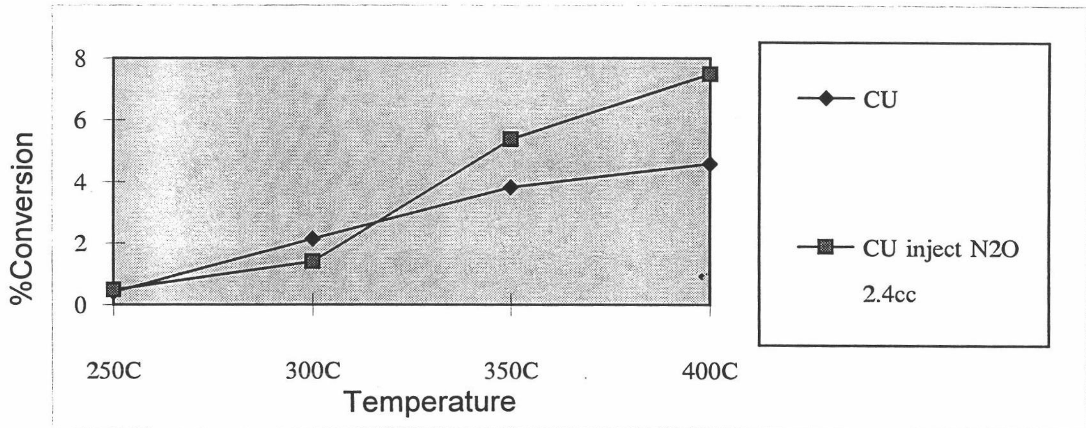

Figure 5.1.2 Effect of reaction temperature on %conversion of CU

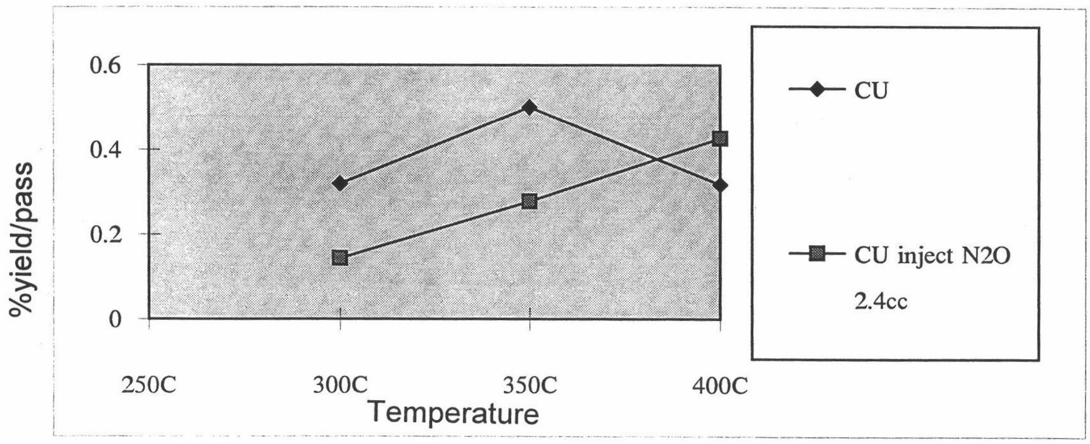

Figure 5.1.3 Effect of reaction temperature on %yield/pass of CU

Figures 5.1.1-5.1.3 show that, %selectivity of methanol synthesis over Cu-based catalyst decreases with increasing temperature especially between 350-400°C it shows strongly decrease. In contrast, %conversion increases with increasing temperature all the way to 400°C and %yield per pass also increases with increasing temperature and reach a maximum, 0.5%, at 350°C then decrease.

It can be concluded that %selectivity and %yield per pass decrease with temperature increase in the range of 350-400°C as Chin chen [6] has reported that sintering of Cu particles would appear at high temperature and Campbell [27] showed that copper surface area was a criticle factor for methanol synthesis activity.

5.2 Commercial catalyst

To compare with in-house catalysts, we have used a commercial catalyst part No MK 101 VNR 22803 The investigation results are shown in figure 5.2.1-5.2.3

When change to the commercial catalyst, it was observed that the commercial catalyst showed higher %selectivity, %conversion and %yield per pass than catalyst CU all over temperature range 250°C-400°C In this temperature range %selectivity is around 70-71%. Both %conversion and % yield per pass increase with the increase of temperature and reach a maximum of 11.13% and 7.86% respectively at the same temperature 400°C

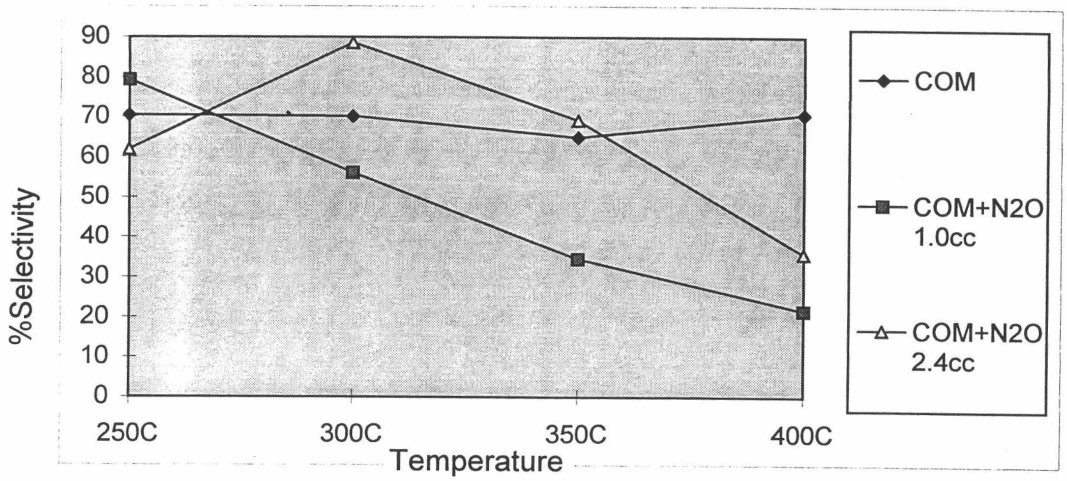

Figure 5.2.1 Effect of reaction on %selectivity of COM

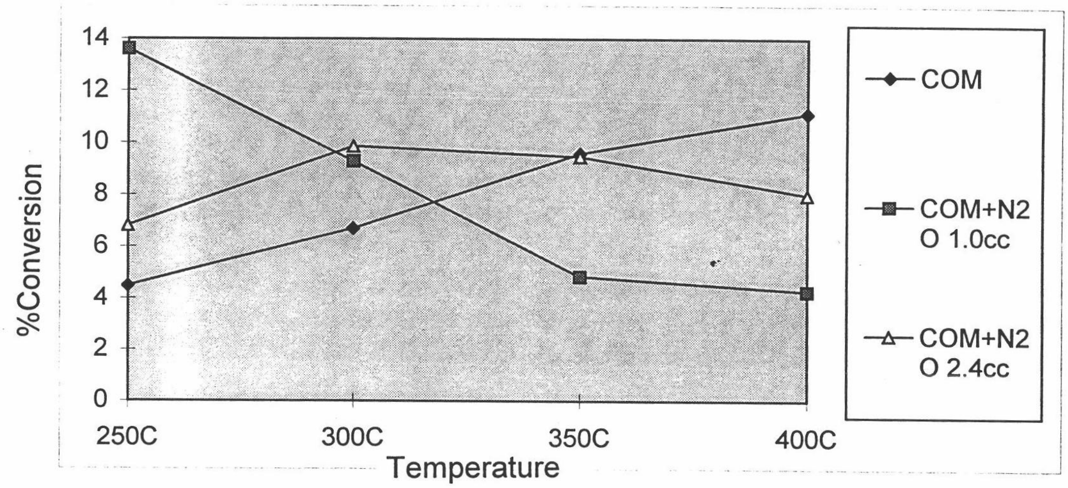

Figure 5.2.2 Effect of reaction on %conversion of COM

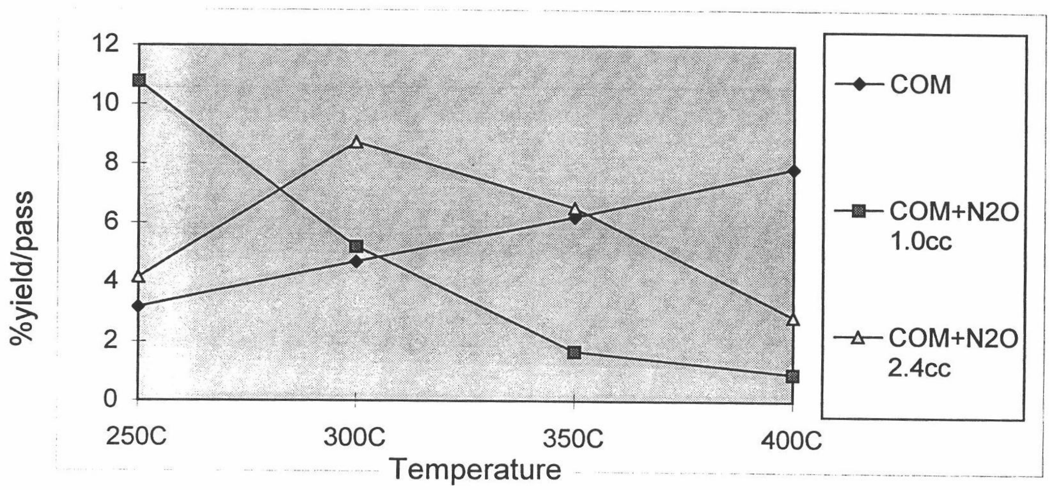

Figure 5.2.3 Effect of reaction on %yield/pass of COM

5.3 Effect of Zn loading on catalytic performance

The addition of Zn is improve the thermal stability of the Cu catalyst resulted from the formation of metal oxides.

5.3.1 Fixed 2%Cu

The experiment shows the effect of Zn loading of various ratios on catalytic performance. The results are shown in figures 5.3.1.1-5.3.1.3 Then, selected the best composition to find optimum Cu amount in catalysts and the results are shown in table 5.3.1

Figures 5.3.1.1.1-5.3.1.3, present the %selectivity of ZN3, show the same direction as CU catalyust by decreases as increasing temperature in range of 300°C-400°C. ZN1 show the maximum %selectivity, 21.25% at 400 °C. All compositions show increase of %conversion with increasing temperature through all the range of 250-400°C and ZN2 shows the maximum 5.76% at 400°C which higher than CU catalyst. Zn loading show the methanol yield higher than Cu base catalyst at higher temperature as shown in ZN1 for 0.61%yield per pass at 400°C

As agreed with Herman [1] that ZnO being present to distribute the copper which dissolved in ZnO lattices and ZnO also was suggested to be increased the dispersion of Cu which was the active species. With high copper surface area being related to well dispersed small Cu crytallites [27].

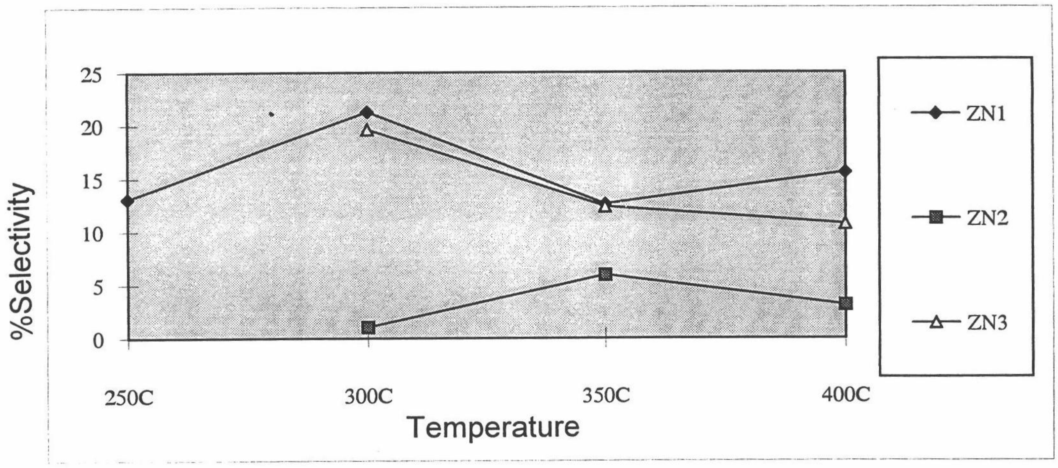

Figure 5.3.1.1 Effect of reaction temperature on %selectivity of ZN

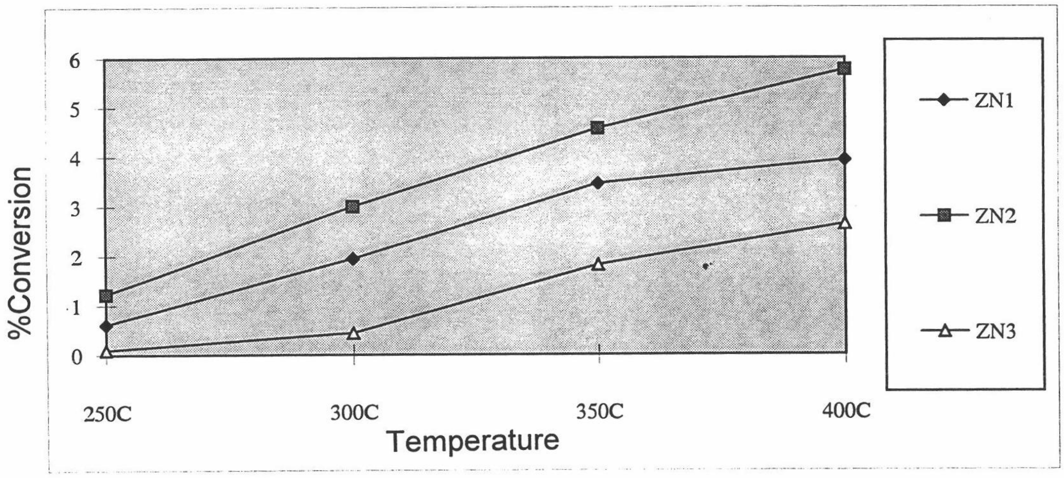

Figure 5.3.1.2 Effect of reaction temperature on %conversion of ZN

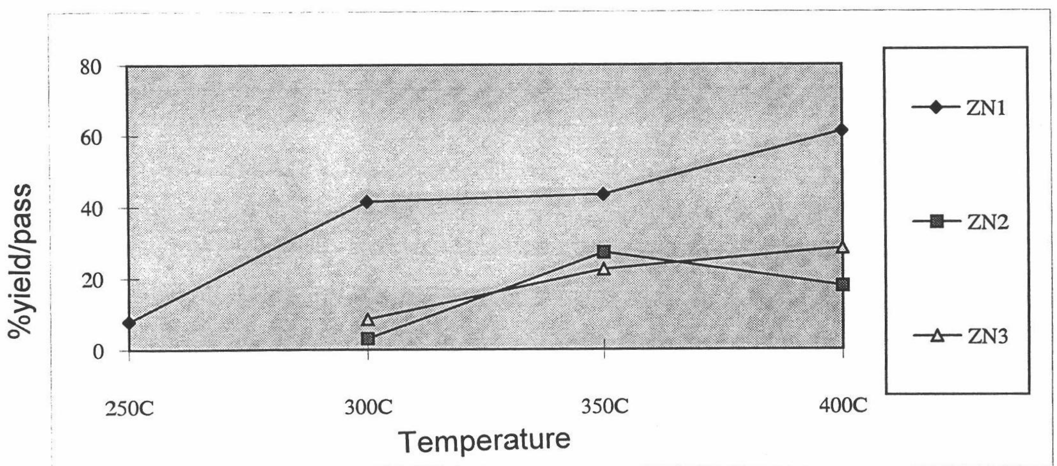

Figure 5.3.1.3 Effect of reaction temperature on %yield/pass of ZN

5.3.2 Fixed 4%Zn

The previously experiment, shows that more Zn loading in the 2% Cu catalyst gives more methanol yield than unpromoted Cu catalyst. It has been suggested that the dispersion of ZnO on the Cu surface increases with the ZnO loading [10]. The effect of Cu content in the fix 4% Zn is shown in figure 5.3.2.1-5.3.2.3

Figures 5.3.2.1-5.3.2.3 illustrate that, ZN4 and ZN5 show decreasing of %selectivity as temperature is increased, while ZN6 shows the maximum %conversion 20.65% at 400°C. All of the Zn/Cu compositions show increase in %conversion with increasing of temperature. The maximum %conversion show in ZN5 at 350°C for 4.42%.

In temperature range of 300°C-350°C, %yield per pass of ZN4, ZN5 and ZN6 increase as temperature increase, and then decrease. It shows the, exceptional for ZN6 which increases strongly in temperature range of 350°C-400°C and shows the maximum %yield per pass 0.52% at 400°C.

However, Friedrich et.al.[3] reported that the active component in Raney Cu-Zn catalyst for hydrogenation of CO to methanol is copper. Greatest activity was exhibited by catalysts containing ~97%wt copper. While, the surface area was found to increase with increasing precursor alloy zinc content. The activity of catalyst decrease which zinc content in the precursor alloy down to 20%wt or more.

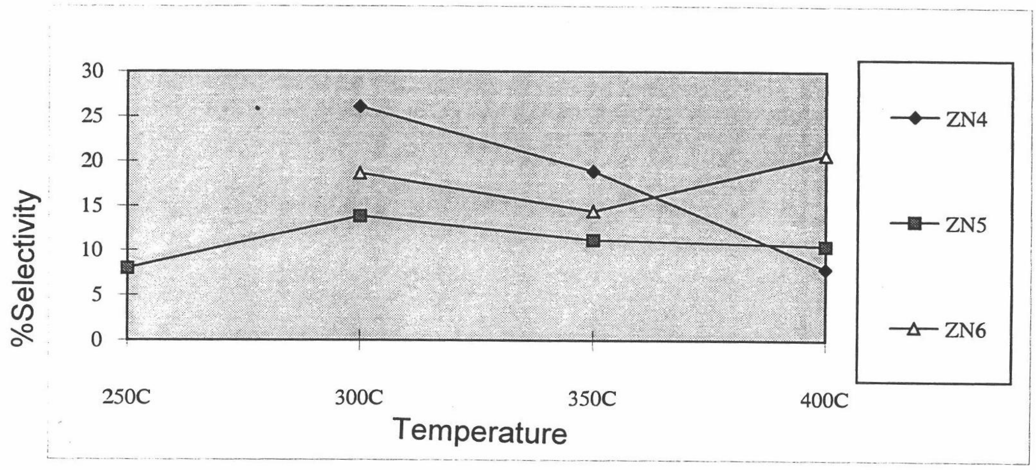

Figure 5.3.2.1 Effect of reaction temperature on %selectivity of ZN

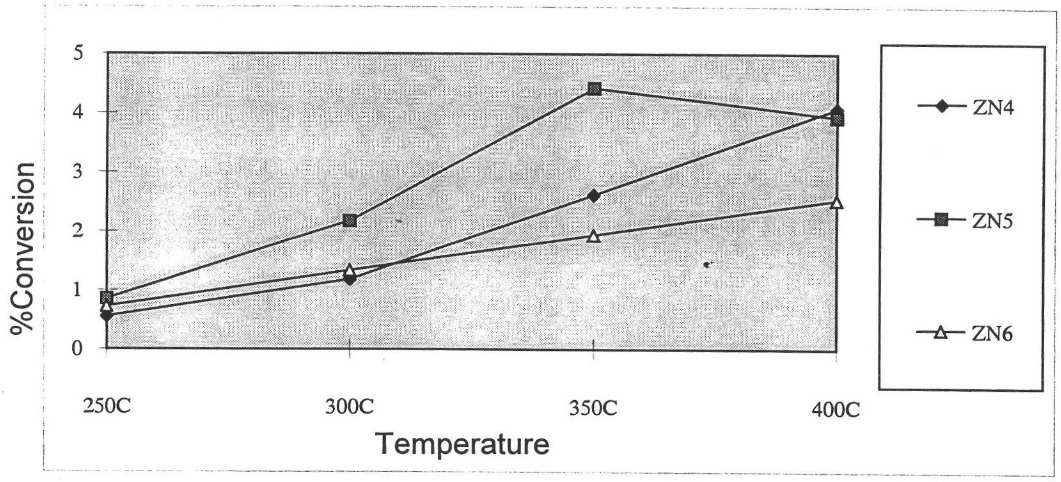

Figure 5.3.2.2 Effect of reaction temperature on %conversion of ZN

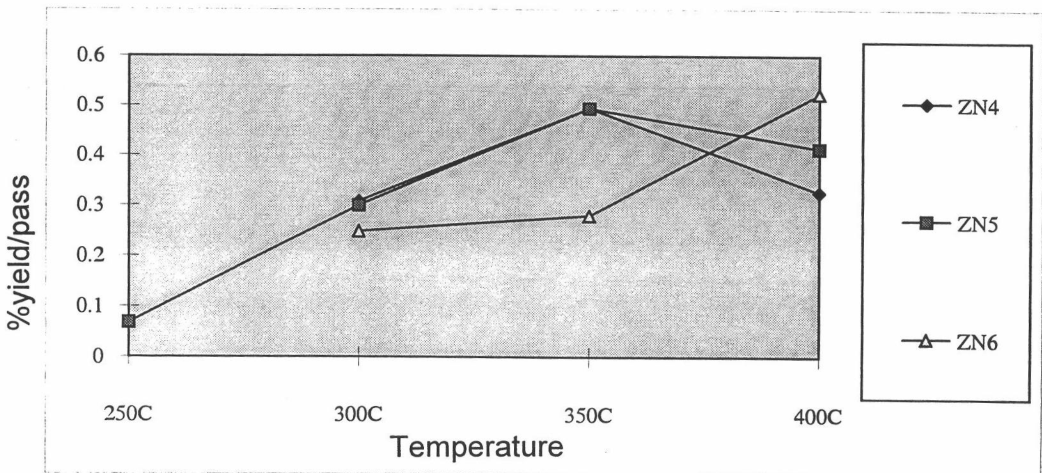

Figure 5.3.2.3 Effect of reaction temperature on %yield/pass of ZN

5.4 Effect of Sm loading on the catalytic performance

We will use Sm as a promoter at various ratio and %Cu was fixed at 2%. The results of experiment are shown in figure 5.4.1-5.4.3

Effect of Sm loading to Cu catalyst is presented in figures 5.4.1-5.4.3. The figures show that %selectivities of SM1, SM4 are less than that of CU catalyst through out the temperature range 250°C-400°C. SM4 shows the maximum %selectivity 7.72% at 300°C while SM1 reach the maximum 5.14% at 350°C before decreasing. In this experimental, shows that % conversion increase compared with CU catalyst all over temperature range of 250°C to 400°C. For %yield per pass of SM4 also increases in this temperature range and similar to CU catalyst at 350°C, then going up to 0.625% at 400°C, while SM1 pass through the maximum 0.24% at 350°C

5.5 Effect of Zr loading on the catalytic performance

This experiment uses Zr as a promoter at various ratios and fixed % Cu base catalyst at 2%.

Effect of Zr loading on catalytic performance are shown in figures 5.5.1-5.5.3. It was presented that %selectivity of ZR1.2 increased to 82.95% as temperature was increased up to 350°C before decreasing rapidly when temperature passed 350°C to 400°C. For ZR0.25, the curve shows slowly selectivity increase in the temperature range of 250°C-400°C. ZR0.75 shows the increase of %conversion more than CU catalyst through out the temperature range 350°C-400°C and reach the maximum value 5.7%, at 400°C. It also shows %yield per pass of both ZR0.75 and ZR1.2 are higher than CU catalyst. ZR1.2 shows the maximum of 1.84 %yield per pass at 350 °C before decreasing.

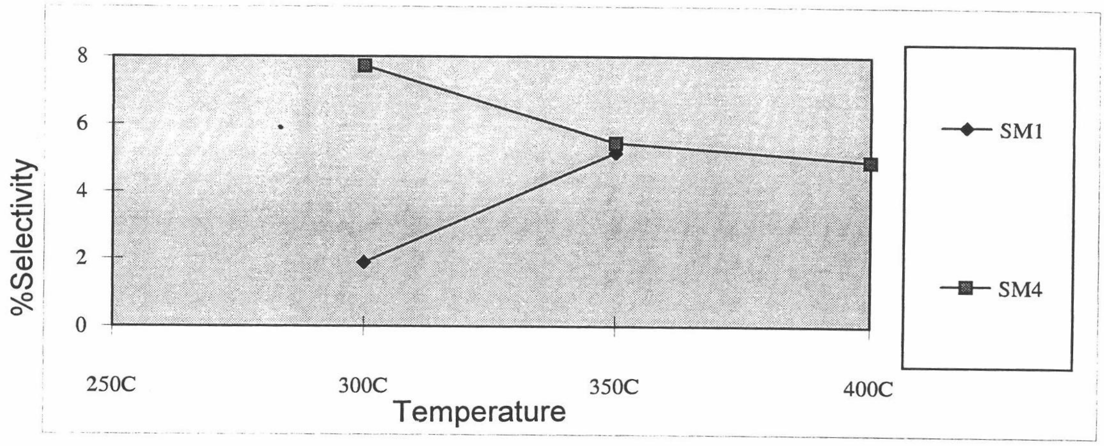

Figure 5.4.1 Effect of reaction temperature on %selectivity of SM

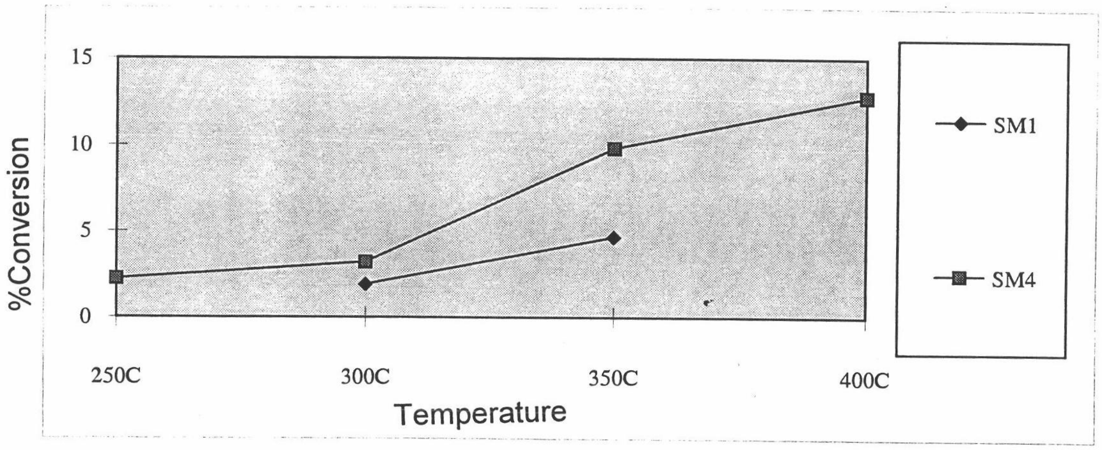

Figure 5.4.2 Effect of reaction temperature on %conversion of SM

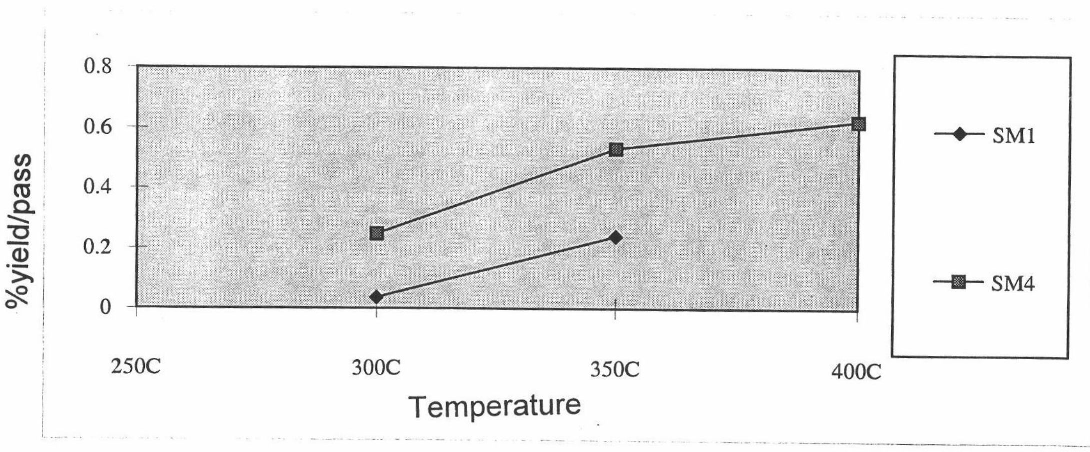

Figure 5.4.3 Effect of reaction temperature on %yield/pass of SM

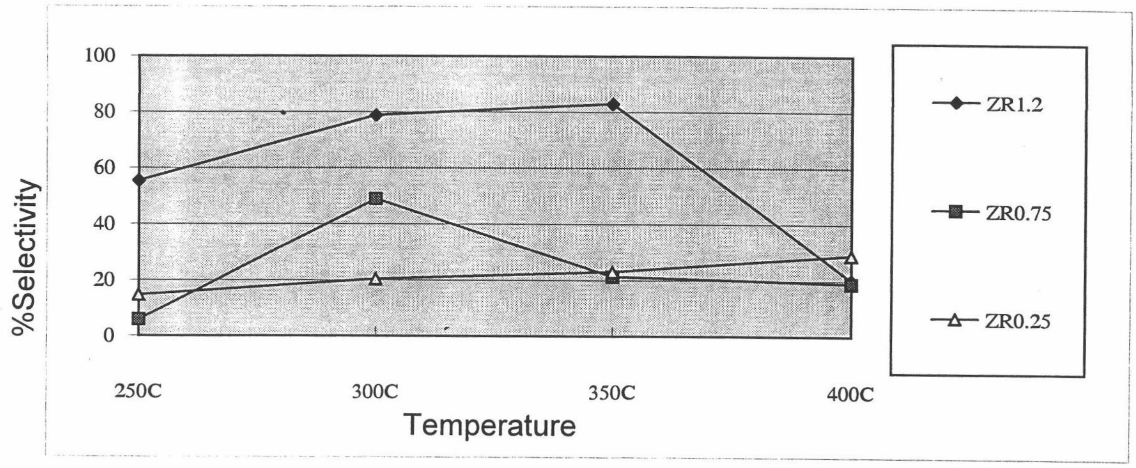

Figure 5.5.1 Effect of reaction temperature on %selectivity of ZR

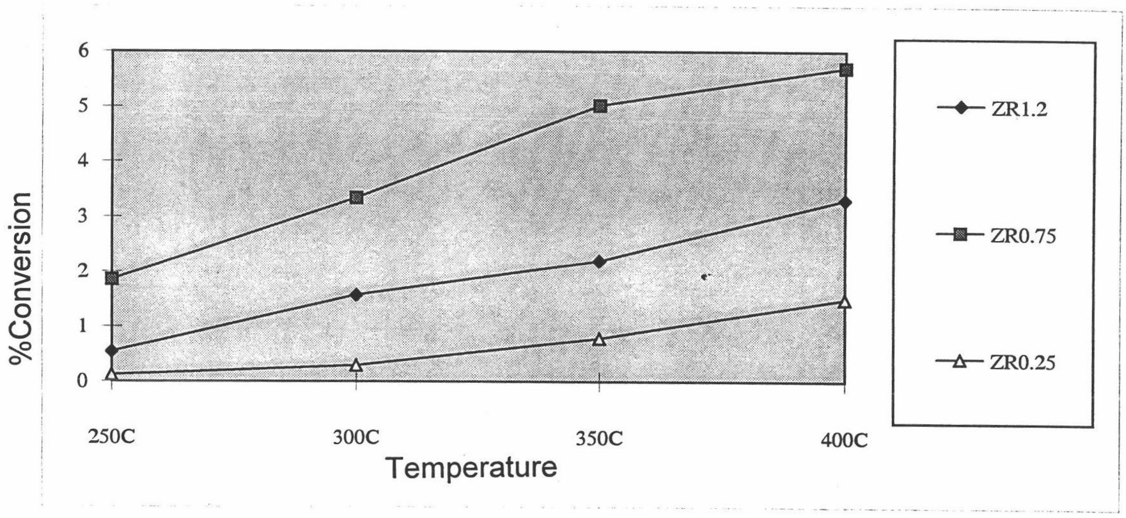

Figure 5.5.2 Effect of reaction temperature on %conversion of ZR

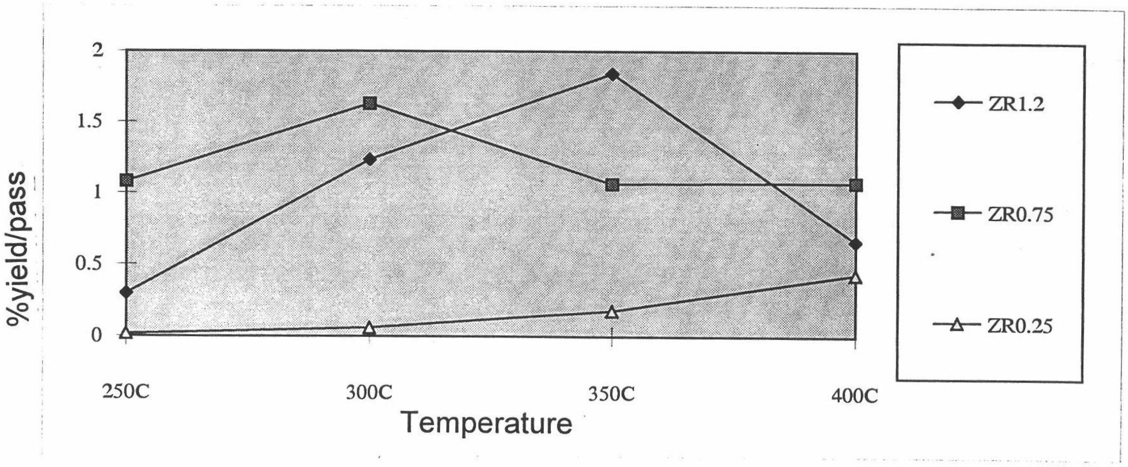

Figure 5.5.3 Effect of reaction temperature on %yield/pass of ZR

Gasser D. et.al.[8] suggested the behavior of Zr in amorphous Cu_7Zr_3 alloy that, the amorphous Cu_7Zr_3 alloy was transformed into metallic copper and ZrO_2 phase during reaction. Zirconium was oxidized to ZrO_2 by water or trace amount of impurity oxygen in the mixed gas, and copper segregrated onto the surface. This process increase the catalyst surface area by dispersing Cu particles in ZrO_2.

5.6 Effect of Sm & Zr loading on catalytic performance

In this experimental, we investigated the effect of 2 types of metal loading on catalytic performance. Figures 5.6.1-5.6.3 shows the experimental results.

Figures 5.6.1-5.6.3 show that, %selectivity and %yield per pass of SZ3 increases as increasing of temperature all over temperature range 250 °C-350°C and reach the maximum 42.78% and 0.60% respectively which higher than CU catalyst, then decreasing through temperarure 400°C. We also see that, %conversion results less than CU catalyst and increases with temperature (only SZ1 show decreased of %conversion at temperature between 350°C-400°C)

These results difference from the tendency it should to be for promoted metal oxide. It might be explained that, from previously experiment of Sm loading on 2%Cu catalyst. It found that, SM4 was the optimum catalyst which presented %yield per pass 0.53% at 350°C same as CU and %selectivity lower than CU catalyst at same temperature. (It supposed to be better results than unpromoted CU catalyst). In addition, the Zr loading shows the excellent results by reach 1.84%yield at 350°C.

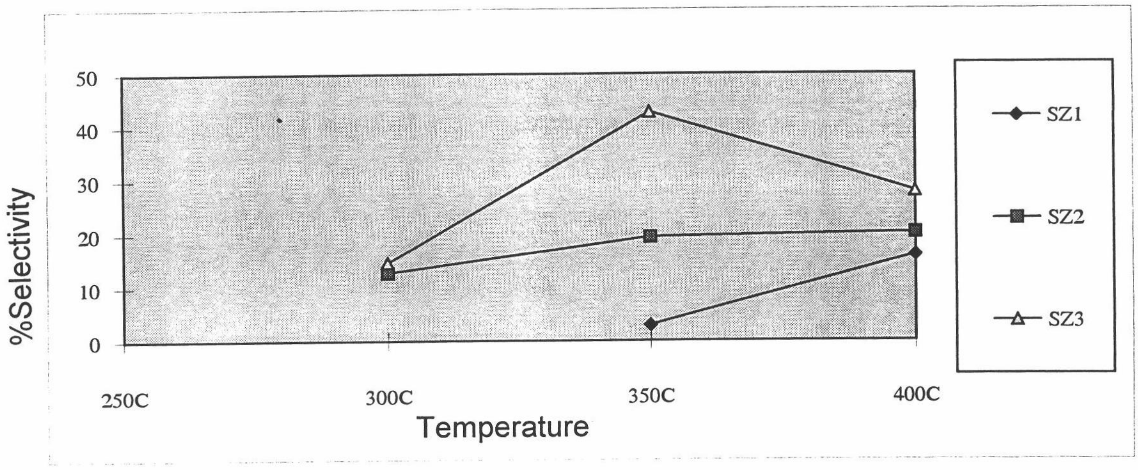

Figure 5.6.1 Effect of reaction temperature on %selectivity of SZ

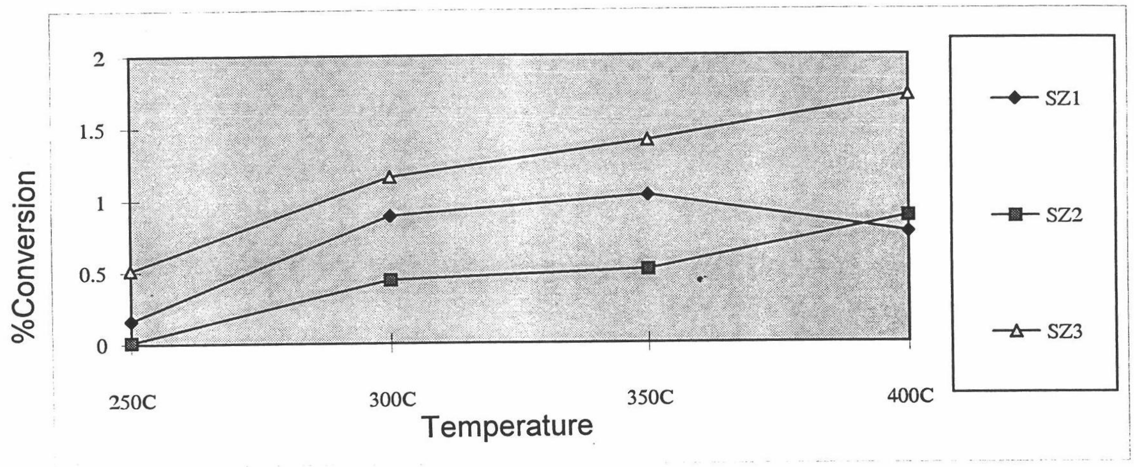

Figure 5.6.2 Effect of reaction temperature on %conversion of SZ

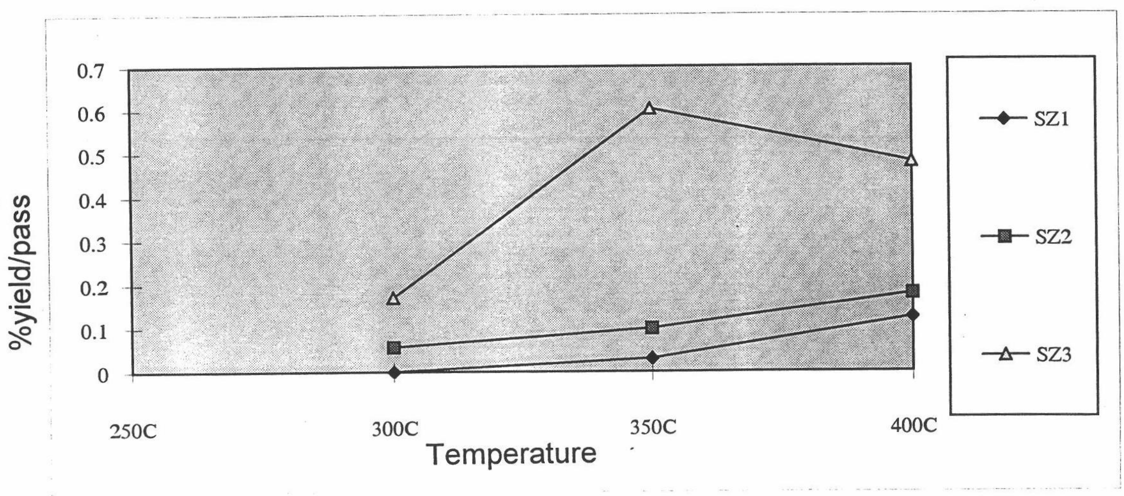

Figure 5.6.3 Effect of reaction temperature on %yield/pass of SZ

In this experiment, we prepared the catalyst by co-impregnation method, Sm may cover Zr surface and Caused Zr less activity according to surface area. Owen, G. and Jenning, J.R.[29,30] investigated the methanol synthesis over catalyst which prepared by in-situ activation of Cu/rare earth binary and ternary alloys in the CO/H_2 gas and reported that catalysts derive from ternary alloys are less active than those derived from their binary counter parts.

5.7 Effect of Nd loading on catalytic performance

The experiment shows the effect of Nd loading in various ratio on catalytic performance and the results show in figures 5.7.1-5.7.3

Figures 5.7.1-5.7.3 are presented that, %selectivity of ND0.25 and ND4 similar to CU catalyst at 300°C but after temperature pass to 350°C, we see that ND0.25 increases rapidly to maximum 30.88%selectivity and higher than CU catalyst. On the other hand, %conversion and %yield per pass of ND4 show the maximum of 9.39% and 1.58% respectively at 350°C which strongly increases than Cu catalyst in this temperature range.

5.8 Effect of Pr loading on the catalytic performance

We used Pr as a promoter at various ratio and 2%Cu was fixed. The effect shows in figures 5.8.1-5.8.3

We can see the effect of Pr loading via figures 5.8.1-5.8.3 which show that, %selectivity of PR1 decreases as temperature increased from 300°C-350°C. PR0.25 and PR4 shows %selectivity similar to CU catalyst. Both PR0.25 and PR4 show %conversion and %yield per pass increase as

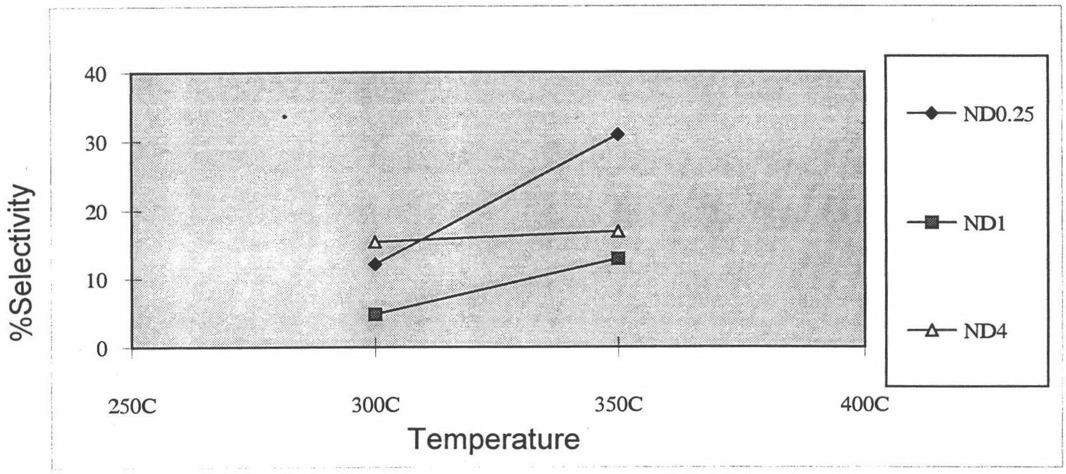

Figure 5.7.1 Effect of reaction temperature on %selectivity of ND

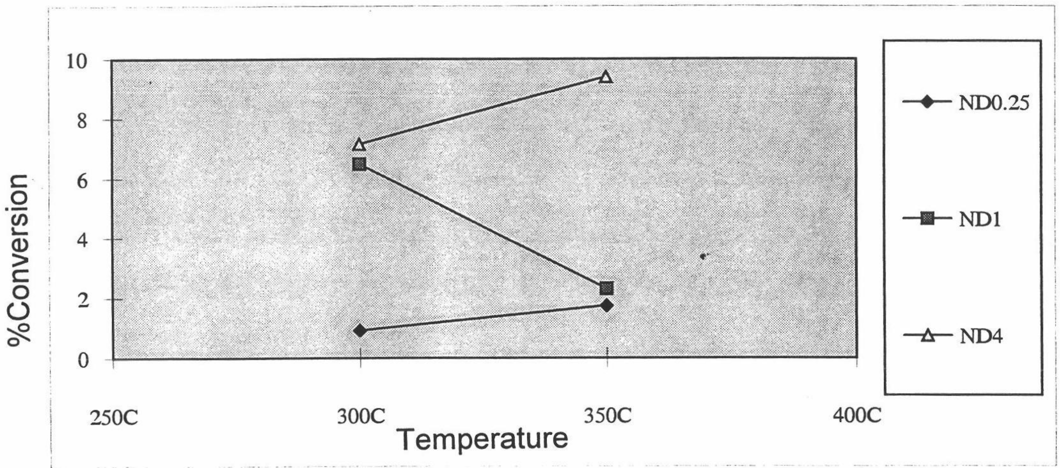

Figure 5.7.2 Effect of reaction temperature on %conversion of ND

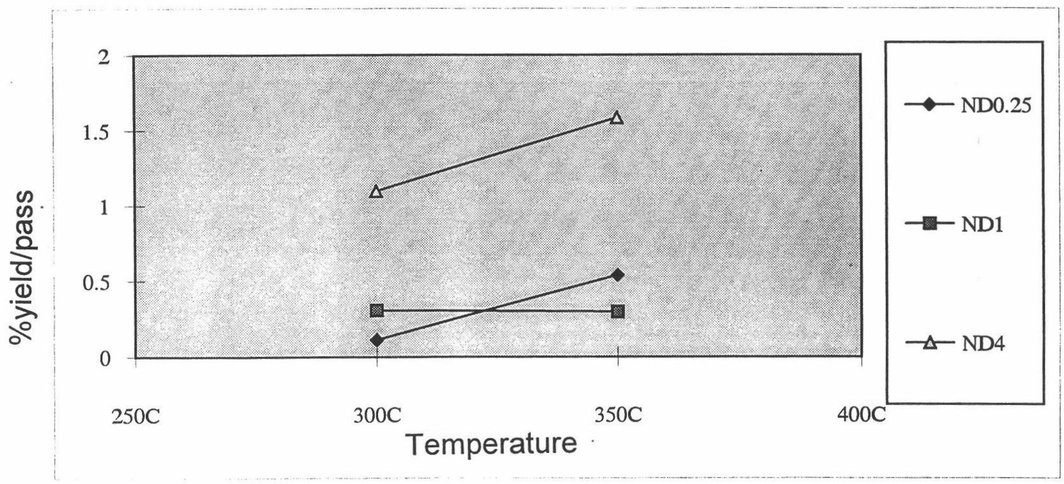

Figure 5.7.3 Effect of reaction temperature on %yield/pass of ND

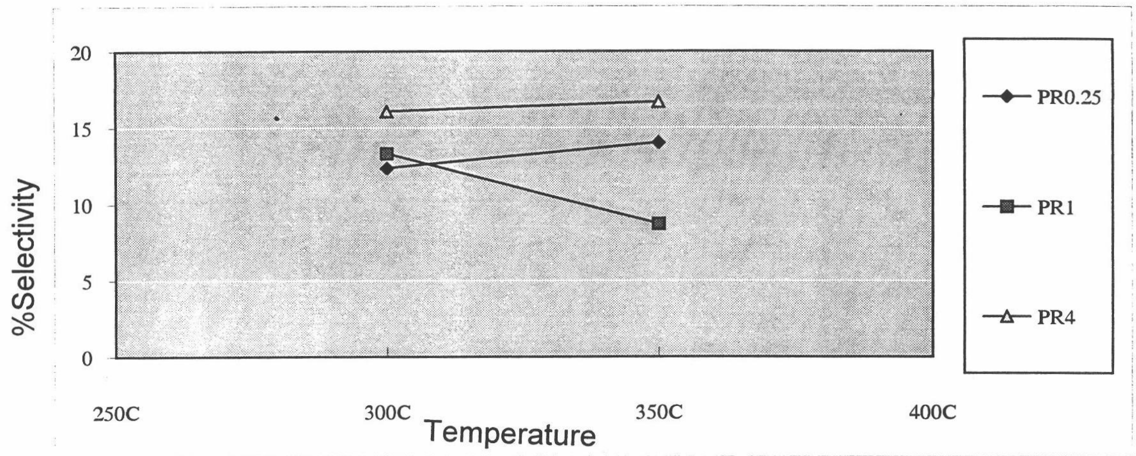

Figure 5.8.1 Effect of reaction temperature on %selectivity of PR

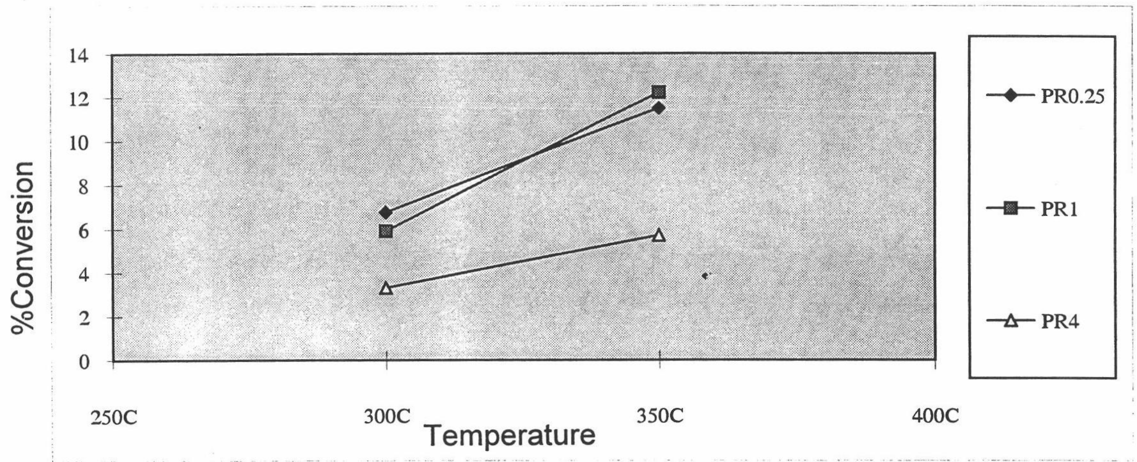

Figure 5.8.2 Effect of reaction temperature on %conversion of PR

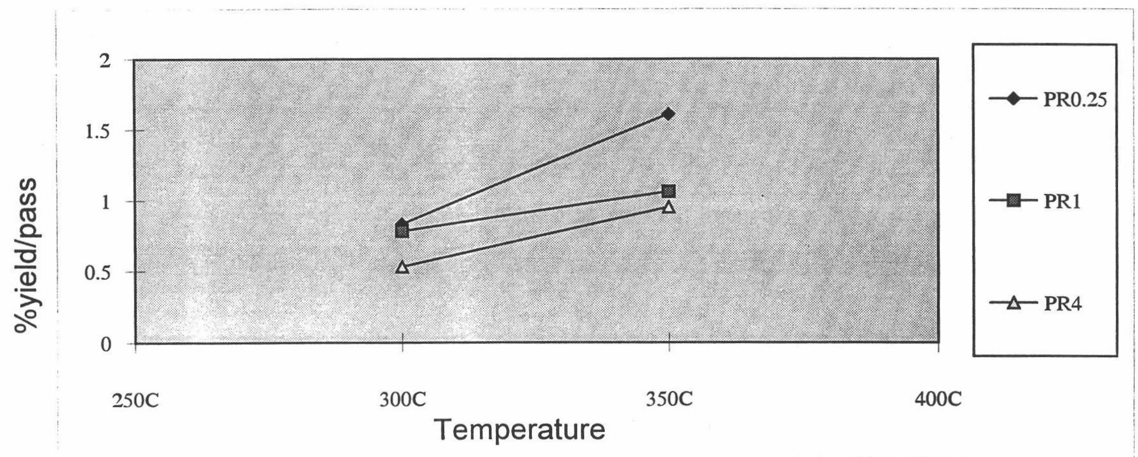

Figure 5.8.3 Effect of reaction temperature on %yield/pass of PR

temperature increase, and PR1 reached the maximum %conversion of 12.21% at 350°C, and PR0.25 show maximum 1.61%yield per pass which higher than CU catalyst at the same temperature.

5.9 Effect of Ce loading on the catalytic performance

5.9.1 Fixed 2%Cu

In this experiment , we investigate Ce as promoter in various ratio and show the result in figures 5.9.1.1-5.9.1.3.

Figures 5.9.1.1-5.9.1.3 show that %selectivity increases all over temperature range 250°C to 350°C then decreases. We can see the strongly increasing in CE2 reached 30.75 %selectivity higher than CU catalyst. Most of them also show higher %conversion than CU catalyst and increases as temperature increased. CE2 reach the maximum of 3.09%yield per pass at 400°C and increases as increasing temperature except CE1 has slightly decrease within temperature range of 350°C-400°C.

5.9.2 Fixed 1%Ce

Previously experiment we found that the best composition of Ce promoter was 1%Ce. So, we will investigate the optimum of Cu amount in the composition of catalysts by use Cu in various ratio. Figures 5.9.2.1-5.9.2.3 shows the experiment results.

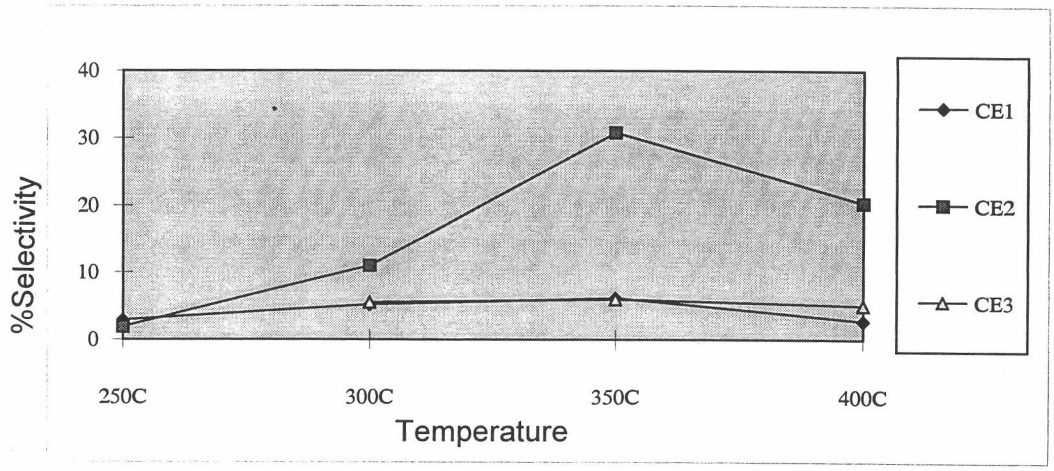

Figure 5.9.1.1 Effect of reaction temperature on %selectivity of CE

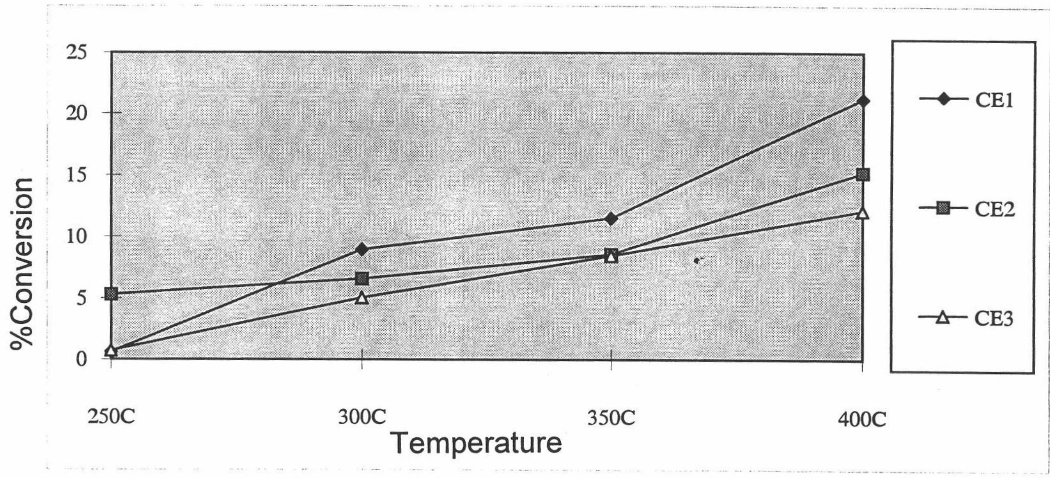

Figure 5.9.1.2 Effect of reaction temperature on %conversion of CE

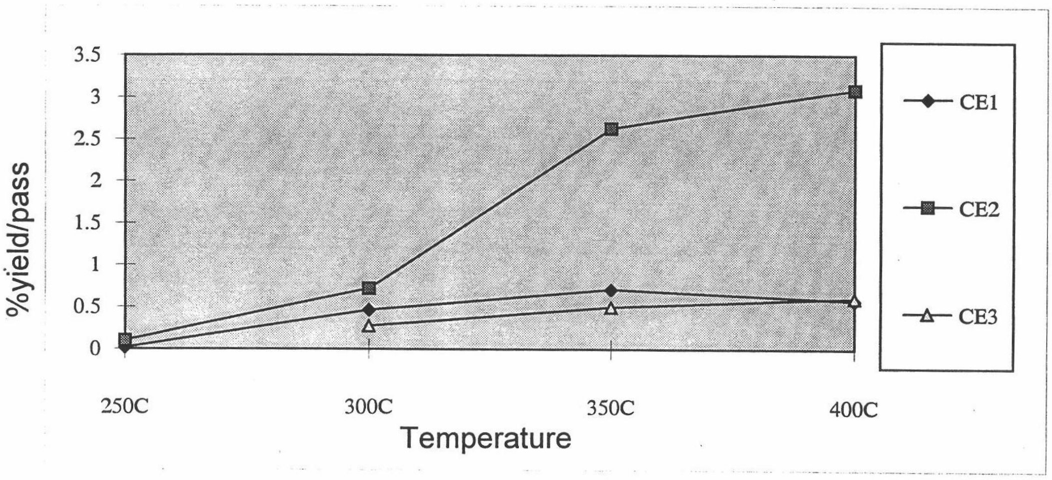

Figure 5.9.1.3 Effect of reaction temperature on %yield/pass of CE

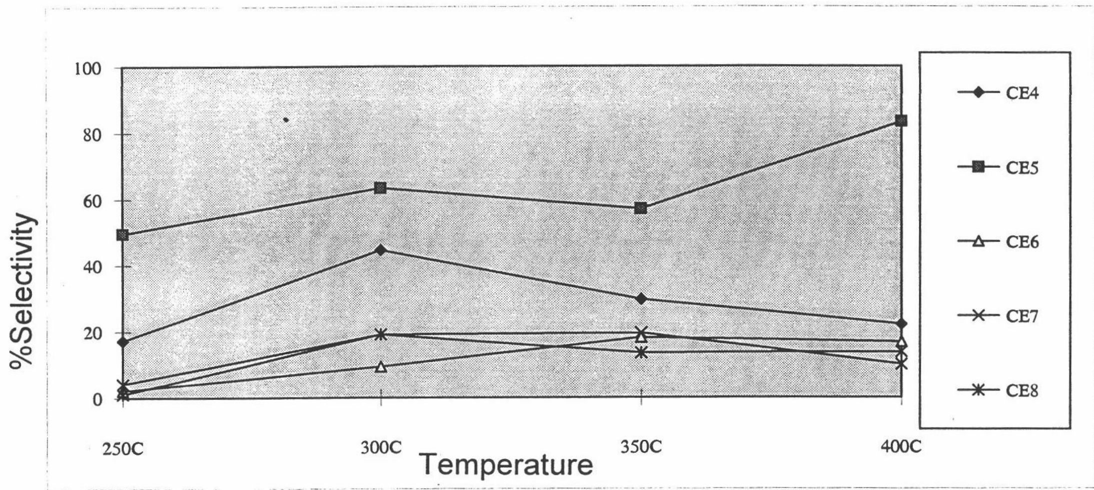

Figure 5.9.2.1 Effect of reaction temperature on %selectivity of CE

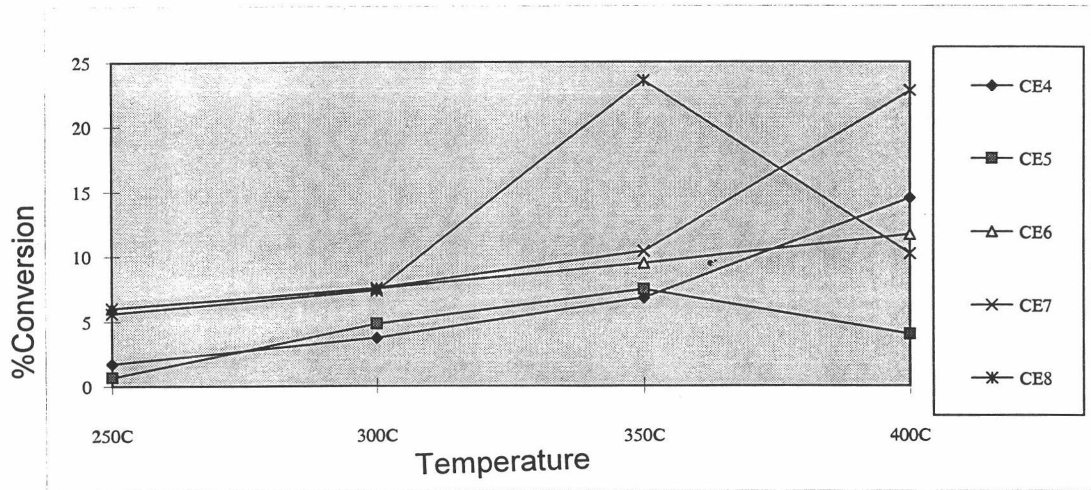

Figure 5.9.2.2 Effect of reaction temperature on %conversion of CE

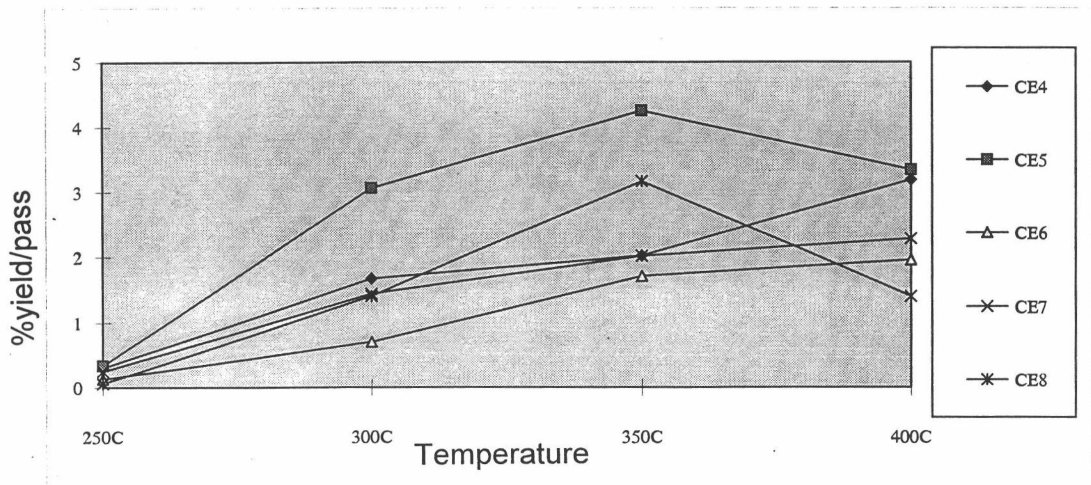

Figure 5.9.2.3 Effect of reaction temperature on %yield/pass of CE

Figures 5.9.2.1-5.9.2.3 are presented that CE5 show higher % selectivity than CU catalyst all over temperature range 250°C-400°C and reach a maximum 83.31%selectivity at 400°C. For CE6, CE7 and CE8 which has the amount of Cu more than 2% show %selectivity less than CU catalyst in temperature range 350°C-400°C. It also shows that, %conversion of all ratio higher than CU at the same temperature except CE5.

The experimental results show that, CE6, CE7 and CE8 have the similar %conversion at 300°C. All the compositions show increasing of % conversion all over temperature range 250°C-400°C except CE5 and CE8 which decreases in the temperature range 350°C-400°C. CE8 show the maximum 23.57%conversion at 350°C.

For %yield per pass, we can see that, CE4, CE5 which have CU content less than 2% show higher %yield per pass than CE2 in temperature range of 250°C-400°C especially for CE5 reach maximum at 4.25%yield per pass at 350°C. CE6, CE7 and CE8 show the same direction as CE5 which increases all over temperature range 250°C-400°C except CE8 (maximum amount of Cu) shows decrease of %yield per pass at temperature between 350°C-400°C.

5.10 Effect of pressure on catalytic performance

In this study, we investigate through the pressure 10 bar, which less than normal pressure 20 bar. We select the best result of Nd, Pr, Zn promoter from previously experiment. The results of each promoter are shown in tables 5.10.1-5.10.3.

Figures 5.10.1.1-5.10.1.3 present that at the same temperature, % selectivity and %yield per pass show the result less than normal pressure (20 bar). However, the maximum %selectivity, %conversion and %yield per pass reach at 350°C for 2.8%, 14.47% and 0.40% respectively.

Figures 5.10.2.1-5.10.2.3 presented that, when use pressure 10 bar it shows the lower results of %selectivity, %conversion and %yield per pass than using pressure 20 bar, at the same temperature. We can see the maximum of %selectivity, %conversion and %yield per pass at 350°C for 3.32%, 6.31% and 0.21% respectively.

From figures 5.10.3.1-5.10.3.3, we can see the similar results as ND4 catalyst when use pressure 10 bar that, only %conversion shows higher than pressure 20 bar experimental. All %selectivity, %conversion and % yield per pass show the same direction as using pressure 20 bar. % Selectivity reach maximum of 2.71% at 300°C, while %conversion and % yield per pass show maximum of 6.39% and 0.12% respectively at 350°C.

It can be conclude that, pressure has a considerable effect on the yield of methanol. From the experiment, it showed that, decreasing of pressure effected to decrease methanol yield as agree with [25].

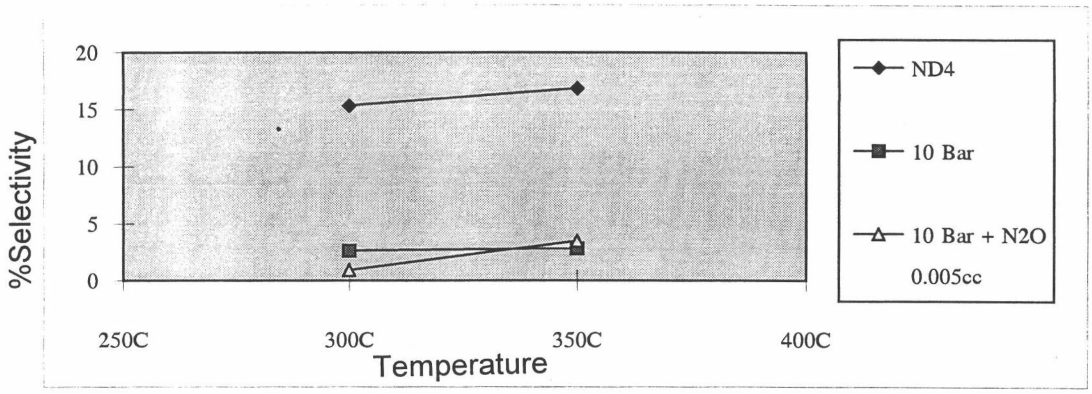

Figure 5.10.1.1 Effect of reaction pressure on %selectivity of ND4

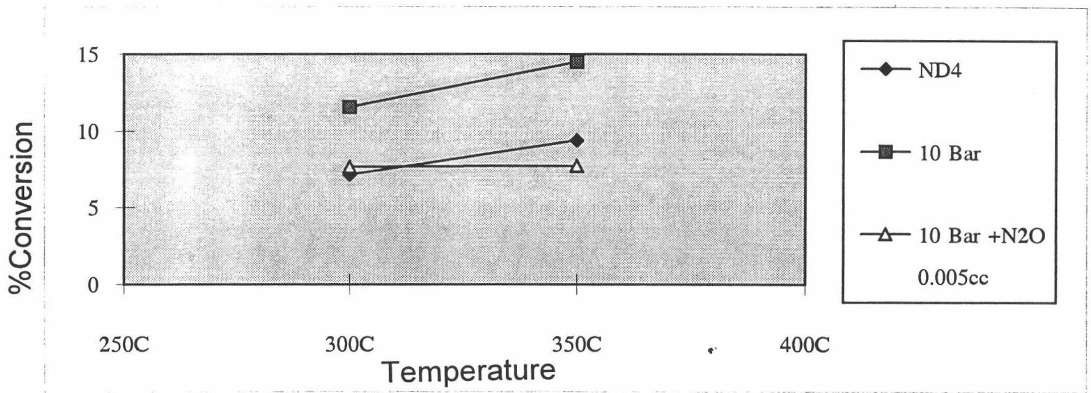

Figure 5.10.1.2 Effect of reaction pressure on %conversion of ND4

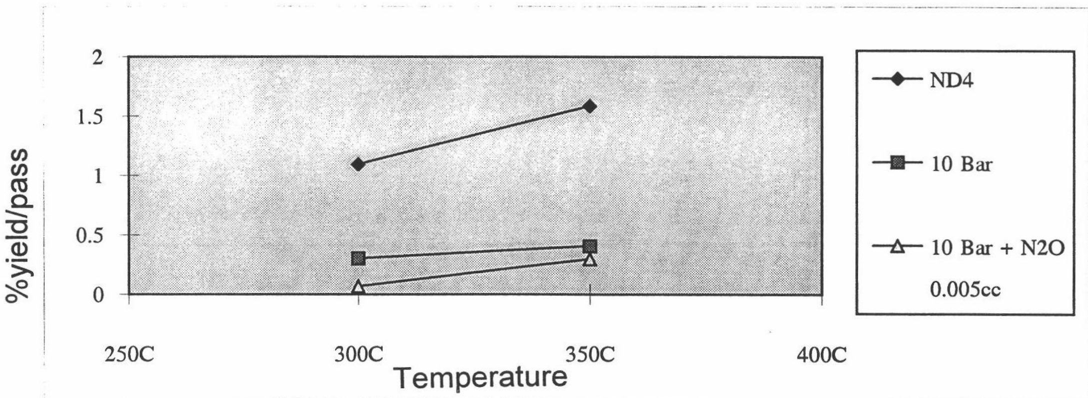

Figure 5.10.1.3 Effect of reaction pressure on %yield/pass of ND4

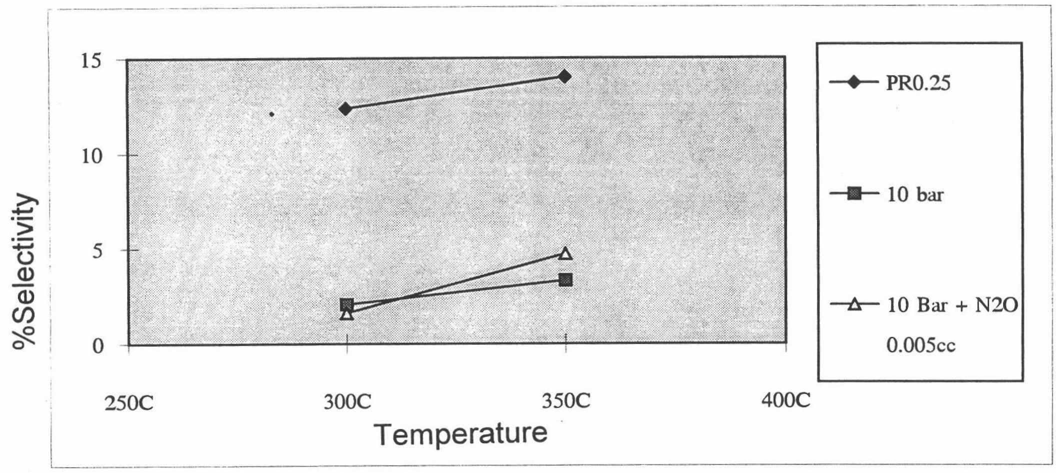

Figure 5.10.2.1 Effect of reaction pressure on %selectivity of PR0.25

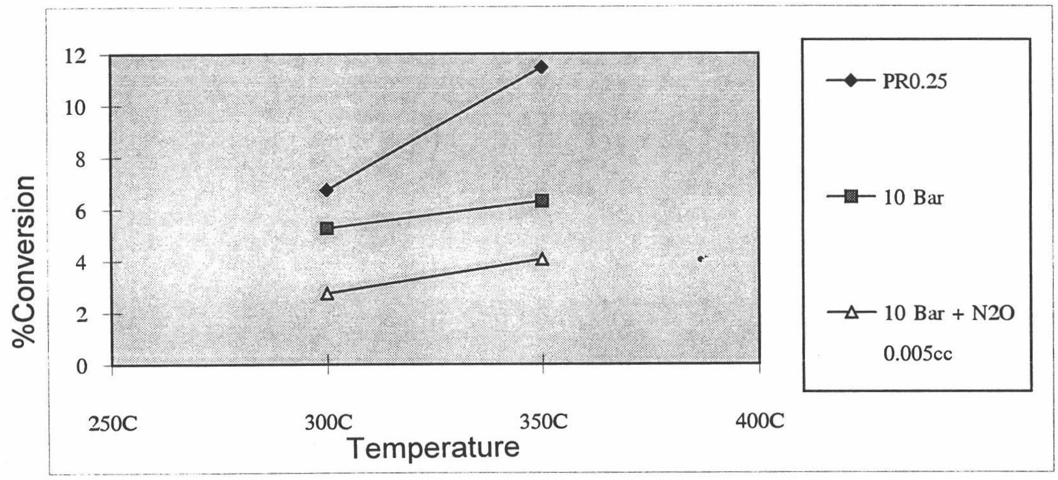

Figure 5.10.2.2 Effect of reaction pressure on %conversion of PR0.25

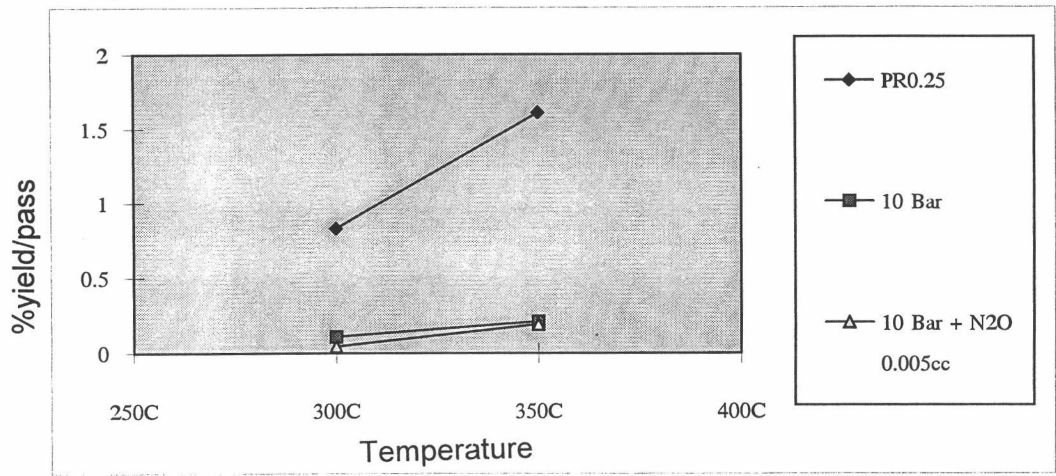

Figure 5.10.2.3 Effect of reaction pressure on %yield/pass of PR0.25

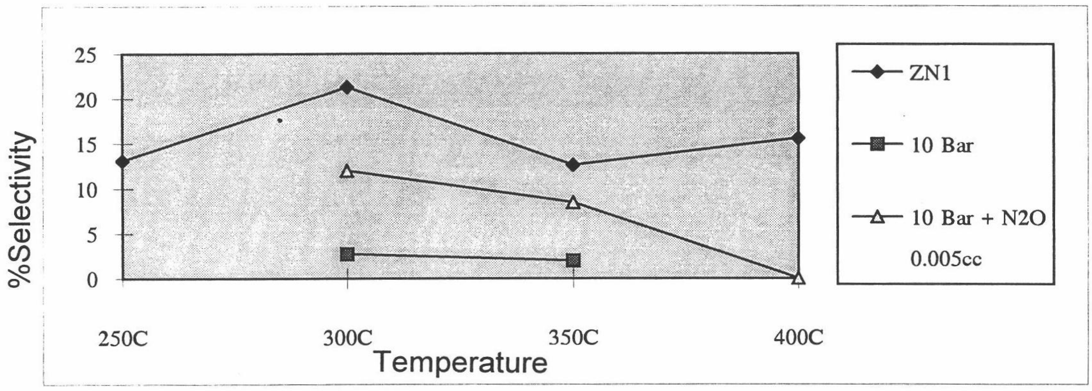

Figure 5.10.3.1 Effect of reaction pressure on %selectivity of ZN1

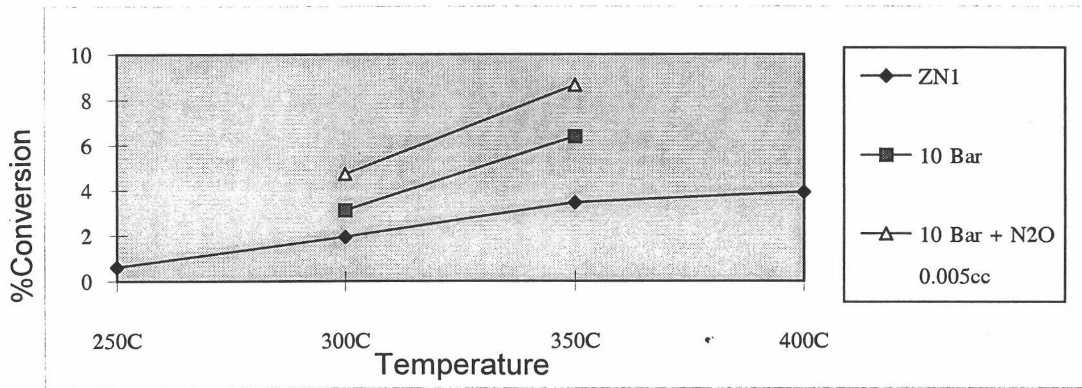

Figure 5.10.3.2 Effect of reaction pressure on %conversion of ZN1

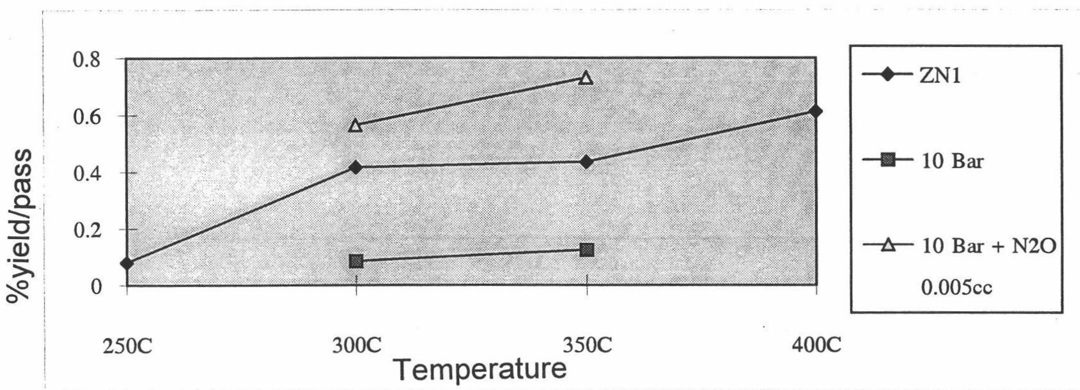

Figure 5.10.3.3 Effect of reaction pressure on %yield/pass of ZN1

5.11 Effect of N_2O on catalytic performance

Herman et.al.[1] presented that the use of synthesis gas free from oxidisinf gases such as water, oxygen or CO_2 resulted in extensive reduction and deactivation of the catalysts.

The same suggestion of Jennings et.al.[31] that pulsing injection of the oxidant led significant transient increase in the exit methanol concentration with the effectiveness decreasing in the order O_2>N_2O>CO_2.

5.11.1 Effect of N_2O on CU

In this experimental, we inject 2.4cc. of N_2O into the system and investigated. The results are shown in table 5.11.1

From figures 5.1.1-5.1.3, when injection N_2O into the sysyem it show lower %selectivity than CU catalyst without N_2O all the temperature range of 300°C-400°C and show maximum 10.3%selectivity at 300°C. Both % conversion and %yield per pass increase as temperature increase and reach maximum at 400°C for 7.49% and 0.043% respectively. However, the maximum %yield per pass of Cu with N_2O content still shows the result less than maximum of CU catalyst without N_2O at 350°C.

5.11.2 Effect of N_2O on commercial catalyst

In case of commercial catalyst, we also compare by inject 1.0 cc and 2.4 cc of N_2O. The results. of investigated through catalytic performance are shown in table 5.11.2.

From figures 5.2.1-5.2.3, we can see that as temperature increases, %selectivity of inject 1.0 cc N_2O decreases through 400°C and inject 2.4 cc

N_2O shows increasing of %selectivity as temperature increase through 300 °C then, decreases. Inject 2.4 cc N_2O reach maximum of 88.57%selectivity at 300°C which higher than COM without N_2O content. %conversion and % yield per pass of inject N_2O show higher than COM in temperature range of 250°C-300°C, and decrease after passes 350°C to 400°C and also less than COM without N_2O content. It were shown that both %conversion and % yield per pass of COM with 1.0 cc N_2O show maximum of 13.61% and 10.77% respectively. at 250°C

5.11.3 Effect of N_2O on SM4

In this review, we use 2.4cc N_2O inject into the system at 350°C and show the results in table 5.11.3

Figures 5.11.3.1-5.11.3.3 show that, as we inject 2.4 cc N_2O at 350°C %selectivity show 7.43% which higher than SM4

5.11.4 Effect of N_2O on CE5

In this experiment, we inject N_2O in various quantity on CE5 catalyst which the best results show from previously experiment. The result of investigate through catalytic performance can be seen from table 5.11.4.

Figures 5.11.4.1-5.11.4.3 present the injection of N_2O in any ratio which show the lower % selectivity than CE5 all temperature range of 250°C -400°C. The maximum %selectivity of 0.005 cc N_2O content shows at 5.53%, 300°C. For temperature between 300°C-350°C, %conversion of CE5 with 1.0 cc N_2O shows the maximum of 21.28% at 400°C which higher than CE5. It absolutely shows that, CE5 without N_2O show higher %yield per pass than CE% with N_2O all over temperature range of 250°C-400°C. The maximum 1.10 %yield per pass was CE5 with 0.005cc N_2O at 300°C.

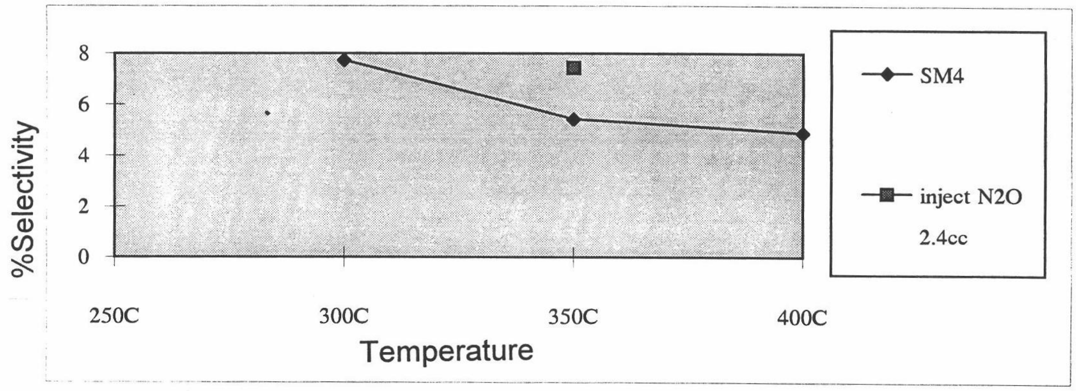

Figure 5.11.3.1 Effect of N2O on %selectivity of SM4

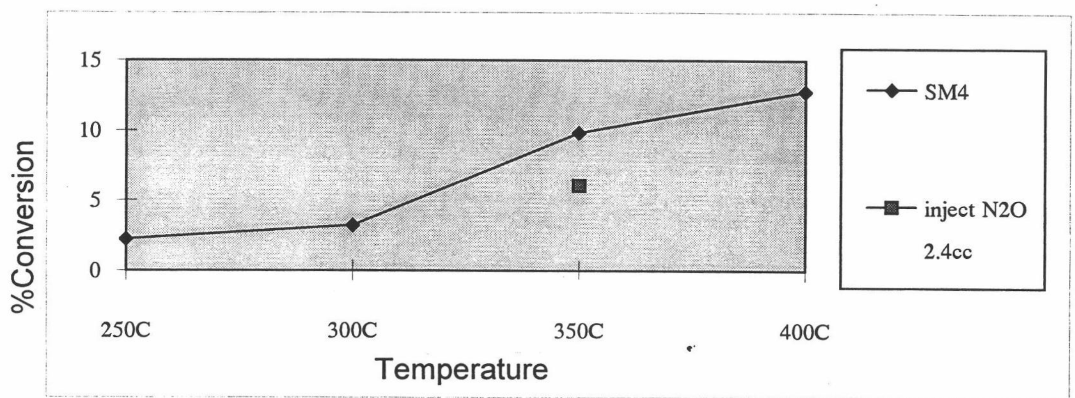

Figure 5.11.3.2 Effect of N2O on %conversion of SM4

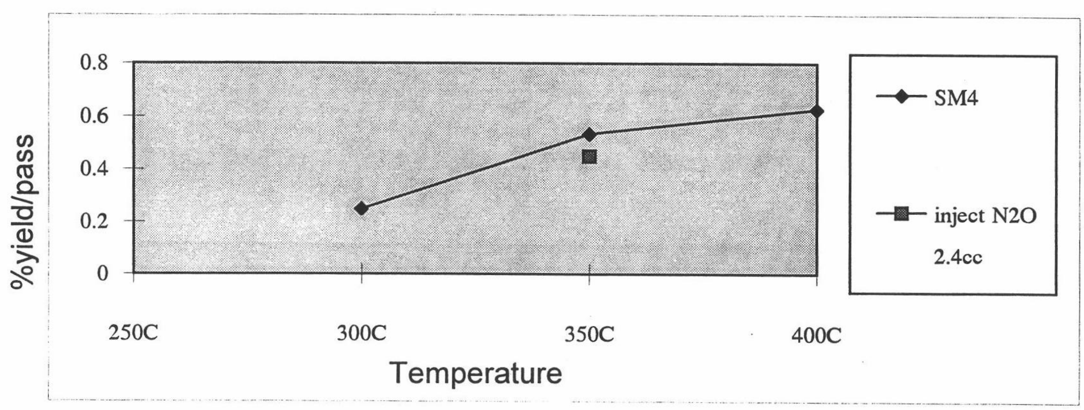

Figure 5.11.3.3 Effect of N2O on %yield/pass of SM4

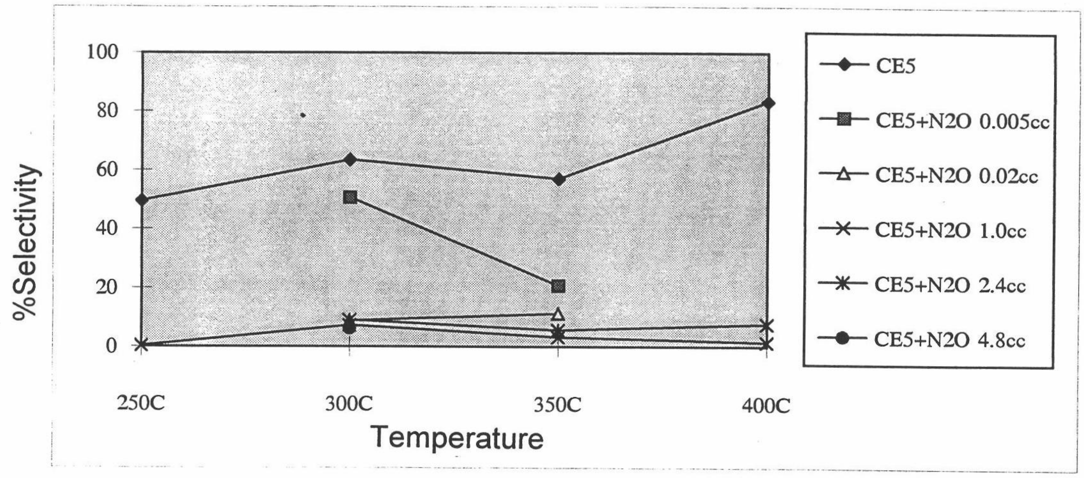

Figure 5.11.4.1 Effect of N2O on %selectivity of CE5

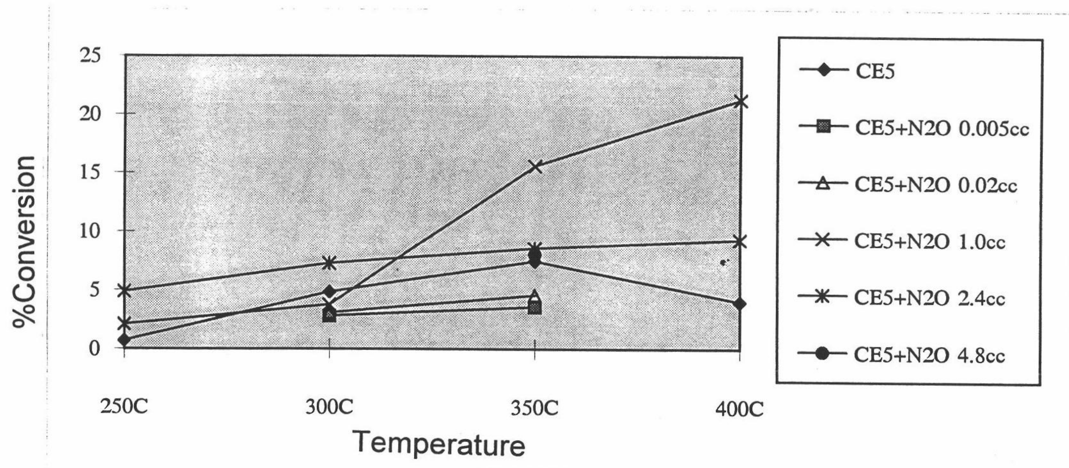

Figure 5.11.4.2 Effect of N2O on %conversion of CE5

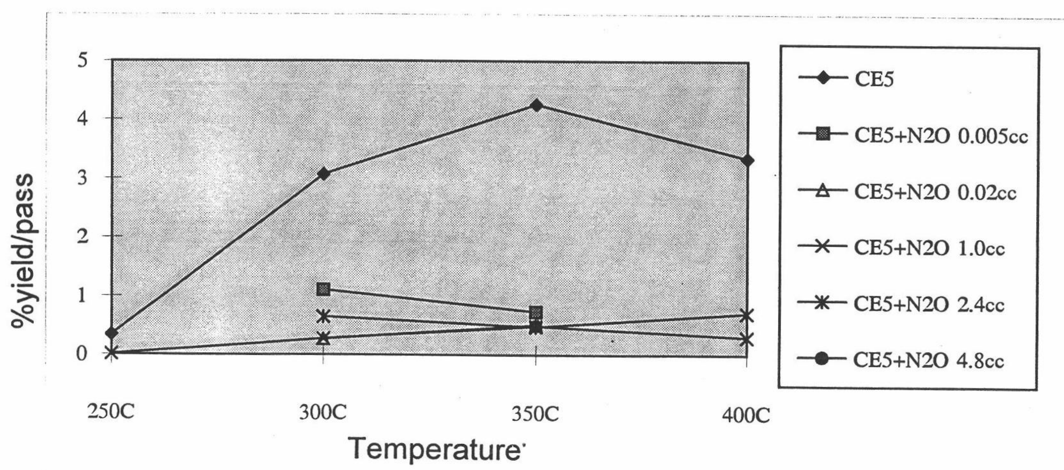

Figure 5.11.4.3 Effect of N2O on %yield/pass of CE5

5.11.5 Effect of N_2O on ND4

In this experiment, we inject 0.005cc N_2O into the system which use ND4 as the catalyst. It shows the results in table 5.11.5.

Figures 5.11.5.1-5.11.5.3 show that when inject 0.005cc of N_2O to ND4 %selectivity, %conversion and %yield per pass increase as temperature increase same direction as ND4 without N_2O content. ND4 with 0.005cc N_2O show higher result of %selectivity than ND4 without N_2O and reach maximum 85.82% at 350°C. For %conversion and %yield per pass, it show the maximum 0.95% and 0.82% respectively at same temperature.

5.11.6 Effect of N_2O on ND4 (Pressure 10 bar)

In this review, we change both conditions of ND4 by inject 0.005cc N_2O and decrease pressure from 20 bar to 10 bar. The results of investigation are shown in table 5.11.6.

Figures 5.10.1.1-5.10.1.3 present that, when decreases pressure from 20 bar to 10 bar, ND4 with 0.005cc N_2O content show lower % selectivity than ND4 without N_2O in temperature range 300°C-350°C. It shows 3.48% selectivity maximum at 350°C in which higher than ND4 without N_2O.

For %conversion, it show lower results than ND4 without N_2O in temperature rang 300°C-350°C. But show higher results if compare with the same amount N_2O and pressure 20 bar

When inject N_2O, we can see that ND4 with 10 bar of pressure show less %yield per pass than ND4 at pressure 20 bar. It can be concluded

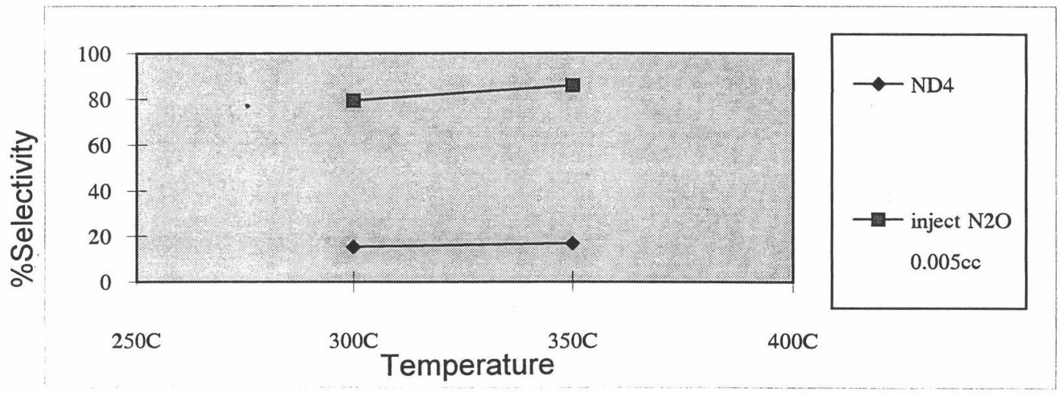

Figure 5.11.5.1 Effect of N2O on %selectivity of ND4

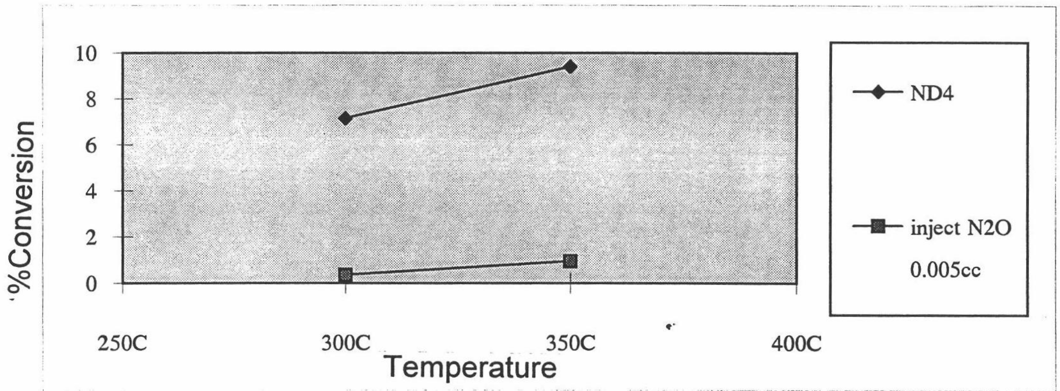

Figure 5.11.5.2 Effect of N2O on %conversion of ND4

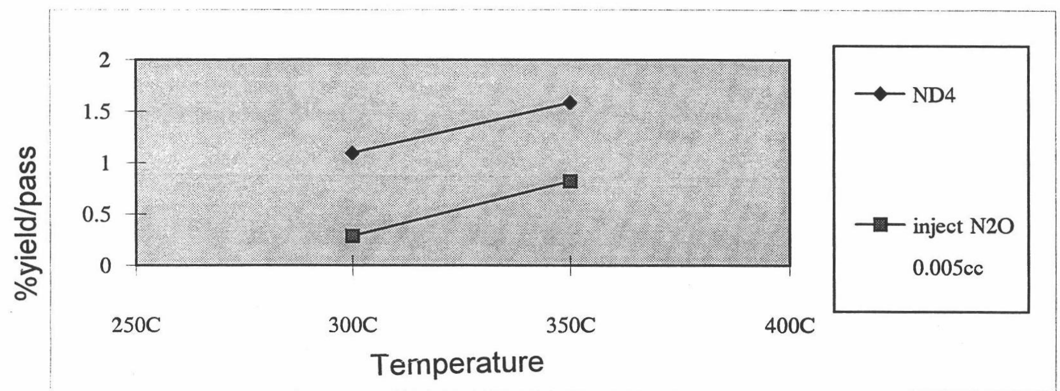

Figure 5.11.5.3 Effect of N2O on %yield/pass of ND4

thatND4 with N_2O show lower %yield per pass than ND4 catalyst without N_2O.

5.11.7 Effect of N_2O on PR0.25 (pressure 10 bar)

When we change both conditions by inject N_2O and decreases pressure to 10 bar and investigate the result through catalytic performance. The results are shown in table 5.11.7.

From figure 5.10.2.1-5.10.2.3,it show that, after we inject N_2O 0.005 cc into PR0.25 catalyst %selectivity, %conversion and %yield per pass show lower than PR0.25 without N_2O at temperature between 300°C-350°C. However, it show increasing of %selectivity at temperature 350°C and reach maximum at 4.72%. For %conversion and %yield per pass, it show maximum at same temperature of 350°C for 4.05% and 0.0191% respectively.

5.11.8 Effect of N_2O on ZN1 (pressure 10 bar)

The results of using ZN1, the catalyst which has the best performance, with N2O treatment at 10 bar are shown in table 5.11.8.

Figure 5.10.3.1-5.10.3.3 are presented that, %selectivity of ZN1 catalyst at pressure 20 bar shows higher than ZN1 with decreasing pressure to 10 bar. at temperature range of 300°C-350°C. However, ZN1 with injection of N2O shows higher %selectivity than ZN1 without N2O and same pressure (10 bar) at the same temperature range and decrease as temperature passes to 400°C. The maximum %selectivity of ZN1 with N_2O injection shows at 11.97% 300°C. We can see that, both %conversion and %yield per pass increase with increasing of temperature and show higher result even compares with ZN1 or ZN1 at 10 bar and reach maximum at same temperature of 350°C for 8.65% and 0.73% respectively.

In the above experiment, CU, SM4, CE5, ND4, and PR0.25 in the presence of N_2O show lower methanol yield than catalyst without N_2O which much different from suggestion by Herman et al.[1] and Jennings et al.[31].

In addition, Jennings et al. [31] suggested that, the "dead time" of the test unit corresponded to a time lapse of about 45 seconds after which the oxidant underwent interaction with the catalyst, causing a rise in the exit concentration of methanol which reach a maximum some 10 seconds after its apperance threshold signal. The methanol signal then decayed slowly, falling to its original level some 50 seconds later. Figure 5.11.9 shows the concentration of methanol as a function of time with oxidizing gases.

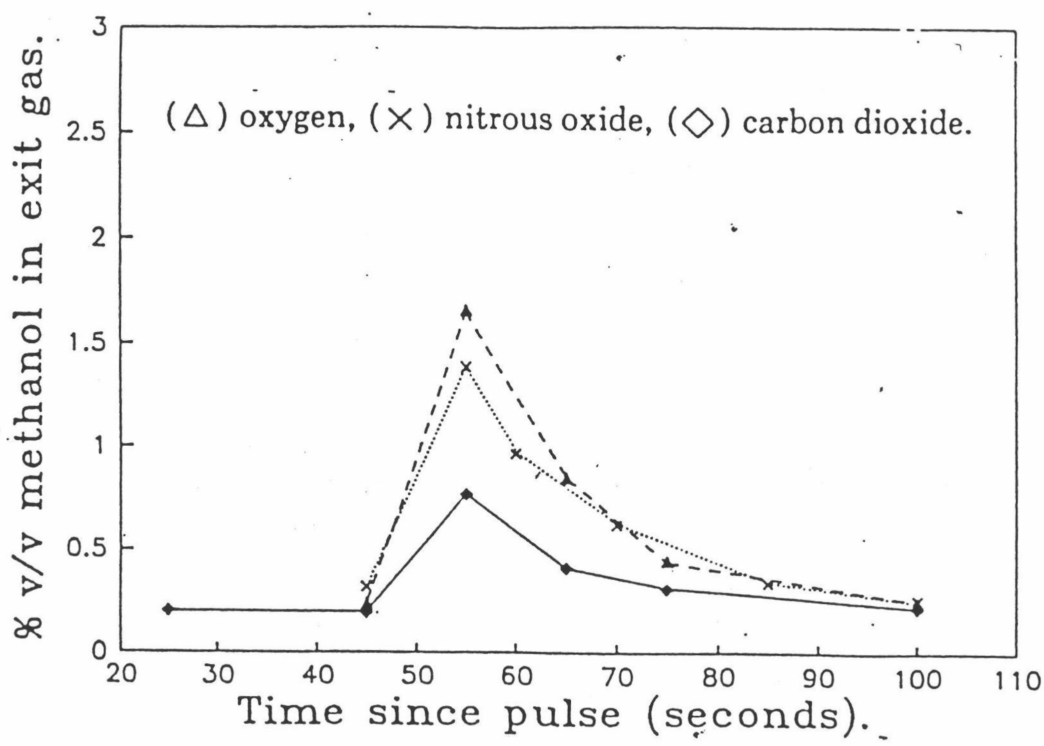

Figure 5.11.9 Comparison of transient excess methanol yield for pulses of different oxidising gases [31]

We had repeated the experiment by investigating the catalytic performance of PR0.25 and ND4 catalyst in the presence of air and follow Jennings [31] in terms of time to measure methanol .Our results show that after injecting air 10 μl for 60 seconds, methanol yield increases and shows the result higher than PR0.25 and ND4 without air.as shown in figures 5.11.9.1-5.11.9.9.

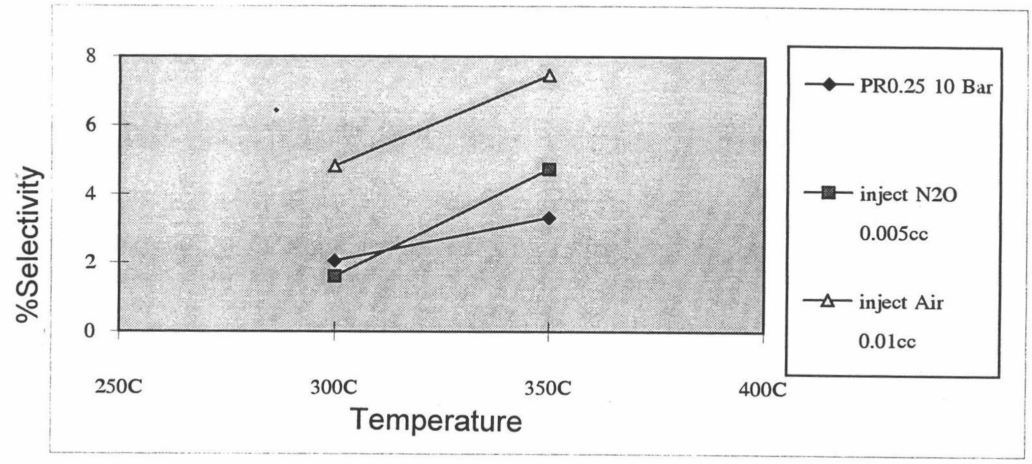

Figure 5.11.9.1 Effect of oxidant on %Selectivity of PR0.25

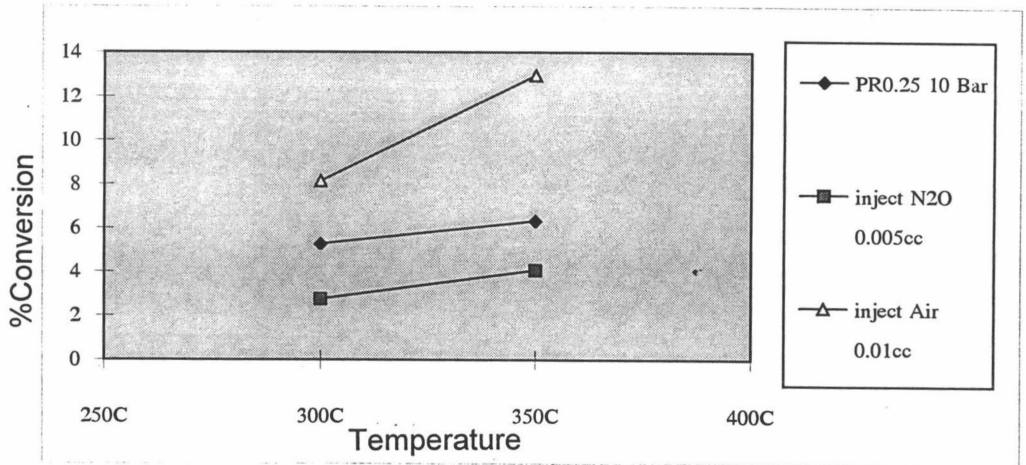

Figure 5.11.9.2 Effect of oxidant on %Conversion of PR0.25

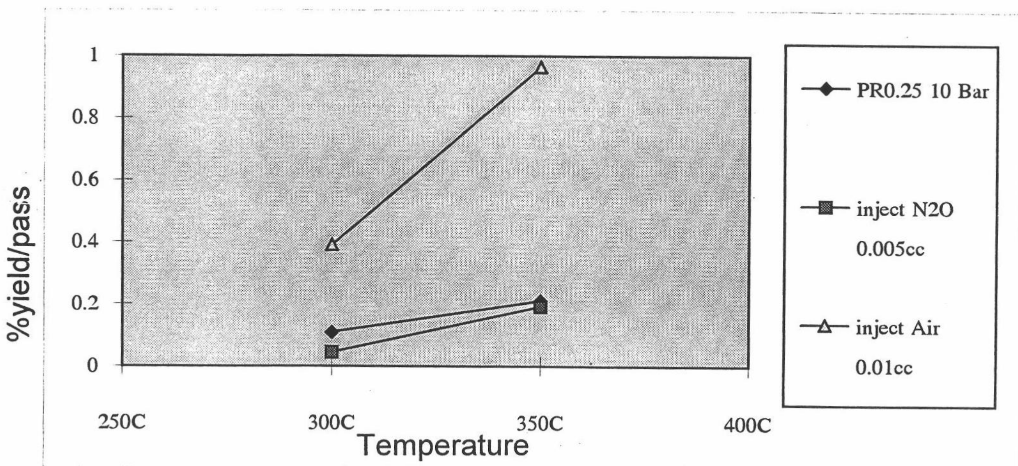

Figure 5.11.9.3 Effect of oxidant on %Yield/Pass of PR0.25

Table 5.11.9.1 Effect of Air on PR0.25 (Pressure 10 Bar)

		300C				350C
	5 min	15 min-10	30 min-20	60 min-20	90 min -0	15 min-20
%Selectivity	3.89	5.87	5.78	4.81	6.34	7.45
%Conversion	4.2	4.4	5.93	8.13	5.53	12.95
%Yield/pass	0.16338	0.2582	0.3428	0.3914	0.3504	0.9642

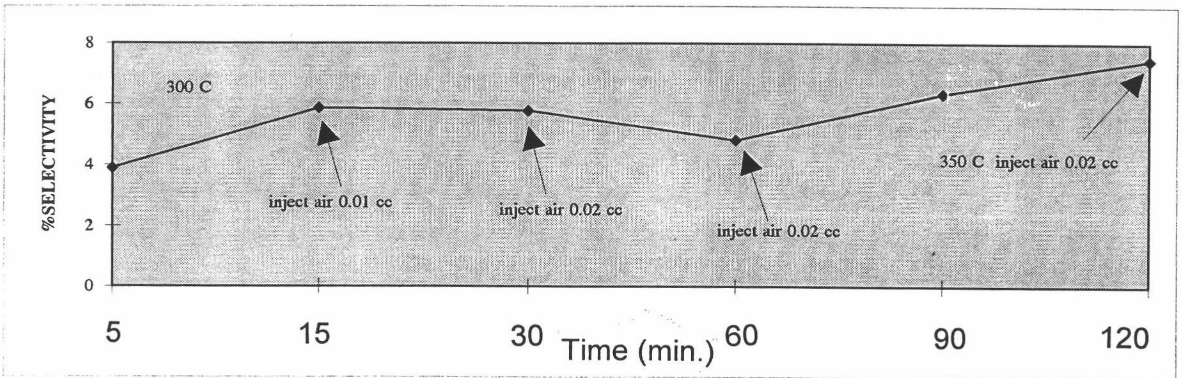

Figure 5.11.9.4 Effect of Air on %Selectivity of PR0.25

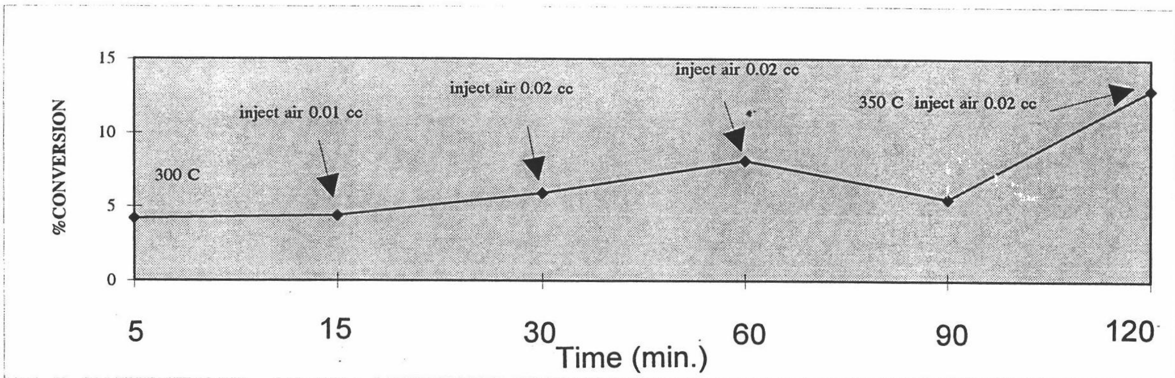

Figure 5.11.9.5 Effect of Air on %Conversion of PR0.25

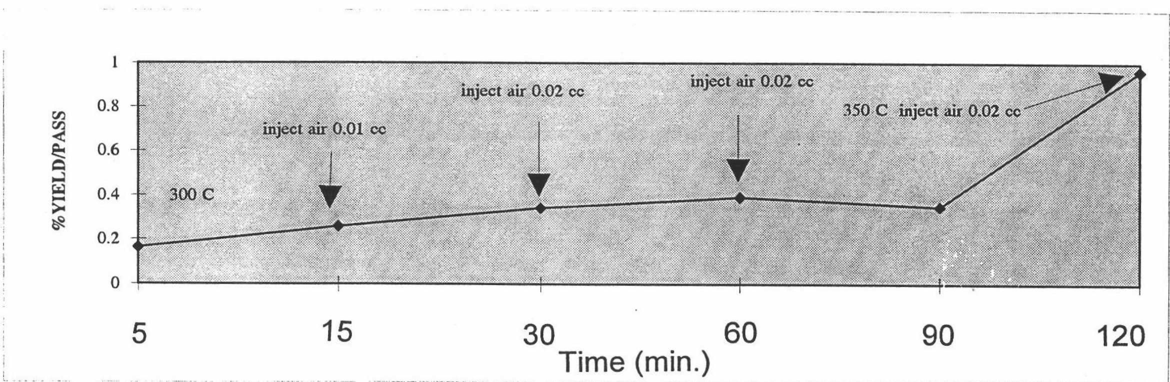

Figure 5.11.9.6 Effect of Air on %Yield/Pass of PR0.25

Table 5.11.9.2 Effect of Air on ND4 (Pressure 10 Bar)

		300C				350C
	5 min	15 min-10	30 min-20	60 min-20	90 min -0	15 min-20
%Selectivity	6.81	7.46	6.44	7.43	7.75	9.02
%Conversion	4.41	4.22	4.94	5.16	4.77	4.85
%Yield/pass	0.3	0.32	0.32	0.38	0.37	0.44

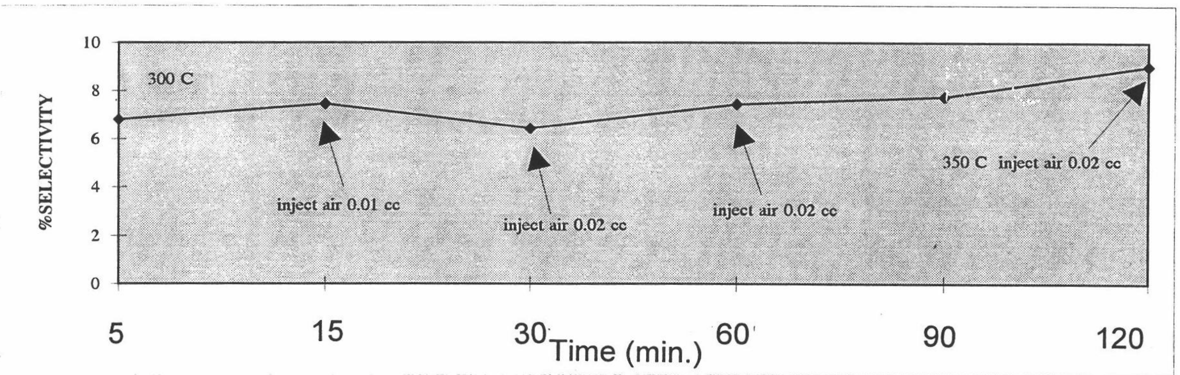

Figure 5.11.9.7 Effect of Air on %Selectivity of ND4

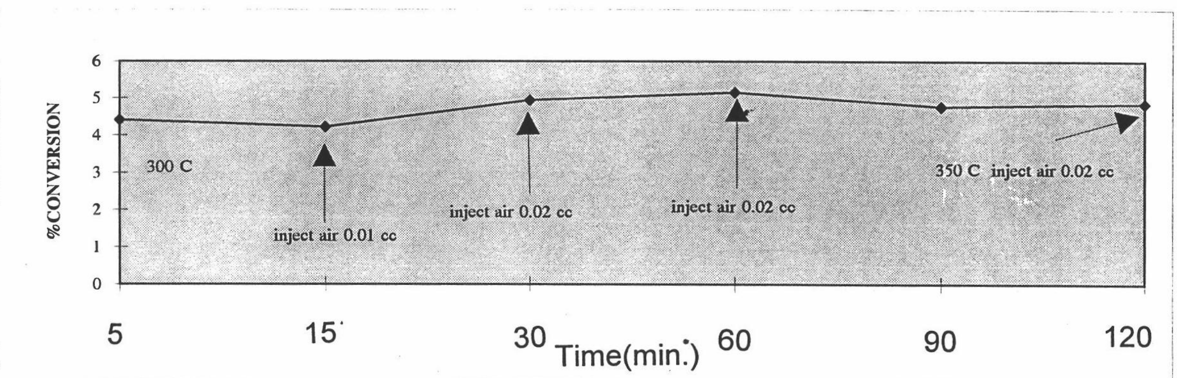

Figure 5.11.9.8 Effect of Air on %Conversion of ND4

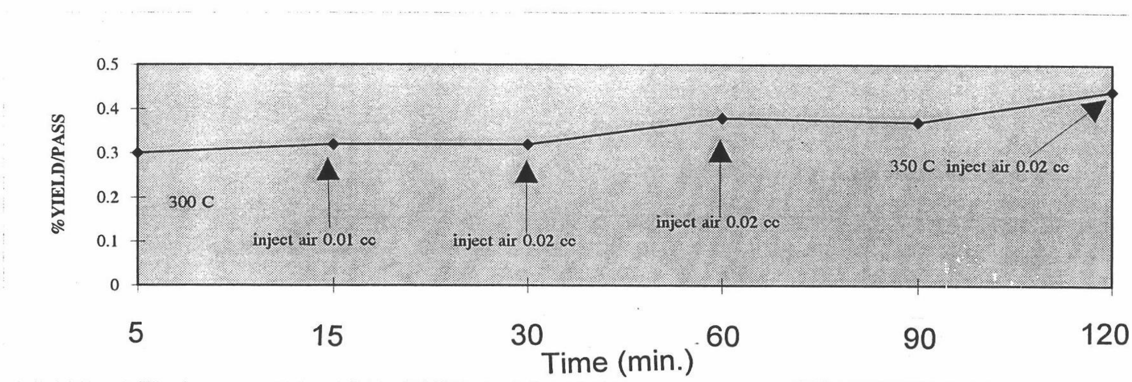

Figure 5.11.9.9 Effect of Air on %Yield/Pass of ND4