CHAPTER 6

EXPERIMENTS ON METHANOL SYNTHESIS

Experiments were carried out on methanol synthesis from one part of CO in the presence of two parts of H_2 at various temperatures, pressures. Two types of catalysts were used. One of them was prepared in the laboratory with atomic ratios of Cu,Zn and Cr = 31:38:10 The other catalyst was solicited from a Japanese company with Zn:Cr=1.8-2.2

For the prepared catalyst, the reaction pressure was varied from 20 to 40 atg; the reaction temperature, from 200-300°C; and the space velocity, from around 2000 - 16000 ml of synthesis gas/ml cat.hr. For the industrial catalyst, the reaction pressure was again varied from 20 to 40 atg; the reaction temperature, from 280 - 400°C; and the space velocity, from 2000 - 16000 ml synthesis gas/ml cat.hr.

Before carrying out the experiments, the catalyst of interest was packed in the reactor tube at a point where there is uniform heating and thus uniform axial temperature in the furnace. Three CA (chromel-alumel) thermocouples were inserted into a thermowell in the reactor tube to measure the reaction temperature at the top, the middle and the bottom of the catalyst bed (about 3 - 4 cm high).

6.1 Experimental Procedure of Methanol Synthesis (see fig. 5.1 and 5.2)

1. The GC (gas chromatography) (Shimadzu-Model 8AIT) with a MS-5A (molecular sieve 5A) and a PT (porapak T) column was started up first, as follows. (see fig. 6.1 and 6.2)
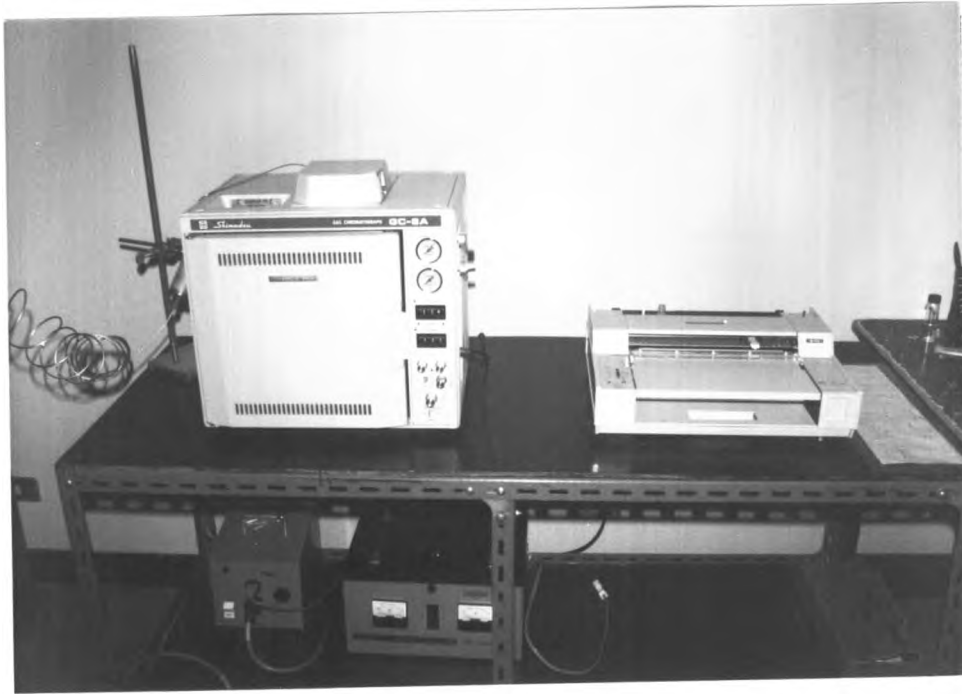
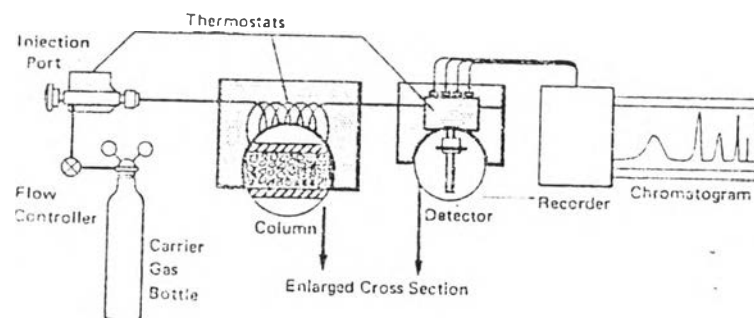Figure 6.1 Shimadzu TCD Gas Chromatography (Model 8 AIT)

Figure 6.2 Schematic Drawing of a Gas Chromatographic System

1.1 Open the stop valve of the helium carrier gas cylinder and set the secondary pressure of the regulator at 7 - 8 atg.

1.2 Adujst the carrier gas pressures at about 3.4 - 3.5 atg and 5 atg for the MS-5A and PT columns and set the gas flows around 10 ml/10 sec and 10 ml/19 sec, respectively.

1.3 Set the inject/detector (inj/det) temperature at $150^{\circ}C$, and the column temperture at $125^{\circ}C$.

1.4 Switch on the GC

1.5 Confirm that carrier gas comes out of vents. Set current at 60 mA.

1.6 Set the polarity, and attenuation to the propriate position for the analysis. (Generally polarity = + and atten. = 1 (for H_2, CH_4) and 4 (for CO) for MS-5A; polarity = - and atten = 1 for PT.)

1.7 Turn on the recorder and wait for the base line to stabilize.

2. Prepare the wet gas meter by pouring in clean water until the water level reaches the needle point. Next connect both the inlet and outlet rubber tubes to the meter, and check for leak.

3. Open the stop valves (SV - 1.) of the synthesis gas cylinder (containing $CO:H_2 = 1:2$) and set the outlet pressure of the pressure control valve (PI-2) at 5 atg for about 30 minutes, so that synthesis gas will purge all N_2 out of the system. Ensure that there is no N_2 gas left by sampling and analyzing the synthesis gas at SP-1.

4. Turn the pressure control valve (PVC) and NV-1 to adjust the pressure of synthesis gas at PI-3 as desired. It may be 20,30, and 40 atg.

5. Turn on NV-2, and adjust it along with NV-1 to obtain the desired gas flow rate (space velocity).

6. Put lumps of ice to the condenser unit (CU). Occasionally drain out water and add ice during the experiment.

7. Start up the heating furnace. Increase temperature gradually by adjusting the slidacs until the desired reaction temperature is reached and maintained.

8. At the maintained temperature, sample the reaction gas at SP-2 (0.5 ml) using the syringe and inject it into the MS-5A column (GC 8AIT) to analyse the concentrations of H_2, CH_4, and CO in the reaction gas.

9. Next sample another 0.5 ml or 1 ml of the reaction gas at SP-1 and inject it into the PT column of the same GC to analyse the concentrations of hydrocarbons (eg. C_2H_6, C_3H_8), DME (dimethyl ether) and alcohols (especially methanol). Since methanol was in the form of vapor, the syringe used for sampling should kept above $78^{o}C$, the boiling point of methanol, to prevent the condensation of methanol. The syringe was insulated and always kept in an oven set at $150^{o}C$.

10. After the analysis of the both samples has been completed, we are ready to proceed to a new reaction temperature, by returning to step 4. Otherwise, proceed to step 11 to shut down the experiment.

11. First switch off heating furnace and keep the synthesis gas flowing through the catalyst bed until its temperature drops lower than $50^{\circ}C$. Then stop the synthesis gas flow and wait until the pressure in the line drops to 5 atg. Next purge the synthesis gas with N_2 at 5-10 atg about 30 minutes. Meanwhile, shut down the GC step by step as follows.

11.1 Reset both the column and inj/det temperatures to $0^{\circ}C$ and open wide the GC oven.

11.2 Turn off the recorder, and the current of the detector.

11.3 Confirm that the inj/det and column temperatures have dropped below $100 - 150^{\circ}C$.

11.4 Switch off the main power of the GC.

11.5 Shut off the carrier gas.

6.2 Analysis of Experiment Data

Determination of the reaction gas composition was carried out via gas chromatography. The basis for gas chromatographic separation is the distribution of sample components between two phases. One of the phases is a stationary bed of large surface area and the other is a gas which percolates through the stationary bed in the column along with an inert gas (carrier gas). The stationary bed selectively retards the sample components according to their different distribution coefficients until they form separate bands in the carrier gas. These component bands leave the GC column with the gas stream and their amounts and retention times are detected by a thermal conductivity detector. The basic parts of a GC, as shown in fig. 6.2, are :

1. Cylinder of carrier gas

2. Flow controller and pressure regulator

3. Injection port (sample inlet)

4. Column

5. Detector (with necessary electronics)

6. Recorder

7. Thermostats for the injector, column and detector

Recorded GC data are usually in the form of a continuous curve with numerous peaks at corresponding retention times. The retention time data are useful for qualitative analysis to identify the components in the mixture. Quantitative analysis can be based either on peak heights or on peak areas, which are calibrated a priori against known concentrations of the components of interest. In this work, a relationship between the analytical peak area and the concentration (mole of the component in the gas mixture) was determined empirically using a set of standard gas mixtures. Fig. 6.3 shows a typical calibration curve thus obtained. It is important that the conditions of the GC must be identical during all analyses of the samples and standards. In this way experimental data from the GC may be interpreted for the composition of the gas mixture. Calibration curves for CO_2, CH_4, H_2, C_2H_6, C_3H_8, CO, DME, H_2O and CH_3OH (methanol) presented in Appendix A.

As an illustration, analysis of experimental data obtained at 40 atg, 265°C and 8000 hr^{-1} with our prepared catalyst would carried out in detail to show how to determine the reaction gas composition, the percent conversion per pass of CO to methanol, catalyst selectivity and space time yield. Fig. 6.4 and 6.5 show respectively actual gas chromatographical data obtained from MS-5A and PT columns for reaction
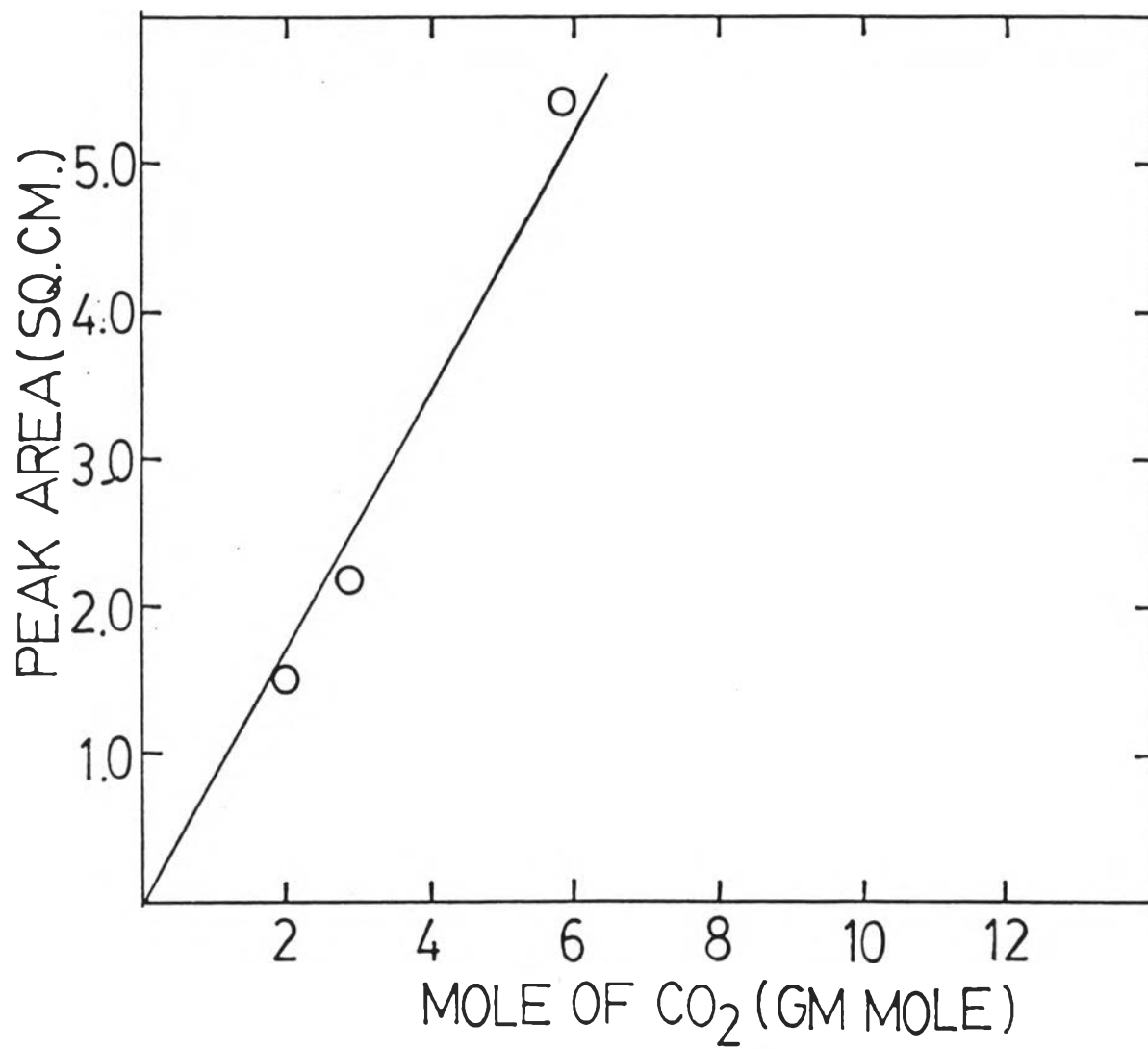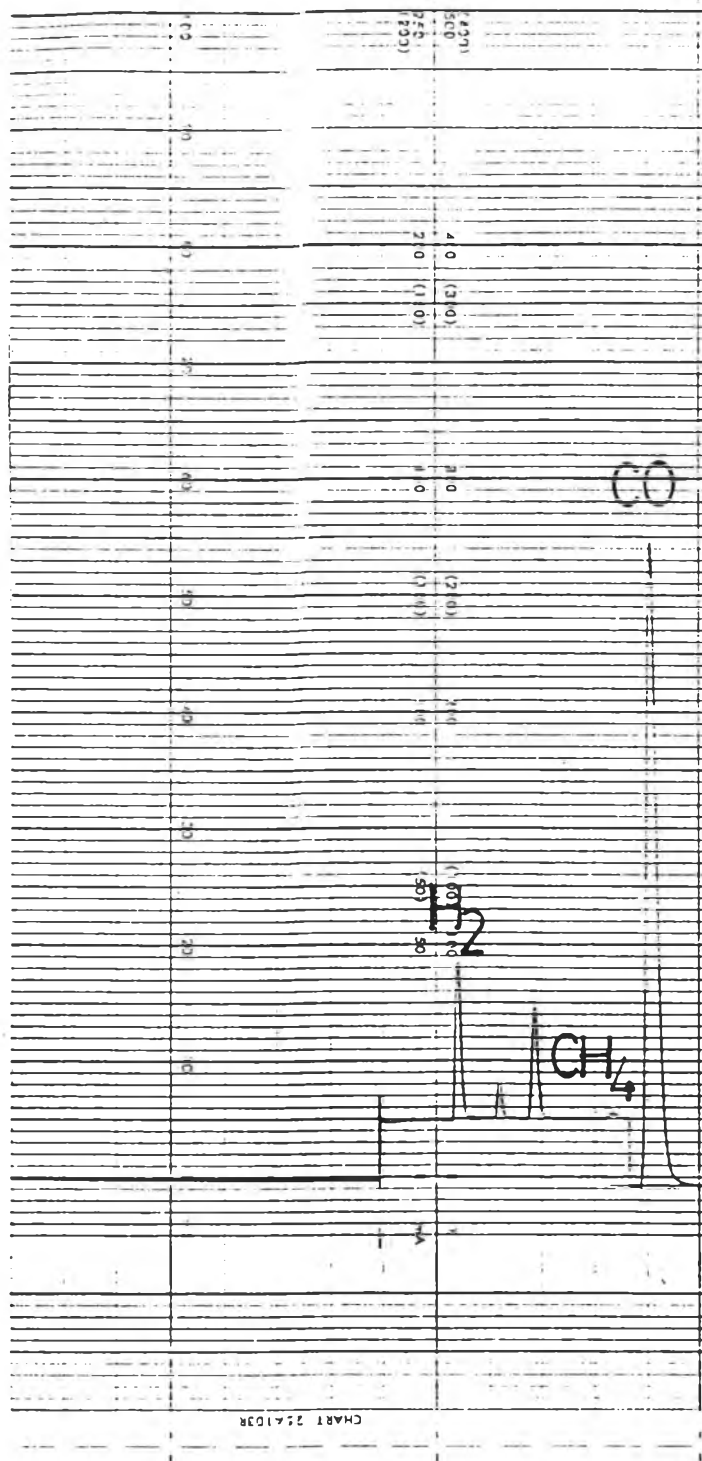
Figure 6.3 Calibration Curve of CO_2

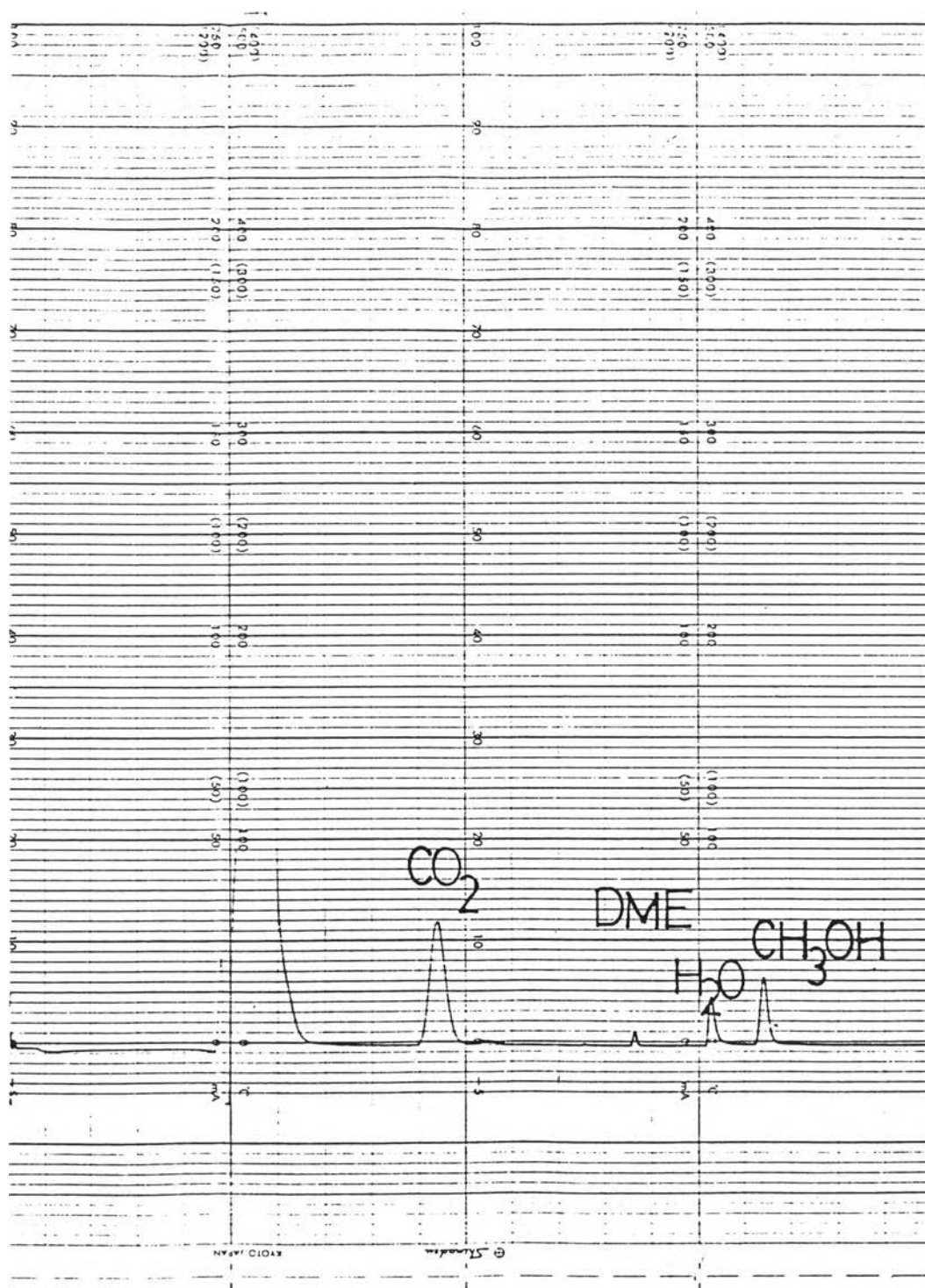Figure 6.4   Gas Chromatographic Data from MS-5A

Figure 6.5 Gas Chromatographic Data from Porapak T

conditions of 40 atg, 265°C and 8000 hr^{-1}. Table 6.1 summarized the results interpreted from peak areas in fig. 6.4 and 6.5 with the aid of calibration curves (Appendix A). Note that the amount of gas sample at SP-1 was 0.5 cc or 1 cc, while only 0.5 cc was taken at SP-2. Furthermore, the sample temperatures were different, and the gas sample at SP-2 contained no condesible vapors (i.e. no methanol or water vapors). So the amount of sample gas at SP-2 had to be adjusted accordingly to make it comparable to the gas sample at SP-1. The method of adjustment is as follows.

Let x = total moles of condensible vapors/moles of dry gas mixtures.

a = total moles of CO, H_2, and CH_4 detected by MS-5A from a 0.5 - cc sample at SP-2 (see fig. 5.1), (The gas mixture at SP-2 is at 32°C)

b = total moles of C_2H_6, C_3H_8, CO_2, CH_3OCH_3, CH_3OH and H_2O detected by PT from a 0.5 - cc or 1 - cc sample at SP-1 with syringe temperature being 100°C.

c = total mole fractions of methanol and H_2O in a sample at SP-1.

d = temperature conversion factor; for example

$$d = \frac{273 + 100}{273 + 32} = 1.223 \quad \text{for conversion from}$$

32°C to 100°C.

From mass balance,

Table 6.1 Example of Experimental Data

Cat : prepared catalyst   CO : H_2 feed = 2 : 1   Date 8 14 August 27 1984

P : 40 atg.   S.V. : 8000 hr^{-1} T : 265°C

	Raw Data					Total Wet gas	g-atom of feed			% CONV = 11.3	Reaction
	SP_2 Dry gas (32°C)		SP_1 Wet. gas (~100°C)							%Selectivity	
	Area cm^2	0.5 c.c mole	Area cm^2	0.5 c.c mole	1.0 c.c mole	0.5 c.c. mole	C	H	O		
CO	2.384	5.25×10^{-6}	–	–	–	4.16025×10^{-6}	4.16025×10^{-6}	–	4.16025×10^{-6}	–	
H_2	.29	107×10^{-7}	–	–	–	8.47898×10^{-6}	–	1.69579×10^{-5}	–	–	
CH_4	0.015	0.1×10^{-7}				7.92428×10^{-9}	7.92428×10^{-9}	3.16971×10^{-8}		1.50	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$
C_2H_6			0.04	0.175×15^{8}	0.35×10^{-8}	0.175×10^{-8}	3.5×10^{-9}	1.05×10^{-8}		0.66	$2CO+5H_2 \rightleftharpoons C_2H_6+2H_2O$
C_3H_8											$3CO+7H_2 \rightleftharpoons C_3H_8+3H_2O$
CO_2			0.975	0.55×10^{-7}	1.1×10^{-7}	0.55×10^{-7}	0.55×10^{-7}		1.1×10^{-7}	10.38	$CO+H_2O \rightleftharpoons CO_2+H_2$
CH_3OCH_3			0.03	0.15×10^{-7}	0.3×10^{-7}	0.15×10^{-7}	0.3×10^{-7}	0.90×10^{-7}	0.15×10^{-7}	5.66	$2CO+4H_2 \rightleftharpoons CH_3OCH_3+H_2$
CH_3OH			0.284	2.45×10^{-7}	4.9×10^{-7}	2.45×10^{-7}	2.45×10^{-7}	9.8×10^{-7}	2.45×10^{-7}	46.23	$CO+2H_2 \rightleftharpoons CH_3CH$
H_2O			0.15	1.6×10^{-7}	3.2×10^{-7}	1.6×10^{-7}		3.2×10^{-7}	1.6×10^{-7}		
C_mH_n							(1.8858×10^{-7})	(3.7716×10^{-7})		35.58	$mCO+(m+\frac{n}{2})H_2 \rightleftharpoons C_mH_n+mH_2O$
Other											
Total		1.596×10^{-5}		4.7675×10^{-7}		1.31239×10^{-5}	4.50167×10^{-6}	1.83901×10^{-5}	4.69025×10^{-6}		C:O = 0.95979
Total adjust							4.69025×10^{-6}	(1.8767×10^{-5})		100.01	H:O = 3.9209332

(a) d = 1.223   (b) $c = 4.05 \times 10^{-7}$

$\alpha = 2c - \frac{a}{d} - b = -1.2716 \times 10^{-5}$

$\beta = C - b = -7.175 \times 10^{-8}$

$\gamma = \alpha^2 - 4\beta c = 1.27211 \times 10^{-5}$

$x = \frac{-\alpha - \delta}{2\beta} = 0.0318423$

wet : $= \text{day} \times \frac{1}{d} \times \frac{1}{1+x}$

wet $= \text{day} \times 0.7924287$

C_mH_n = m = 1, n = 2

H:C = 4.0851816

H:C = 4.0013347

$$\frac{bx}{1+x} + \frac{ax}{d(1+x)(1+x)} = c$$

This can be rewritten as

$$(c-b)x^2 + (2c-\frac{a}{d} - b)x+c = 0$$

If we let $\beta = c-b$

$$\alpha = (2c-\frac{a}{d} -b)$$

$$\gamma = \sqrt{\gamma^2 - 4\beta c}$$

then $x = \dfrac{-\gamma-\beta}{2\beta}$

A dry gas mixture could be converted to a " wet " gas mixture at the same conditions by multiplying with $\frac{1}{d} \cdot \frac{1}{1+x}$. In this manner, the moles of all gasous and vapor components in a dry gas mixture can be transformed to those of a wet gas mixture. Gram-atom (gm-atom) of carbon(C), hydrogen(H), and oxygen(O) in the feed can readily be calculated from stoichiometry, since the atomic ratios of both H:O and H:C in the feed are both 4:1. Other missing hydrocarbons that the MS-5A and PT columns fail to detect would be accounted for by adjusting the atomic ratios of both H:O and H:C in the product to be 4:1. Conversion per pass of CO and % product selectivity are calculated from

$$\text{conversion per pass of CO} = \frac{\text{moles of CO that has been converted}}{\text{total moles of CO in feed}}$$

$$\text{selectivity of i-component} = \frac{\text{moles of CO that were converted to i-component}}{\text{moles of CO that has been coverted}}$$

As an illustration, we find from table 6.1 that

$$a = 5.25 \times 10^{-6} + 107 \times 10^{-6} + 0.1 \times 10^{-7} = 1.596 \times 10^{-6}$$

$$b = 0.175 \times 10^{-8} + 0.55 \times 10^{-7} + 2.45 \times 10^{-7} + 1.6 \times 10^{-7}$$

$$= 4.7675 \times 10^{-7}$$

$$c = 2.45 \times 10^{-7} + 1.6 \times 10^{-7} = 4.05 \times 10^{-7}$$

$$d = 1.223$$

$$\alpha = 2 \times 4.05 \times 10^{-7} - \frac{1.596 \times 10^{-6}}{1.223} - 4.7675 \times 10^{-7}$$

$$= -1.2716 \times 10^{-5}$$

$$\beta = 4.05 \times 10^{-7} - 4.7675 \times 10^{-7} = -7.175 \times 10^{-8}$$

$$\gamma = \sqrt{(-1.2716 \times 10^{-5})^2 - 4(-7.175 \times 10^{-8})(4.05 \times 10^{-7})}$$

$$= 1.27211 \times 10^{-5}$$

Therefore, $$x = \frac{-(-1.2716 \times 10^{-5}) - 1.27211 \times 10^{-5}}{2 \times (-7.175 \times 10^{-8})}$$

$$= 0.0318423$$

and $$\frac{1}{d} \cdot \frac{1}{1+x} = \frac{1}{1.223} \cdot \frac{1}{1 + 0.0318423} = 0.792487$$

Hence 1 mole of dry gas mixture is equivalent to 0.79243 of the wet gas mixture. The mole fractions of CO, H_2, CH_4 at $32^{\circ}C$ in 0.5 cc of the dry mixture may be converted to those of the wet mixture (0.5 cc) at $100^{\circ}C$ by multiplying with 0.79243.

Thus, for the wet mixture (0.5 cc at 100°C)

mole of CO $= 5.25 \times 10^{-7} \times 0.79243 = 4.16025 \times 10^{-6}$ mole

mole of $H_2 = 107 \times 10^{-7} \times 0.79243 = 8.47898 \times 10^{-6}$ mole

mole of $CH_4 = 0.1 \times 10^{-7} \times 0.79243 = 7.924287 \times 10^{-9}$ mole

Then the complete analysis of the detectable components in the product gas mixture (0.5 cc of wet mixture at 100°C) are as follows :

$$CO = 4.16025 \times 10^{-7} \text{ mole}$$

$$H_2 = 8.47898 \times 10^{-6} \text{ mole}$$

$$CH_4 = 7.92428 \times 10^{-9} \text{ mole}$$

$$C_2H_6 = 0.175 \times 10^{-8} \text{ mole}$$

$$CO_2 = 0.55 \times 10^{-7} \text{ mole}$$

$$DME(CH_3OCH_3) = 0.15 \times 10^{-7} \text{ mole}$$

$$CH_3OH = 2.45 \times 10^{-7} \text{ mole .}$$

$$H_2O = 1.6 \times 10^{-7} \text{ mole}$$

Next we make a C balance for the wet product gas mixture, as follows :

gm-atom of C in CO $=$ mole of CO $= 4.16025 \times 10^{-7}$

" " " " CH_4 $=$ mole of $CH_4 = 7.9243 \times 10^{-9}$

" " " " C_2H_6 $= 2 \times$ mole of $C_2H_6 = 2 \times 0.175 \times 10^{-8} = 3.5 \times 10^{-9}$

" " " " CO_2 $=$ mole of $CO_2 = 0.55 \times 10^{-7}$

" " " " DME $= 2 \times$ mole or DME $= 2 \times 0.15 \times 10^{-7} = 0.3 \times 10^{-7}$

" " " " CH_3OH $=$ mole of $CH_3OH = 2.45 \times 10^{-7}$
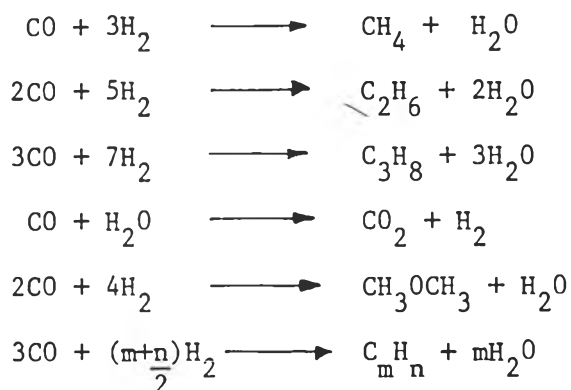
Total gm-atom of C detected in the product gas mixture $= 4.16025 \times 10^{-7}$

$+ 7.9243 \times 10^{-9} + 3.5 \times 10^{-9} + 0.55 \times 10^{-7} + 0.3 \times 10^{-7} + 2.45 \times 10^{-7}$

$= 4.50167 \times 10^{-6}$

Similarly, total gm-atom of H detected in the product gas mixture $= 1.83901 \times 10^{-5}$ and total gm-atom of O detected in the product gas mixture 4.69025×10^{-6}. If we were able to detect all existing components in the product gas mixture, then the atomic ratios of H:C and H:O in the product gas mixture would be both 4:1. By assuming that the missing hydrocarbons can be represented on the average by $C_m H_n$ we find from calculating back that, if m:n = 1:2 and if the gm-atoms of C and H in $C_m H_n$ are 1.8858×10^{-7} mole and 3.7716×10^{-7} mole, respectively, the desired atomic ratios of H:C and H:O equalling 4:1 will be obtained.

In summary, the reactions that contributed to the above product gas mixture are as follows:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

$$2CO + 5H_2 \longrightarrow C_2H_6 + 2H_2O$$

$$3CO + 7H_2 \longrightarrow C_3H_8 + 3H_2O$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$2CO + 4H_2 \longrightarrow CH_3OCH_3 + H_2O$$

$$3CO + \frac{(m+n)}{2}H_2 \longrightarrow C_m H_n + mH_2O$$

The total mole of CO in the feed that has been converted
$= 4.69025 \times 10^{-6} - 4.16025 \times 10^{-6} = 5.3 \times 10^{-7}$ mole

$$\text{conversion per pass of CO} = \frac{5.3 \times 10^{-7} \times 100}{4.69025 \times 10^{-6}} = 11.3\%$$

$$\text{selectivity of CH}_4 = \frac{7.9243 \times 10^{-9} \times 100}{5.3 \times 10^{-7}} = 1.5\%$$

$$"\quad"\quad"\quad" \ C_2H_6 = \frac{3.5 \times 10^{-9}}{5.3 \times 10^{-7}} = 0.66\%$$

$$\text{selectivity of } CO_2 \quad = \quad \frac{0.55 \times 10^{-7}}{5.3 \times 10^{-7}} \quad = \quad 10.38\%$$

$$\text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad DME \quad = \quad \frac{0.3 \times 10^{-7}}{5.3 \times 10^{-7}} \quad = \quad 5.66\%$$

$$\text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad CH_3OH \quad = \quad \frac{2.45 \times 10^{-7}}{5.3 \times 10^{-7}} \quad = \quad 46.23\%$$

$$\text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad H.C. \quad = \quad \frac{1.8858 \times 10^{-7}}{5.3 \times 10^{-7}} \quad = \quad 35.58\%$$

Furthermore, the space time yield (STY) (in terms of moles of product i/(liter catalyst)$(hr)^{-1}$) is given by

$$\text{STY of product } i \quad = \quad \frac{\text{space velocity x \% conversion x \% selectivity}}{22.4 \times 3 \times 100 \times 100}$$

Thus STY of CH_3OH $\quad = \quad \dfrac{8000 \times 11.3 \times 46.23}{22.4 \times 3 \times 100 \times 100} \quad = \quad 6.219$

STY of DME $\quad = \quad \dfrac{8000 \times 11.3 \times 5.66}{22.4 \times 3 \times 100 \times 2 \times 100} \quad = \quad 0.3807$

The above data analysis results are for the case of space velocity = 8000 hr^{-1} and reaction conditions = 40 atg., $265^{o}C$.