



CHAPTER 5

EXPERIMENTAL ON ISOPROPANOL SYNTHESIS

Experiments were carried out on isopropanol synthesis from one part of C_3H_8 in the presence of one to twelve parts of H_2O at various temperatures, pressures and space velocities. Two types of catalysts were used. One of them was Na-Y zeolite, with mole ratio of $Si_2O/Al_2O_3 = 5.6$ which was ion exchanged with NH_4NO_3 to H-Y zeolite. The other catalyst was offretite/erionite, ion exchanged with NH_4NO_3 to H form, with mole ratio of $SiO_2/Al_2O_3 = 7.7$, $Na_2O/Al_2O_3 = .25$ and $K_2O/Al_2O_3 = 0.78$. Both catalysts were ion exchanged and calcined by us at Chemical Engineering Dept. Chulalongkorn University.

In the case of Na-Y the reaction pressure was varied from 45 to 105 psig, the reaction temperature from 200 - 280 °C, and the space velocity from around 2000 - 8000 ml of total feed gas/ml.cat.hr. In the case of offretite/erionite, the reaction pressure was likewise varied from 45 to 105 psig, the reaction temperature from 150 - 250 °C, and the space velocity, from 2000 - 8000 ml.total feed gas/ml cat.hr.

5.1 Experimental Procedure of Isopropanol Synthesis

1. The GC (gas chromatography) (Shimadzu-Model 8AIT) with PQ (Porapak Q) column and the GC (Shimadzu - Model 8AIF) with a PQ column were started up first, as follows. See (Fig. 5.1).

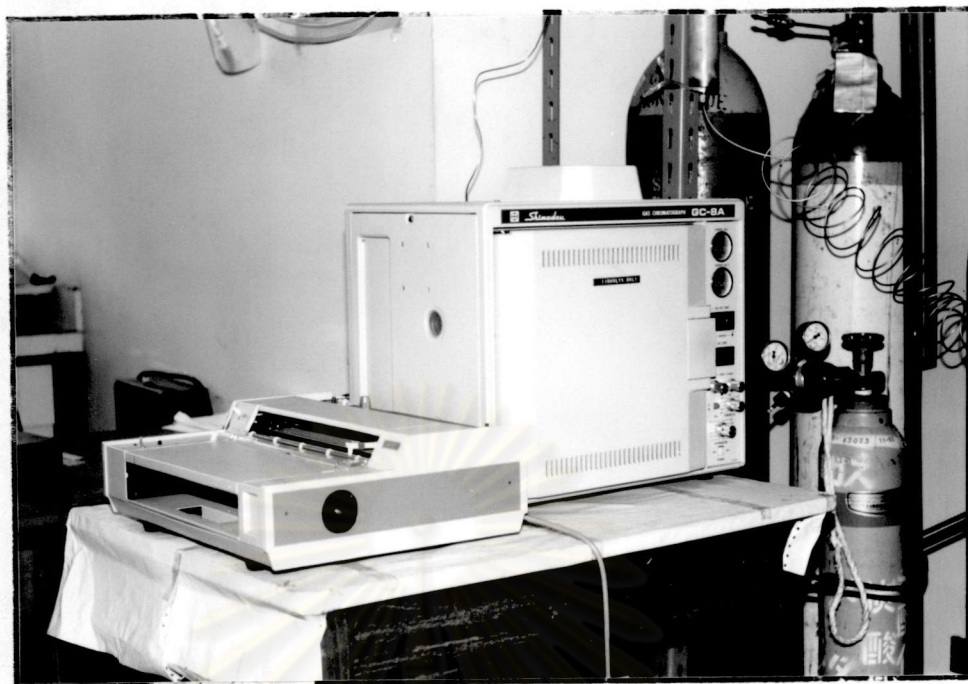


Fig. 5.1 Shimadzu TCD Gas Chromatography (Model 8AIT)

For example, in the case of the GC-8AIT

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

1.2 Adjust the carrier gas pressures to approximately 3.5 atg for the PQ column and set the gas flow around 10 ml/25 sec.

1.3 Set the injector/detector (Inj/Det) temperature at 150°C and the column temperature at 125°C

1.4 Switch on the GC.

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

1.6 Set the polarity, and attenuation to the appropriate position for the analysis. (Generally polarity = + and attenuation = 32 (for C_3H_8) and 256 (for H_2O) for the porapak Q column.

1.7 Turn on the recorder for the GC-8AIT and wait for the base line to stabilize.



Fig. 5.2 Shimadzu FID Gas Chromatography (Model 8A1F)

1.8 Open the main valve of the N_2 carrier gas cylinder and set the secondary pressure of its regulator at 7-8 atg.

1.9 Adjust the carrier gas pressure to about 2.5 atg for the PQ column

1.10 Set the Inj/Det temperature at $200^\circ C$ and set the column temperature at $50^\circ C$ for preheating.

1.11 Set temperature read out selection at column position.

1.12 Switch on the GC. Indicator lights of "Inj" and "Col" should go on the temperature reaches $50^\circ C$.

1.13 Change temperature readout switch to "Inj."

1.14 Feed air and H_2 to the FID and set the pressure at $0.1-0.2 \text{ kg/cm}^2$ and H_2 pressure at $0.9-1 \text{ kg/cm}^2$.

1.15 Ignite the FID and confirm the ignition succeeds with a mirror or shiny object.

1.16 Adjust flow rate of H_2 to 0.4-0.7 kg/cm². Visible condensation of water vapor on the surface indicator indicates proper ignition.

1.17 Turn on the recorder for GC-8AIF.

1.18 Check that the Inj/Det temperature has risen to the desired value. When the temperature is reached, the Inj DEMAND light will flicker.

1.19 Set the Col temperature at 180°C. Check if Col indicator light is on.

1.20 Confirm that the column temperature has stabilized. Check if the Col indicator light flickers regularly.

1.21 Set the polarity, range, and attenuation to the appropriate positions for the analysis (Generally polarity = +, range = 10^{-2} , Att = 2 (for C_2H_4 , C_2H_5OH , $i-C_3H_7OH$, $n-C_3H_7OH$, $t-C_4H_9OH$, $2-C_4H_9OH$))

1.22 Check if the base line of the recorder has stabilized.

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

3. Open the main valve of N_2 cylinder no 2. and set the outlet pressure of the pressure control valve to 75-135 psig. Open SV4 to build up pressure in the H_2O bottle. Open SV3 slowly, and adjust the water flow rate by turning NV2, micrometering valve no. 1 and micrometering valve no. 2 slightly.

4. After the desired water flow rate has been reached, turn on the water pre-heater (130°C).

5. After the desired temperatures have been reached and maintained, measure to confirm the water (steam) flow rate.

6. Open the main valve of the propylene cylinder and set the desired outlet pressure by the pressure control valve. Adjust the flow rate by opening NV1 slightly and measure the total flow of feed with the wet test meter. Simultaneously, make fine adjustment of the furnace temperature.

7. Check the $H_2O : C_3H_8$ feed mole ratio with the aid of the GC-8AIF and GC-8AIT. Ensure that there is no N_2 gas left and put lumps of ice to the condensor unit. Occasionally drain out the water and ice during the experiment.

8. When everything is all right, open micrometering valve no.3, so that a sample of the reaction products (liquid components) is now collected in the condensor. Record the time, and also measure the flow of the dried gas.

9. Take the liquid sample through SP2 and also take a gas sample through SP1.

10. At the maintained temperature, sample the reaction gas at SP1 (0.5 ml) using one preheated insulated syringe and inject it into the PQ column (GC-8AIT) and the other inject it into the PQ column (GC-8AIF) to analyse the concentration of hydrocarbons water and alcohols, for the reaction liquid sample at the sampling pot (5 microlitre) using the micro-syringe and inject it into the PQ column (GC-8AIF) to analyse the concentration of C_2H_5OH and i-propanol.

11. Record the temperature, amount of reaction liquid, total gas reaction, etc., regularly.

12. When all the analysis is finished, vary the furnace temperature to see the effect of reaction temperature by returning to step 5. Otherwise, proceed to step 13 to shut down the experiment.

13. After the analysis of both samples has been completed, switch off the furnace and the pre-heater. Open wide the furnace and

blow at it with an electric fan. Keep the propylene gas and water flowing through the catalyst bed until the bed temperature drops lower than 50°C. Then stop propylene gas and water flow. Next purge out the propylene and water with nitrogen at 45 psig about 30 minutes. Meanwhile, shut down the GC step by step, as follows.

14. For the GC-8AIT :

14.1 Reset the column and Inj/Det temperature to 0°C and open wide the GC oven.

14.2 Turn off the recorder, and the current to the detector.

14.3 confirm that the Inj/Det and column temperatures have dropped below 100-150°C

14.4 Switch off the main power of the GC.

14.5 Shut off the carrier gas.

14.6 Switch off the stabilizer.

For GC-8AIF :

14.7 Reset the column temperature to 20°C, push RESET, and open wide the column oven door.

14.8 Turn off the detection system :

- turn off the recorder

- stop the H₂ supply

14.9 Reset the Inj/Det temperature to 0°C.

14.10 Confirm that the Inj/Det, Col temperatures have lowered to at least 100-150°C.

14.11 Turn off the main power switch of the GC.

14.12 Shut off the air stream.

14.13 Close the main valves of the carrier gas and hydrogen gas cylinders.

14.14 Switch off the stabilizer.

5.2 Analysis of Experimental Data

Analytical determination of the reaction gas composition was carried out using gas chromatography. The basis for gas chromatographic separation is the distribution of sample components between two phases. One of the phase 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 an appropriate detector fig. 5.3, such as a thermal conductivity detector. The basic parts of a GC, as shown in fig 5.4, 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

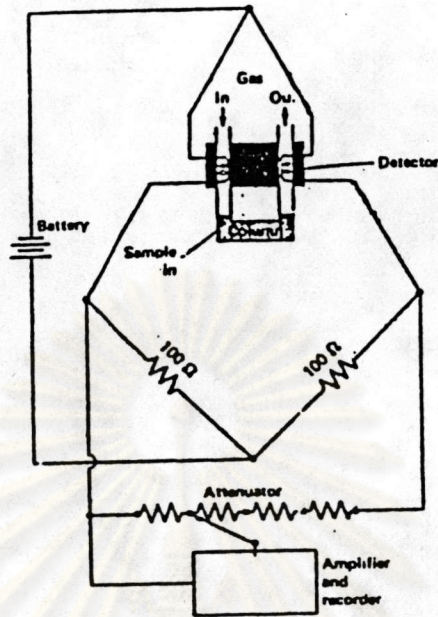


Figure 5.3 Schematic Diagram of a Thermal Conductivity Detector.

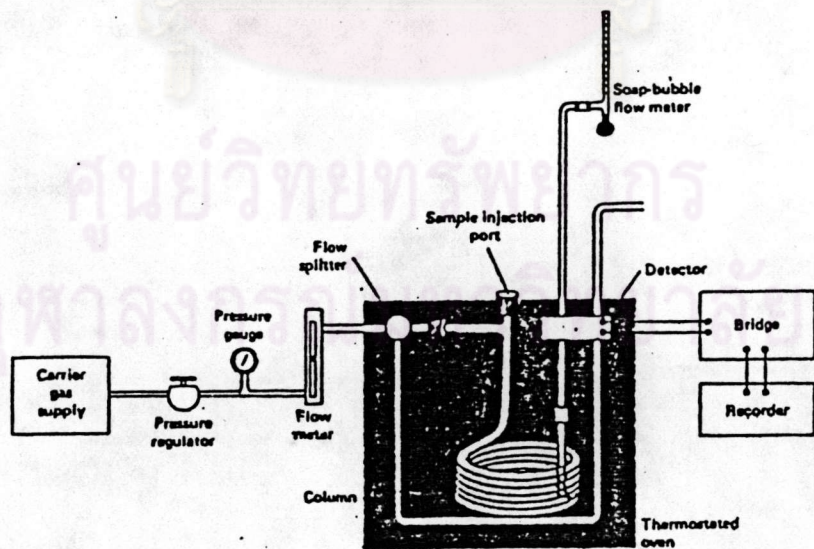


Figure 5.4 Schematic Diagram of a Gas Chromatography.

work, a relationship between the analytical peak area and the concentration (moles of the component in the gas or liquid mixture) was determined empirically using a set of standard gas mixtures. Fig. 5.5 show a typical calibration curve thus obtained. It is important that the conditions of the GC must be identical during the analyses of all the samples and standards. In this way experimental data from the GC (8AIT) may be interpreted for the composition of the gas mixture as well as liquid mixture. Calibration curves for C_3H_8 , H_2O are presented in Appendix A.

The flame ionization detector makes use of the fact that most organic compounds, when pyrolyzed at the temperature of a hydrogen/air flame, produce ionic intermediates that provide a mechanism by which electricity can be carried through the flame. By employing an apparatus such as that shown in Figure. 5.6, these ions can be collected and the resulting ion current measured. The electrical resistance of the flame is very high (around $10^{12} \Omega$) and the resulting currents are therefore minuscule. Thus an electrometer must be employed for their measurement. (12)

The ionization of carbon compounds in a flame is a poorly understood process, although it is known that the number of ions produced is roughly proportional to the number of reduced carbon atom in the flame, Functional groups such as carbonyls, alcohols, and amines produce fewer ions or none at all.

The hydrogen flame detector is currently one of the most popular and most sensitive detectors. It is more complicated and more expensive than the thermal conductivity detector, but has the advantage of higher sensitivity. In addition, it has a wide range of linear response. It is, of course, destructive of the sample. Experimental data from the GC (8AIF) are interpreted for the

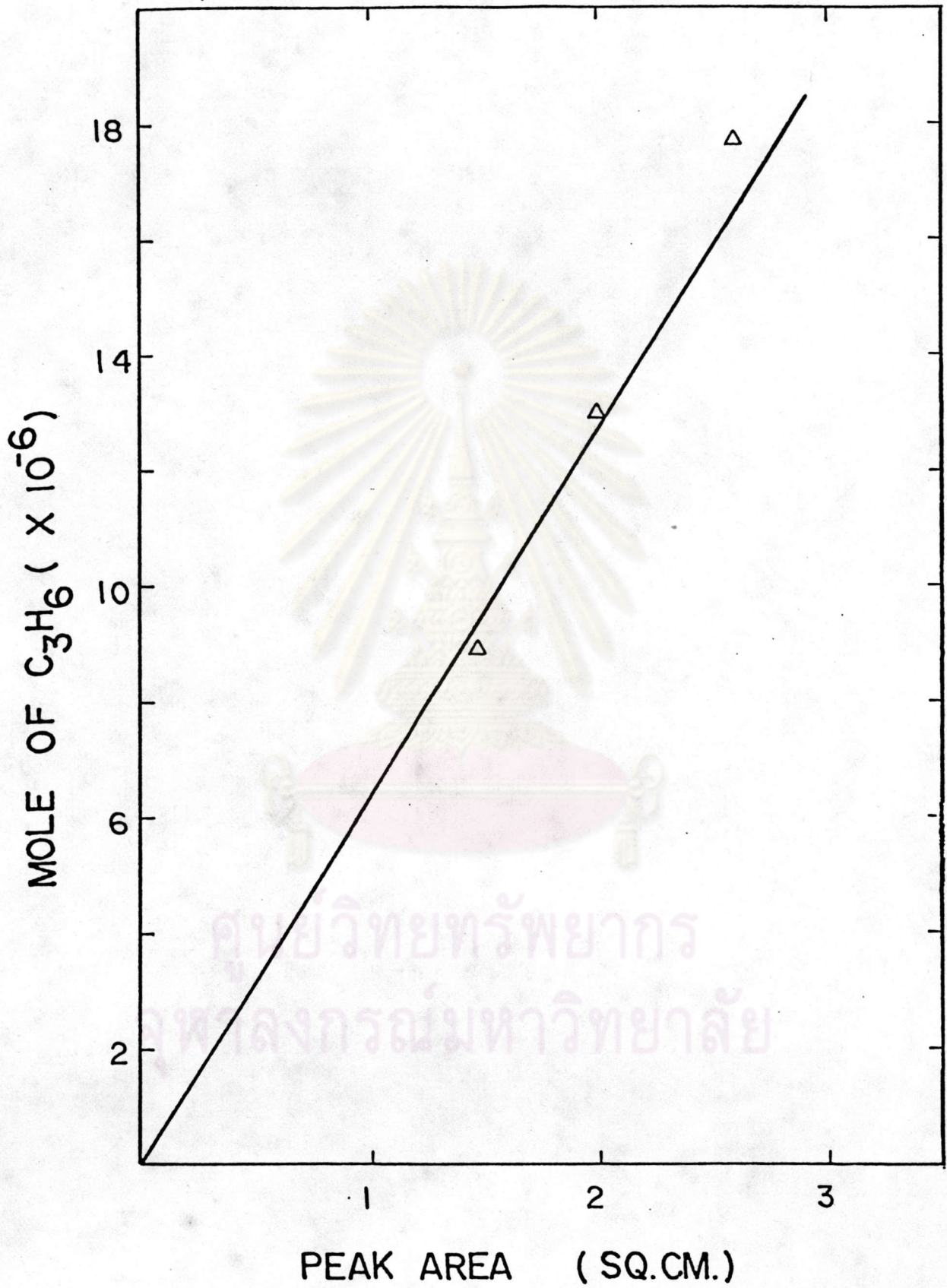


Figure 5.5 Calibration Curve for Propylene

composition of the gas as well as liquid mixture. Calibration curves for C_2H_4 , C_2H_5OH , $i-C_3H_7OH$, $n-C_3H_7OH$, $1-C_4H_8$, $i-C_4H_8$, $ter-C_4H_9OH$, $2-C_4H_9OH$, $n-C_4H_9OH$ are presented in Appendix A.

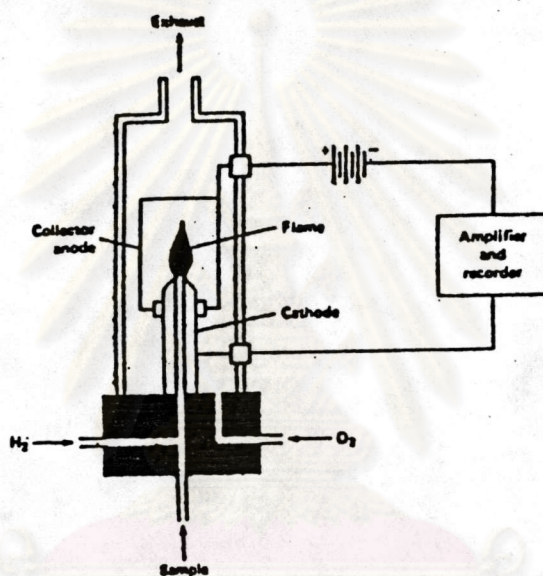


Figure 5.6 Hydrogen Flame-ionization Detector.

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As an illustration, analysis of the set of experimental data obtained at 45 psig, 250 °C and S.V. 5000 hr⁻¹ with catalyst no 1 is carried out in details here to show how the reaction product composition, the percent conversion per pass of C₃H₈ to isopropanol, catalyst selectivity and space time yield are determined. Figs 5.7 and 5.8 show the gas chromatographical data obtained using the PQ (GC 8AIT) and PQ (GC 8AIF) columns, respectively, at 45 psig, 250 °C and S.V. 5000 hr⁻¹. Table 5.1 summarizes the results interpreted from the peak areas in Figs. 5.7 and 5.8 with the aid of the calibration curves (see Appendix A.)

Gram-atom (gm-atom) of carbon (C), hydrogen (H), and oxygen (O) in the feed can readily be calculated from stoichiometry, since the feed atomic ratios are C:O = 3:4-10 and H:O = 3:14-26. Conversion per pass of C₃H₈ and product selectivity (%) are defined as follows:

$$\text{Conversion per pass of C}_3\text{H}_8 = \frac{\text{moles of C}_3\text{H}_8 \text{ that has been converted}}{\text{total moles of C}_3\text{H}_8 \text{ in feed}}$$

selectivity for component i

$$= \frac{\text{moles of C}_3\text{H}_8 \text{ that were converted to compound.}}{\text{total moles of C}_3\text{H}_8 \text{ that has been converted}}$$

Analytical results for total liquid mixture (at 32 °C) :

mole of H ₂ O	=	.023	mole
mole of C ₂ H ₅ OH	=	2.59 x 10 ⁻⁵	mole
mole of i-C ₃ H ₇ OH	=	9.17 x 10 ⁻⁴	mole
mole of n-C ₃ H ₇ OH	=	5.96 x 10 ⁻⁶	mole
mole of t-C ₄ H ₉ OH	=	5.17 x 10 ⁻⁵	mole
mole of 2-C ₄ H ₉ OH	=	2.65 x 10 ⁻⁵	mole
mole of n-C ₄ H ₉ OH	=	1.58 x 10 ⁻⁸	mole

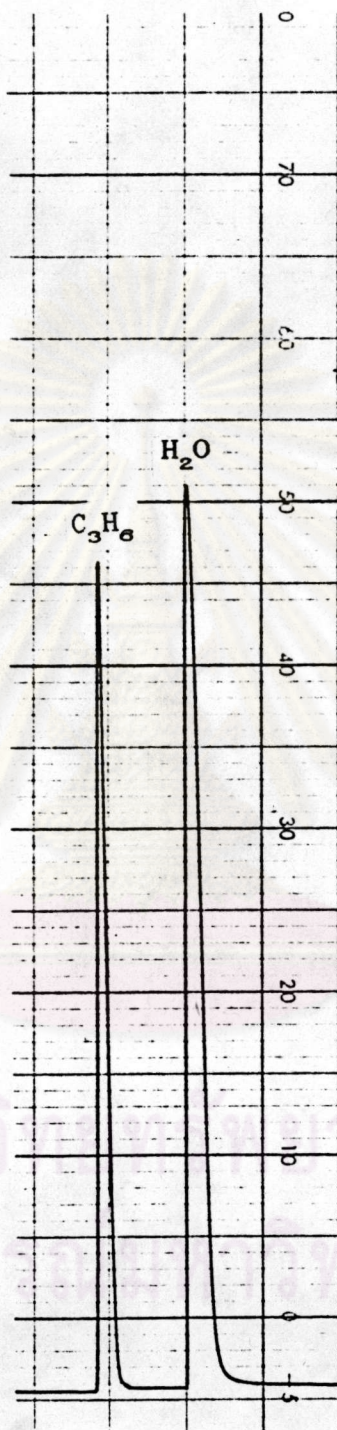


Figure 5.7 Gas Chromatographical Data Using the PQ (GC-8AIT) Column.

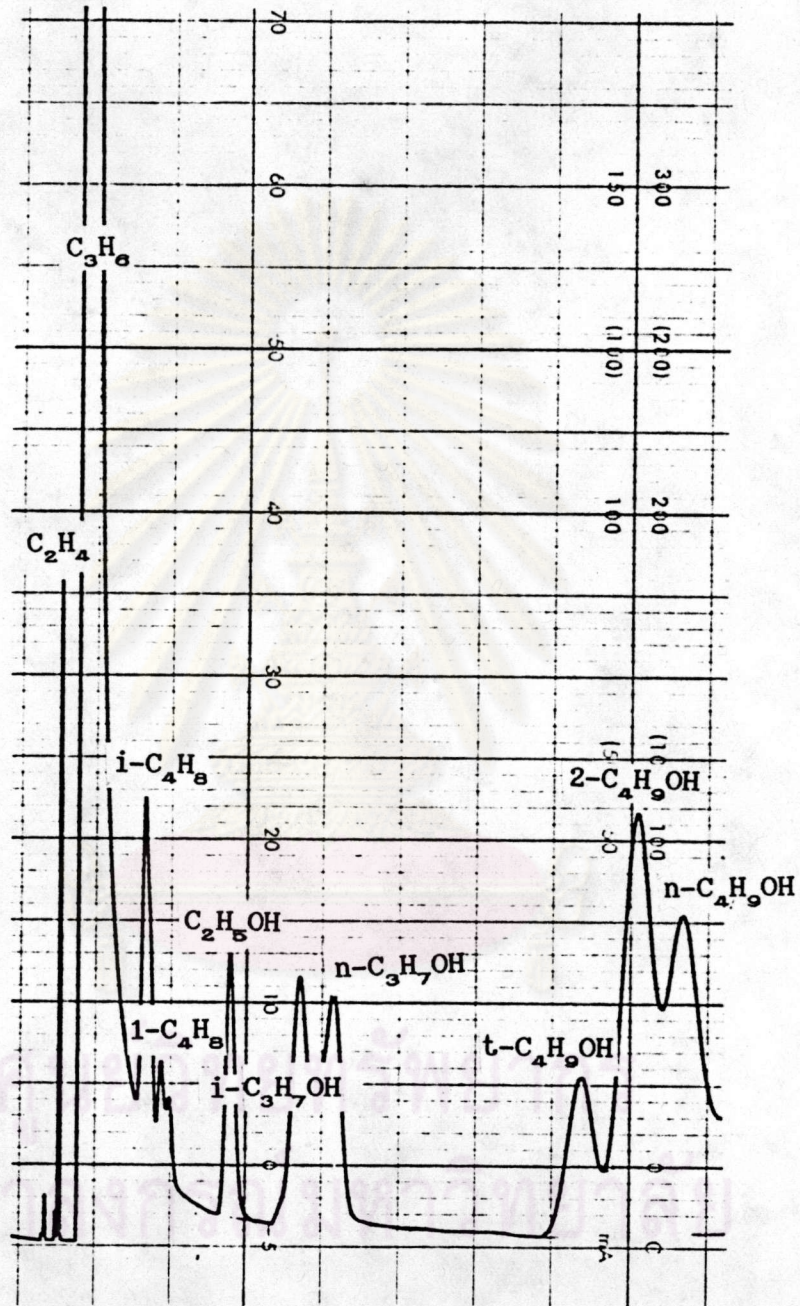


Figure 5.8 Gas Chromatographical Data Using the PQ (GC-8AIF) Column.

Analytical results for total gas mixture (at 32° C) :

mole of C_2H_4	=	3.24×10^{-8}	mole
mole of C_3H_6	=	.023	mole
mole of $i-C_4H_8$	=	4.39×10^{-6}	mole
mole of $1-C_4H_8$	=	7.47×10^{-7}	mole

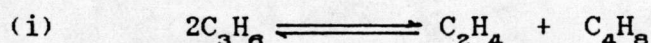
Next we make a C balance for the wet product gas mixture, as follows.

gm-atom of C in C_2H_4	=	2 x mole of C_2H_4	=	6.48×10^{-8}	mole
gm-atom of C in C_2H_5OH	=	2 x mole of C_2H_5OH	=	5.18×10^{-5}	mole
gm-atom of C in C_3H_6	=	3 x mole of C_3H_6	=	.069	mole
gm-atom of C in $i-C_3H_7OH$	=	3 x mole of $i-C_3H_7OH$	=	2.75×10^{-3}	mole
gm-atom of C in $n-C_3H_7OH$	=	3 x mole of $n-C_3H_7OH$	=	1.78×10^{-5}	mole
gm-atom of C in $i-C_4H_8$	=	4 x mole of $i-C_4H_8$	=	1.756×10^{-5}	mole
gm-atom of C in $1-C_4H_8$	=	4 x mole of $1-C_4H_8$	=	2.98×10^{-6}	mole
gm-atom of C in $ter-C_4H_9OH$	=	4 x mole of $ter-C_4H_9OH$	=	2.06×10^{-5}	mole
gm-atom of C in $2-C_4H_9OH$	=	4 x mole of $2-C_4H_9OH$	=	1.06×10^{-4}	mole
gm-atom of C in $n-C_4H_9OH$	=	4 x mole of $n-C_4H_9OH$	=	6.32×10^{-5}	mole

Total g-atom of C detected in the product mixture = .072 mole

Similarly, total gm-atom of H detected in the product gas mixture and product liquid mixture = .390 mole, and total gm-atom of O detected in the product mixture = .122 mole.

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



The disproportionation of propylene to ethylene and butenes is not unique propylene and can, in fact, be applied to a variety of feed olefins, in each case producing two other olefins, with a lower chain length and one with a higher chain length. Since three olefins

Table 5.1 Example of Experimental Data

Cat: NaY catalyst Feed $C_3H_6:H_2O = 1:6$ Date 5/7/31 P = 45 psig S.V. = 5000 hr ⁻¹ T = 250 °C												
	Raw Data						Total moles	g-atoms of Feed			% Conversion = 4.3 % Selectivity	Reaction Involved
	Gas Sample			Liquid Sample (32 °C)				C	H	O		
	Area/cm ²	mol/.5CC	mol/550CC	Area/cm ²	mole/5µl	mole/2.7CC						
C ₃ H ₆	3.36	2.15x10 ⁻⁵	.023				.023	.069	.138	-		
H ₂ O				2.36	2.73x10 ⁻⁴	.122	.122	-	.244	.122		
C ₂ H ₄	1.6	2.95x10 ⁻⁶	3.24x10 ⁻⁶				3.24x10 ⁻⁶	6.48x10 ⁻⁶	1.296x10 ⁻⁷	-	3.13	2-C ₃ H ₆ ⇌ C ₂ H ₄ +C ₄ H ₆
iso-C ₄ H ₆	.06	3.99x10 ⁻⁹	4.39x10 ⁻⁶				4.39x10 ⁻⁶	1.756x10 ⁻⁵	3.512x10 ⁻⁵	-	.424	C ₄ H ₆ ⇌ i-C ₄ H ₆
n-C ₄ H ₆	.045	7.47x10 ⁻¹⁰	8.21x10 ⁻⁷				7.47x10 ⁻⁷	2.98x10 ⁻⁶	5.97x10 ⁻⁶	-	.079	2-C ₃ H ₆ ⇌ C ₂ H ₄ +C ₄ H ₆
C ₂ H ₅ OH				6x10 ⁻³	4.8x10 ⁻⁶	2.59x10 ⁻⁵	2.59x10 ⁻⁵	5.18x10 ⁻⁵	1.55x10 ⁻⁴	2.59x10 ⁻⁵	2.5	C ₂ H ₄ +H ₂ O ⇌ C ₂ H ₅ OH
2-C ₃ H ₇ OH				.45	1.69x10 ⁻⁶	9.17x10 ⁻⁴	9.17x10 ⁻⁴	2.75x10 ⁻³	7.33x10 ⁻⁴	9.17x10 ⁻⁴	88.68	C ₃ H ₆ +H ₂ O ⇌ i-C ₃ H ₇ OH
n-C ₃ H ₇ OH				2.5x10 ⁻³	5.42x10 ⁻⁶	5.96x10 ⁻⁶	5.96x10 ⁻⁶	1.78x10 ⁻⁵	4.76x10 ⁻⁵	5.96x10 ⁻⁶	.576	C ₃ H ₆ +H ₂ O ⇌ n-C ₃ H ₇ OH
ter-C ₄ H ₉ OH				2.5x10 ⁻³	4.7x10 ⁻⁶	5.17x10 ⁻⁶	5.17x10 ⁻⁶	2.06x10 ⁻⁵	5.17x10 ⁻⁵	5.17x10 ⁻⁶	.5	i-C ₄ H ₈ +H ₂ O ⇌ ter-C ₄ H ₉ OH
2-C ₄ H ₉ OH				.017	2.41x10 ⁻⁶	2.65x10 ⁻⁵	2.65x10 ⁻⁵	1.06x10 ⁻⁴	2.65x10 ⁻⁴	2.65x10 ⁻⁵	2.56	C ₄ H ₆ +H ₂ O ⇌ 2-C ₄ H ₉ OH
n-C ₄ H ₉ OH				.015	1.44x10 ⁻⁶	1.58x10 ⁻⁵	1.58x10 ⁻⁵	6.32x10 ⁻⁵	1.58x10 ⁻⁴	1.58x10 ⁻⁵	1.52	C ₄ H ₆ +H ₂ O ⇌ n-C ₄ H ₉ OH
Total			5.24x10 ⁻⁶			.1229	.146	.072	.390	.122	99.96	
												C:O = .59
												H:O = 3.196
												H:C = 5.41

are thus involved, the process has been called the "Triol process".

(ii) $C_3H_6 + H_2O \longrightarrow i-C_3H_7OH$ (direct catalytic hydration of propylene to isopropanol)

(iii) $C_3H_6 + H_2O \longrightarrow n-C_3H_7OH$

In this case an alternative reaction might take place to give n-propanol

(iv) $C_2H_4 + H_2O \longrightarrow C_2H_5OH$ (direct catalytic hydration of ethylene)

(v) $1-C_4H_8 + H_2O \longrightarrow 2-C_4H_9OH$ (direct catalytic hydration of 1-butene)

(vi) $i-C_4H_8 + H_2O \longrightarrow ter-C_4H_9OH$ (direct catalytic hydration of i-butene)

(vii) $1-C_4H_8 + H_2O \longrightarrow n-C_4H_9OH$ (minor product)

The total mole of C_3H_6 in the feed that has been converted
= .001 mole

Conversion per pass of C_3H_6	=	4.3 %
Selectivity for C_2H_4	=	3.13 %
Selectivity for $i-C_4H_8$	=	.424 %
Selectivity for $1-C_4H_8$	=	.079 %
Selectivity for C_2H_5OH	=	2.5 %
Selectivity for $i-C_3H_7OH$	=	88.68 %
Selectivity for $n-C_3H_7OH$	=	.576 %
Selectivity for $t-C_4H_9OH$	=	.5 %
Selectivity for $2-C_4H_9OH$	=	2.56 %
Selectivity for C_4H_9OH	=	1.52 %

Furthermore, the space time yield (STY) in terms of moles of product i/(liter catalyst) (hr) is defined here as STY of product

= space velocity x % conversion x % selectivity x mole ratio of C_3H_6/H_2O

22.4 x 100 x 100

$$= \frac{5000 \times 4.3 \times 88.68 \times 1}{22.4 \times 100 \times 100 \times 7}$$

Thus STY of $i\text{-C}_3\text{H}_7\text{OH}$ = 1.21

Note that the above analytical results are for the case of space velocity = 5000 hr^{-1} and reaction conditions 45 psig, 250°C .



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