

CHAPTER III

EXPERIMENTAL

The experiment for the study of kinetics of COS adsorption on Selexsorb[®] COS was operated in 15 cc. continuous flow tube reactor installed in an oven of gas chromatograph as the temperature control system. Another gas chromatograph equipped with a pulse flame photometric detector was used as the analytical system in order to determine the COS conversion after adsorption. The order of reaction and the activation energy of adsorption was calculated from the experimental data varying using different COS concentrations and operating temperatures, respectively.

3.1 Materials

3.1.1 Reactant Gases

Carbonyl sulfide in propylene was used as the feed gas. The sample was collected from the C₃ hydrogenation tower of the ethylene cracking plant of Thai Petrochemical Industry Co., Ltd. in Rayong, as shown in Table 3.1

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Table 3.1 Feed compositions

Composition	Concentration
Carbonyl Sulfide	0.4-5 ppm wt
Hydrogen Sulfide	trace
Carbon disulfide	trace
Propadiene	2-3 % wt
Propyne	2-3 % wt
Propane	5 % wt
Carbonmonoxide	10-50 ppm vol
Carbondioxide	10-50 ppm vol

3.1.2 Absorbent

The adsorbent used was Alcoa Selexsorb[®] COS. This adsorbent selectively remove carbonyl sulfide, hydrogen sulfide, carbondisulfide as well as carbondisulfide from the gas feedstocks . Typical physical and chemical properties of Selexsorb COS are as shown in Table 3.2 and Table 3.3, respectively.

Table 3.2 Typical physical properties Alcoa Selexsorb[®] COS

Property	Detail
Diameter	3.2 mm (1/8 inch)
Surface area	270 m ² /gram
Total pore volume	0.5 cc/gram
Alumina XRD	Amorphous Chi, & gamma
Crush strength	14 kgs (31 lbs)
Packed bulk density	785 kgs/m ³ (49 lbs/ft ³)

Table 3.3 Typical chemical properties Alcoa Selexsorb[®] COS

Composition	%wt
Al ₂ O ₃ + Proprietary Modifier	93.1% wt
SiO ₂	0.02% wt
Fe ₂ O ₃	0.02% wt
Na ₂ O	0.30% wt
Loss of ignition (250 -1200°C)	6.5% wt

3.2. Experimental Equipment

3.2.1 Reactor

The reactor consisted of a 300 mm. long, 8 mm. outer diameter, 6 mm. inner diameter of Swagelok teflon tube installed in column oven of the Perkin Elmer Autosystem model gas chromatograph as if column. The temperature of the system was controlled using the thermocouple PT-100 indicated in the reactor and PT-400 in the oven.

3.2.2 Gas Manifold

Carbonyl sulfide in propylene was fed from Swagelok 300 cc- internal Teflon coated stainless steel and controlled feed flow rate with verify pressure regulator (stainless steel diaphragm and material), needle valve and rotameter. Together the regulator and the rotameter made it possible to reproduce the feed stream accurately and consistently. The gas flow lines were constructed of 316 stainless steel tubing and 1/8 inch Teflon tube with Swagelok connections.

3.3 Analytical Instrument

The analytical system consisted of a Varian Model 3400 gas chromatograph used for the determination of trace carbonyl sulfide. It was equipped with pulse flame photometric detector (PFPD) and installed with 56 in x 1/8 in Teflon packed column 1.5 % XE - 60 and 1% H₃PO₄ 60/80 Carbopack B packing material supplied by Varian Associates, Inc. The gas chromatograph was previously, calibrated by using known COS , 1.8 wt. ppm in nitrogen balance (Linde certified standard gas). The external standard calibration curves is shown in appendix D. The appropriate operating conditions of the gas chromatograph were studied as follows :

Flow rate of carrier gas (Nitrogen 99.9995 %)	26	ml/min
Flow rate of oxidant I (Air zero)	24.4	ml/min
Flow rate of oxidant II (Air zero)	10	ml/min
Flow rate of fuel (Hydrogen 99.99%)	19.7	ml/min
Flow rate of carrier gas (at PFPD outlet)	7.2	ml/min
Split flow (before detector)	18.8	ml/min
Injector temperature	150	°C
Oven temperature	50	°C
Detector temperature	200	°C
The inlet pressure for N ₂ carrier gas is set to	60	psig

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3.4 Experimental Procedure

3.4.1 System Preconditioning

After loading give the amount of adsorbent into the reactor, checking for leaks, pretreatment by 99.9995 % nitrogen purge and bringing the temperature to the desired value, the system was allowed to come to equilibrium for 20 minutes.

3.4.2 Procedure for COS Adsorption.

The reactant, COS in liquid propylene, was evaporated in teflon coil immersed in a water bath (Heto DT model) at 40 °C and passed through a bypass give reference to diagram of experimental and its compositions verified by using gas chromatographs. The needle valve (SV-3 to SV-6)(see Figure 3.2)has been switched over for flow through the reactor. The gas stream was regulated until the desired value was reached at atmospheric pressure, after which the reaction was ready to start.

Continuously flow of gas stream was passed from the reactor outlet through the 1 cc - gas sampling teflon loop connected in the six-port gas sampling valve in the injection oven of the analytical gas chromatograph and vented to the sample-out line to the Varian digital flow meter for flowrate of 50-1000 mL/min or the bubble flow meter for higher flow rate. After every five minutes of reaction, manually the analysis was synchronously operated with automatically switching gas sampling valve to the "ON" position, called sample discharge step in order to introduce the sample into the analytical GC column by carrier gas. The six-port valve was switched automatically to the "OFF" position, called sample charge step when the analysis was completed after four-minute analysis time. The gas sample passed through the sampling for every new experimenting loop again and went back to analysis cycle at "OFF" position of gas sampling valve for 1 hour fresh adsorbent was used and stored to the preconditioning system step.

The process control diagram and the sketch of experimental equipments and instrument are shown as Figure 3.1 and Figure 3.2, respectively. Systematically, the

experimental step for this study was ordered as Figure 3.3 and the details of each experiment are presented in Table 3.4 based on the experimental strategies shown in Figure 3.3.

Table 3.4 Details of the experiments.

Experiment	Temperature (°C)	COS reactant (ppm)	Flow rate (mL/min)
A	40	1.08	50, 109, 144, 181, 210
B	40	1.53	50, 110, 305, 410, 508
C	40	3.80	104, 206, 307, 401, 450
D	40	4.90	50, 150, 250, 300, 340
E	40	6.68	73, 150, 250, 400, 450
F	30	0.82	50, 153, 253, 303, 402
G	40	0.82	60, 151, 251, 351, 450
H	45	0.86	50, 150, 251, 351, 450
I	50	0.86	50, 152, 252, 345, 457
J	60	0.86	50, 151, 251, 351, 452

3.5 Methods for Determination of Kinetic Parameters

The result of the determination of carbonyl sulfide in effluent after 1- hour of reaction time were, first, calculated to the COS conversion (shown in the equation 3.1). Afterward, a conversion curve was plotted between COS conversion versus time.

$$\text{COS conversion, } X_{\text{COS}} = (C_{\text{eff}} - C_0)/C_0 \quad (3.1)$$

where

C_{eff} = COS concentration in effluent, wt ppm or mol/m³

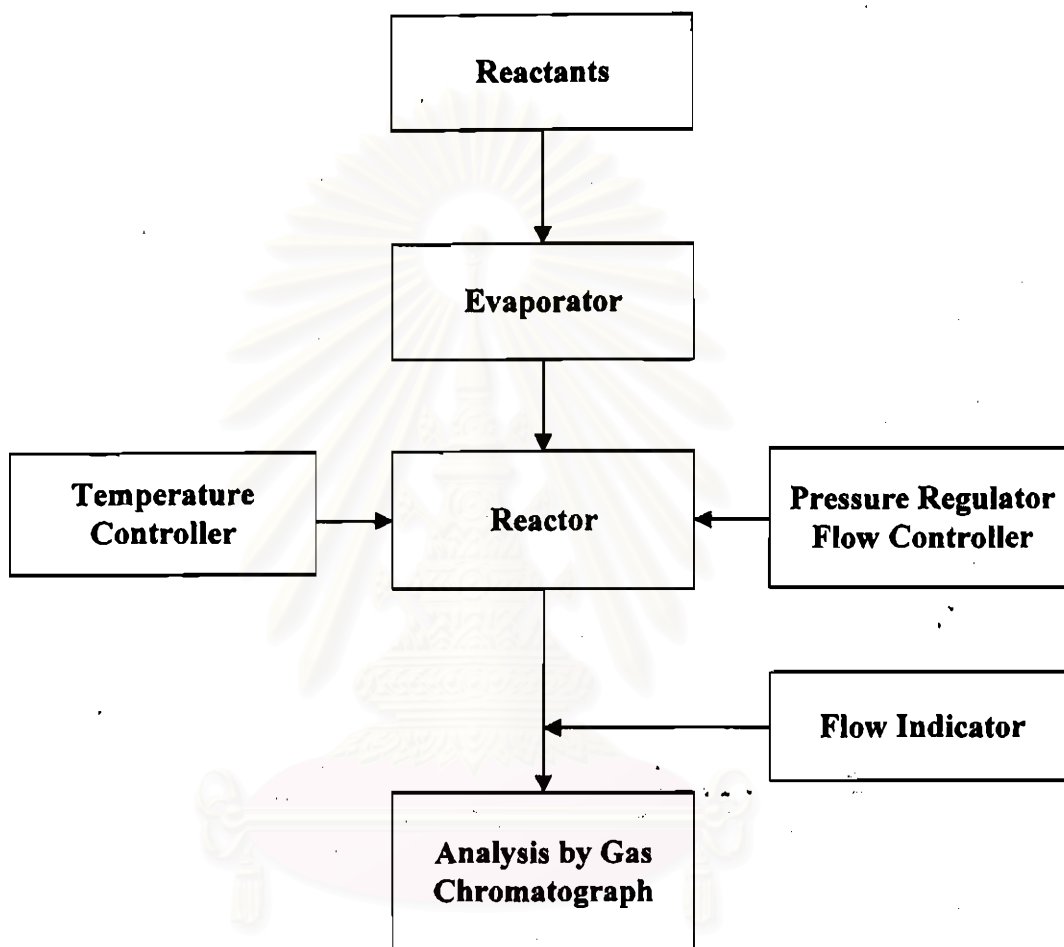
C_0 = COS concentration in feed, wt ppm or mol/m³

From the conversion curve, it was noticed an amount of COS in effluent at steady - state and record data as C_{eff} at that condition and parameter. After varying flow rate of reactant until five values, a plot between conversion and $W/ F_{o,cos}$ was given polynomial equation and taken the first derivation. The initial slope, obtained from a substituting of $W/F_{o,cos}$ or time = 0, is represented to the initial rate. It was assumed that, this reaction is unimolecular. It could be therefore used the equation (2.20) and (2.21) for the determination of the partial order of reaction with respect to COS concentration and rate constant with the aid of linear regression.

The activation energy was determination by the equation (2.10), and taking natural logarithm. The E_a and k_o were obtained with the aid of linear regression also.

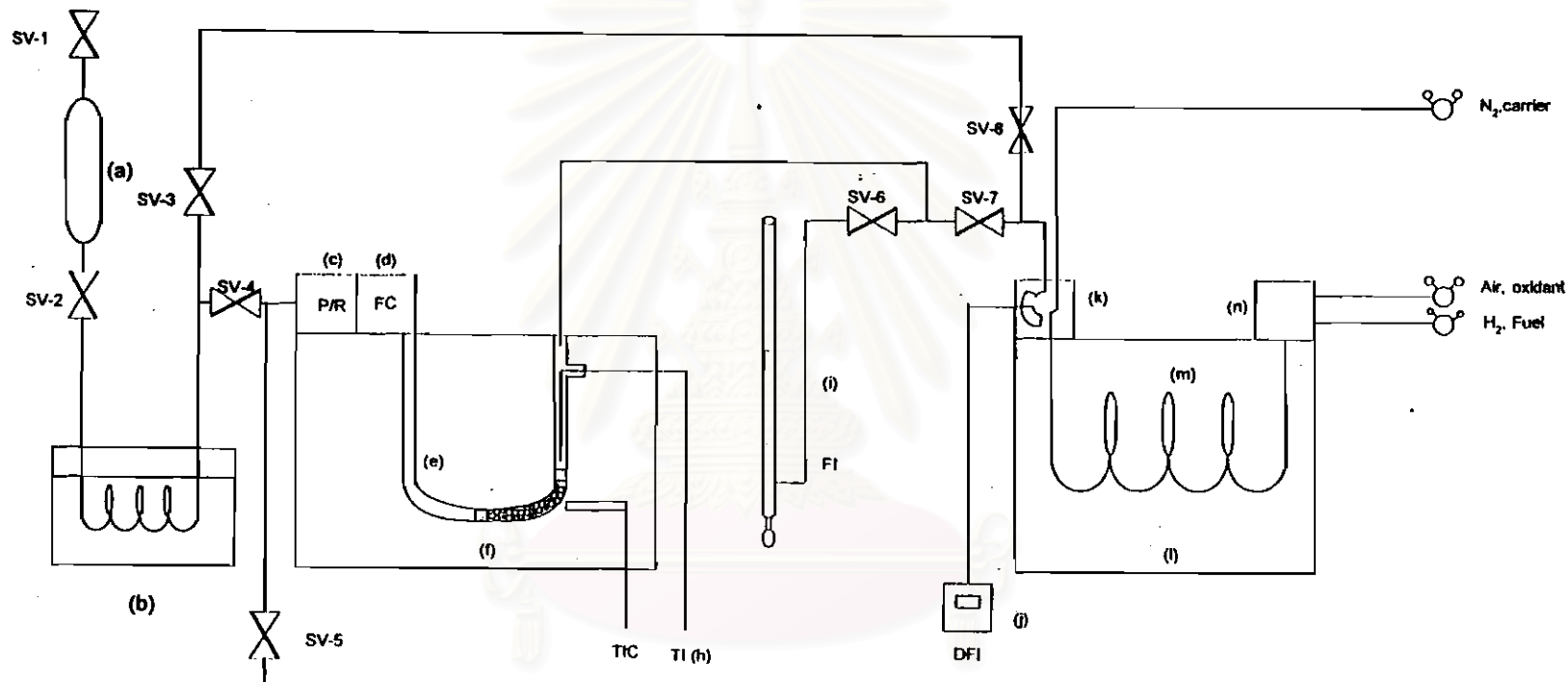


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Figure 3.1 Experimental procedure



- | | | |
|-------------------------------------|---------------------------|--------------------------------------|
| (a) Gas Cylinder Bomb | (f) GC-Oven | (k) Gas Sampling Valve |
| (b) Evaporation Device (water bath) | (g) Temperature Indicator | (l) Analytical GC |
| (c) Pressure Regulator | (h) Temperature Indicator | (m) Analytical Column |
| (d) Flow Controller | (i) Bubble Flow Meter | (n) Pulse Flame Photometric Detector |
| (e) Teflon Tube Reactor | (j) Digital Flow Meter | (o) SV-1 to SV-7 as toggle valve |

Figure 3.2 Sketch of Experimental Equipments and Instrument

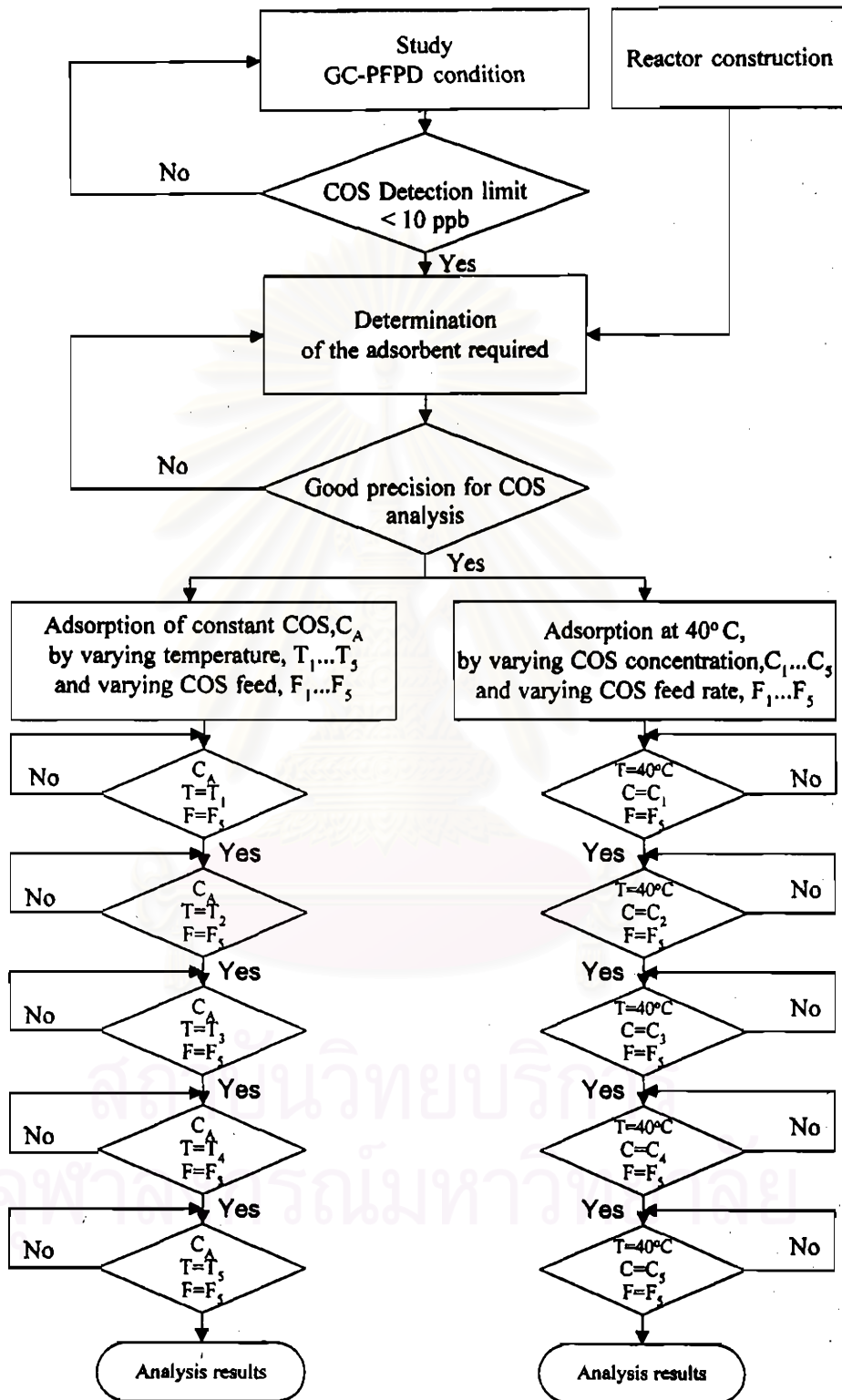


Figure 3.3 Flow chart of experiment plan

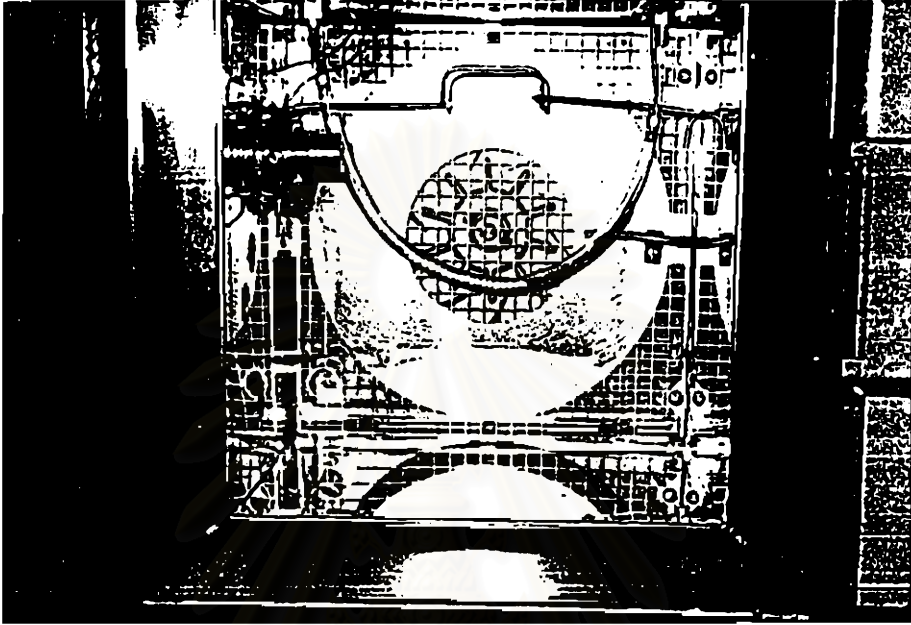


Figure 3.4 Photo of tube reactor installed in a gas chromatograph.

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