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APPENDIX A

Table A-1 Impurities Common in Olefins and Catalysts for their Removal

Impurity to Remove	BASF Catalyst	Composition
Acetylenes	H 0-22	0.3 % Pd on Al_2O_3
Arsine	H 3-12	$CuO + ZnO + Al_2O_3$
CO	R 3-11, R 3-15	$CuO, CuO + ZnO$
COS	R 3-12	$CuO + ZnO + Al_2O_3$
Dienes	H 0-22	0.3 % Pd on Al_2O_3
H_2S	R 3-12	$CuO + ZnO + Al_2O_3$
Mercaptans	R 3-12	$CuO + ZnO + Al_2O_3$
Oxygen	R 3-11, R 3-15	$CuO, CuO + ZnO$

APPENDIX B

Table B-1 Propylene (polymer grade) Specification

Component	Specification	Unit
Propylene	greater 99.5	% by wt
Methane, Ethane	max 500	ppm by wt
Ethylene	max 10	ppm by wt
Acetylene	max 1	ppm by wt
Propyne, Propadiene	max 5	ppm by wt
C4-Hydrocarbon	max 7	ppm by wt
Carbon monoxide	max 2	ppm by wt
Carbon dioxide	max 2	ppm by wt
Hydrogen	max 1	ppm by wt
Oxygen	max 3	ppm by wt
Water	max 2	ppm by wt
Methanol, Ketones	max 4	ppm by wt
Total sulphur	max 2	ppm by wt
Carbonyl sulfide	max 20	ppb by wt
Propane		remainder

APPENDIX C

Raw data obtained the experiments

Table C-1 The COS Concentration in Effluent after Adsorption of the Experiment A and B.

Time	COS concentration in effluent (ppm)									
(min)	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
5	0.635	0.609	0.575	0.622	0.484	0.246	0.207	0.207	0.121	0.143
10	0.600	0.575	0.562	0.600	0.419	0.216	0.181	0.207	0.125	0.134
20	0.570	0.562	0.553	0.570	0.410	0.207	0.168	0.168	0.082	0.125
30	0.575	0.562	0.549	0.540	0.384	0.194	0.160	0.160	0.073	0.060
40	0.570	0.562	0.553	0.531	0.246	0.186	0.160	0.095	0.069	0.043
50	0.579	0.562	0.549	0.518	0.242	0.181	0.160	0.095	0.065	0.043
60	0.575	0.540	0.540	0.510	0.233	0.177	0.125	0.091	0.065	0.043

Table C-2 The COS Concentration in Effluent after Adsorption of the Experiment C and D.

Time	COS concentration in effluent (ppm)									
(min)	C1	C2	C3	C4	C5	D1	D2	D3	D4	D5
5	3.015	3.572	3.317	2.704	3.205	4.423	3.624	2.527	5.654	4.423
10	2.894	3.326	3.222	2.043	2.160	3.071	2.199	1.957	4.138	2.324
20	2.769	2.678	2.678	1.546	1.469	2.955	2.112	1.702	2.281	1.741
30	2.587	2.423	2.423	1.162	0.825	2.622	1.991	1.598	1.343	1.235
40	2.410	2.384	2.384	1.123	0.769	2.587	1.965	1.572	0.557	0.587
50	2.246	2.082	2.082	0.994	0.752	2.540	1.957	1.434	0.549	0.536
60	2.160	1.935	1.935	0.985	0.721	2.549	1.948	1.352	0.518	0.514

Table C-3 The COS Concentration in Effluent after Adsorption of the Experiment E and F.

Time	COS concentration in effluent (ppm)									
(min)	E1	E2	E3	E4	E5	F1	F2	F3	F4	F5
5	5.408	4.747	3.084	3.888	2.946	0.717	1.011	0.510	0.475	0.419
10	5.270	3.888	2.946	2.782	1.970	0.670	0.639	0.492	0.419	0.315
20	5.045	3.819	2.454	1.927	1.326	0.626	0.592	0.479	0.393	0.311
30	4.415	3.762	2.419	1.667	1.197	0.605	0.518	0.471	0.393	0.251
40	4.125	3.689	2.376	1.654	1.153	0.531	0.484	0.419	0.376	0.242
50	4.082	3.663	2.333	1.650	1.123	0.518	0.484	0.410	0.371	0.233
60	4.065	3.603	2.177	1.309	0.916	0.527	1.948	0.402	0.367	0.216

Table C-4 The COS Concentration in Effluent after Adsorption of the Experiment G and H.

Time	COS concentration in effluent (ppm)									
(min)	G1	G2	G3	G4	G5	H1	H2	H3	H4	H5
5	0.346	0.410	0.337	0.354	0.229	0.320	0.389	0.415	0.108	0.104
10	0.328	0.337	0.285	0.242	0.147	0.302	0.307	0.229	0.104	0.078
20	0.324	0.302	0.268	0.130	0.065	0.259	0.181	0.207	0.082	0.065
30	0.276	0.276	0.225	0.121	0.043	0.255	0.164	0.134	0.082	0.043
40	0.285	0.272	0.220	0.112	0.039	0.242	0.173	0.130	0.078	0.039
50	0.255	0.272	0.216	-	0.035	0.246	0.177	0.125	-	-
60	-	-	-	-	-	-	-	-	-	-

Table C-5 The COS Concentration in Effluent after Adsorption of the Experiment I and J.

Time	COS concentration in effluent (ppm)									
(min)	I1	I2	I3	I4	I5	J1	J2	J3	J4	J5
5	0.367	0.354	0.276	0.272	0.263	0.263	0.251	0.194	0.173	0.138
10	0.242	0.298	0.233	0.225	0.246	0.143	0.151	0.117	0.108	0.086
20	0.238	0.229	0.194	0.168	0.125	0.134	0.091	0.086	0.086	0.043
30	0.229	0.220	0.177	0.160	0.112	0.134	0.099	0.078	0.091	0.030
40	0.229	0.216	0.186	0.151	0.117	0.130	0.095	0.091	0.095	0.030
50	-	-	-	-	-	-	-	-	-	-
60	-	-	-	-	-	-	-	-	-	-
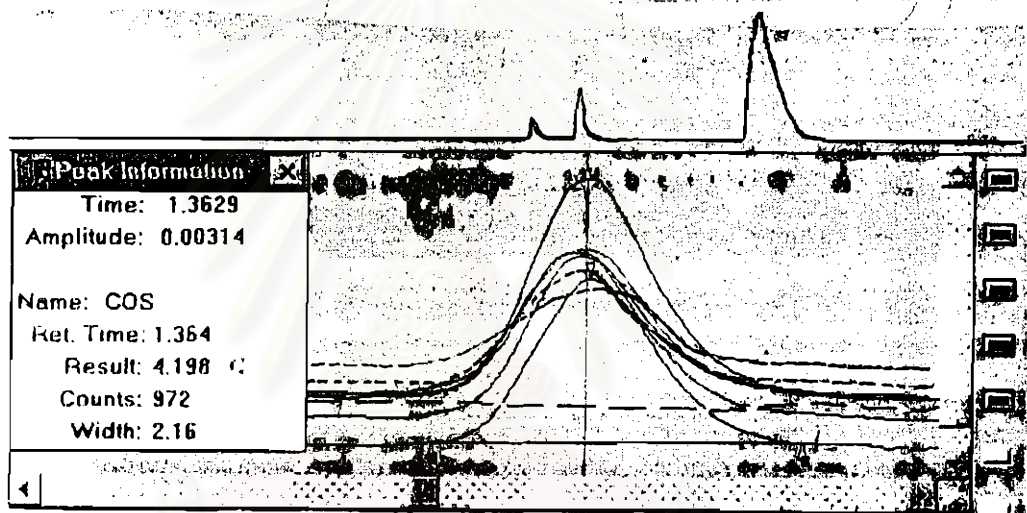
Figure D-1 Chromatogram of the Determination of COS in Effluent after
Adsorption

COS

External Standard Analysis
Curve Type: Linear
Origin: Include
y = +2.315185e+002x +5.118128e-014

Resp. Fact. RSD: 5.063%
Corr. Coef.(R²): 0.993211
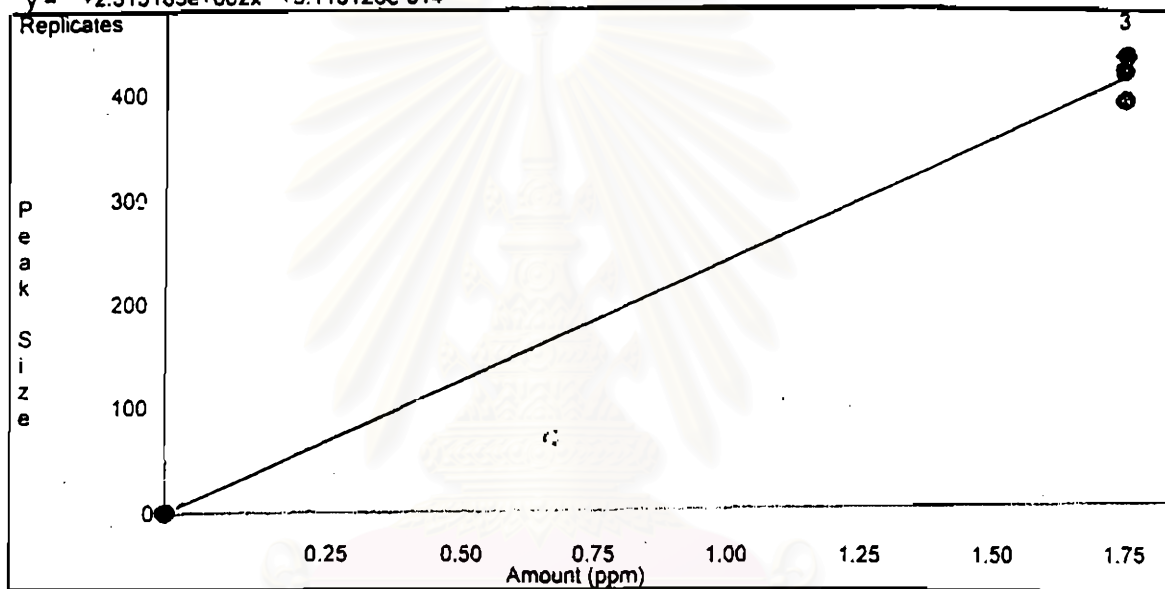
Figure D-2 External Standard Calibration Curve using 1.8 wt.ppm of COS
Standard Gas in nitrogen balance

APPENDIX E

1. Concentration unit conversion

The conversion unit in wt.ppm of COS in propylene (wt by wt) can be converted to mole of COS in volume of propylene.

$$1 \text{ ppm} = 42.08 / (22.4 * 60.07) \quad \text{mol/m}^3$$
$$= 0.0313$$

2. The conversion of volume flow rate to mass flow rate

Mass flow rate of COS in propylene is given by,

$$F_m = (C * F_v) / (6.0 * 10^7)$$

where

F_m = mass flow rate of COS in propylene, mol/s

C = COS concentration in propylene, wt.ppm

F_v = volume flow rate of COS in propylene, ml/min

3. The calculation of initial rate of reaction of continuous-flow reactor

From mass balance, the rate of reaction have to be considered the conversion at the space time as shown below:

$$(-r_A) = d X_A / (W/F_{0,A})$$

An initial slope of a relationship between X_A and $W/F_{0,A}$ is represented to the initial rate which can be determined by means of two methods, the differential method and the graphical method.

3.1 The differential method

The fitting of the relationship between X_A and $W/F_{0,A}$ is operated by the polynomial equation with the most suitable order. The third order and the second order were used for fitting the curve.

Afterthat, each curve equation was taken by the first derivative; f'(x). A result of f'(0) substitution was assumed to be an initial reaction rate as shown in table E-1, appendix E.

3.2 The graphical method

Each conversion curve was drawn manually, then draw a linear line contacting that curve that give the maximum slope. The initial rate of experiment is the initial slope of each curve.

<u>Example1</u>   From figure 4.3, experiment C

$$r \qquad = \qquad dXcos /(W/F_{0,cos}) \qquad = slope$$
$$\Delta y/\Delta x \qquad = \qquad 0.2/48.72 \qquad = 4.11*10^{-3}$$

The initial reaction rate for the experiment C from differential method and the graphical method are $4.2*10^{-3}$ and $4.11*10^{-3}$, respectively.

4. Computation of Mass Diffusivity

Predict the value of $\mathcal{D}_{AB}$ for mixtures of propylene (A) and carbonyl sulfide (B) at 313 K and 1 atm total pressure.

Solution. From Table B-1 , appendix B [22] we obtain the following constants :

$$M_A = 42.08 \quad ; \quad \sigma_A \approx Propane = 5.061 \ ^\circ A \quad ; \quad \epsilon_A/K = 254 \ K$$
$$M_B = 60.07 \quad ; \quad \sigma_B = 4.13 \quad ^\circ A \quad ; \quad \epsilon_B/K = 335 \ K$$

The parameters σAB and ϵ_{AB}/K for collisions of propylene with carbonyl sulfide may be estimated by means of equation:

$$\sigma_{AB} \quad = \quad (\sigma A + \sigma B)$$
$$\sigma_{AB} \quad = \quad (5.061 + 4.13) = 4.595 \ ^\circ C$$
$$\epsilon_{AB} \quad = \quad [(254)(335)]^{0.5} = 291.70 \ K$$

This gives $KT/\epsilon_{AB} = 313/291.70 \quad = \quad 1.07$, and from Table B-2 , appendix B [22] we then obtian $\Omega AB = 1.394$. Substitation of the forgoing values into equation :

$$\mathcal{D}_{AB} \quad = \quad 0.0018583*[T3 \ (\ 1/M_A + 1/M_B \ )/(\phi\sigma_{AB}^2\Omega \ D_{AB})]^{0.5}$$
$$= \quad 0.070283$$

Table E-1 The first derivatives of the relationship between conversion and space time

Experiment	3rd polynomial equation [f(x)]	1st derivative [f'(x)]	f'(0)
A	$(8 \times 10^{-11})x^3 - (5 \times 10^{-7})x^2 + (9 \times 10^{-4})x + (1.2 \times 10^{-3})$	$(2.4 \times 10^{-10})x^2 - (1 \times 10^{-6})x + (9 \times 10^{-4})$	9×10^{-4}
B	$(5 \times 10^{-10})x^3 - (2 \times 10^{-6})x^2 + (2.3 \times 10^{-3})x + (8.6 \times 10^{-3})$	$(1 \times 10^{-9})x^2 - (4 \times 10^{-6})x + (2.3 \times 10^{-3})$	2.3×10^{-3}
C	$(-5 \times 10^{-11})x^2 + (4.2 \times 10^{-3})x - (4 \times 10^{-3})$	$(-1 \times 10^{-5})x - (4.2 \times 10^{-3})$	4.2×10^{-3}
D	$(-5 \times 10^{-6})x^2 + (4.9 \times 10^{-3})x$	$(-1 \times 10^{-5})x - (4.9 \times 10^{-3})$	4.9×10^{-3}
E	$(3 \times 10^{-8})x^3 - (3 \times 10^{-5})x^2 + (8.1 \times 10^{-3})x$	$(6 \times 10^{-8})x^2 - (1 \times 10^{-6})x + (8.1 \times 10^{-3})$	8.1×10^{-3}
F	$(4 \times 10^{-10})x^3 - (1 \times 10^{-6})x^2 + (1.6 \times 10^{-3})x + (6 \times 10^{-4})$	$(1.2 \times 10^{-9})x^2 - (2 \times 10^{-6})x + (1.6 \times 10^{-3})$	1.6×10^{-3}
G	$(1 \times 10^{-9})x^3 - (3 \times 10^{-6})x^2 + (2.6 \times 10^{-3})x + (4 \times 10^{-5})$	$(2 \times 10^{-9})x^2 - (6 \times 10^{-6})x + (2.6 \times 10^{-3})$	3.0×10^{-3}
H	$(1 \times 10^{-9})x^3 - (3 \times 10^{-6})x^2 + (3 \times 10^{-3})x + (3 \times 10^{-4})$	$(6 \times 10^{-9})x^2 - (8 \times 10^{-6})x + (3.2 \times 10^{-3})$	3.2×10^{-3}
I	$(2 \times 10^{-9})x^3 - (4 \times 10^{-6})x^2 + (3.2 \times 10^{-3})x + (1.5 \times 10^{-3})$	$(6 \times 10^{-9})x^2 - (1 \times 10^{-5})x + (3.6 \times 10^{-3})$	3.0×10^{-3}
J	$(2 \times 10^{-9})x^3 - (5 \times 10^{-6})x^2 + (2.6 \times 10^{-3})x + (4 \times 10^{-5})$	$(3 \times 10^{-9})x^2 - (6 \times 10^{-6})x + (3 \times 10^{-3})$	2.6×10^{-3}

APPENDIX F

Analysis of Selexsorb COS

1.   Scanning Electron Micrograph

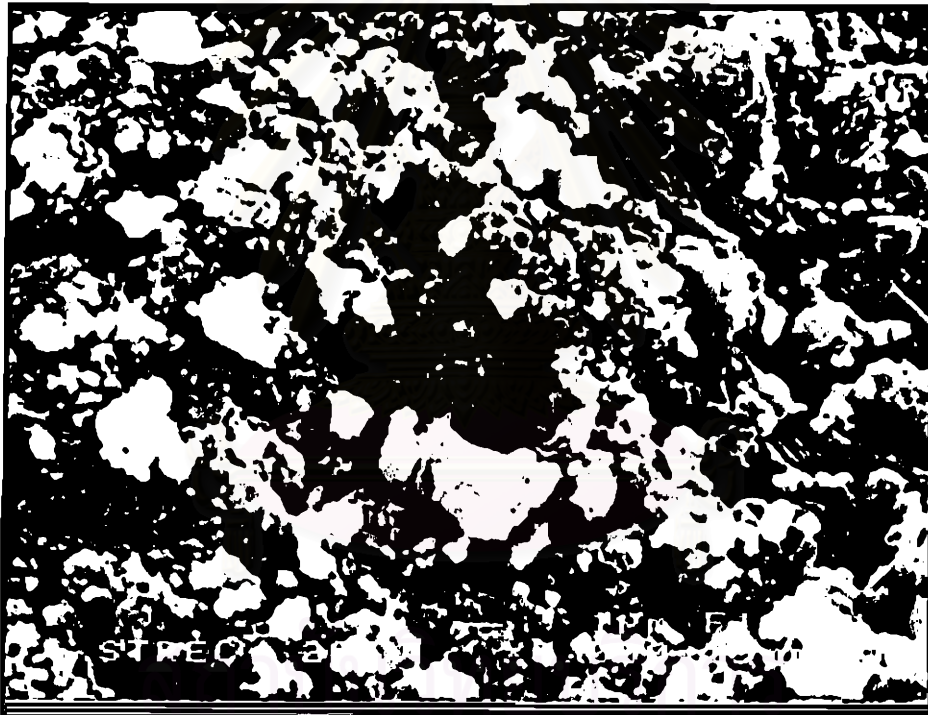The micrograph of Selexsorb COS was studied by the scanning electron microscope, JSM-6400 JELO showh in Figure F-1.

Figure F-1   Scanning electron Micrograph of Selexsorb COS

2. Elemental Analysis

2.1 X-Ray Fluorescence Spectroscopy

The semiquantitative analysis of metal oxides by means of Philips Analytical X-Ray, PW 2400 obtained the results shown in Table F-1. It was considered that the alkali metal compound and alkali earth metal compound that impregnated into the Selexsorb COS may be sodium oxide, Na_2O and calcium oxide, CaO, respectively.

Table F-1 results of metal compounds analysis by X-Ray Fluorescence.

Compound	Unit	Concentration
Al_2O_3	%wt	95.15
Na_2O	%wt	4.80
CaO	%wt	0.05

2.2 CHNS Analysis

The C, H, N contents were quantitatively analyzed by CHNS/O analyzer, Perkin Elmer, PE 2400 series II, and sulfur content was determined by means of microcoulometry using Sulfur Analyzer, Rosemount Dorhmann MCTS 120/130 shown in Table F-2. This result was implied that the mixture impregnated into Selexsorb® COS may be amine compounds.

Table F-2 The results of elemental analysis

Element	Unit	Concentration
C	% wt	0.41
H	% wt	1.79
N	% wt	2.03
S	ppm wt	20

VITA

Mr. Pattanapong Amphan was born on April 2, 1967. He received a Bachelor degree of Science in Chemistry with the second class honour from the Faculty of Sciencee at Burapha University in 1992. He has joined the Thai Petrochemical Industry (Public) Co.,Ltd. since 1992. In 1998, he has accepted as graduate student (part-time program for Msc. in Petrochemistry and Polymer Science) in the Department of Chemistry, Chulalongkorn University. He received a master's Degree of Science in 1998.