CHAPTER IV

EXPERIMENTS AND EXPERIMENTAL RESULTS

In this study, there were a total of six experiments, labeled preliminary experiment and experiment 1 through 5.

Detailed of each experiment will be presented follow by analysis results of each experimental sample.

4.1 Experiments

Before start-up of each experiment, the reactor was packed with 10 grams of catalyst to the height of 15.24 centimeters (6 inches). The catalyst was packed only in the middle section of the reactor and the bottom end of the reactor was packed with glass beads. The reactor was then connected to gas feed and liquid feed lines at the top and to sample bombs at the bottom. The system was checked for leaks by gradually pressurizing the system with nitrogen gas. The pressure test was conducted at 4.14 MPa (600 psig) which is 0.69 MPa (100 psig) higher than the reactor operating pressure. A pressure drop of 68.95 kPa (10 psig) in one hour was the maximum acceptible leak.

The catalyst was calcined to remove moisture and adsorbed gas on the surface by slowly increasing the reactor temperature from room temperature to 200°C (392°F) under the flow of nitrogen gas. The temperature was maintained at 200°C (392°F) for 1.5 hours.

Since the catalyst was originally in its oxide form, it must be sulfided before each experiment. Carbondisulfide was used as sulfiding agent. The sulfidation step was conducted at 350°C (662°F) for 2.5 hours. Detailed description of this step was documented elsewhere [224].

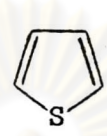
Toluene is an unsaturated heterocyclic hydrocarbon compound. It is a non-polar solvent commonly used in cool liquid extraction [205]. Toluene is considered to be a feed carrier which has a good solubility for thiophene and organometallic compounds. Thiophene serves as an excellent model of the organosulfur compounds popularly used for studying hydrodesulfurization reaction [6, 10, 140]. Organometallic compounds used in these experimental runs were ferrocene, titanocene dichloride, and vanadyl acetylacetonate. The catalyst used in this study is 1/8 inch extrudate Ni-Mo/Al_2O_3, donated by Thai Oil Refinery Company Limited.

Properties of thiophene, toluene, ferrocene, titanocene dichloride and vanadyl acetylacetonate are given in Tables 4.1 to 4.5, respectively.

A preliminary experiment was conducted to find a suitable operating condition for hydrodesulfurization of thiophene in toluene solution. In this experiment, operating temperature was varied from 100 to 300°C (212 - 572°F) at a step size of 100°C. Other operating conditions are listed in Table 4.6. The suitable operating temperature was subsequently used in experiment 1 to experiment 5.

The study of organometallic compounds was conducted by adding 100 ppm of metal directly into the feedstock and

TABLE 4.1 Properties of Thiophene*

Formula	C_4H_4S
Structure	
Chemical Name	Thiophene
Physical Properties	
Molecular weight	84.14
Form	liquid
Color	colorless
Melting Point (°C)	-38.2
Boiling Point (°C)	82-84
Specific gravity	1.063
Solubility	Soluble in alcohol, ether, actone, benzene and pyrimidine
Purity	> 98 % (by supplier)
Supplier	Fluka

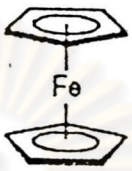
* From Supplier

TABLE 4.2 Properties of Toluene*

Formula	$C_6H_5CH_3$
Structure	
Chemical Name	Methylbenzene
Physical Properties	
Molecular weight	92.14
Form	liquid
Color	colorless
Melting Point (°C)	-95
Boiling Point (°C)	109-112
Specific gravity	0.87
Solubility	Soluble in alcohol, ether, acetone, benzene and pyrimidine Insoluble in water
Purity	> 99.5 % (by supplier)
Supplier	Merck

* From Supplier

TABLE 4.3 Properties of Ferrocene*

Formula	$(C_5H_5)_2Fe$
Structure	
Chemical Name	Bis(cyclopentadienyl) iron, Dicyclopentadienyliron
Physical Properties	
Molecular weight	186.04
Form	crystalline solid
Color	orange
Melting Point (°C)	172-174
Iron Content	30.02%
Solubility	Soluble in toluene, alcohol, ether, acetone and benzene
Purity	> 98 % (by supplier)
Supplier	Fluka

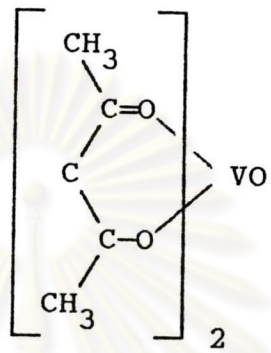
* From Supplier

TABLE 4.4 Properties of Titanocene Dichloride*

Formula	$(C_5H_5)_2Cl_2Ti$
Structure	
Chemical Name	Bis(cyclopentadienyl) titanium dichloride, Dicyclopentadienyl titanium dichloride
Physical Properties	
Molcular weight	248.93
Form	crystalline solid
Color	red
Melting Point (°C)	260-280
Titanium Content	19.24 %
Solubility	Moderately soluble in toluene and chloroform and in alcohol and other hydroxylic solvents
Purity	97 % (by supplier)
Supplier	Fluka

* From Supplier

TABLE 4.5 Properties of Vanadyl Acetylacetonate*

Formula	$OV(C_5H_7O_2)_2$
Structure	
Chemical Name	Vanadiumoxy acetylacetonate, Vanadium (IV) oxide acetylacetonate
Physical Properties	
Molecular weight	265.16
Form	crystalline solid
Color	dark green
Melting Point (°C)	256-259
Vanadium Content	19.21%
Solubility	Moderately soluble in toluene and chloroform
Purity	95 % (by supplier)
Supplier	Fluka

* From Supplier

TABLE 4.6 Experimental Conditions

Operating Conditions :	
Reactor Temperature	: 100 - 300°C (212 - 572°F) for Preliminary Experiment
	: 220°C (428°F) for Experiment 1 - 5
Pressure	: 3.45 MPa (500 psig)
Feedstock flowrate	: 30 cm^3/hour
Hydrogen flowrate	: 400 cm^3/minute
Liquid Hourly - Space Velocity (LHSV)	: 2.1 hr^{-1}
Duration of run	: 72 hrs
Sampling	: every 12 hrs
Catalyst	: 1/8" Extrudate of Ni-Mo /γ-Al_2O_3
Catalyst weight	: 10 grams

hydrodesulfurized it. Table 4.7 shows compositions of feed stocks used in each experiment. The operating conditions were identical to the ones used in preliminary experiment except the temperature which was 220°C (428°F)

The hydrodesulfurization experiments were conducted at a pressure of 3.45 MPa (500 psig) and a temperature of 220°C (428°F). Because the conversion of thiophene at 200°C is 31.98 %. It is not as high as we expect so used temperature in experiment 1 through 5 is 220°C. In a new condition, thiophene conversion is moderate, approximately 47%.

4.2 Experimental Results

During each experiment, liquid samples were taken every 6 hours. The samples of every 12 hours were analyzed for their compositions and metal contents.

A Perkin Elmer model 8700 Gas Chromatograph equipped with OV-1 GL Sciences capillary column was used to analyze for the composition of each compound in liquid samples. The outputs from the chromatogram were used to calculate weight percent of thiophene and toluene in every sample. Conversion of thiophene was then calculated by:

$$\% \text{ conversion of thiophene} = (1 - C_t / C_{to}) * 100$$

where

C_{to} = weight % of thiophene in feed

C_t = weight % of thiophene in product sample

Table 4.8 shows the conversion of thiophene in the preliminary experiment. The temperature was varied from 100 to 300°C (212-572 F). Tables 4.9 to 4.13 show the conversion of thiophene in each experiment. Conversion of toluene

TABLE 4.7 Feed Compositions

Feedstock:	
Preliminary Experiment	- Toluene + 3 wt% sulfur (as Thiophene)
Experiment 1	- Toluene + 3 wt% sulfur (as Thiophene)
Experiment 2	- Toluene + 3 wt% sulfur (as Thiophene)+ 100 ppm of iron (as Ferrocene)
Experiment 3	- Toluene + 3 wt% sulfur (as Thiophene)
Experiment 4	- Toluene + 3 wt% sulfur (as Thiophene) + 100 ppm of titanium (as Titanocene dichloride)
Experiment 5	- Toluene + 3 wt% sulfur (as Thiophene) + 100 ppm of vanadium (as Vanadyl acetylacetonate)

TABLE 4.8 Conversion of Thiophene in the Preliminary Experiment

Temp. (°C)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
Feed	94.69	4.97	-
100	94.70	4.95	-
200	95.51	3.41	31.98
300	88.53	0	100

TABLE 4.9 Conversion of Thiophene in Experiment 1

Time (hr)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
0	95.02	4.96	-
12	96.23	2.69	46.56
24	96.24	2.80	44.29
36	95.96	2.76	44.99
48	96.52	2.75	45.44
60	96.49	2.62	47.95
72	96.43	2.60	48.47

TABLE 4.10 Conversion of Thiophene in Experiment 2

Time (hr)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
0	94.97	4.89	-
12	97.26	1.61	68.02
24	97.21	2.24	55.33
36	96.53	2.65	46.63
48	96.60	2.69	45.96
60	95.98	2.74	44.63
72	96.35	2.78	43.97

TABLE 4.11 Conversion of Thiophene in Experiment 3

Time (hr)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
0	94.94	5.06	-
12	96.73	2.09	59.38
24	96.70	2.24	56.54
36	96.99	2.02	60.96
48	96.60	2.23	56.96
60	96.90	2.29	55.61
72	96.44	2.35	54.21

TABLE 4.12 Conversion of Thiophene in Experiment 4

Time (hr)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
0	95.01	4.98	-
12	96.09	2.62	47.99
24	96.03	3.05	39.35
36	95.78	3.11	38.00
48	95.80	3.29	34.43
60	95.58	3.54	29.20
72	95.56	3.61	27.95

TABLE 4.13 Conversion of Thiophene in Experiment 5

Time (hr)	wt %		% Conversion of Thiophene
	Toluene	Thiophene	
0	95.26	4.69	-
12	97.02	2.23	53.40
24	96.88	2.27	52.36
36	96.61	2.30	52.77
48	96.72	2.36	50.52
60	96.44	2.54	46.59
72	96.71	2.57	49.04

is 0 % at this operating condition.

The metal concentrations in the feedstock and product oils were determined by a Instrumentation Laborytory Model IL 551 Atomic Emission Spectrometers. The deviation of the results was so high that the results were belived not to be reliable.

The coke content in each catalyst was analyzed by burning the catalyst at 550°C (1022°F) for 60 hours to calculate the weight percent of loss of carbonaceous material. Approximately 0.2 gram of the catalyst are weight at room temperature and placed in a furnace at 550°C (1022°F) to burn off their carbonaceous material for 60 hours. The samples are allowed to cool down to room temperature then weighed. Three sampled catalysts were analyzed for coke content in each section and then their coke contents were averaged in each section. Tables 4.14 to 4.18 show the weight percent of coke content in each experiment.

Metal distribution in catalyst pellets of experiments 2, 4, and 5 were analyzed by using a JEOL Model JSM - T220A Scanning Microscope equipped with a LINK Model EDX 860 Energy Dispersive X-Ray Analyzer. The outputs of the X-ray analyzer were integrated and printed as relative amounts of metal contents in each location. Tables 4.19 to 4.21 show iron, titanium and vanadium distribution in each experiment, respectively.

TABLE 4.14 Coke Content on Catalyst in Experiment 1

Section	wt% Coke in Each Sampling			Average wt% Coke
	1	2	3	
Top	23.59	25.10	24.58	24.42
Middle	21.95	23.37	23.58	22.97
Bottom	22.44	23.13	23.75	23.11

TABLE 4.15 Coke Content on Catalyst in Experiment 2

Section	wt% Coke in Each Sampling			Average wt% Coke
	1	2	3	
Top	19.69	19.11	18.38	19.06
Middle	21.53	21.58	22.34	21.82
Bottom	21.74	20.75	22.19	21.56

TABLE 4.16 Coke Content on Catalyst inExperiment 3

Section	wt% Coke in Each Sampling			Average wt% Coke
	1	2	3	
Top	23.03	22.86	23.00	22.96
Middle	22.46	22.28	22.06	22.27
Bottom	21.72	23.05	22.39	22.39

TABLE 4.17 Coke Content on Catalyst in Experiment 4

Section	wt% Coke in Each Sampling			Average wt% Coke
	1	2	3	
Top	12.56	12.25	12.09	12.30
Middle	14.10	10.99	13.96	13.02
Bottom	13.10	13.15	13.35	13.20

TABLE 4.18 Coke Content on Catalyst in Experiment 5

Section	wt% Coke in Each Sampling			Average wt% Coke
	1	2	3	
Top	13.58	14.40	14.56	14.18
Middle	14.88	14.81	14.97	14.89
Bottom	13.18	13.76	14.13	13.69

TABLE 4.19 Iron Distribution on Catalyst in Experiment 2

Section	Point	Iron Distribution in the Catalyst Extrudate
Top	Center	1
	x	0.63
	y	0.54
	Edge	0.46
Middle	Center	0.41
	x	0.26
	y	0.09
	Edge	0.02
Bottom	Center	0.14
	x	0.09
	y	0.03
	Edge	0.002

TABLE 4.20 Titanium Distribution on Catalyst in Experiment 4

Section	Point	Titanium Distribution in the Catalyst Extrudate
Top	Center	1
	x	0.79
	y	0.24
	Edge	0.13
Middle	Center	0.74
	x	0.44
	y	0.19
	Edge	0.05
Bottom	Center	0.19
	x	0.07
	y	0.04
	Edge	0

TABLE 4.21 Vanadium Distribution on Catalyst in Experiment 5

Section	Point	Vanadium Distribution in the Catalyst Extrudate
Top	Center	1
	x	0.76
	y	0.70
	Edge	0.20
Middle	Center	0.10
	x	0.06
	y	0.04
	Edge	0.01
Bottom	Center	0.08
	x	0.07
	y	0.02
	Edge	0