

Chapter III
Materials
and
Methods



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MATERIALS and METHODS

3.1 Feed Stocks:

Heavy vacuum gas oil (HVGO) kindly supplied from Suez Petroleum Company and a synthetic feed blend (40 - 60), 40 % heavy vacuum gas oil and 60 % heavy vacuum residue (HVR) have been used as feed stocks in the present investigation. The main characteristics of feeds are indicated in *Table (1)*.

Table (1): Main Characteristics of Feed Stocks

<i>Characteristics</i>	<i>HVGO</i>	<i>Feed Blend</i>
Density at 15 °C	0.8744	0.9829
Sulfur content, wt %	1.83	3.95
Nitrogen content, wt %	0.063	-
Conradson carbon residue, wt %	-	13.01
Asphaltene content, wt %	-	7.74
Pour point, °C	12	-
Aniline point, °F	168.8	-
Olefins content, wt %	12.9	-
Color	5.5	-
<i>Component analysis, wt %:</i>		
Total Saturates	55.96	10.61
Total aromatics	42.63	79.92
Resins	1.41	9.47
<i>Metal analysis, ppm:</i>		
Vanadium (V)	-	98.4
Nickel (Ni)	-	82.8

3.2 Catalyst:

A commercially CoO MoO₃ / Al₂O₃ - hydrotreated catalyst was used in the catalytic activity tests. The chemical and main physical characteristics of the catalyst are illustrated in *Table (2)*.

Table (2): Catalyst Characteristics

<i>Characteristics</i>	<i>Value</i>
Shape, extrudates, mm	4.3
Bulk density, g / cc	0.67
Crushing strength, Kg / Cm	19.43
Surface area, m ² /g	175.53
Total pore volume, cc/g	0.4254
Average pore diameter, Å	194
CoO, wt %	4.1
MoO ₃ , wt %	12.8

3.3 Chemicals:

The solvents used in the present study are as follows:

a) Solvents used in component analysis:

1. Toluene: rectified (pure reagent for analysis) (El Nasr pharmaceutical chemicals Co. Egypt) ADWIC.
2. n-Hexane: (reagent for analysis) ADWIC
3. Chloroform: (laboratory fine chemicals) BIO. CHEM
4. Methanol: (Analytical reagent) ADWIC

b) Solvents for catalyst regeneration:

5. Ethyl alcohol: (Locally laboratory chemicals)

6. Tetra hydro furane (THF): (HONIL LIMITED) England

3.4 Catalytic Activity Test:

3.4.1 Apparatus:

Catalyst performance and hydrotreating runs were carried out in a down flow, fixed - bed high pressure micro- reactor unit (cata – test unit) as shown in *Figure (2)*.

The unit consists of a stainless steel reactor (internal diameter 19 mm, external diameter 27 mm, length 50 cm) and divided into three zones, each of them is heated and separately temperature controlled. The reactor was equipped with a calibrated burette connected to feed jar, a metric pump, a gas liquid separator, and wet gas meter and product collector.

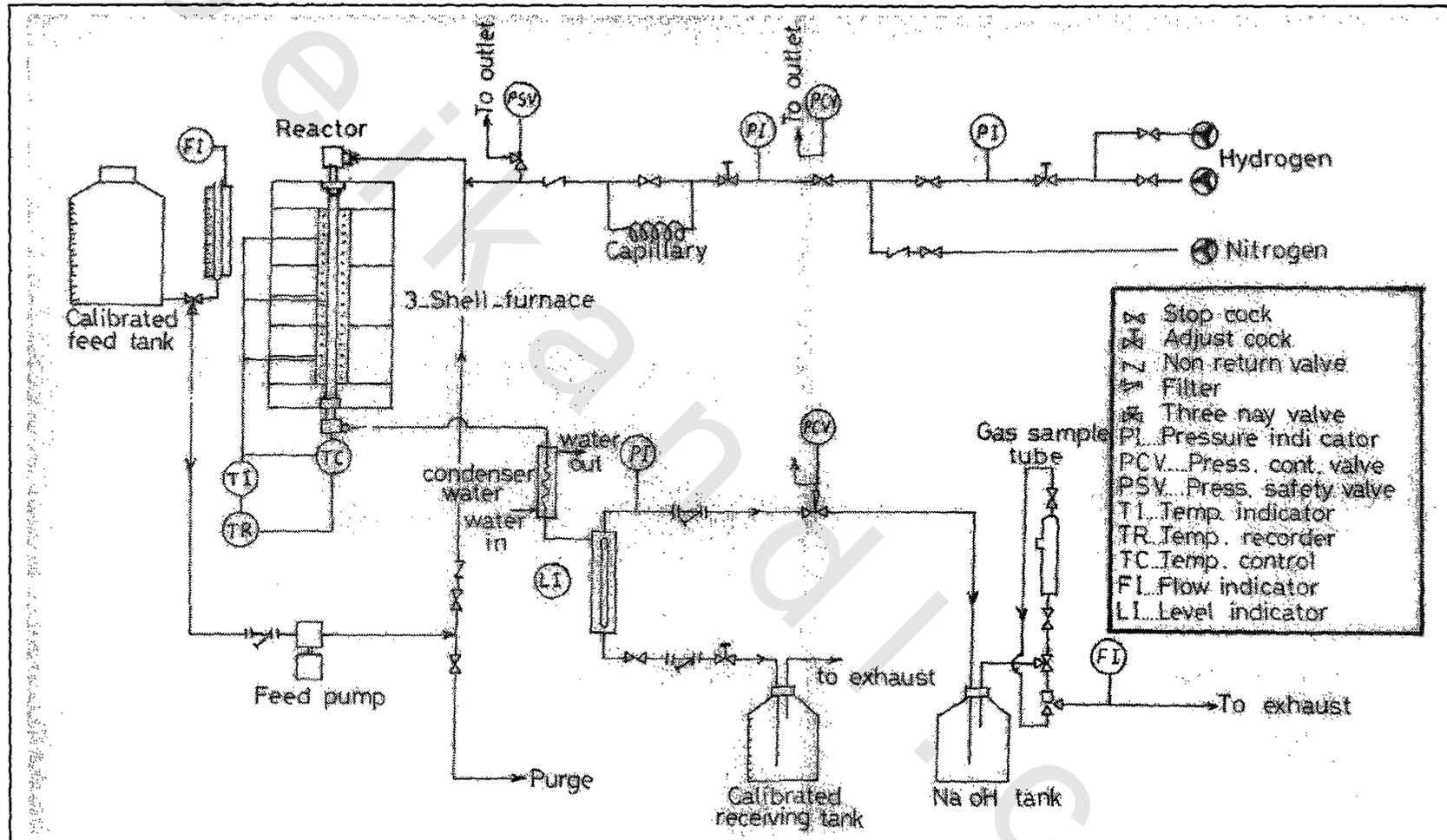


Figure (2): High Pressure Catalyst Activity Testing Unit

3.4.2 Procedure:

3.4.2.1 Catalyst Presulfiding:

The catalyst is pre-sulfided by using gas oil as feed stock mixed with dimethyl disulfide (DMDS) as spiking agent (8% of the catalyst volume) under 15 bar initial hydrogen pressure and at 350 °C reaction temperature for 6 hours.

3.4.2.2 Hydrotreating Runs:

The hydrotreating experiments with varying operating conditions indicated in *Table (3)*. Were conducted in a fixed-bed cata-test unit.

100 ml of the catalyst is loaded inside the middle zone of the reactor (40 Cm, length) divided into three zones; glass beads and glass wool separate each from other. Where as the upper and lower zones of the reactor is filled with 5ml of glass beads. After charging the reactor with predetermined quantity of the catalyst, the leakage of the unit is checked by putting the unit under pressure (100 bar) of the hydrogen gas over night.

The required operating conditions are adjusted before introducing the charge stock under investigation. The liquid feed and hydrogen gas are injected under pressure at the top of the reactor.

The mixture crosses the different zones of the reactor in down - flow direction as shown in *Figure (2)*.

The density of the reactor effluent (liquid product) is measured continuously during the test. When density becomes stable, a stable catalyst activity is attained and samples of the reactor effluent are collected every 9 hours.

Table (3): Catalytic Activity Operating Conditions

<i>Feed stock Conditions</i>	<i>Hydrotreating heavy vacuum gas oil</i>	<i>Deactivation feed Blend + HVGO</i>
Reaction temperature, °C	300,325, 350, 375,400,425	350
Hydrogen pressure, bar	15, 35, 50,65	50
L.H.S.V., h ⁻¹	0.50,0.75, 1.00,1.25, 1.50	0.5
H ₂ / feed L/L	250	250
Time of test run, h	9	3, 6, 9, 12, 24
Catalyst volume, ml	100	50 : 50

The most important properties of product are measured using the standard methods indicated in *Table (4)*. The physical properties and coke deposition of the catalyst were also determined.

Table (4): Standard Methods (ASTM)

<i>Analysis</i>	<i>Standard method</i>
Density @ 15, °C	ASTM D-1298
ASTM- Color	ASTM D-1500
Pour point, °C	ASTM D 97-88
Aniline point, °F	ASTM D 611-82
Sulfur content, wt%	IP - 336
Conradson- carbon residue, wt%	ASTM D-189
Asphaltene content, wt%	IP – 143
Hydrocarbon component analysis, wt %	[Mair and Rossina, 1958]

3.4.2.3 Time on Stream (TOS) for Catalyst Deactivation:

Fifty milliliters of catalyst diluted with an equal amount of glass beads was charged in the reactor and used in each run. Two feeds were used: HVGO and a blend of 40 % HVGO and 60 % HVR as shown in *Table (I)*.

Deactivation study was carried out at the following constant conditions: 350°C of reaction temperature, 50 bar of total H₂ pressure, 250 L/L hydrogen - to - oil ratio, 0.5 h⁻¹ of liquid hourly space velocity (LHSV) and time on stream (TOS) 3, 6, 9, 12 and 24 h. The effluent from the reactor is cooled in a water condenser and passes to the high pressure separator where the liquid phase is separated from the gas phase. The liquid product is then collected in a receiver for analysis.

3.4.2.4 Spent Catalyst Regeneration:

3.4.2.4.1 Catalyst Washing:

The samples of tested catalyst from the TOS - runs were washed with different organic solvents, ethanol then n- hexane.

3.4.2.4.2 Coke Determination by Burn off Method:

The washed catalyst is then heated at different temperatures in an electric oven to eliminate the carbon and sulfur residues in air as Co₂ and So₂ respectively.

The temperature is first increased from 100 to 350 °C at a rate of 50 °C / h then the catalyst is maintained at 350 °C for 1h, then heated to 450 °C with a rate of 25 °C / h, and maintained at this temperature for 24h [Ackerman et al., 1994].

After cooling to room temperature the percentage of coke was determined by loss of weight of the catalyst sample before and after burn off.

3.4.2.4.3 Coke Determination by Extraction Method:

The spent catalyst from various (TOS) experiments (3, 6, 9, 12& 24 h) were soxhlet- extracted with tetra hydro furane (THF) until no coloration of the solvent took place any more. For each extraction, about 2g of used catalyst was placed in a whatman filter paper number 42 which was fitted in the soxhlet apparatus.

During extraction the compartment containing the catalyst was siphoned every 5 min; the extraction temperature was about 64 °C. After extraction the sample was dried until its weight is fixed. The weight before and after extraction were then taken [Hauser et al., 2005].

3.4.2.5 Spent Catalyst Activity Test:

The regenerated catalyst samples from step (3.4.2.4.2) for both HVGO - runs and blend of HVGO and HVR runs were used for testing their hydrotreating activities using HVGO as a feed stock and under the following

operating conditions: 350 °C of reaction temperature, 50 bar of total H₂ pressure, and 250 L/L hydrogen - to - oil ratio, 0.5 h⁻¹ of liquid hourly space velocity (LHSV). At the end of each run, the effluent from the reactor is cooled in a water condenser and passes to the high pressure separator where the liquid phase is separated from gas phase and taken for analysis.

3.4.2.6 Catalyst Characterization:

3.4.2.6.1 Surface Area and Pore Volume:

Surface area, pore volume and average pore diameter of catalyst samples are measured using quanta chrome (Nova automated sorption system model 2002) at Central Metallurgical Research and Development Institute.

3.4.2.6.2 Coke Deposition:

As described before (3.4.2.4.2)

3.4.2.6.3 Catalyst Crushing Strength:

The side crushing (mechanical) strength for catalyst samples were determined by using Erweka, type TP 24 tablet hardness tester.

3.4.2.6.4 Infra Red Spectroscopic Analysis (FT-IR):

IR measurements were carried out by using an ATI Mattson Genesis Ser FTIR Tm infra red spectrophotometric at ambient conditions using KBr disks.

The spectrometer was used in the transmission mode. The measurements were recorded at room temperature at a wave number in the range of 500- 4000 Cm^{-1} .

3.4.2.6.5 X-Ray Diffraction:

X-ray powder diffraction (XRD) analysis for catalyst samples were carried out on a Rigaku C/max-2500 diffractometer using graphite filtered Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 100 mA with a scanning rate of 8° min^{-1} from $2\theta = 5^\circ$ to $2\theta = 80^\circ$. The XRD phases present in the samples were identified with the help of JCPDS Powder Data Files.
