

Chapter 1

1. Introduction

Crude oil is a complex mixture containing thousands of different organic hydrocarbon molecules weight and other organic compounds.

The main purpose of an oil refinery is to turn crude oil into more valuable products that meet consumer demands and environmental specifications.

One of the most important products is the diesel oil. Which is a complex mixture consisting of different classes of hydrocarbons typically in the range C₁₀ to C₂₅, It consists of normal, branched and cyclic paraffins, and compounds containing single as well as fused aromatic rings. [1]

Certain compounds contain heteroatom, such as sulfur, nitrogen, oxygen, metals and aromatic compounds. In addition to that, the cracking processes in the refinery generate of certain amount of unsaturated compounds like olefins and Acetylenic compounds.

For over three decades, refiners worldwide have been implementing various projects in their facilities to accommodate a variety of regulations to improve the quality of transportation fuels in order to reduce vehicle emissions. [2]

Hydrotreating is an established refinery process for reducing sulfur, nitrogen and aromatics while enhancing cetane number, density and smoke point. The refining industry's efforts to meet the global trend for more-stringent clean fuels specifications, the growing demand for transportation fuels and the shift toward diesel mean that hydrotreating has become an increasingly important refinery process in recent years.

Hydrotreating process combines advanced process technology, high-performance catalyst systems and efficient reactor internal designs. This technology has helped many refiners to rise to the clean fuels challenges facing their businesses; operators around the world have licensed new units for their grass-roots facilities. [4]

One of the key areas of interest has been the reduction of sulfur in diesel fuel to very low levels. For example, since mid-2006, the maximum sulfur content of on-road diesel fuel in the US has been limited to 15 wppm. [1]

1.1 Problem statement:

Reducing pollution from the use of diesel oil as a transportation fuel is an ongoing endeavor and important area of research. Which affect not only for human but all the organic life in our plant. That leads all the world conduct a lot of researches to reduce this emission.

In this research will focus in reducing the impurities to the minimum level according to international standard specification by using hydrogenation technology taking diesel hydrotreating unit (DHTU) in Khartoum refinery as the main case of study.

1.2 Objectives:

The objectives of the research are:

1. Improve the quality of the produced diesel.
2. Reach to the minimum sulfur content.
3. Optimum design for DHT unit to maintain and optimize the currently running unit of DHT in Khartoum Refinery Company.

Chapter 2

2. Literature Review

2.1 Previous Studies about Hydrotreating:-

2.1.1 Although the chemical reactions of hydrogenation for organic compounds were known before 1897, Pool Sabbath who was made fixing reactions for hydrogen on hydrocarbons (like benzene and ethylene) by using powder of nickel, by that way he could to convert unsaturated hydrocarbons in gas phase to saturated hydrocarbons by using hydrogen gas in appearance of metallic catalyst. This step is considered the basic of hydrogenation catalytic in this time. [4]

2.1.2 In 1902 Philelm Norman the Germanic chemistry converted the unsaturated acidic or glycerides for saturated compounds, for that effort he patent in Germany and United Kingdom in 1903. All that let the hydrogenation technique spread all around the world. [5]

2.1.3 In 2009 Ed Palmer, Stan Polcar and Anne Wong prepared a research about clean diesel hydrotreating and mentioned as Design considerations for clean diesel hydrotreating. Critical issues are discussed when designing a hydrotreating facility to produce diesel fuel with very low levels of total sulfur. [2]

2.1.4 In 2010 Abdelazeez Maarefy is a researcher from Kuwait institute for scientific research prepared study about producing high quality diesel by decreasing the sulfur content to prevent the environment and human health and get the maximum profit. [6]

2.2 The Background of Hydrogenation Technology:-

In German before the Second World War the hydrogenation technology of modern times originated from the high pressure hydrogenation process of coal and coal tar, which appeared, and had been put into widely application in 1926.

In 1949, the platinum reforming technology appeared. That requires the feedstock being refined to get sulfur content of less than 1 ppm. On the other hand, it provides a great deal of free hydrogen gas.

All these accelerated the development of hydro refining technology; After 1950's, the auto-industry progressed rapidly. Therefore, the consumption of gasoline in USA and kerosene and diesel in EU and Japan increased rapidly. The straight run fractions could not meet the requirement of consumption and quality simultaneity, so hydro-cracking process which can neatly produce naphtha or mid-distillates was born.

In 1959, the first hydrocracking process was opened out.

In 1960's, most of residue was burn off as industrial fuel and thus a large amount of SOx sent to air, the pollution became more and more severity. USA, Japan and many of European countries adopted measure to limit the sulfur content of fuel oil, so residue HDS process had been studied.

In 1967, the first residue HDS unit was commercialized in Japan.

In 1970, in order to obtain more quantity of diesel fuel, EEC relaxed the limitation of FBP of diesel fuels, while the increase of pour point was not allowed. Hence, along with the increase of needs on low pour point and colorless middle fractions, the hydro dewaxing process for middle fractions had been applied. The successful application of hydro-dewaxing on medium fractions provided an example for lube oils. Before long, in 1981, the first hydro-dewaxing unit for lube oil production had been put into application.

From industry studies covering unit performance from 1998 to 2006, a comparison of Shell hydrodesulphurization (HDS) units with the average industry performance shows clear and sustained advantages.

From industry studies covering unit performance from 1998 to 2006 Mechanical availability was 1-5%, On-stream factor was 2-9%, Utilization was 5%, and Turnaround duration was 8-16 days.

Now days the studies talk about Ultra-Low Sulfur Diesel specifications with IsoTherming Hydroprocessing Technology, it is a commercially proven process with a long track record in providing refiners with a more economical means to produce today's transportation fuels. The core of IsoTherming technology is the ability to provide the hydrogen necessary for the reactions through a liquid stream, rather than a recycle gas system. IsoTherming technology is also very versatile in use as it is suitable for a wide range of grassroots and revamp applications, including kerosene hydrotreating, transmix hydrotreating, diesel hydrotreating, FCC feed hydrotreating, mild hydrocracking, dewaxing, gas to liquid (GTL) upgrading and heavy oil

upgrading. IsoTherming capacities range from 1500 bpd up to 80 000 bpd processing feed stocks such as 100% kerosene, 100% light cycle oil (LCO) and various mixtures of distillates and heavy gas oils, including Coker blends. [7]

2.3 Catalyst

The hydro treating process takes place in a reactor containing two fixed beds of catalyst which is commercially called RN-10

2.3.1 Catalyst specifications

2.3.1.1 Physical properties of catalyst:

- ▶ The specific surface area.
- ▶ The dispersion rate of the active agents on the support.
- ▶ The pore distribution of the support.

2.3.1.2 Chemical properties of catalyst:

- ▶ The activity which is the catalyst ability to increase the rate of the reactions.
- ▶ The selectivity expresses the catalyst ability to fastvour desirable reactions.
- ▶ The stability characterizes the change with time of the catalyst performance.

2.3.1.3 Mechanical properties of catalyst:

- ▶ Abrasion resistance
- ▶ Crush strength
- ▶ Attrition resistance

The catalyst RN-10 was developed by changing catalyst manufacturer.

Table (2.1): Specification of Catalyst RN-10

Catalyst	RN-10
Chemical component , m%	
WO ₃	≥26.0
NiO	≥2.6
Physical property :	
Specific surface area m ² /g	≥100
Pore volume: ml/g	≥0.25
Crushing strength: N/mm	≥18.0
Shape	Clover (tri)
Equivalent diameter: mm	1.4
bulk density : t/m ³	0.89~0.95

2.3.2 Hydro-Catalyst Deactivation Reasons:

Hydro-catalysts lose their activity in several ways:

- (1) Sintering of the active phase into large crystal units;
- (2) Degradation of the active phase (reduction reaction).
- (3) Covering of the active sites by reactants and/or products including coke.
- (4) Deposition of inactive metal sulfides (such as V sulfide).
- (5) Deposition of other impurities such as salt, silica.

2.4 Diesel Feed Stock:

Diesel Feed stock be characterized as high sulfur and nitrogen content

2.4.1 Feed Stock of RFCC Diesel Specifications:

Table (2.2): RFCC Diesel Specification

Distillation range	204
10%	228
20%	242
30%	254
50%	278
70%	309
80%	323
90%	337
Sulfur, ppm	600
D, kg/m ³	856
Nitrogen, ppm	283
Freezing point	-2
Bromine value mgBr/100g	15.4
Cetane index	33.0

2.4.2 Hydrogen

The hydrogen source required by the unit is mainly provided by the reformed hydrogen from the reforming unit, and the insufficient part will be provided by the hydrogen from the hydrogen recovery part.

Table (2.3): Composition of Reformed Hydrogen

Component	H ₂	CH ₂	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	Subtotal	Molecular weight
V%	94.60	2.00	1.60	1.00	0.50	0.30	100.00	3.657

Table (2.4): Composition of PSA Hydrogen

Composition	H ₂	C ₁	N ₂	O ₂	H ₂ O	Sum total
V%	99.9	100ppm	20ppm	<10ppm	50ppm	100

2.5 Product Specification:

The raw gasoline produced by the hydrotreating part can be used as the blending components of the gasoline in the whole refinery or delivered to RFCC for reprocessing, and the diesel oil distillates can be used as the blending components of the diesel oil in the whole refinery:

Table (2.5): The Characteristics of the Main Products

Properties	Refined diesel oil		Raw gasoline	
Item	Value provided by the Research Institute	Calculated value	Value provided by the Research Institute	Calculated value
Distillation range	ASTMD-86		ASTMD-86	
IBP		196		
10%	226	223		64
30%	253	253		95
50%	277	277		106
70%	307	306		110
90%/95%	335	335		158/179
Density (20C ⁰) g/cm ³	0.8930	0.903		0.716
Sulfur, ppm	61			-
Nitrogen, ppm	45			-
Cetane value D-976	36.5			-
Viscosity, mm ² /S (40C ⁰)	3.3			-
Viscosity,mm ² /S (100C ⁰)	1.3			-
Freezing point, C ⁰	-4			-

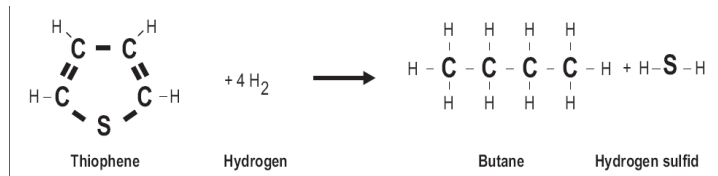
2.6 Reaction Principles:

Under a certain temperature, pressure, hydrogen oil ratio and space velocity conditions, convert the impurities in the secondary processed diesel oil that are harmful to the oil properties such as sulfur, nitrogen, and oxygen, etc. into hydrogen sulfide, water and ammonia that can be removed easily, saturate the unstable alkenes and some condensed aromatics, and eliminate metal impurities by virtue of catalyst's

function and through hydrogenation measure so as to improve the safety, corrosiveness, and combustion performance of the oil product and obtain the product with excellent quality.

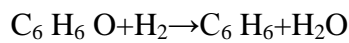
2.6.1 Main Chemical Reactions:

- Desulfurization reaction:

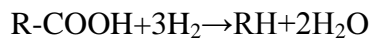


- Deoxidation reaction

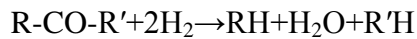
Phenols



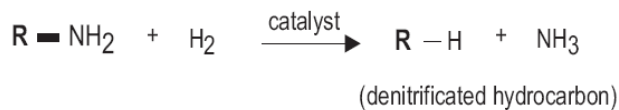
Acid



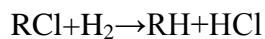
Kenton



- Denitrification reaction

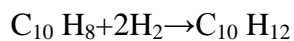
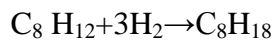


- Dehalogenation reaction

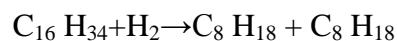


- Alkenes saturation

Straight chain alkenes:



- Hydrogenation cracking



Chapter 3

Materials and Methods

3.1 Materials

The data used in this research obtained from Khartoum refinery and it is properly used to perform the material and energy balance to the unit.

In the design stage we are going to design a stripper column which is play a great role to improve the quality of diesel specification precisely the flash point.

3.2 Methods:

3.2.1 Process Description

The catalytic diesel oil from tank farm is pumped under level control of feedstock surge drum via the feedstock relay pump, then, removes the particles bigger than 25 μ m through feedstock filter, and then, enters feedstock surge drum. The feedstock coming from surge drum boosts its pressure to 9.2MPa through hydro-treating feeding pump, then, exchanges heat through the reaction effluent/feedstock heat exchangers under flow rate control, then, blends with the mixed hydrogen and enters the reaction effluent/reaction feeding heat exchangers, and then, is heated to the reaction temperature through the reaction feeding heating furnace, and then, enters the hydro-treating reactor. The reactor is set with two catalyst beds, between which is set with quench hydrogen.

The reaction effluent from reactor passes through heat exchanger and then, passes through reaction effluent air cooler and reaction effluent water cooler to cool down to 45°C, and then, enters the high pressure separator (HPS).

To prevent the ammonium salt in the reaction effluent from being separated out at low-temperature positions, desalted water will be injected into the pipeline at the upstream (or downstream) of last heat exchanger through water injection pump .

The cooled reaction effluent is collected in the cold HP separator where three phases are separated gas, hydrocarbon liquid and sour water. The gas phase (recycle hydrogen) goes to separates liquid through the knock out drum at the suction of the recycle hydrogen compressor, then, enters the recycle hydrogen side. In the make

upside /circulating hydrogen compressor pressurize to 8.7MPa, then, is divided into two routes: one route is used as the reactor's quench hydrogen; the other route mixes with the make upside from the outlet of the make upside side, and the product hydrogen from the hydrogen recovery part. The mixed hydrogen will mix with the feedstock as the reaction feeding. The sour water containing ammonium salts is sent to the sour water stripping unit.

The hydrocarbon liquid is sent to the low pressure separator (LPS) through the pressure reduction adjusting valve under liquid level control; then, the gas of flash distillation from LPS will be discharged to the fuel gas pipe network or flare.

The LPS-effluent oil passes through diesel oil/LPS-effluent oil heat exchangers exchanges heat with refined diesel oil and reaction effluent separately, then, enters diesel oil steam stripping tower. The low-pressure and high- pressure separators sourer water will be discharged from the unit together, but reflux drum sour water sent to sour water plant separately.

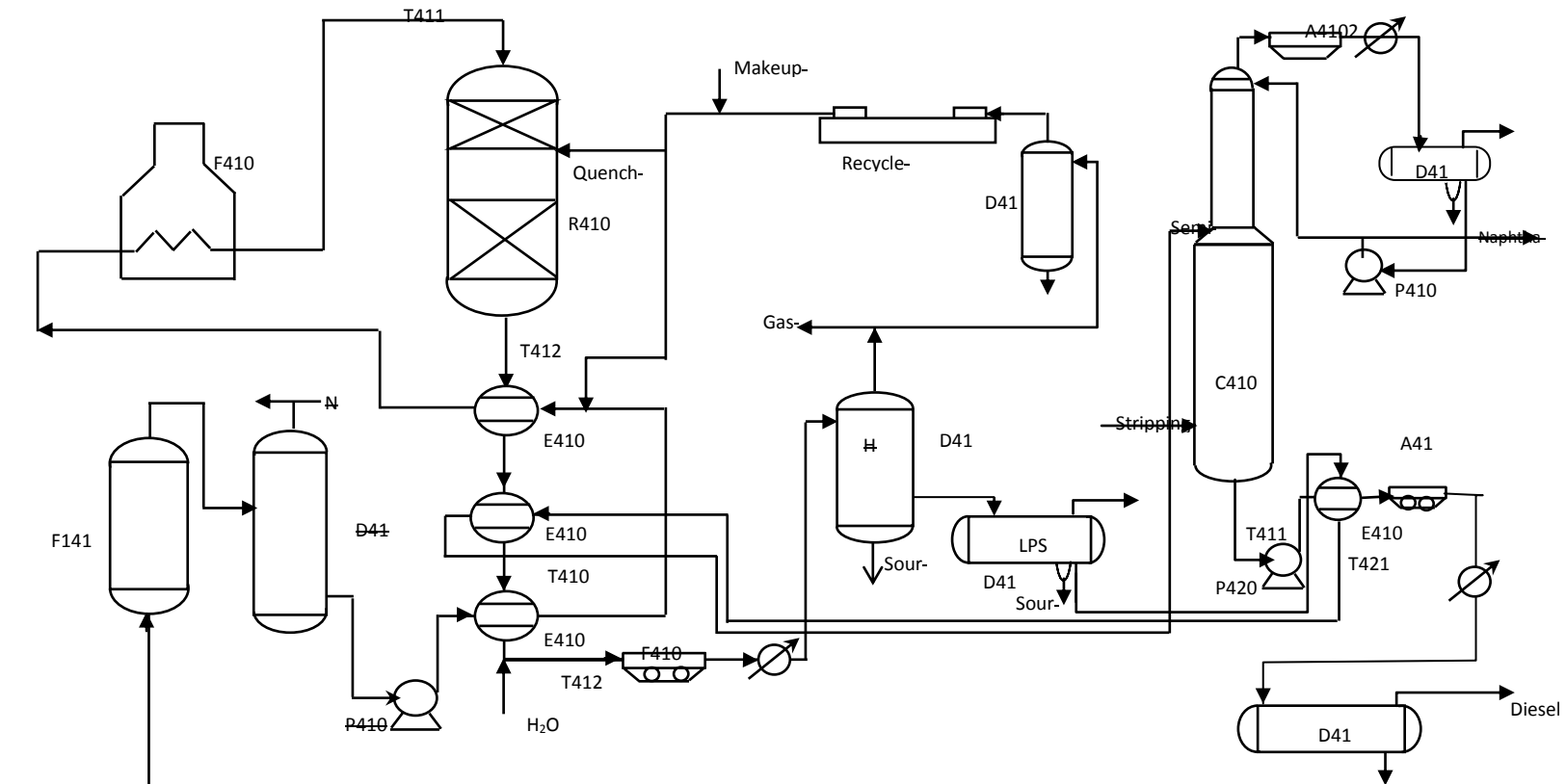


Figure (3.1): Flow Chart of Diesel Hydrotreating unit

Equipment	Symbol	Equipment	Symbol
Pump	P	H.E	E
Filter	F1	Drum	D
Furnace	F	Column	C
Reactor	R	Air-cooler	A
Stream	T		

3.3 Material Balances:

Material balances are the basis of process design. It considers all the process to determine the quantities of the materials required and product. Also it is a useful tool for the study of plant operation and trouble shooting. And can be used to check performance against design, to reach the proper use of the plant.

The general equation for any process system can be written as:

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady state process the accumulation will be zero. When there is no chemical reaction, the steady state balance reduced to:

$$\text{Material out} = \text{Material In}$$

A balance equation can be written for each separately identifiable species present, elements, compounds, and for the total material.

3.3.1 Material Balance of Diesel Hydrotreating Unit:

Table (3.1): Material Balance of DHT

No.	Material name	Measuring unit					
		rate %		Kg/h		t/d	
		Nominal	Actual	nominal	Actual	nominal	Actual
	Input part						
1	catalytic diesel	100	100	62500	54975	1500	1319.40
2	reformed hydrogen	2.36	2.39	1474	1317	35.38	31.61
3	hydrogen*	0.25	0.24	156	131	3.74	3.14
4	desalted water	4.8	5.46	3000	3000	72.00	72.00
5	steam stripping	2.08	2.09	1300	1150	31.20	27.60
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75
	Output part						
1	refined diesel oil	99.08	99.08	61925	54472	1486.2	1307.33
2	crude gasoline	1.03	1.03	644	568	15.46	13.63
3	low-component	0.66	0.64	411	351	9.86	8.42
4	tower top gas	1.7	1.67	1060	920	25.44	22.08
5	acid sewage	6.55	7.29	4094	4008	98.26	96.19
6	oil-bearing	0.30	0.30	188	167	4.51	4.01
7	Loss	0.17	0.17	108	87	2.59	2.09
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75

3.3.2 Material Balance of Hydrogen:

The hydrogen source required by the unit is mainly provided by the reformed hydrogen from the reforming unit, and the insufficient part will be provided by the hydrogen from the hydrogen recovery part.

Table (3.2): Composition of Reformed Hydrogen

Component	H ₂	C ₁	C ₂	C ₃	iC ₄	nC ₄	C ₅₊	Sum total
V%	85.43	5.83	4.48	2.54	0.72	0.24	0.76	100

Table (3.3): Composition of PSA Hydrogen

Composition	H ₂	C ₁	N ₂	O ₂	H ₂ O	Sum total
V%	>99.9	100ppm	20ppm	<10ppm	50ppm	100

3.4 Energy Balance

3.4.1 Introduction:

The conservation of energy differs from that of Mass in that energy can be generated or consumed in a chemical process. The total enthalpy of the outlet streams will not equal that of the inlet streams if energy is generated or consumed in the process.

In process design, energy balances are made to determine the energy requirements of the process: the heating, cooling and power required. In plant operation an energy balance on the plant will show the pattern of energy usage and suggest areas for conservation and saving.

3.4.2 Conservation of the Energy:

A general equation can be written for the conservation of energy:

Energy out = Energy in + Generation – Consumption – Accumulation.

For steady state processes the accumulation term will be zero. Energy can exist in many forms and this makes an energy balance more complicated.

A simplified form of the energy balance equation with is sufficient for estimating the heating and cooling requirements of the various unit operations involved in chemical processes is:

$$H_2 - H_1 = Q - W$$

This equation is applicable to both static (non-flow) and flow systems, therefore it can be used to estimate the energy requirements for batch processes.

For many processes the work term will be zero, or negligibly small and the equation reduces to the simple heat balance equation:

$$Q = H_2 - H_1$$

Where:

H_1 \equiv enthalpy of the inlet stream.

H_2 \equiv enthalpy of the outlet stream.

+ (positive): for heat entering the system.

- (negative): for heat leaving the system

3.4.3 Assumption:

- (1) Heat losses to the surrounding are neglected.
- (2) Specific heats of solids are assumed to be constant.
- (3) Specific heat of water and water vapor calculated at $(T+T_0) / 2$.

3.4.4 Energy Balance Calculation:

We calculate the specific heat c_p (kJ / kg. k) for feed and products in various temperatures (T) according to the following equation:

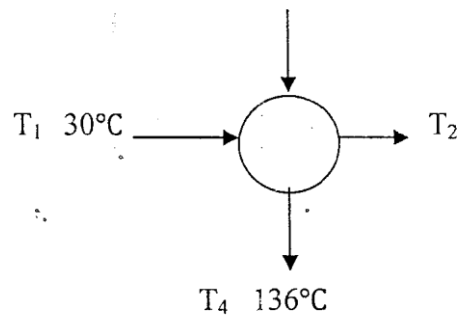
$$C_p = a + bT + cT^2 \dots\dots\dots (3.1)$$

3.4.4.1 Energy Balance around Heat Exchanger (E4 103) T3 190°

Objective:

Calculate the exit temperature (t_2)

$$Q = m * C_p * \Delta T$$



$$M_1 \cdot CP_1 \cdot (T_2 - T_1) = M_2 \cdot CP_2 \cdot (T_4 - T_3)$$

3.4.4.2 Calculated Specific Heat of Diesel at Various Temperatures:

Table (3.4): Specific Heat of Diesel at Various Temperatures

T (C ⁰)	CP KJ/Kg K
30	3.42
78	1.92
130	2.96
190	3.22
226	3.35
313	3.65

While $M_1 = M_2$

$$cp_{mean} = \frac{3.22 + 2.96}{2} = 3.09 \text{ kJ/kg k}$$

$$T_2 = \frac{3.09}{3.42} (190 - 136) + 30 = 78.8^\circ\text{C}$$

3.4.4.3 Energy balance around 2nd heat exchanger:

Objective:

Calculate the exit temperature (T_7)

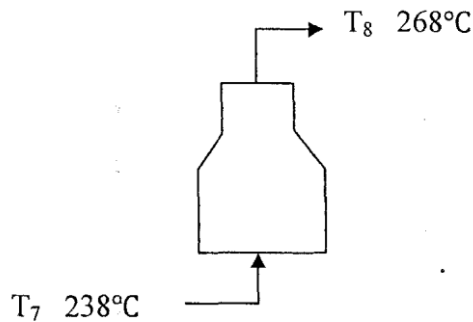
$$Cp \text{ mean} = Cp_4$$

$$cp_{mean} = \frac{cp \text{ at } 313^\circ\text{C} + cp \text{ at } 226^\circ\text{C}}{2}$$

$$= (3.65 + 3.35) / 2 = 3.5 \text{ KJ/Kg K}^0$$

$$T_7 = \frac{3.5}{1.92} (313 - 226) + 78.8 = 237^\circ\text{C}$$

3.4.4.4 Energy Balance Around furnace:



Calculate the heat transferred from furnace to diesel

$$Q = m \cdot C_p \cdot (T_8 - T_7)$$

$$Q = (100) \cdot (3.65) \cdot (268 - 237) = 11315 \text{ kJ}$$

3.4.4.5 Energy Balance around Reactor:

T_{ref} is 313°C (586K)

$$Q = \Delta H = rH_r(313^\circ\text{C}) + \sum_{out} n_i H_i - \sum_{in} n_i H_i \quad \dots\dots\dots (3.2)$$

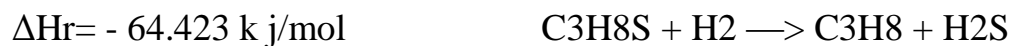
$$H_i = \int_{T_{ref}}^T c_{p_i} dT \quad \dots\dots\dots (3.3)$$

But Firstly we have to calculate H_r at (313°C)

T_{ref} For H_r at (313°C) 25°C (298 K)

3.4.4.5.1 Desulfurization Reaction (Q1)

Calculate the heat transferred through Desulfurization reaction



$$\begin{aligned} \Delta H_r(586 \text{ K}) &= \Delta H_r(298 \text{ K}) + \int_{298}^{586} c_{p(\text{C}_3\text{H}_8)} dT + \int_{298}^{586} c_{p(\text{H}_2\text{S})} dT - \\ &\quad \int_{298}^{586} c_{p(\text{C}_3\text{H}_8\text{S})} dT - \int_{298}^{586} c_{p(\text{H}_2)} dT \\ &= -64.423 + 10.25 + 0.5317 - 14.47 - 0.43 = -73.83 \text{ kJ/mol} \end{aligned}$$

$$H_{in(H_2)}^{\wedge} = \int_{586}^{541} cp_{(H_2)} dT = -12.58 \text{ kJ/mol}$$

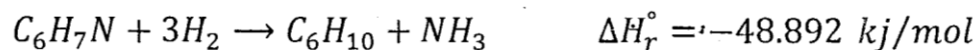
$$H_{in(C_3H_8S)}^{\wedge} = \int_{586}^{541} cp_{(C_3H_8S)} dT = -64.76 \text{ kJ/mol}$$

$$\therefore Q_1 = -66.31 \text{ kJ}$$

3.4.4.5.2 Denitrification Reaction (Q2):

Objective:

Calculate the heat transferred through De nitrification reaction



$$\Delta H_r^{\wedge}(586 \text{ k}) = \Delta H_r^{\circ}(298 \text{ k}) + \sum_{out} n_i H_i^{\wedge} - \sum_{in} n_i H_i^{\wedge}$$

$$= \Delta H_r^{\circ}(298 \text{ k}) + \int_{298}^{586} cp_{(C_6H_{10})} dT + \int_{298}^{586} cp_{(NH_3)} dT - \int_{298}^{586} cp_{(C_6H_7N)} dT - \int_{298}^{586} 3 cp_{(H_2)} dT$$

$$H_r^{\wedge}(586) = -48.892 + 38.86 + 11.8 - 64.38 - 82.21 = -21.98 \text{ kJ/mol}$$

$$H_{in(H_2)}^{\wedge} = \int_{586}^{541} cp_{(H_2)} dT = -12.72 \text{ kJ/mol}$$

$$H_{in(C_6H_7N)}^{\wedge} = \int_{586}^{541} cp_{(C_6H_7N)} dT = -13.31 \text{ kJ/mol}$$

$$\therefore Q_2 = -19.767 \text{ kJ}$$

3.4.4.5.3 De Oxygenation reaction (Q3):

Objective:

Calculate the heat transferred through Deoxygenating reaction (Q3)



$$\Delta H_r^{\wedge}(586 \text{ k}) = \Delta H_r^{\circ}(298 \text{ k}) + \sum_{out} n_i H_i^{\wedge} - \sum_{in} n_i H_i^{\wedge}$$

$$= \Delta H_r^{\circ}(298 \text{ k}) + \int_{298}^{586} cp_{(C_6H_6)} dT + \int_{298}^{586} cp_{(H_2O)} dT - \int_{298}^{586} cp_{(C_6H_6O)} dT - \int_{298}^{586} cp_{(H_2)} dT$$

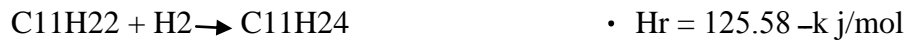
$$H_r^{\wedge}(586) = -62.581 - 136.65 + 10.63 - 35.78 - 81.4 = -305.78 \text{ kJ/mol}$$

$$H_{in(H_2)}^{\wedge} = \int_{586}^{541} cp_{(H_2)} dT = -12.59 \text{ kJ/mol}$$

$$H_{in(C_6H_6O)}^{\wedge} = \int_{586}^{541} cp_{(C_6H_6O)} dT = -66.48 \text{ kJ/mol}$$

$$Q_3 = -45.342 \text{ kJ}$$

3.4.4.5.4 Reaction for saturation (Q4):



$$\Delta H_r^\wedge(586 \text{ k}) = \Delta H_r^\circ(298 \text{ k}) + \int_{298}^{586} c_{p(C_{11}H_{24})} dT - \int_{298}^{586} c_{p(C_{11}H_{22})} dT - \int_{298}^{586} c_{p(H_2)} dT$$

$H_r^\wedge(586) = -125.58 + 95.59 - 96.91 - 81.39 = -207.93 \text{ kJ/mol}$

$H_{in(H_2)}^\wedge = \int_{586}^{541} c_{p(H_2)} dT = -12.59 \text{ kJ/mol}$

$H_{in(C_{11}H_{22})}^\wedge = \int_{586}^{541} c_{p(C_{11}H_{22})} dT = -17.14 \text{ kJ/mol}$

Q4 = - 187.13KJ

Q = Q1 + Q2 + Q3 + Q4

= - 66.31 - 19.767 - 45.342 - 187.13 = -318.36 KJ

3.4.4.6 Energy Balance around Striper:

Objective:

Calculate the Energy Balance around Striper

Q = n • H

Q1+Qs = Q2 + Q3

• H of diesel = 91.335 KJ/mol

n = 2.14

Q1 = 2.14 x 91.335 = 195.84K

• H at T2 = 52.36 KJ/mol

n = 0.023

Q2 = 0.023 x 52.36 = 1.184KJ

• H of steam at 240° C and 10 bar= 2921 k j/kg n = 2.08

..Qs = 2.08 *2921=6075 KJ

..Q3 =Q1 + Qs - Q2

= 195.84 + 6075 - 1.184 = 6269KJ

3.5 Design:

3.5.1 Introduction to Design:

Equipment must be located, design, constructed, adapted and maintained to suit the operation to be carried out. The layout and design of equipment must aim to minimize the risk of errors and permit affective cleaning and maintenance in order to avoid cross-contamination, build –up of dust or dirt, and, in general, and adverse effect on the quality of products.

Production equipment should not present any hazard to the production the part of the production equipment that com in the contact with the product the part of the product must not be reactive .additive .or absorptive .or absorptive to an extent that would affect the quality of the product.

3.5.2 Distillation Column Design:

3.5.2.1 Introduction:

The design consists of three steps:

1. Choice of type of column.
2. Number of trays.
3. Column diameter.

3.5.2.2 The choice between packed and plate column:

The following are the basic choice:

(a) System Factor, Divided into the Following:

1. Scale; for diameter. Less than approximately 1m packed tower are preferred because of fabrication cost of small trays. For large column plate tower are preferred since liquid distribution is problem and also the weight of large volume of packing.
2. Foaming (forth) it is produced by the bubbling action of the vapor thro' the liquid and, therefore packed column is preferred when foaming substance is used.

3. Fouling system, if system contains suspended solids or sludge plate tower are preferred.
4. Corrosive system, since corrosion —resistant ceramics are used in

Packed tower, packed tower is preferred (cheap).
5. Heat evolution, for removing of heat plate columns preferred, coil of cooling can be used.
6. Pressure drop (ΔP), in plate tower generally less P if the number of plate is not great.

(b) Physical Consideration:

- i) Maintenance, cleaning is easy in plate column, while in packet column packing must be remove.
- ii) Weight, packed column are heavier and need heavy support and foundation.

(c) Side stream:

Withdrawal of side streams easier in plate column, while in packed column is impossible.

3.5.2.3 Trays

There are three common types of trays these are:

- i) bubble cup trays
- ii) sieve trays
- iii) valve trays

Bubble cups are less preferred than sieve and valve trays, since sieve trays are lighter ,cheaper ,higher vapor liquid handling capacity, also pressure drop low and their construction is simple.

3.5.2.4 Operation problems of plate tower

- i) Entrainment, large amount of turbulence is set-up and liquid particles become entrained within gas carryover of these particles from tray to tray above is

known as entrainment, which reduces the concentration charge per tray, decreasing the efficiency.

- ii) Weeping, this happens when liquid leakage thro' the plate holes become excessive, as result that the vapor velocity is minimum.

3.5.2.5 Design procedures

1. Contacting device

- 1) No. of plate
- 2) Tray spacing
- 3) Feed point location
- 4) Column diameter
- 5) down corner cross sectional area
- 6) No. of holes

3.5.2.6 Calculation of No. of Plate:

Relative volatility (α) of components;

All the design procedure followed in the design stay is obtained from “Chemical Engineering vol.6”,

$$\alpha_{i,j} = \frac{k_i}{k_j} = \frac{p_i}{p_t} \div \frac{p_j}{p_t} = \frac{p_i}{p_j} = 1.23 \dots\dots\dots (3.4)$$

Where:

- P °i is vapor pressure of light component.
- P °j is vapor pressure of heavy component.
- We used Fenske equation to calculate no. of plates

$$N_{min} = \log \left(\frac{x_{lk}}{x_{hk}} \right)_D \left(\frac{x_{hk}}{x_{lk}} \right)_B / \log \alpha_{i,j} \dots\dots\dots (3.5)$$

Where:

N_{min} : minimum number of stage.

$\alpha_{i,j}$: average relative volatility.

$x_{,hk D}$: concentration of the heavy key in the top product.

$x_{,lk D}$: concentration of the light key in the top product.

$x_{,hk B}$: concentration of the heavy key if in the bottom product.

$x_{,lk B}$: concentration of the light key if in the bottom product.

$$N_{min} = \log \left[\frac{(0.80/0.15)(0.997/0.003)}{(1.23)} \right] = 3.159 \approx 4$$

Then we have to calculate the minimum reflux:

$$(1 - q) = \sum_i \left[\frac{\alpha_i x_{f,i}}{\alpha_i - \lambda} \right] \dots \dots (3.6)$$

$$V_{min} = \sum_i \frac{\alpha_i D x_{i,D}}{\alpha_i - \lambda_i} \dots \dots (3.7)$$

$$L_{min} = V_{min} - D \dots \dots (3.8)$$

$$R_{min} = L_{min} / D \dots \dots (3.9)$$

Where :

q: the feed condition .

α_i : the volatility of the keys

$x_{f,i}$: the concentration of the key component

L_{min} : minimum liquid flow

V_{min} : minimum Vapor flow

R_{min} : minimum Reflex Ratio

$$R_{min} = 1.27$$

Assume that $R=2 \cdot R_{\min}$ \longrightarrow $R = 2.54$

Calculate the No. of moles of liquid and vapor

From Gilliland equation

$$X = \frac{R - R_{\min}}{R + 1} = \frac{2.54 - 1.27}{2.54 + 1} = 0.35 \text{ moles} \quad \dots\dots\dots (3.10)$$

$$Y = 1 - X^{0.2} = 1 - 0.35^{0.2} = 0.185 \text{ moles}$$

Theoretical No. of plate N_{th} from Gilliland correlation:

$$N_{th} = \frac{N_{\min} + Y}{1 + Y} = \frac{4 + 0.185}{1 + 0.185} = 5.13, \approx 6 \text{ plates} \quad \dots\dots\dots (3.11)$$

Actual No. of plate can be found from knowledge of efficiency (η) of plate where is equal (75%)

$$\text{There fore, } N_a = \frac{N_{th} - 1}{\eta} = \frac{6 - 1}{0.75} = 6.67 \approx 7 \text{ plates} \quad \dots\dots\dots (3.12)$$

3.5.2.7 Feed Point Location:

We used Kirdbride equation:

$$\log \frac{N_r}{N_s} = 0.206 \log \left[\left(\frac{B}{D} \right) \left(\frac{x_{f,hk}}{x_{f,lk}} \right) \left(\frac{x_{b,lk}}{x_{d,hk}} \right)^2 \right] \quad \dots\dots\dots (3.13)$$

Where:

N_r : number of stages above the feed, including any partial condenser.

N_s : number of stages below the feed, including the reboiler.

B : molar flow bottom product.

D : molar flow top product.

$X_{f,hk}$: concentration of the heavy key in the feed.

$X_{f,lk}$: concentration of the light key in the feed.

$X_{d,hk}$: concentration of the heavy key in the top product.

$X_{b,lk}$: concentration of the light key if in the bottom product.

$$\frac{N_r}{N_s} = 0.68 \quad ; \quad N_r = 0.68N_s$$

$$N_s + N_r = 6$$

$$N_r = 6 - N_s$$

$$6 - N_s = 0.68N_s$$

$$N_s = \frac{6}{1.68} = 3.56 \approx 4 \text{ plate}$$

So the feed point in the fourth stage.

3.5.2.8 Diameter of the column (Dc):

$$D_c = \sqrt{\frac{4v_w}{\pi \rho_v u_v}} \dots\dots\dots (3.14)$$

$$U_v = -0.171L_t^2 + 0.27 - 0.047 \left[\frac{\rho_1 - \rho_v}{\rho_v} \right]^{0.5} \dots\dots\dots (3.15)$$

where:

U_v : max allowable vapor velocity

L_t : Plate spacing, m (range 0.5-1.5)

$$\rho_1 = 780 \text{ kg/m}^3$$

$$\rho_v = 3.11 \text{ kg/m}^3$$

Take $L_t = 0.6\text{m}$ there for $U_v = 0.844\text{m/s}$

$$D = 1.12 \text{ m}$$

3.5.2.9 Plate Area:

A_t , Tower cross sectional area (m^2) A_t

$$A_t = \frac{\pi}{4} D_c^2 = 1m^2 \dots\dots\dots (3.16)$$

Where:

A_d , down corner cross sectional area (m^2) $= 0.12A_t = 0.12 m^2$

A_n , net area $= A_t - A_d = 1 - 0.12 = 0.88 m^2$

A_a , active area $= A_t - 2A_d = 1 - (2 * 0.12) = 0.76m^2$

A_o , hole area take 10 percent at $= 0.1 * 1 = 0.1m^2$

Diameter of hole 8mm (assumed).

$$\text{No. of holes} = \frac{A_o}{\frac{\pi d_o^2}{4}} = 0.1 * 4/\pi * (0.008)^2 = 1989.43 = 1990 \text{holes}$$

Diameter of tray D_n

$$D_n = D_c - D_d = 1.12 - 0.39 = 0.72m$$

3.5.2.10 Height of Tower (Ht)

$$H_t = (N_a - 1) L_t + N_a/10 + T_s + T_B \dots\dots\dots (3.17)$$

Where:

T_s : height of top tower

T_B : height of bottom tower

$T_s + T_B$ taken as 20% of $[(N_a - 1) L_t + N_a/10]$

$$H_t = (7-1) (0.6) + 7/10 + 0.20 [(7- 1) (0.6) + 7/10] = 5.16m$$

3.5.2.12 Summary of design procedure:

Table (3.5): Design Summary

No.	Material	Unit
1	Column diameter	1.12m
2	Column cross sectional	1m ²
3	Down comer cross sectional area	0.12m ²
4	Hole area	0.1m ²
5	Height of column	5.16 m
6	No. of minimum. Plate	5
7	No. of theory plate	6
8	No. of actual plate	7
9	No. of holes	1990

Chapter 4

4. Results and Discussion

4.1 Results:

From the material balance and the design of stripper, these results were obtained:

Table (4.1): Material Balance of DHT

No.	Material name	Measuring unit					
		rate %		Kg/h		t/d	
		Nominal	Actual	nominal	actual	nominal	Actual
	Input part						
1	catalytic diesel oil	100	100	62500	54975	1500	1319.40
2	reformed hydrogen	2.36	2.39	1474	1317	35.38	31.61
3	hydrogen*	0.25	0.24	156	131	3.74	3.14
4	desalted water	4.8	5.46	3000	3000	72.00	72.00
5	steam stripping	2.08	2.09	1300	1150	31.20	27.60
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75
	Output part						
1	refined diesel oil	99.08	99.08	61925	54472	1486.2	1307.33
2	crude gasoline	1.03	1.03	644	568	15.46	13.63
3	low-component	0.66	0.64	411	351	9.86	8.42
4	tower top gas	1.7	1.67	1060	920	25.44	22.08
5	acid sewage	6.55	7.29	4094	4008	98.26	96.19
6	oil-bearing	0.30	0.30	188	167	4.51	4.01
7	Loss	0.17	0.17	108	87	2.59	2.09
	Sum total	109.49	110.18	68430	60573	1642.3	1453.75

Table (4.2): Design Summary

No.	Material	Unit
1	Column diameter	1.12m
2	Column cross sectional	1m ²
3	Down comer cross sectional area	0.12m ²
4	Hole area	0.1m ²
5	Height of column	5.16 m
6	No. of minimum. Plate	5
7	No. of theory plate	6
8	No. of actual plate	7
9	No. of holes	1990

4.2 Discussion:

From the catalyst property found that the maximum operating temperature is 350c⁰ so that the optimum operating conditions (pressure, temperature) is applied to the unit so nothing can be happen to the reaction part.

For the physical stage which is mainly content separation process. Firstly the most important part is the stripping column which is aim mainly to adjust the flash point by separating the lights, from design stage found that the optimum dimension required is mentioned in table (4.2).

Secondly, other important result is all the gas formed is collected and then processed and used as source of energy for the heating equipment, and the output liquid from the bottom of the column is near free of sulfur, which is the final product (diesel).

Chapter 5

5. Conclusion and Recommendations

5.1 Conclusion:

From the above discussion in chapter 4 it is concluded that the unit operates at the optimum and suitable operating conditions against the designed capability, which is led to the improved quality of the produced diesel and minimum sulfur content.

5.2 Recommendations:

From the previous results it is strongly recommended that:

- 1- Using Ultra Low Sulfur Diesel (ULSD) technology as a development technology in the hydrotreating process.
- 2- Using other or modified type of catalyst which can be used in hard condition to enhance the reaction part.
- 3- More studies must be done in this field to reach the free sulfur content of the diesel.

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