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Simulation of Hydrodesulphurization (HDS) Unit of Kaduna Refining and Petrochemical Company Limited

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Abstract

This research was carried out to simulate the Hydrodesulphurization unit using ASPEN HYSYS with the aim of removing impurities such as Sulphur, Nitrogen and Oxygen in raw Kerosene. The simulation is based on conditions and parameters (mass flow rates, temperature and pressure readings) obtained from the Linear Alkyl Benzene (LAB) plant of the Kaduna Refining and Petrochemical Company (KRPC). After the successful completion of the simulation, total removal of impurities was achieved as the concentration of sulphur, nitrogen and oxygen in mole fraction present in the treated Kerosene stream was approximately zero. The treated Kerosene composition indicated 0.0021, 0.3342, 0.3322 and 0.3315 mole fractions of n-C13, n-C14, n-C15 and n-C16 respectively.

Key words: Simulation, Hydrodesulphurization, Aspen Hysys, Impurities.

1. Introduction

Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove impurities mainly sulphur containing compounds from hydrocarbon products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. Sulphur, Nitrogen and Oxygen are already present in crude oil while unsaturated components are produced at the refineries. The purpose of removing the impurities mainly sulphur is to reduce the sulphur dioxide(SO_2) emissions that result from using those fuels in automotive vehicles, aircrafts, rail/road locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion. An HDS unit in the petroleum refining industry is also often referred to as a hydrotreater [1].

Hydrotreating or hydroprocessing refers to a variety of hydrogenation processes which saturate unsaturated hydrocarbons and remove Sulphur [by hydrodesulphurization (HDS)], Nitrogen [by hydrodenitrogenation (HDN)], Oxygen [by hydrodeoxygenation (HDO)] and metals [byhydrodemetallization (HDM)] from different petroleum product streams in a refinery. The main aim of hydrotreating is to minimise air pollution emissions, to avoid poisoning of noble metals and acid catalysts used in catalytic reforming and cracking and to improve the fuel quality [2].

The Kerosene hydrodesulphurization process is a catalytic hydrogenation method used to upgrade and desulphurize the kerosene feedstock with negligible effect on the boiling range of the feed, in the presence of large amount of hydrogen. The reaction is carried out at high pressure and moderate temperature [3]. Liquid hydrocarbon fuel such as Kerosene is promising energy source of fuel cell owing to their high energy density and easy handling. [4] and [5], although sulphur compounds in commercial Kerosene are more refractory than those in city gas or liquefied petroleum gas (LPG) [4].

The industrial hydrodesulphurization processes include facilities for the capture and removal of impurities such as hydrogen sulphide (H_2S) gas, ammonia (NH_3) and steam (H_2O). In petroleum refineries, the hydrogen sulphide gas is then subsequently converted into byproduct elemental sulphur or sulphuric acid (H_2SO_4). In fact, the vast majority of sulphur produced worldwide was byproduct of sulphur from refineries and other hydrocarbon processing plants [6] and [7].

The Kerosene hydrodesulphurization unit can be subdivided into three sections namely reaction, compression and stripping sections respectively. In every section an operation or a definite number of related operations are carried out [3].

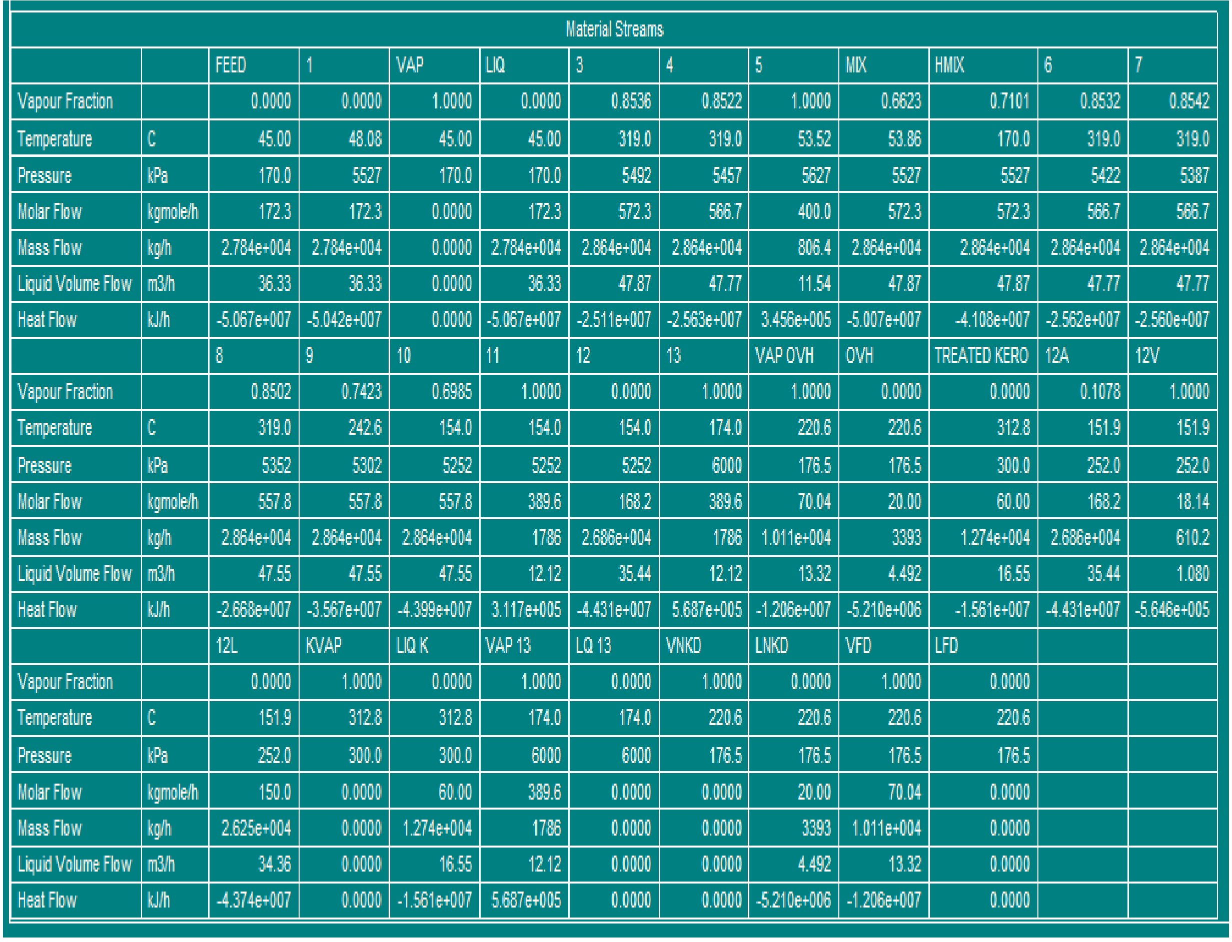
The impurities such as Sulphur, Nitrogen and Oxygen found in crude oil and its byproducts cause serious impact on both environment and plant operation and in turn on the company’s economy.

2. Theory

Aspen Hysys

ASPEN HYSYS is software for simulation of process plants and refineries. It has an extensive database, reliable thermodynamic models and rigorous equipment models, as well as tools for estimation of physical properties, liquid-vapour phase equilibrium, energy and material balances. ASPEN HYSYS facilitate the design, sizing, simulation and optimization of a chemical and/or a refinery plant and the required equipment. Although user-friendly, considerable effort must be expended to master its use [8]. ASPEN HYSYS was used to simulate the Kerosene hydrodesulphurization unit. The process parameters and state conditions for all the streams are presented in table 1.

Table 1: Process parameters and state conditions for the streams



Material Streams												
		FEED	1	VAP	LIQ	3	4	5	MIX	HMIX	6	7
Vapour Fraction		0.0000	0.0000	1.0000	0.0000	0.8536	0.8522	1.0000	0.6623	0.7101	0.8532	0.8542
Temperature	C	45.00	48.08	45.00	45.00	319.0	319.0	53.52	53.86	170.0	319.0	319.0
Pressure	kPa	170.0	5527	170.0	170.0	5492	5457	5627	5527	5527	5422	5387
Molar Flow	kgmole/h	172.3	172.3	0.0000	172.3	572.3	566.7	400.0	572.3	572.3	566.7	566.7
Mass Flow	kg/h	2.784e+004	2.784e+004	0.0000	2.784e+004	2.864e+004	2.864e+004	806.4	2.864e+004	2.864e+004	2.864e+004	2.864e+004
Liquid Volume Flow	m3/h	36.33	36.33	0.0000	36.33	47.87	47.77	11.54	47.87	47.87	47.77	47.77
Heat Flow	kJ/h	-5.067e+007	-5.042e+007	0.0000	-5.067e+007	-2.511e+007	-2.563e+007	3.456e+005	-5.007e+007	-4.108e+007	-2.562e+007	-2.560e+007
		8	9	10	11	12	13	VAP OVH	OVH	TREATED KERO	12A	12V
Vapour Fraction		0.8502	0.7423	0.6985	1.0000	0.0000	1.0000	1.0000	0.0000	0.0000	0.1078	1.0000
Temperature	C	319.0	242.6	154.0	154.0	154.0	174.0	220.6	220.6	312.8	151.9	151.9
Pressure	kPa	5352	5302	5252	5252	5252	6000	176.5	176.5	300.0	252.0	252.0
Molar Flow	kgmole/h	557.8	557.8	557.8	389.6	168.2	389.6	70.04	20.00	60.00	168.2	18.14
Mass Flow	kg/h	2.864e+004	2.864e+004	2.864e+004	1786	2.686e+004	1786	1.011e+004	3393	1.274e+004	2.686e+004	610.2
Liquid Volume Flow	m3/h	47.55	47.55	47.55	12.12	35.44	12.12	13.32	4.492	16.55	35.44	1.080
Heat Flow	kJ/h	-2.668e+007	-3.567e+007	-4.399e+007	3.117e+005	-4.431e+007	5.687e+005	-1.206e+007	-5.210e+006	-1.561e+007	-4.431e+007	-5.646e+005
		12L	KVAP	LIQ K	VAP 13	LQ 13	VNKD	LNKD	VFD	LFD		
Vapour Fraction		0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000	1.0000	0.0000		
Temperature	C	151.9	312.8	312.8	174.0	174.0	220.6	220.6	220.6	220.6		
Pressure	kPa	252.0	300.0	300.0	6000	6000	176.5	176.5	176.5	176.5		
Molar Flow	kgmole/h	150.0	0.0000	60.00	389.6	0.0000	0.0000	20.00	70.04	0.0000		
Mass Flow	kg/h	2.625e+004	0.0000	1.274e+004	1786	0.0000	0.0000	3393	1.011e+004	0.0000		
Liquid Volume Flow	m3/h	34.36	0.0000	16.55	12.12	0.0000	0.0000	4.492	13.32	0.0000		
Heat Flow	kJ/h	-4.374e+007	0.0000	-1.561e+007	5.687e+005	0.0000	0.0000	-5.210e+006	-1.206e+007	0.0000		

3. Methodology

The scope will be limited to the use of the software to illustrate how a Kerosene hydrodesulphurization (HDS) unit can be created and tested virtually, based on conditions and parameters obtained from the Linear Alkyl Benzene (LAB) plant of Kaduna Refining and Petrochemical Company (KRPC). Simulation of the HDS was carried out in order to generate enough data for the analysis. The unit was simulated using ASPEN HYSYS software version 7.2 employing KRPC, HDS unit data log sheet (daily mass flow, temperature and pressure readings). The temperature, pressure, molar flow rates, vapour fraction, liquid volume flow and heat flow used for the analyses were obtained from the simulation results. The modification involves using four reactors arranged in series as a unit while pumps and other auxiliary equipment were unaltered. The process flow diagram of the unit is shown in figure 1.

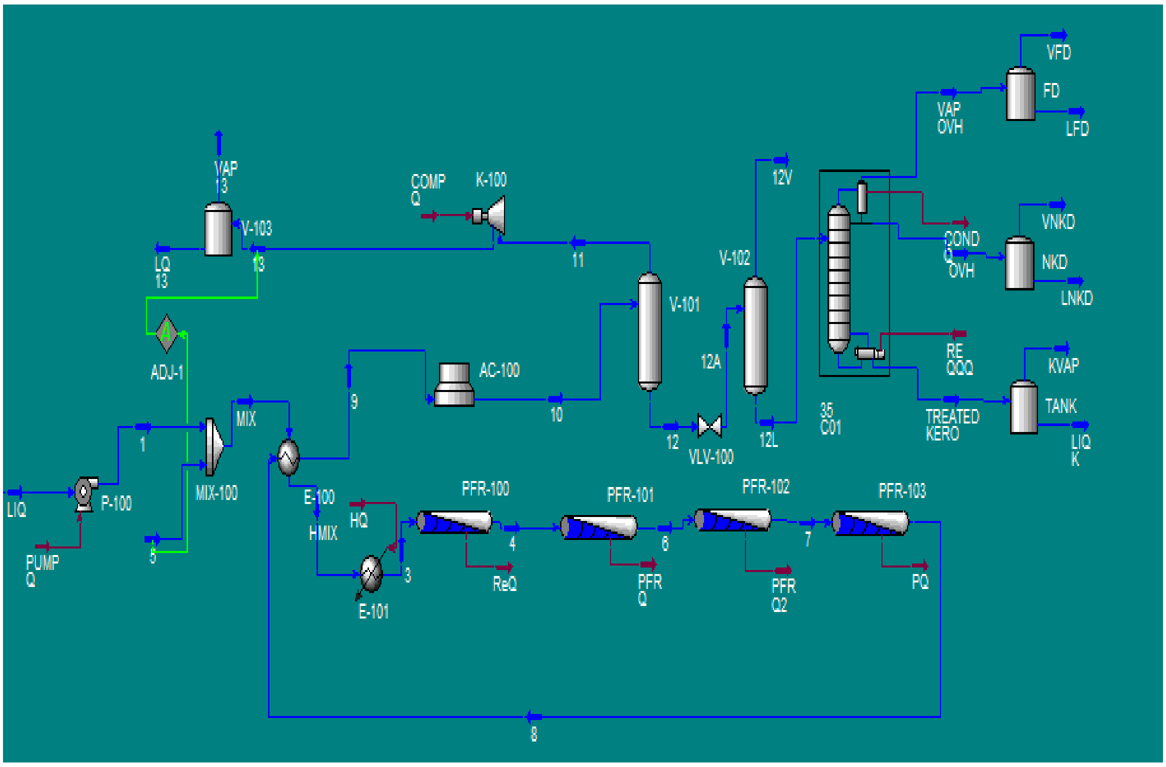


Figure1: Process flow diagram of the HDS Unit

3.1 Process Description

The liquid feed (stream LIQ) is pumped up to the required elevated pressure of 5527kPa and is joined by a stream of rich hydrogen gas (stream 5). The resulting liquid-gas mixture is preheated by flowing through a heat exchanger (E-100). The preheated feed then flows through a fired heater (E-101) where the feed mixture is totally vaporised and heated to the required elevated temperature of 319^{o}C before entering the reactors PFR-100, PFR-101, PFR-102 and PFR-103 respectively, and flowing through a fixed-bed of catalyst where the hydrodesulphurisation reaction takes place.

The hot reaction products are partially cooled by flowing through the heat exchanger (the tube side of E-100) where the reactor feed was preheated and then flows through an air-fin cooler (AC-100) before it flows to a flash separator (V-101) where the reaction products are flashed out together with the hydrogen gas. The bottom i.e. the liquid outlet of the flash separator flows to a low pressure flash separator (V-102) to remove the stubborn gases that could not be removed from the first separator.

The liquid from the flash separator (V-102) vessel is routed through a reboiled stripper distillation tower (35-C01). The bottom product from the stripper is the final desulphurised liquid product from the hydrodesulphurisation unit.

The overhead traces of sour gas from the stripper (35-C01) contain hydrogen, methane, ethane, hydrogen sulphide, propane and perhaps, some butane and heavier components which are condensed and collected in the overhead receiver tank (FD). The heavier components retrieved as liquid naphtha flows to tank (NKD) which is later sent for refining. The treated Kerosene is finally taken from the bottoms of the stripper column and sent to a storage tank.

4. Result and Discussion

The HDS plant basically consists of three sections namely; Reaction section, Stripping section and the Compression section. Reaction and Stripping sections have been considered as they are the area of interest.

4.1 Reaction Section

The operating temperature and pressure of the reaction section of the simulated HDS unit are 319^{o}C and 5492kPa (56kg/cm^{2}) respectively. At this condition, the pure hydrogen gas and the major impurities such as Sulphur from Thiopene, Nitrogen from Pyridine, Oxygen from Phenols and the Olefins become ionized and charged hence weakening their bonds and charged into the reactor. The reactor effluent is then cooled with an air fin cooler and then sent to the stripping section.

4.2 Rate of Reaction

The plot of rate of reaction against length of reactor is shown below for the various reactions.

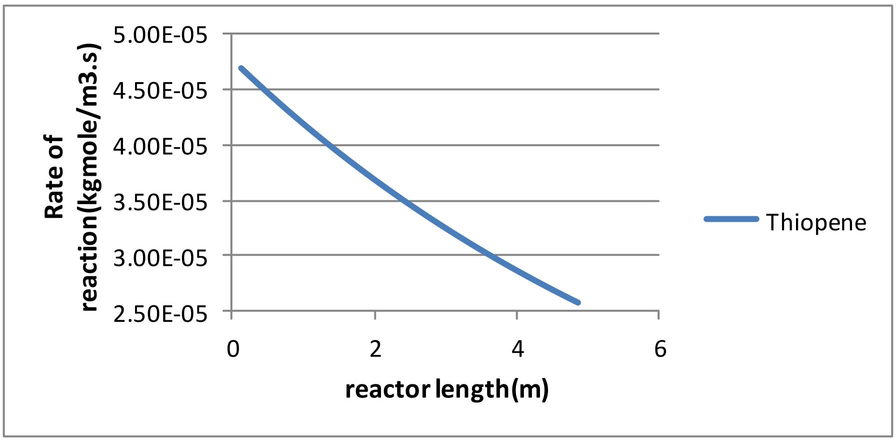


Figure 2: Rate of Reaction for Thiopene (Sulphur containing molecule)

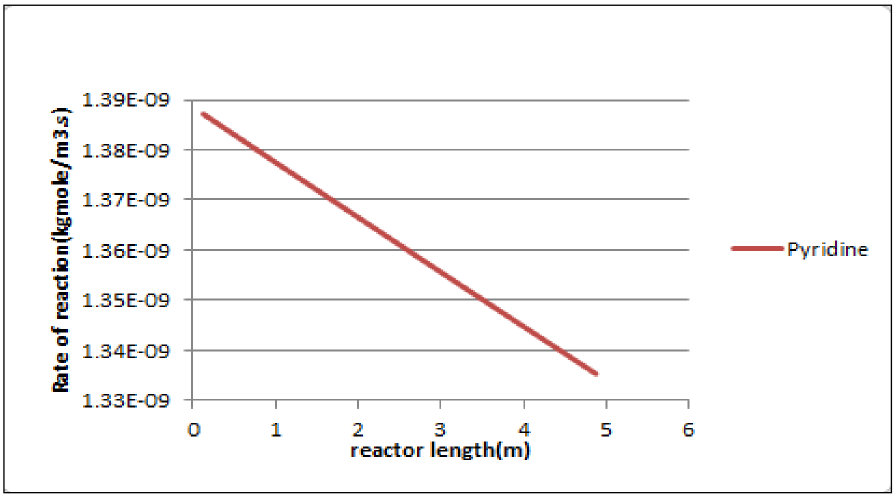


Figure 3: Rate of Reaction for Pyridine (Nitrogen containing molecule)

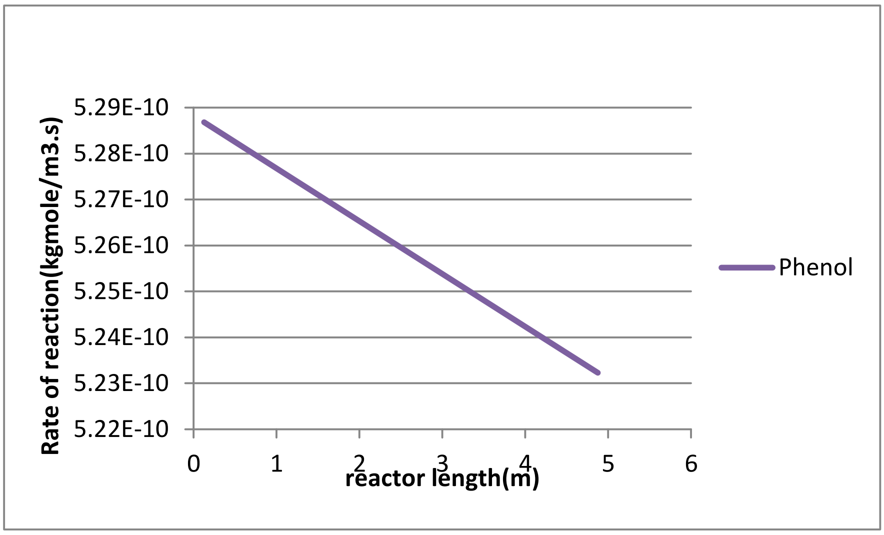


Figure 4: Rate of reaction for phenols (Oxygen containing molecule)

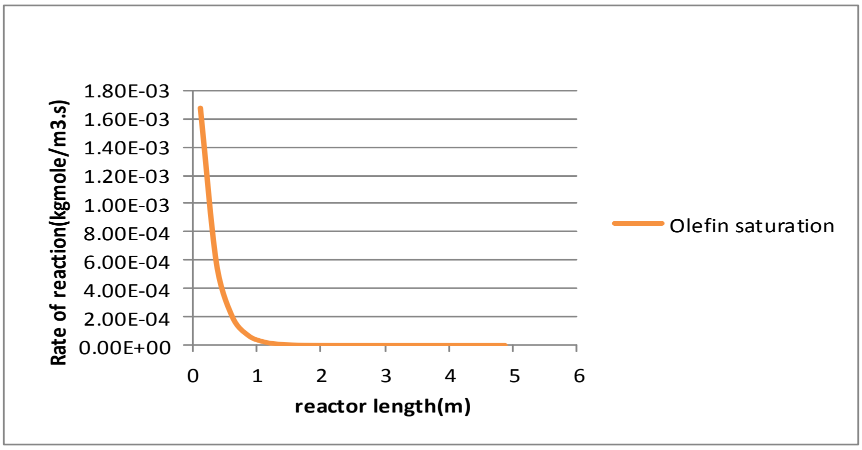


Figure 5: Rate of Reaction for Olefin

The various plots in Figures 2, 3 and 4 of the rate of reactions across the reactor length show that the rate of reaction decreases with length of reactor, with all the reactions being exothermic, the reaction proceeds immediately when the process fluid is charged into the reactor and then decrease as the limiting reactant is exhausted.

As for the reaction of olefin saturation in figure 5, it was observed that the rate of reaction terminates within one meter of the Plug Flow Reactor (PFR) as seen from the plot. This may be attributed to the reaction constants or the selected thermodynamic data.

4.3 Stripping Section

The stripping section consists essentially of a stripper with 27 trays column, reboiler and a reflux condenser for the effluents and receivers (tanks) for the overheads and bottoms.

The mixture of the reactor effluent, make up gas enters the reactor products separator (V-101) at a high pressure of 5492kPa (56kg/cm^2) where the hydrocarbon, water and gas phase are separated and removed individually. A circumferential mesh mat is placed in the separator to help separate the hydrocarbons and water from the gas phase.The liquid hydrocarbon phase is drawn from the bottom of the reactor product separator (V-101) and sent to the low pressure flash drum operating at 490kPa (5kg/cm^2).At this lower pressure, the gases that were absorbed by the kerosene(such as H_2S,C3,C4 etc) flash out and are separated from the hydrocarbon phase.

The liquid hydrocarbon phase is drawn from the bottom of the low pressure flash drum and fed to the stripper column at the ninth tray. The top temperature and pressure of the stripper column are 220^{o}C and 176.5kPa (1.8kg/cm^2) while the bottom temperature is 312^{o}C. In the stripper column, all the light materials are removed from the treated kerosene in order to meet flash point specifications.

The vapours leaving the top of the tower are condensed and collected in the overhead receiver tank (FD). The overhead hydrocarbon is also condensed and collected in a tank (NKD), the net overhead liquid is sent to the refinery. The treated Kerosene is finally taken from the bottoms of the stripper column and sent to a storage tank or sent to the MOLEX unit.

4.4 Composition of Impurities in Treated Kerosene

A plot of composition of impurities against tray position within the stripper column is shown in figure 6.

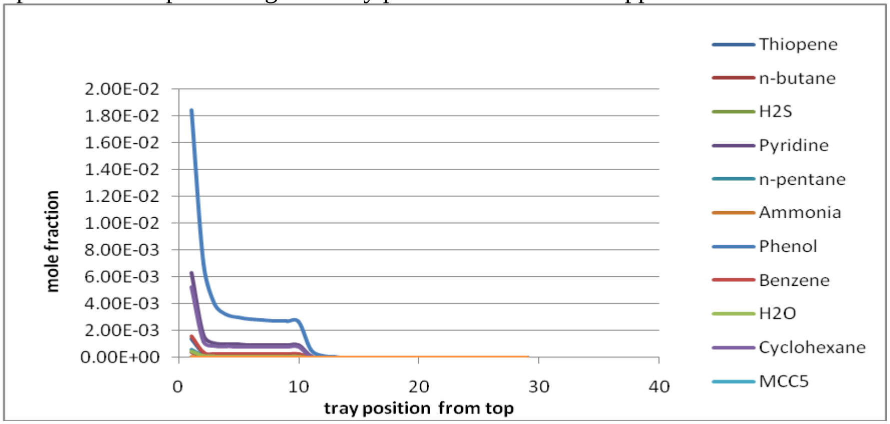


Figure 6: Composition of Impurities across the Stripper Column form the top

From figure 6, it seems that the composition of impurities was higher at the top of the column; the composition is highest at the condenser. No impurity is present at the bottom as from the thirteenth tray. This is because all the components are in a vapor phase and rise up to the top. The plot shows that there is a perfect separation in the column since the bottom of the stripper is free of impurities as pure treated Kerosene is collected from the bottom.

The plot of composition of treated Kerosene across stripper column is shown below:

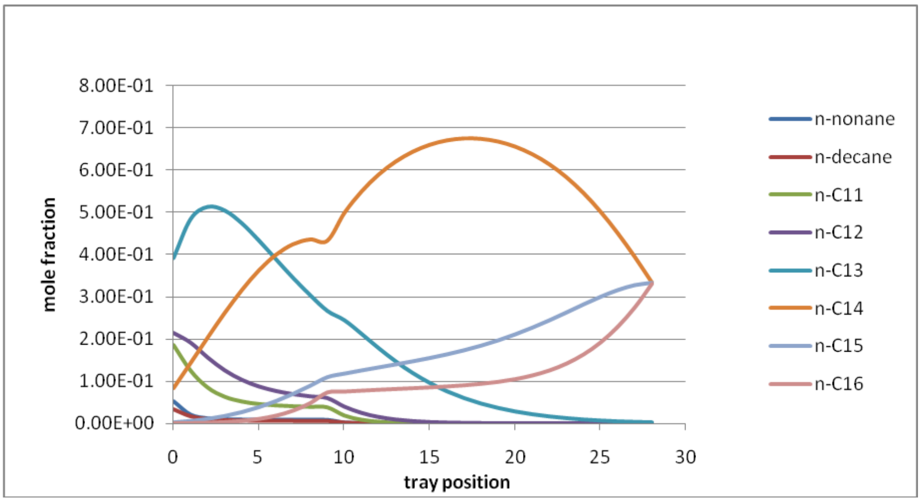


Figure 7: Composition of treated Kerosene with respect to the tray position from the top

The above plot (Figure 7) shows the distribution of the components of pure Kerosene across stripper column. The components of the treated Kerosene are n-C13,n-C14,n-C15 and n-C16 respectively with compositions of 0.0021,0.3342,0.3322 and 0.3315 respectively, which were predominant at the bottom of the column, while the lighter components such as n-nonane,n-decane,n-C11,n-C12 and n-C13 are predominant at the top of the column. This may be as a result of the temperature as the higher the temperature, the more the lighter components rise up. The above result is in good agreement with literature as pure Dual Purpose Kerosene (DPK) components ranges between n-nonane to n-C16.

The Temperature and Pressure distribution across Stripper from the top of tray position is graphically shown in figure 8.

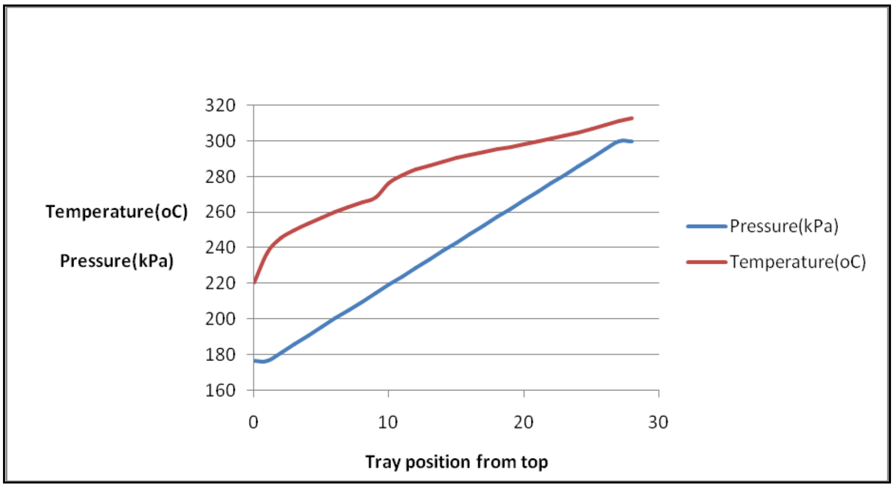


Figure 8: Temperature and Pressure against Tray position.

From the above plot (Fig. 8), it can be seen that the temperature and pressure was higher and higher coming from the top to the bottom of the stripper. Higher temperature in the bottom is as a result of the reboiler which heats the content of the bottom, while a lower temperature at the top is as a result of the reflux condenser. High temperature is required at the bottom of the column so that the light key will rise up to the top of the column because the higher the temperature, the lower the density. Hence lighter components at the bottom rise up the top of the column. From design, the pressure of the feed entering the stripper is higher than the condenser pressure and lower than the reboiler pressure.

5. Conclusion

The Hydrodesulphurization unit was successfully simulated under feasible working conditions, and the applicability of Aspen Hysys as a simulation software package has been demonstrated by studying the effect of the process variables on the plants throughput or efficiency. The following findings were deduced from the simulated plant;

1. The components of the treated Kerosene are n-C13,n-C14,n-C15 and n-C16 respectively with compositions of 0.0021,0.3342,0.3322 and 0.3315 mole fractions respectively.

2. Roughly100% removal of impurities was achieved.

3. The optimized working temperature and pressure of the reaction section are 319°C and 5492kPa (56kg/cm^2) respectively. All the reactions are exothermic and proceeds immediately when the reactor feed is charged and decreases as the limiting reactant is exhausted.

4. Only a 1.5m reactor length is required for the reaction of olefin saturation.

Recommendation

Provisions should be made to simulate multiple reactions in one reactor.

Acknowledgement

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