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Design and Simulation of Plug Flow Reactor and Distillation Column for the Production of Aniline via Nitrobenzene Hydrogenation

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ABSTRACT
The objective of this study is to design a plug flow reactor and distillation column for the production of 95% purity aniline from the hydrogenation of nitrobenzene. The hydrogenation of nitrobenzene took place in a plug flow reactor via the heating and mixing of nitrobenzene with hydrogen at 300^0C for aniline production and the produced aniline was purified via a distillation column. Aspen Hysys software and MatLab simulation tool were applied in carrying out this research study, and the simulation converged effectively yielding 251.47kmol of aniline at 95% purity, reflux ratio of 1.816, boil up ratio of 28.98 with a condenser duty of 3.02 x 10^7 kJ/hr. The design parameters such as column internal configurations, column tray, weir geometry, downcomer geometry and plug flow reactor were simulated using MatLab simulation tool and Aspen Hysys software, and results were compared, which yielded minimal deviations that shows the effectiveness of the operational process. Thus, the hydraulic plot showed entrainment of 0% weeping and 0% downcomer backup, and the column internals gave a weir height of 50.8mm, a downcomer clearance of 38.1mm and a side weir length of 1.628m at constant pressure. Hence, the research study operational process yielded an improved Aniline product purity with less convergence time.

KEYWORDS: *Aniline, Nitrobenzene, Distillation Column, Plug Flow reactor, Aspen Hysys, MatLab*

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I. INTRODUCTION

Aniline, also known as aminobenzene or phenylamine, has 6 carbon atoms, 7 hydrogen atoms, and 1 nitrogen atom in its chemical formula of C_6H_7N or $C_6H_5NH_2$. Due to the amino group in aniline's structure, it is also an amine, and thus classified as an aromatic amine [1]. Aniline is used in rubber accelerators and anti-oxidants, dyes and intermediates, photographic chemicals, as isocyanates for urethane foams, in pharmaceuticals, explosives, petroleum refining; and in production of diphenylamine, phenolics, herbicides and fungicides [2]. It ignites readily, burns with a smoky flame, which is a characteristic of aromatic compound [3]. It is generally colourless, oxidizes slowly in air and gives a red-brown tint to age samples. The structural formula of aniline is shown in Figure 1 [4].

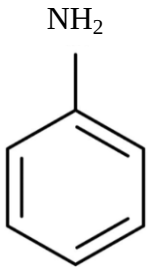

Figure 1: Aniline Structure

The International Union of Pure and Applied Chemistry (IUPAC) name for aniline is Phenyl-amine, while other names includes Aminobenzene and Benzamine. The global consumption of Aniline reached about 6.7million tonnes in 2019 [2]. It was first produced by Otto Unverdorbeni in 1826 by the destructive dry

distillation from the leaves of indigo plant, called indigofera[5]. Several methods or techniques for production of aniline includes catalytic vapour phase reduction of Nitrobenzene, reduction of Nitrobenzene with iron fillings using hydrochloric acid as catalyst, catalytic reaction of Chlorobenzene and aqueous Ammonia, ammonolysis of Phenoletc[6, 7, 8, 9].This mechanism was first proposed by Haber in 1826and it is reliable and widely accepted[10]. Thus, the production of aniline viathe hydrogenation of Nitrobenzene is an important method that produces aniline in commercial quantity. The main importance of this study is in the purity of aniline produced via the plug flow reactor, which is improved to 95% purity through distillation operation. The use of AspenHysys simulation in this project has enhance efficiency, accuracy and speed up or accelerates the production of Aniline.

Therefore, this research study focused on design and simulation of a plug flow reactor and distillation column for the production of 95% purity aniline via hydrogenation of nitrobenzene using Aspen Hysys as the simulation tool. The economic viability of the process, the effects of operational parameters on the yield of aniline and comparison of MatLabsimulated result with Aspen Hysys software were also investigated.

II. MATERIALS AND METHODS

2.1 Materials

The materials and unit operations used for this research study includes nitrobenzene, hydrogen, plug flow reactor, distillation column, Mixer, Aspen Hysysetc.

2.2 Aspen Hysys Process Description

The reaction equation for the production of aniline via the hydrogenation of nitrobenzene is expressed thus.

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O. \qquad (1)$$

The process flow sheet for the production of aniline from hydrogenation of nitrobenzene from Aspen Hysys is shown in Figure 1.Nitrobenzene is heated above its room temperature of 24℃ to 300℃, the heated nitrobenzene is then sent to the Mixer (Mix-100), where it is mixed with Hydrogen. The mixed feed is then fed into a plug flow reactor (PFR-100: I.D 15mm and 500mm long) at atmospheric pressure and temperature of 300^0C via a separator (CRV-100). Excess hydrogen from the effluent is recycled back to the mixer from the separator. At the top of the separator, the water generated is removed as the overhead product while the bottom mixture stream (aniline and nitrobenzene) is sent to the distillation column (T-101) for separation of aniline and nitrobenzene based on difference in boiling point. The produced aniline is recovered at the top with about 95% purity while at the bottom product is unconverted nitrobenzene. The Aniline is cooled and then stored.

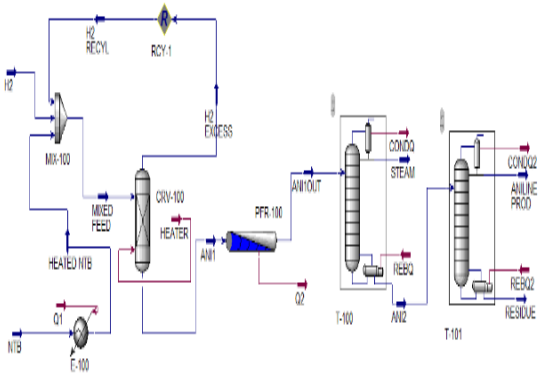

Fig. 2: Process Flow Diagram from Aspen Hysys.

2.3 Design Model Equations

Plug Flow Reactor is a tubular reactor with a continuous flow and often used for both liquid-Phase and gas-phase reaction [11]. The reactants are continually fed into a cylindrical tube and the products are continuously withdrawn [12]. Also, the distillation column is used to separate a liquid or vapour mixture of two or more substance into its component fraction of desired purity, and it is divided into the stripping andrectifying sections respectively[13]. The principle adopted in the column is the difference in boiling point or relative volatility of the constituent mixtures. The difference that exist between the liquid and the vapour composition forms the basis for the separation [14]. The design and energy balance equations for the plug flow reactor and distillation column are discussed.

2.3.1 Design Models for Plug Flow Reactor

A tubular liquid-phase plug flow reactor is shown in Figure 3

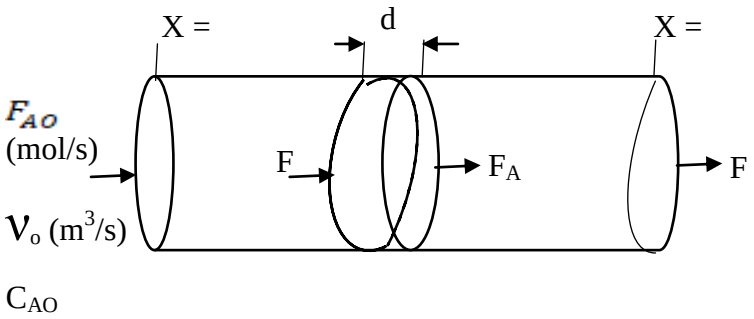

Fig. 3: Schematic Plug Flow Reactor.

The following assumptions were applied in modellingthe tubular plug flow reactor

i. A steady state tubular plug flow reactor is considered.
ii. The hydrogenation process is in liquid phase operation.
iii. The gases behaviour are assumed to be ideal.
iv. The reaction rate equation is assumed to be linear first order

Based on the above assumptions, the following steps were adopted.

i. Determine general mole balance for the Reactor.
ii. Deduce the reaction equations in terms of conversion.
iii. Express the rate law as a function of conversion in reaction rate -$r_A = f(x)$.
iv. Determine the rate law from concentration (C_A) and more of stoichiometric tables.
v. If no change in moles and pressure drop, then combine Rate law and stoichiometric tables.
vi. Evaluate your equations and solve the problem

Therefore, the general material balance equation for a steady state tubular plug flow reactor is expressed as

$$\begin{bmatrix}\text{Rate of}\\ \text{inflow of}\\ \text{materials}\\ \text{into the}\\ \text{Reactor}\end{bmatrix} = \begin{bmatrix}\text{Rate of outflow}\\ \text{of material from}\\ \text{the Reactor}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\ \text{Generation of}\\ \text{Material in}\\ \text{the Reactor}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\ \text{accumulation}\\ \text{of materials}\\ \text{in the Reactor}\end{bmatrix} \quad (2)$$

Hence, based on the above assumptions and steps involved in this research analysis, the length of the tubular plug flow reactor in terms of fractional conversion is expressed as

$$L_R = \frac{4F_{Ao}}{\pi(D)^2} k \int_o^{X_A} \frac{dX_A}{C_{Ao}} \quad (3)$$

2.3.2 Energy Balance for Plug Flow Reactor

The general energy balance equation for the plug flow reactor in terms of rate equation is expressed as:

Accumulation = Energy in – Energy out + Heat added. (4)

Thus, based on the above assumptions and solution steps highlighted above, the steady state energy equation for this research study is expressed as

$$\left(F_A C_{P_A} + F_B C_{P_B} + F_C C_{P_C}\right)\frac{dT}{A_x dz} = \Delta H_R(-r_A) + UA(T - T_C) \quad (5)$$

2.3.3 Design Models of the Distillation Column.

The distillation column is essential for the separation of liquid mixtures. As stated earlier, changes in the relative volatility is used (difference in vapour pressure) [15]. In this research study, a perforated plate is applied in the column and the number of plates in the column, as well as the liquid and vapour flow rates for both the top and bottom sections were deduced. The following steps were applied in the analysis of the distillation column

i. Obtain the physical properties of the system - density, viscosity and surface tension.
ii. Take or select a prior plate spacing.
iii. Determine the column diameter.
iv. Evaluate the liquid flow arrangement

v. Make a provisional tray layout-down comer area and active area.
vi. Check the weeping rate, if not satisfactory, return to step (VI), if YES, go to step (viii).
vii. Check plate pressure drop. If two high, go to step (VI), if okay then go to step (IX).
viii. Check downcomer backup, if too high, go to step (VI) or (III). If okay, go to steep(X).
ix. Decide plate layout, if unsatisfactory, go to step(VI), if yes go to step (II)
x. Recalculate the percentage flooding.
xi. Check entrainment, if too high, return to step (IV).
xii. Optimize design – Repeat (III)-(IX) to obtain smallest diameters.
xiii. Finalize the design
xiv. Sketch the layout.

2.3.4 Distillation Column Model Equations

From Figure 3, given the feed stream F with flow rate in mol/hr with feed concentration x_f, which delivers Dmol/hr of product at the distillate of concentration x_D and a bottom product Bmol/hr with concentration x_B.

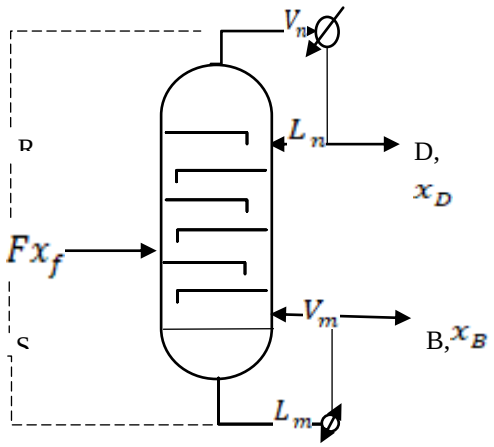

Fig 4:Schematic Diagram of a Distillation Column

The overall material balance is expressed as

$$F = D + B \quad (6)$$

While the component balance is

$$Fx_f = Dx_D + Bx_B \quad (7)$$

When the feed enters below the boiling point, then the molar heat flux is obtained thus.

$$q = 1 + \frac{C_{p_w}(T_{f_s} - T_f)}{\lambda_w} \quad (8)$$

Material balance around the rectifying section of the distillation column yields its operating line equation as

$$y_n = \frac{L_n}{V_n}x_n + \frac{D}{V_n}x_D \quad (9)$$

Equation 39 can be rewritten in terms of the Reflux ratio as

$$y_n = \frac{R}{R+1}x_n + \frac{1}{R+1}x_D \quad (10)$$

Since the reflux ratio is defined as

$$R = \frac{flow\ returned\ as\ reflux}{flow\ of\ top\ product\ taken\ off}$$

$$R = \frac{L_n}{D} \quad (11)$$

Furthermore, material balance analysis on the stripping section of the distillation column yields its operating line equation as

$$y_m = \frac{L_m}{V_m}x_m - \frac{B}{V_m}x_B \quad (12)$$

The q –line equation is defined as heat to vaporize one mole of feed by molar latent heat of feed and it expressed mathematically as [16]

$$Y_q = -\left(\frac{q}{1-q}\right)x_q + \frac{x_f}{(1-q)} \quad (13)$$

2.3.5 Plate Area and Column Diameter.

The total column cross-sectional area (A_c) is given as maximum volumetric vapour flow rate$V(m^3/s)$ by actual vapour velocity $U_n(m/s)$, mathematically stated as,

$$A_c = V \times U_n \quad (14)$$

Other areas used in the design are the net area (A_n), which is given as;

$$A_n = A_C - A_d \quad (15)$$

The column Diameter is obtained from the flooding correlation for a chosen plate spacing. It is given as

$$(D_c) = \sqrt{\frac{4Q_{max}}{\pi \rho_v \rho_l}} \quad (16)$$

The flooding velocity U_f at 70% flooding is given as,

$$U_f = K_l\sqrt{\frac{\rho_l - \rho_v}{\rho_v}} \quad (17)$$

$$K_{1new} = K_1\left(\frac{\sigma}{0.02}\right) \quad (18)$$

$$U_n = 70\%\ U_f \quad (19)$$

Column Height (H) = Plate spacing × Number of plates

$$H_T = 10\%\ H + H \quad (20)$$

The flooding velocity is obtained from

$$U_{nf} = C_{sbf}\left(\frac{\sigma}{20}\right)^{0.5}\left(\frac{\rho_l - \rho_v}{\rho_v}\right)^{0.5} \quad (21)$$

2.3.6 Design Parameters

The following parameters were applied in performing this research study. These includes Antoine constants, physical parameters and feed stream of the tubular plug flow reactor as depicted in Tables 1, 2 and 3 respectively.

Table 1: Antoine Constants [17]

Compound	A	B	C
Aniline	7.29291	1668.15	93.636
Nitrobenzene	7.11562	746.586	201.783

The operating pressure P_T is 760mmHg (1atm). The partial pressure of aniline and nitrobenzene are deduced thus:

$$Log(P^A, mmHg) = 7.2929 - \frac{1668.15}{93.636 + T} \quad (22)$$

And

$$Log(P^B, mmHg) = 7.11562 - \frac{746.586}{201.783 + T} \quad (23)$$

A is for Aniline while B is for Nitrobenzene. This is determined for the range of temperature 184.3℃ to 210.6℃.

Table 2: Physical Parameter[2]

Component	Boiling Point (℃)	Surface Tension (N/m)	Critical Pressure (atm)	Critical Temp (℃)
Aniline	184.3	42.9	52.4	425.7
Nitrobenzene	210.6	22.68	47.62	447

III. RESULTS AND DISCUSSION

3.1 Products Yield and Dimensions of Tubular Plug Flow Reactor

The design of tubular plug flow reactor yielded the tubular plug flow reactor of volume 8.836m^3, length of reactor of 5m, tubular reactor diameter of 1.5m, reactor wall thickness of 0.005mand a single number of tube for the reactor. Also, the feed stream (product yields) from the tubular reactor into the distillation column is highlighted in Table 3

Table 3: Feed Streams from Plug Flow Reactor

Species	Mole Flow(kgmole/hr)	Mole Fraction
Nitrobenzene	38.15	0.0791
Hydrogen	0.048	0.0001
Water	84.82	0.1750
Aniline	359.82	0.7459
Total	482.838	1.00

In addition, the products yield from the tubular plug flow reactor showed molar flow rates of aniline, water and unconverted nitrobenzene as 359.82kgmol/hr, 84.82kgmole/hr and 38.15kgmol/hr respectively with 74.59% yield for aniline, 17.5% yield of water and unconverted nitrobenzene of 7.91%.

3.2 Vapour Liquid Equilibrium Data

As a result of the partial pressures of aniline and nitrobenzene deduced within the temperature range of 184.3^{0}C and 210.6^{0}C at an operating pressure of 760mmHg, the vapour liquid equilibrium (liquid and vapour mole fractions) data were generated using Excel software as depicted in Table 4. Therefore, the average relative volatility (α_{ave}) was obtained as 1.94.

Table 4: Vapour Liquid Equilibrium Data for Aniline and Nitrobenzene

Temp (℃)	P^A (mmHg)	P^B (mmHg)	$\alpha = \frac{P_A}{P_B}$	$x_A = \frac{P_T - P_B}{P_A - P_B}$	$y_A = \frac{P_A P_B}{P_T}$
210.6	1466.30	759.05	1.932	0.00	0.003
207.0	1346.30	696.58	1.933	0.098	0.173
2040	1252.30	647.71	1.934	0.185	0.306
201.0	1163.70	601.62	1.934	0.281	0.431
198.0	1080.10	558.19	1.935	0.387	0.550
195.0	1001.30	517.31	1.936	0.501	0.661
192.0	927.25	478.87	1.936	0.627	0.765
189.0	857.59	442.75	1.937	0.765	0.863
186.0	792.19	408.87	1.938	0.916	0.955
184.3	756.95	390.62	1.938	1.008	1.000

3.3 Characterization of Column Parameters

The distillation column parameters that include column internal properties (column number of stages, total height of column etc), tray geometry, weir geometry and downcommer geometry were determined or evaluated using MatLab software and its simulated data compared with the Aspen Hysys software data as shown in Tables 5, 6, 7 and 8 respectively.

Table 5: Column Internal Parameters

Column Internal Parameters	Aspen HysysSimulation	MatLabSimulation
Total Height(m)	6.096	6
Total Headloss(mm)	1231	136.73
Total Pressure drop(mbar)	108.7	389
Number of Sections	2	2
Number of Diameter	2	2
Heat flow at top(Joules)	1.895x 10^3	1.895x 10^3
Approach to flood	80	80
Pressure drop CS-1-4 (KPa)	42.19	169.9
Pressure drop CS-5-10- (KPa)	66.53	219.11

Table 6: Column Tray Geometry

	Aspen Simulation	MatLabSimulation
Tray Type	**Sieve**	**Sieve**
Diameter(m)	2.240	2.27
Tray Spacing	0.609	0.6
Number of Passes	1	1
Hole diameter(mm)	12.70	12
Hole Area(AA)	0.1	0.486
Deck Guage Thickness	10 Gauge	
Deck Guage Thickness value	3.404	
Cross-sectional Area	3.942	5.47
Active Area(AA) m^2	3.153	3.24
Net Area(m^2)	3.548	3.65
Section Height(m)	3.658	3
Section Head loss(mm)	733.4	136
Trays with weeping	None	None
Section pressure drop(mbar)	66.53	79.83

Table 7: Column Weir Geometry

	Aspen HysysSimulation	MatLabSimulation
Property	**Size**	**Size**
Weir Height(mm)	50.80	40
Weir length(mm)	1.628	1.66

Table 8: Column Downcomer Geometry

Properties	**Aspen Hysys Simulation**	**MatLabSimulation**
Downcomer Clearance(mm)	38.10	49.8
Downcomer width Top(mm)	350.5	300
Downcomer width Bottom	350.5	300
Downcomer Area Top(m^2)	0.3942	0.405
Downcomer Area Bottom(m^2)	0.3942	0.405

Furthermore, it can be deduced from the above respective tables for column parameters that the simulated data via MatLab and Aspen Hysyssoftwares were very close with little or no deviation when compared. Thus, these tends to the correctness or accuracy of the deduced and applied equations in this research study. Also, the reboiler and condenser applied in the distillation column operation were sized and its sizing values and shape orientation shown in Table 9

Table 9: Vessel Sizing

Vessel	**Reboiler**	**Condenser**
Diameter(m)	1.193	1.193
Length(m)	1.789	1.789
Volume(m^3)	2.00	2.00
Orientation	Horizontal	Horizontal
Duty(KJ/h)	3.033E7	3.026E7
Reflux flow rate	Outflow 22.53kmol/hr	480.8kmol/hr

3.4 Distillation Column Products Yield

The products (mixture of aniline, water and unconverted nitrobenzene)from the tubular plug flow reactor were distilled in a distillation column for recovery of desired aniline product from the products mixture. The desired aniline product of 95% purity was recovered as product from the rectifying section of molar flow rate of 251.47kgmole/hr while 5% of unconverted nitrobenzene reactant was recovered and recycled into the tubular plug flow reactor for further operational process.

IV. CONCLUSION

Aspen Hysys software and models for the simulation of plug flow reactor and distillation column were developed for the production of 95% purity Aniline via the hydrogenation of Nitrobenzene. Thus, this research study focused on improving the percentage purity of produced aniline from plug flow reactor through the distillation operation.Distillation column components such as column internal parameters, column tray geometry, weir geometry, downcomer geometry, condenser and reboiler sizing results were compared (MatLab

simulation and Aspen Hysys software) as highlighted in the results with little or minimal deviations. Therefore, the comparison results of Aspen Hysys and MatLab simulationfor plug flow reactor and distillation column designshowed a close mapping with minimal deviation or absolute error, which confirms the efficiency and effectiveness of the operational process. Therefore, the results and findings of this study are in tandem with other previous studies on production of aniline with improved purity of aniline production via the distillation process.

REFERENCE

[1]. Zhu, J. &Aikawa, B. Determination of Aniline and Related Mono-Aromatic Amines in Indoor Air in Selected Canadian Residences by a Modified Thermal Desorption GC/MS Method. Environmental International Canada, (30): 135-143, (2014)

[2]. IARC. Some Aromatics Amines and Related Compounds. IARC Monographs on the Identification of Carcinogenic Hazards to Humans, Lyon, France, (2021)

[3]. Uzoukwu, B. A., Manilla, P. N. &Ogali, R. E. Undergraduate Chemistry Fundamental Principles. Lagos: Timi Hyacinth Enterprises, (2005)

[4]. Belykh, L. B., Skripov, N. I., Schmidt, F. K. & Stepanova, T. P. Liquid Phase Hydrogenation of Nitrobenzene and O-nitrochlorobenzene in the Presence of Phosphorus containing Palladium Nanoparticles. Kinetics and Catalyst, 56(2): 181-189, (2015)

[5]. Ibrahem, A. S. &Dzulkifil, A. System Identification and Analysis to Optimize Plant Design of Aniline. Journal of Purity, Utility Reaction and Environment, 1(2): 351-362, (2012)

[6]. Doluda, V. Y., Filatov, A. E., Sul'man, E. M., Matveeva, V. G., Mikhailov, S. P, Sidorov, A. I. &Kosivtsov, Y. Y. Studying the Three Phase Hydrogenation of Nitrobenzene to Aniline in the Presence of Ruthenium catalyst. Journal of Catalysis in Chemical and Petrochemical Industry, 10(4): 328 -334, (2018)

[7]. Rick, T. D., Peter, K., Lydwien, M., Ruo, Z., Louis, G. J. V. D. H., Henk, V. D. B. &Arend, J. Z. Industrial Process Design for the Pproduction of Aniline by Direct Amination. Chemical Engineering & Technology, 5(40): 838-846, (2017)

[8]. Javaid, A. &Bîldea, C. S. Design and Control of an Integrated Toluene-Aniline Production Plant a Preliminary Study. International Journal of Chemical Engineering and Applications, 8:267-271, (2017)

[9]. Keypour, H. Application of Response Surface Methodology for Catalytic Hydrogenation of Nitrobenzene to Aniline using Ruthenium Fullerene Nano Catalyst. Iranian Journal of Chemistry and Chemical Engineering, 34(1): 21-33, (2015)

[10]. Wong, E.W. &Birkhoff, R. Dupoint KBR. Aniline Process. New York: McGraw – Hills Handbook, (2005)

[11]. Ghosh, D. Design of Ideal Reactors. Department of Chemical Engineering, Birla Institute of Technology, Mesra, India, (2020)

[12]. Abowei, M. F. N. &Goodhead, T.O. Design of Isothermal Plug Flow Reactor Adsorption Tower for sulphur Trioxide Hydration using Vanadium Catalyst. International Journal of Innovative Science and Modern Engineering, 2(9): 9-13, (2014)

[13]. Igbagara, P. W**.,** Adeloye, O. M.&Olayebi, O. Design of Three Phase Separator for 12.5BPD Crude Oil Atmospheric Distillation Unit. FUPRE Journal of Scientific and Industrial Research, 7(1): 127-137, (2023)

[14]. Adeloye, O. M.,Akpa, J. G., Dagde, K. K. &Ehirim, E. O. Process Simulation and Performance Models for Enhanced Modular Refinery Operations in Nigeria. International Journal of Chemical Engineering and Application, 14(1): 1-13, (2023)

[15]. Rizwan, S. M. A. An Efficient Design of Multicomponent Distillation Column by Approximate and Rigorous method. International Journal and Magazine of Engineering Technology Management and Research.2(11): 1116-1121, (2015)

[16]. Ademuliyi, F. T. (2017). Process Plant Design Manual (with Hysys). Lecture Material, Chemical Engineering, Rivers State University, Port Harcourt.

[17]. Iranian Chemical Engineers (2021). Antoine Data and Vapour liquid Equilibrium Calculations. Available: www.IrChe.com [Accessed: 2021, Nov.23].