Process Simulation Analysis of HF Stripping Column Using HYSYS Process Simulator

Thaer A. Abdulla, Assistant Lecture, University of Tikrit

Abstract

HYSYS process simulator is used for the analysis of existing HF stripping column in LAB plant (Arab Detergent Company, Baiji-Iraq). Simulated column performance and profiles curves are constructed. The variables considered are the thermodynamic model option, bottom temperature, feed temperature, and column profiles for the temperature, vapor flow rate, liquid flow rate and composition. The five thermodynamic models options used (Margules, UNIQUAC, van laar, Antoine, and Zudkevitch-Joffee), affecting the results within (0.1-58%) variation for the most cases.

The simulated results show that about 4% of paraffin (C10 & C11) presents at the top stream, which may cause a problem in the LAB production plant. The major variations were noticed for the total top vapor flow rate with bottom temperature and with feed composition. The column profiles maintain fairly constants from tray 5 to tray 18. The study gives evidence about a successful simulation with HYSYS because the results correspond with the real plant operation data.

Keywords: Process Simulation, HYSYS Simulator, Multicomponents Distillation, LAB, HF Stripper.

المحاكاة النظرية لتحليل عمود انتزاع حامض الهيدروفلوريك باستخدام برنبامج المحاكاة HYSYS

الخلاصة

استعمل البرنامج الجاهز HYSYS للتحليل الهندسي لعمود انتزاع حامض الهيدروفلوريك لمصنع انتاج الالكيل بنزين المستقيم للشركة العربية في بيجي. رسمت منحنيات أداء عمود الانتزاع للمتغيرات : موديل ديناميك الحرارة، درجة حرارة اسفل العمود ، درجة حرارة المواد الداخلة. ورسمت ايضا المخططات الداخلية للعمود لتغير (Margules, درجة حرارة المواد والتركيز . استعمل خمسة موديلات لديناميك الحرارة , ومعدل تدفق الاطوار والتركيز . استعمل خمسة موديلات لديناميك الحرارة (Margules, ومعدل تدفق الاطوار والتركيز . استعمل خمسة موديلات لديناميك الحرارة (معدل تدفق الاطوار والتركيز . استعمل خمسة موديلات لديناميك الحرارة . ومعدل تدفق الاطوار والتركيز . استعمل خمسة موديلات لديناميك الحرارة . ومعدل تدفق الاطوار والتركيز . استعمل خمسة موديلات لديناميك الحرارة معدود (1.0- (0.1)) معظم الحالات . تبين من نتائج المحاكاة ان هنالك 4% من البارافين في مجرى العلوي والذي قد يسبب مشكلة في المصنع. وتم ملاحظة اكبر تغير في معدل تدفق البخار في اعلى العمود مع تغير درجة حرارة اسفل المواد والذي قد يسبب مشكلة في المصنع. وتم ملاحظة اكبر تغير في معدل تدفق البخار في اعلى العمود مع تغير درجة حرارة اسفل المواد الداخلة. وتبين من نتائج المحاكاة ان هنالك 4% من البارافين في مجرى العلوي والذي قد يسبب مشكلة في المصنع. وتم ملاحظة اكبر تغير في معدل تدفق البخار في اعلى العمود مع تغير درجة حرارة اسفل العمود وتركيز المواد الداخلة. وتبين ايضا بان المخططات الداخلية للعمود انها ثابتة نسبيا بين الصينية رقم 5 الى المحود وتركيز المواد الداخلة. وتبين ايضا بان المخططات الداخلية العمود انها ثابتة نسبيا بين الصينية رقم 5 الى الصينية رقم 5 الى المحيات المحاكاة الماليزامج الجاهز HYSYS بنجاح في الصينية رقم 5 الى المحاكاة النظرية لعمود انتزاع حامض الهيدروفاوريك المستخدم.

الكلمات الدالة:المحاكاة، برنامج HYSYS ، تقطير متعدد الاطوار ، الالكيل بنزين المستقيم، انتزاع حامض الهيدروفلوريك.

Abbreviations

ESSO K: Empirical K-value model uses the Maxwell-Bonnell vapor pressure equation to calculate K-values, used for heavy hydrocarbon materials effectively at pressures below 7 bar. This model can be used to model vacuum towers.

NRTL: Non-Random Two-Liquid Equation based on activity coefficient Equilibrium

thermodynamic model recommended for Polar (Highly Non-Ideal Solutions).

PR: <u>Peng-R</u>obinson thermodynamic model to calculate K-values, based on equation of state recommended for most hydrocarbon systems.

SRK:Soave - Redlich - Kwong thermodynamic model to calculate K-values, based on equation of state recommended for most hydrocarbonsystems.

UNIQUAC:Universal Quasi Chemical activity coefficient equilibrium thermodynamic model

Introduction

Distillation columns have been widely used for separation processes in the petroleum and chemical industries. These columns are not only the most energy-intensive operations, but also determine the quality of products of those industries and many times limit rates^[1]. product process Recent progresses in the computer softwares have possible made extensive application of process simulators in industries. process Distillation simulation has been studied extensively and poses many challenging problems since a distillation column is complex, non-linear, multivariable highly process^[2-4]. Process simulation is a computer representation of an individual unit operation, or multiple connected units or an entire plant. It is applicable in different fields of the process engineering; analysis of existing processes (rating), synthesis of new processes (design), and operator training (process dynamic startup & shutdown). The authors of many chemical engineering textbooks added a chapter dealing with process simulation & process simulation softwares (Process Simulators)^[5-10]. Currently available modern process Simulators are shown in Table (1). Major sections of typical process simulator are:

1. Unit operation (block) model library.

recommended for polar (highly non-ideal solutions).

Antoine: Modified Antoine Equation (vapor pressure model) is applicable for lowpressure systems (below 7 bar) that behave ideally, for hydrocarbon components which has not vapor pressure coefficients. As such, crude and vacuum towers can be modeled with this equation.

LKP: Lee Kesler <u>Plöcker</u> Equation is an accurate general method for non-polar substances and mixtures

- **2.**Physical properties & thermodynamic model selection.
- **3.**General flowsheeting, steady state material and energy balance, recycle processes, and dynamic processes.

The process simulation softwares (Process Simulators) consist of standard chemical engineering relationships and models. These are material balance, energy balance, kinetics relationships, equilibrium relationships and dynamic & control relationships. Typically, steady state simulation involves the solution of algebraic equations. while dynamic simulation involves the solution of ordinary differential equations. The disadvantage of commercial simulators is that they do not provide the simulator's source code; the user must rely on closed black box for the unit operation process.

To take advantage of the existing chemical plants in Iraq for engineering process analysis research & development, Linear Alkyl Benzene (LAB) plant (Arab Detergent Company/Beiji-Iraq) which contain cumulative field data of plant operation, especially one of the major equipment; HF-stripper column, was used as a case study using the process simulation software (HYSYS).

LAB now accounts for nearly all of the worldwide production of alkylbenzene

sulfonates that are frequently used as raw material of biodegradable household detergents. A LAB complex consists of two major steps: production of normal paraffins, and production of LAB from normal paraffins. The straight run kerosene from a refinery is used to produce normal paraffins through kerosene prefractionation, distillate unionfining process and Molex process. Then, the normal paraffins are dehydrogenated to corresponding mono-olefins over a highly selective and active catalyst. Lastly, benzene is alkylated with mono-olefins to LAB using hydrofluoric (HF) acid as the catalyst in alkylation process. The alkylation process includes two major sections: alkylation section and distillation section. The HF-stripper column in the distillation section is researched this paper. The feed of this column is a mixed LAB stream with HF, benzene and paraffin from alkylation section, which passes through a feed heat exchanger enters at the top tray. The HF vapor is vented to the HF recovery system. The hot oil to the reboiler is on flow control. The bottom level is directly controlled by adjusting bottom product flow to the benzene column. The bottom temperature is a key variable that reflects fractionation effect^[11,12]

HYSYS Process Simulator

is a process HYSYS simulation environment designed to serve many processing industries especially oil and gas and refining. Rigorous steady state and dynamic models for plant design, performance monitoring, troubleshooting, improvement, operational business planning and asset management can be created using HYSYS. The built-in property packages in HYSYS provide accurate thermodynamic, physical and property predictions for transport hydrocarbon, non-hydrocarbon, petrochemical and chemical fluids. They are divided into five basic methods

{equations of state (LKP, PR, SRK and their modifications) for rigorous treatment of hydrocarbon systems, semi-empirical models (Chao-Seader and Grayson-Streed) and vapour pressure models (Antoine, Braun k10, Esso K) for the heavier hydrocarbon systems, activity coefficient models (Margules, UNIQUAC, Van Laar, NRTL and their modifications, etc.) for finally chemical systems and miscellaneous (special application) models (Amines and steam packages)}. Proper use thermodynamic property package of parameters is to successfully key simulating any chemical process. The database consists of an excess of 1500 components and over 16000 fitted binary coefficients. If a library component cannot be found within the database. a comprehensive selection of estimation methods is available for creating fully defined hypothetical components^{[13,14].}

The calculation method for distillation in HYSYS is done to a high standard in accordance with the matrix method. A quick convergence and short simulation time is therefore guaranteed. In most cases the user need not be concerned with the details of the internal calculation, this is done automatically by HYSYS. The following six basic steps are used to run a flowsheet simulation in HYSYS^[15]:

1.Selecting components.

2.Selecting thermodynamics options.

3.Creating a flow sheet.

4.Defining the feed streams.

5.Input equipment parameters.

6.Running the simulation & Reviewing the results.

Figure (1) shows the HF Stripper distillation column diagram constructed using HYSYS & Table (2) gives a typical simulation results.

Results and Discussions

HF stripping column in LAB production plant has been simulated utilizing plant field data presented in Table (3), using HYSYS simulator.

Effect of Bottom Temperature

Figures (2 to 6) show the effect of bottom temperature on top temperature, total top vapor flow rate & top components weight fractions (benzene, C10 paraffin, C11 paraffin), at different thermodynamic models. The figures effect of show that the the thermodynamic models used (Margules, UNIQUAC, van laar, Antoine and Zudkevitch-Joffee) on the general results is within (0.1-4.5%) variation, except the total top vapor flow rate, the variation is (51-58%). Margules within thermodynamic option gives the average values.

Figure (2) shows the bottom temperature increase of 30°C (from 210°C) cause, 190° C to the top temperature increase of 5.5°C (from 147° C to 152.5° C). From figure (3) it can be seen that the major variation of the total top vapor flow from about 9266 kg/hr to 19638 kg/hr with the 30°C difference of bottom temperature. Figures (4 to 6) show the variation of the top components weight fractions are small ((0.919-0.936) for benzene in figure (4), and approximately constant at about 0.02 for both C10 paraffin & C11 paraffin in figure (5 & 6) respectively).

The simulation results in figures (5 & 6) show that about 4% of paraffin (C10 & C11) presents at top stream which may cause a problem in the LAB production plant.

Effect of Feed Temperature

Figures (7 to 11) show the effect of feed temperature on top temperature, top total vapor flow rate, & top components weight fractions (benzene, C10 paraffin, C11 paraffin), at different thermodynamic models. The figures show that the effect of the thermodynamic models used on the general results is within (1-3%)variation, except the top components

weight fractions of C10 paraffin & C11 paraffin, the variation is within (15-17%). Margules thermodynamic option gives the average values.

Figure (7) shows the feed temperature increase of 20° C (from 90° C to 110° C) cause, the top temperature increase of 4° C (from 148° C to 152° C). The variation of the total top vapor flow rate and the top component weight fraction of benzene are small. The variations are within (1%), figures (8 & 9). Figures (10 & 11) show the major variation of the top components weight fractions of C10 paraffin & C11 paraffin from about (0.018 to 0.022) with the 20° C difference of feed temperature.

Effect of Feed Concentration

Feed concentration presentation is very difficult in multicomponents systems. Table (4) show a comparison between two simulation runs to notice the effect of decreasing light components feed weight fractions (benzene) and increasing heavy components feed weight fractions (C10 paraffin & C11 paraffin). The top temperature decreases (from 150.4 °C to 147.5 °C), where as the total top vapor flow rate decreases (from about 13840 kg/hr to 7713 kg/hr).

HF Stripper Column Profiles

Figures (12 to 17) show the temperature & composition profiles for HF-stripper column. The figures show that the effect of the thermodynamic models used on the general results is within (0.05-5%) variation, except the total top vapor flowrate profile, figure (14), the variation is within (5-11.5%) and tray vapor profiles of c10 paraffin and c11 paraffin, figures (16 & 17), the variation is within (11-26%). In all cases, the profiles remain fairly constant from tray 5 (immediately below feed) through tray 18 (immediately above reboiler). In fact, these trays can be

removed without severely affected the column performance.

Comparison of HF Stripper's Results

The comparison of the simulated results with plant HF-stripping column parameters is shown in Table (5). The high deviations of simulated top weight fractions of components with the plant values due to the difficulty of sampling and the accurate chemical analysis of the top stream because of presence of HF.

Conclusions

- 1. Five different thermodynamic models options (Margules, UNIQUAC, Van-
- laar, Antoine and Zudkevitch-Joffee) were used, affecting the results within (0.05-58.4%) variation for the most cases. Margules thermodynamic option gives the average values.
- **2.**The simulation results show that about 4% of paraffin (C10 & C11) presents at the top stream which may cause a problem in the LAB production plant.
- **3.**The major variations were noticed for the total top vapor flow rate with bottom temperature and with feed composition.
- **4.**The column profiles maintain fairly constants from tray 5 (immediately below feed) through tray 18 (immediately above reboiler). These trays can be removed without severely affected the column profile.
- **5.**Simulation of the HF stripping column in LAB production plant using HYSYS Simulator confirms the real plant operation data and this study gives evidence about a successful simulation with HYSYS.

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Fig.(1) HF Stripper Distillation Column Diagram Constructed Using HYSYS.



Fig. (2) Effect of Bottom Temperature on Top Temperature P _{Top}=461.3 kPa, & T _{Feed} = 102 °C



Fig. (3) Effect of Bottom Temperature on Total Top vapor Flowrate P $_{Top}{=}461.3$ kPa, & T_{Feed} = 102 ^{o}C

16. Arab Detergent Company; "LAB production plant Field data", Baiji-Iraq.



Fig. (4) Effect of Bottom Temperature on Benzene wt. fraction P $_{Top}{=}461.3$ kPa, & T $_{Feed}{=}102\ ^{o}\mathrm{C}$



Fig. (5) Effect of Bottom Temperature on wt. fraction of C10-Paraffin P Top=461.3 kPa, & T_{Feed} = 102 °C



Fig. (6) Effect of Bottom Temperature on wt. fraction of C_{11} -Paraffin P_{Top} =461.3 kPa, & T_{Feed} = 102 °C



Fig. (7) Effect of Feed Temperature on Top Temperature P $_{Top}{=}461.3$ kPa, & $T_{Bottom}{=}200\ ^{o}C$



Fig. (8) Effect of Feed Temperature on Total Top Flowrate P $_{Top}$ = 461.3 kPa, & T_{Bottom} =200 ^{o}C



Fig. (9) Effect of Feed Temperature on Benzene wt fraction P $_{Top}$ =461.3 kPa, & T $_{Bottom}$ =200 ^{o}C



Fig. (10) Effect of Feed Temperature on C10paraffin wt fraction P $_{\rm Top}{=}461.3$ kPa, & $T_{\rm Bottom}{=}200$ $^{o}{\rm C}$



Fig. (11) Effect of Feed Temperature on C11paraffin wt fraction P_{Top} =461.3 kPa, & T_{Bottom}=200 °C



Fig. (12) HF Stripper Tower Temperature Profile P _{Top}=461.3 kPa, T _{Feed} = 102 °C,& T _{Bottom}=200 °C



Fig. (13) HF Stripper Total Liquid Flowrate Profile P $_{Top}$ =461.3 Kpa, T_{Feed} = 102 °C, & T_{Bottom} =200 °C



Fig. (14) HF Stripper Total Vapor Flowrate Tower Profile P_{Top} =461.3 Kpa, T_{Feed} = 102 °C, & T_{Bottom} =200 °C



Fig. (15) Tray Vapor Profile of Benzene wt fraction P $_{Top}$ =461.3 Kpa, T_{Feed} = 102 °C, & T_{Bottom} =200 °C



Fig. (16) Tray Vapor Profile of C_{10} -Paraffin wt fraction P $_{Top}$ =461.3 Kpa, T_{Feed} = 102 °C, & T_{Bottom} =200 °C



Fig. (17) Tray Vapor Profile of C₁₁-Paraffin wt fraction P $_{Top}$ =461.3 kPa, T_{Feed} = 102 °C, & T_{Bottom} =200 °C

Table (1) Current Modern Process Simulation Softwares $({\rm Process}\;{\rm Simulator})^{[5]}$

Process Simulator	Source
ASPENPLUS	Aspen Technology Corp., Cambridge , MA
CHEMCAD	Chemstations, Houston, TX
HYSYS	Hyprotech , Calgary , Alberta
PRO/II	Simulation Sciences , Fullerton , CA
DESIGN II	WinSim Inc., Houston, TX

at $(T_{feed} = 102 \ ^{\circ}C, P_{Top} = 461.3 \ \text{kPa} \ \& \ T_{bottom} = 200 \ ^{\circ}C)$				
Stream Name	HF Stripper Feed	Top Product	Bottom Product	
Temp. (^{0}C)	102.0000	150. 3738	200.0000	
Press. (Kpa)	420.0000	461. 3000	481.3000	
Heat Flow (MJ/h)	-96258.7109	10703898. 5066	-82206790. 3483	
Vapor Mole Fraction	0.0000	0. 9809	0.0000	
Molar Flow (Kmol/h)	715.2983	184. 1606	531.1376	
Mass Flow (Kg/h)	87585.0012	13872. 5486	73712. 4526	
Total std L (m^3/h)	111.1462	15. 6201	95. 3066	
Total std V (m ³ /h)	16912. 8241	4354. 3747	12558. 4494	
	Component Ma	ss Fractions		
HF	0. 003334	0. 021049	0.000000	
Benzene	0. 289344	0. 929452	0.168877	
n-Decane	0. 138489	0. 020125	0. 160765	
n-Undecane	0. 263019	0. 020483	0. 308664	
n-Dodecane	0. 165725	0.007168	0. 195565	
n-Tridecane	0. 070507	0. 001591	0.083477	
n-Decyl-BZ	0. 014799	0. 000054	0.017574	
n-Undecyl-BZ	0. 020896	0. 000046	0. 024820	
n-Dodecyl-BZ	0.016719	0.000022	0. 019861	
n-Tridecyl-BZ	0. 011010	0. 000009	0.001308	
Heavy Alkylate	0. 006158	0. 000001	0.007317	

Table (2) Typical Simulation Results Using Margules Thermodynamic Model
at $(T_{1,1} - 102)^{\circ}C_{1}P_{-} - 461.3 kP_{2}.8 T_{-} - 200)^{\circ}C_{1}$

Table (3) Typical Field Data of HF Stripper (Arab Detergent Company).^[16]

Stream Name	HF Stripper Feed	Top Product	Bottom Product
Temp. (^{0}C)	102.0	150.0	200.0
Press. (KPa)	461.3	461.3	481.3
Mass Flow (Kg/h)	87585.0	11670.0	75915.0
	Component Mass Fract	tions	
HF	0.00333406131	0.025	0.0
Benzene	0.2893438698	0.975	0.183838
n-Decane	0.138489129	?	0.159799
n-Undecane	0.2630186368	?	0.303491
n-Dodecane	0.1657250937	?	0.191226
n-Tridecane	0.07050733071	?	0.081357
n-Decyl-BZ	0.01479858229		0.017076
n-Undecyl-BZ	0.02089618633		0.024112
n-Dodecyl-BZ	0.01671867888		0.019291
n-Tridecyl-BZ	0.01101028361		0.012705
HAB [*]	0.00615814763		0.007106

Internal Specification

Column Diameter D (mm)	2000	
No of Trays	20 sieves tray	
No of Stages	21 stages (with reboiler)	
Trays Pacing (mm)	600	
No. of Holes	1260	
Hole Diameter do (mm)	13	
Reboiler Heat Duty Qr (MJ/hr)21356		

* Heavy Alkylate (Molecular Weight= 366, Normal Boiling Point=397 °C and Specific Gravity at 60 °F=0.875)

? Traces

	HYSYS Runs of HF	-Stripper Column.	
Stream Name	HF Stripper Feed	Top Product	Bottom Product
Temp. (^{0}C)	102.0000 *	150. 3738	200.0000
Press. (KPa)	420.0000 *	461.3000	481.3000
Heat Flow (MJ/h)	-96258.7109	10703898. 5066	-82206790. 3482857
Vapor Mole Fraction	0.0000	0. 9809	0.0000
Molar Flow (Kmol/h)	715. 2983	184. 1606	531. 1376
Mass Flow (Kg/h)	87585.0012	13872. 5486	73712. 4526
Total std L (m ³ /h)	111. 1462	15. 6201	95. 3066
Total std V (m ³ /h)	16912. 8241	4354.3747	12558. 4494
	Component M	ass Fractions	
HF	0. 003334	0. 021049	0.000000
Benzene	0. 289344	0. 929452	0. 168877
n-Decane	0. 138489	0. 020125	0. 160765
n-C11	0. 263019	0. 020483	0. 308664
n-C12	0. 165725	0.007168	0. 195565
n-C13	0. 070507	0. 001591	0.083477
n-Decyl-BZ	0. 014799	0.000054	0.017574
n-Undecyl-BZ	0. 020896	0. 000046	0.024820
n-Dodecyl-BZ	0. 016719	0.000022	0. 019861
n-Tridecyl-BZ	0. 011010	0. 000009	0.001308
HAB^*	0.006158	0.000001	0.007317
Stream Name	HF Stripper Feed	Top Product	Bottom Product
Temp. (^{0}C)	102.0000 *	147. 5285	200.0000
Press. (KPa)	420.0000 *	481.3000	481.3000
Heat Flow (MJ/h)	-109264430. 6933	3757930. 6812	-89473774. 4281
	0,0000	0.0(2)	0,0000

Table (4) Effect of Feed Concentration; a Comparison between Two	
HYSYS Runs of HF-Stripper Column.	

Stream Name	HF Stripper Feed	Top Product	Bottom Product
Temp. (^{0}C)	102. 0000 *	147. 5285	200.0000
Press. (KPa)	420. 0000 *	481. 3000	481. 3000
Heat Flow (MJ/h)	-109264430. 6933	3757930. 6812	-89473774. 4281
Vapor Mole Fraction	0.0000	0. 9636	0.0000
Molar Flow (Kmol/h)	686. 1514	106. 7120	579. 4393
Mass Flow (Kg/h)	87585.0012	7712. 6804	79872. 3208
Total std L (m ³ /h)	109. 3285	8. 6216	103. 4181
Total std V (m ³ /h)	16223.6625	2523. 1463	13700. 5162
Component Mass Fractions			

	Component N	lass Fractions	
HF	0. 003334	0. 037861	0.000000
Benzene	0. 234161	0.902034	0. 169669
n-Decane	0. 171260	0. 026487	0. 185239
n-C11	0. 285434	0. 024047	0.310673
n-C12	0. 165725	0.007724	0. 180981
n-C13	0. 070507	0.001706	0.077150
n-Decyl-BZ	0. 014799	0.000058	0.016222
n-Undecyl-BZ	0. 020896	0. 000049	0. 022909
n-Dodecyl-BZ	0. 016719	0. 000024	0.018331
n-Tridecyl-BZ	0. 011010	0. 000009	0.012072
HAB [*]	0. 006158	0. 000001	0.006752

Table (5) Comparison between simulated and plant data of HF–Stripping Column at;
$T_{freed} = 102 \ {}^{\circ}C$, P $T_{on} = 461.3 \ kPa \ \& \ T_{hottom} = 200 \ {}^{\circ}C$

$\Gamma_{\text{feed}} = 102$ C, $\Gamma_{\text{op}} = 401.5$ KI a & $\Gamma_{\text{bottom}} = 200$ C			
Variable	Plant	Simulated	Deviation %
Top Temperature (°C)	150	150. 37	0.25
Total Top Flow rate (kg/hr)	11670	13872.55	15.88
HF wt fraction	0.025	0. 021	16
Benzene wt fraction	0.975	0.930	4.62
C10-paraffin wt fraction	Traces	0.020	Very High
C11-paraffin wt fraction	Traces	0. 021	Very High