Statistical Analysis and Optimization of the Synthesis of Vinyl Chloride from Acetylene via Simulation

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***Abstract*:- Vinyl chloride (VC) is a colorless, nonirritating gas at standard temperature and pressure; and highly stable in the absence of oxygen or sunlight. Vinyl chloride finds its primary applications in the production of polyvinyl chloride (PVC), which covers 12% of the total use of plastic in the world. The widest application of the PVC is the manufacture of plastic piping. Additional significant importance are found in consumer goods, electrical applications, transport sector and floor coverings. This paper is focused on synthesis of Vinyl chloride from Acetylene (vinylation) via Aspen HYSYS simulation. Second order regression models were developed in order to predict the statistical correlation between actual predictors' value (acetylene and HCl flow rates, kgmole/hr) and the dependent variables (conversion of acetylene (%), conversion of HCl (%) and yield of Vinyl chloride (%)) from central composite design of response surface methodology. The reaction simulation process is found to be exothermic with reaction heat of -2.4 x 10^4 kcal/kgmole. The computer simulation results were analyzed statistically using response surface methodology of Design Expert 10.0.3. Optimum flow rates of 100 kgmole/hr of acetylene and 95.312 kgmole/hr of HCl gives optimum conversions (%) of acetylene and HCl to be 89.0238 % and 93.089 %, respectively; and the optimum yield of vinyl chloride is observed to be 45.7696 %. Hence, approximately equimolar flow rates of the two reactants is needed for maximum conversion and maximum yield in the vinylation process. Validating the second order regression models, against design values obtained from the computer simulation, it is observed that good agreement is achieved.**

Keywords: **Vinyl chloride, Acetylene, Aspen Hysys simulation, Optimization and Statistical analysis.**

I. INTRODUCTION

Vinyl chloride is a colorless gas that was earliest synthetized by dehydration of ethylene dichloride (EDC) with caustic alcoholic potash(Dattani, Devani, & Sahu, 2013). C_2H_3Cl has a mild sweet odour; boiling point within the range -13.4 to -13.8 °C; solubility value in water is found to be 1.1 g/L at 25 °C; very soluble in benzene, diethyl ether and carbon tetrachloride; also has good solubility in ethanol (IARC, 2008). The primary sources of emission, are plants where PVC products are fabricated, VC production plants and facilities for the polymerization of polyvinyl chloride (PVC) (WHO, 2000). Over 95 % of the main use of Vinyl chloride is found in the making of polyvinyl chloride (PVC). Nearly 1% of PVC manufactured from VC is used in the production of copolymer of vinyl acetate/vinyl chloride (WHO, 1999**)**.In the past, Vinyl chloride was used as a refrigerant liquid, as asolvent for the extraction heatsensitive materials that are heat sensitive.Another importance use is in the manufacture of chloroacetaldehyde, which serves significant purpose and finds its main use as an aerosol propellant and in cosmetic and drugs products(IARC, 2008).Slight usages of monomer of vinyl chloride comprise the production of chlorinated solvents and the manufacture of ethylene diamine which is of great importance in the production of resins (WHO, 1999; Commission, 2003). Polyvinyl chloride (PVC) is a frequently used plastics and has an extensive variety of uses. It finds good applications in medical devices, packaging, clothing and construction materials. This application is due to its ability to modify the rigidity of the substance using additives. Hence, there is a great demand for this plastic, having over 40 million tonnes of PVC produced yearly, thus leading to vinyl chloride monomer being a very useful chemical. About 90% of vinyl chloride monomer is used in the production of PVC, and lower fewer quantities usedin the production of chlorinated solvents (Davies et al., 2016).Vinyl chloride can be produced by three main methods: the union of acetylene and hydrogen chloride in the presence of a suitable catalyst; the decomposition of ethylene dichloride; and finally, the reaction of trichloroethane with various bivalent metals such as zinc or iron, or trivalent metals like aluminum. The reaction process that produces vinyl chloride from acetylene is termed vinylation. This reaction process is found to be exothermic, as it involves direct combination of acetylene and hydrogen chloride in the presence of suitable catalyst, such as mercury chloride. Here, the process follows purification, drying, and mixing of the feed gas before entering the process reactors, been packed with mercury chloride (catalysts) on active carbon pellets. This process gives over 98 %selectivity of vinyl chloride and formed 1,1-dichlorethane" on addition of excess HCl to vinyl chloride from a side reaction that occurred (Vinyl Chloride Polymer, 1989).The stoichiometry of the reaction process is given as:

$$C_2H_2 + HCl \longrightarrow CH_2{=}CHCl \qquad (1)$$

Experiments conducted in the Industries defines an evaluation between two or more choices. The interest of the scientist or researcher may be want to relate the result of a certain process to a newly developed one or justify the influence of the process change compared to a prevailing condition (Diamond, 1981). In systematic experimental design, statistical explanation of the results is presumed so that justice can be made that a definitesubstitute performs better than the other with e.g. 95% confidence level or, compatibly, that there is a 5% (α, level of significance or risk) that the conclusion is inaccurate. (Diamond, 1981). Several optimization methods are response surface methodology (Central composite design & Box-Behnken), Taguchi, Optimal design, Simplex method, Artificial neural network, Least square optimization, etc. Response surface methodology, (R.S.M), combines statistical and mathematical methods which is used for the modeling and analysis of experimental problems in which a dependent variable of attention is influenced by quite a few variables and the objective is to optimize this dependent variable(Olawoye, 2016). A very good illustration is the effect of flow rates of acetylene and hydrogen chloride on the conversion of acetylene, conversion of hydrogen chloride and yield of vinyl chloride. The Central Composite design optimization (C.C.D) approach is a form of response surface design (RSM) has 3 level factors and apart from this level factors, it axial (star) point. The star point which symbolized as (α) introduces an increase to the number of levels to 5 levels, by this means providing the flexibility of the designed experiment (Asghar et al., 2014). C.C.D's advantages over it's the other form of experimental design, Box-Behnken is that it permits the designer of the experiment to know the effect of the independent variables (factors) on the response variable, indicating how the experimental designer drives above or below the chosen factor levels(Olawoye, 2016). Conversely, Central Composite Design can accommodate minimum numbers of two factors, either continuous factors or numerical factors(Olawoye, 2016). Simulation describes the rough imitation of a process that represents its operation over time. Simulation is frequently used with scientific modeling of chemical systems to have an insight of thefunction or behavior of the particular system. It shows the eventual real effects of alternative conditions and courses of action(Sokolowski & Banks, 2009). Simulation with computer system models a process in a way it imitates an actual situation with necessary installed software to study how it works, typically on a pilot scale. Aspen HYSYS is a process simulator for conceptual design which finds good applications in industries such as pharmaceutical, chemical, petrochemical, oil, refining, gas sweetening, etc. (Fadayini, et al., 2018). Its robustness enables it to handle both steady state and dynamic state models. Within the simulation environment, exceptional features of the software are safety analysis, oil characterization, energy optimization, control, as well as pinch analysis of interested process route.

II. METHODOLOGY

The synthesis of Vinyl chloride from Acetylene via vinylation process was studied using computer simulation with Aspen Hysys 8.8. The parameters employed in the equipment design of this work are presented in Table 1.0. The Process Flow Diagram (PFD) that describes the process route for the vinylation simulation process is shown in Figure 2.0.

Table 1.0: Equipment Design Parameters

Mixer (MIX 100)	elevation (Base) (m)	elevation (Ground) (m)	Diameter (m)				
	1.00	2.00	2.00				
Compressor (K 100)	Adiabatic head (m)	Polytropic head (m)	Adiabatic eff. (%)	Polytropic eff. (%)	Duty (kW)	Capacity (ACT-m^3/h)	Delta P (bar)
	1.547×10^4	1.623×10^4	75.00	78.678	351.128	4926	4.00
Vinylation Reactor (CRV 100)	Delta P (bar)	Vessel volume(m^3)	Liquid level (%)	Liquid volume (m^3)	Reaction heat (kcal/kgmole)		
	0.0000	300	50.00	150.00	-2.4×10^4		
Cooler (E-100)	Delta P (bar)	Delta T (^{0}C)	Duty (kcal/h)				
	4.00	-1095	2.434×10^6				
Column (T-100)	Condenser pressure (bar)	Reboiler pressure (bar)	External Reflux ratio	Internal Reflux ratio	Min. N0. of Trays	Max. N0. of Trays	Optima feed stage
	1.00	1.00	4.00	2.577	4.267	7.670	5.233

2.1 Description of the Process

The simulated process is presented in figure 2.0. This process is a simplified process flow diagram for the synthesis of Vinyl chloride from Acetylene. The process consists of the following equipment: Feed mixer (MIX 100), Compressor (K 100), Process conversion reactor (CRV 100), reaction product heater (E 100) and SeparatorDistillation column (X 100).The Acetylene and Hydrogen chloride are the feed (reactants)

which are first mixed in the feed mixer in order to create room for homogeneity and collision of the reactant particles. The initial conditions of the acetylene and hydrogen chloride are at ambient temperature and pressure of 25 ^{o}C and 1 bar respectively. Since there's need for enough interaction between reactant particles (Ethylene and Hydrogen chloride) for reaction to take place;Acetyleneand hydrogen chloride are in gaseous state at standard temperature and pressure, then the mixed product of these gases are channeled into a compressor to liquefy them, and then sent into a conversion reactor, where the kinetics of the process is not needed to simulate to convergence, but uses the stoichiometry of the reactant particles and products; and the conversion of the base component (Acetylene).From the Hysys simulation, the heat of reaction is found to be -2.4 x 10^4 kcal/kgmole, indicating the process is highly exothermic (Datanni et al., 2013) and a balance error of zero (0) which depicts the convergence of the reaction.The reactor exit is further cooled with a cooler (E-100) and finally channeled to a separator (T-100), where 99.9 % purity of Vinyl chloride is achieved.

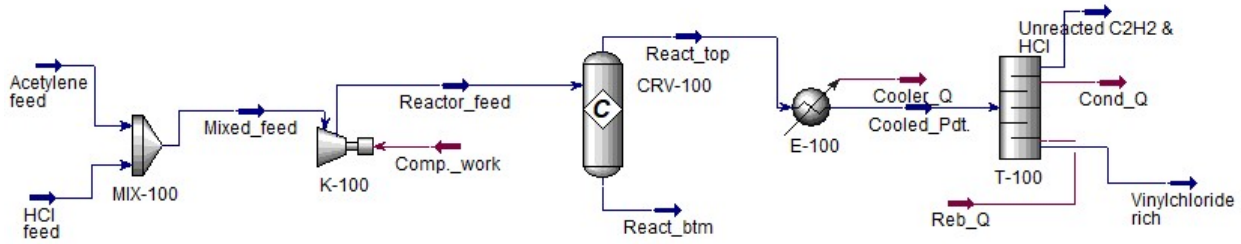

Figure 1.0: Process flow diagram for the Synthesis of Vinyl from Acetylene

2.2: Experimental Design

Central composite design of response surface is used to develop the experimental design, thereby varying the inlet flow rates of acetylene and hydrogen chloride, and observing the effect of these flow rates variation on the responses (conversion of acetylene, conversion of hydrogen chloride and yield of vinyl chloride) as shown in table 2.0.Based on the results generated from the simulated process, mathematical equations (models) were established to illustrate the statisticalrelationship between specified independent variables value of flow rate of acetylene (kgmole/hr) and flow rate of hydrogen chloride (kgmole/hr); the dependent (response) variable of conversion of acetylene (%), conversion of hydrogen chloride (%) and yield of vinyl chloride (%) in order to presume new observations within the limits of the experimental design. These models develops a predicting equation for calculating the conversion of acetylene (%), conversion of hydrogen chloride (%) and yield of vinyl chloride (%). The models adequacy was revealed by the statistical analysis, having three (3)R squared value (coefficient of determination) of 99 %, 100 % and 91 % respectively. The Aspen Hysys results of the computer simulation process for the synthesis of Vinyl chloride from the Acetylene (vinylation), uses experimental design (D.O.E) for variation or randomization of reactants (Acetylene and hydrogen chloride)flow rates and statisticalanalysis with the aid of Central Composite Design of R.S.M of Design Expert 10.0.3.Hence, RSM is an obvious modelling and experimental design approach through the partial regression fitting of the operative variables (Fadayini, et al., 2018). The statistical analysis of the responses conceded the model equations 2, 3 and 4.

These mathematical models offers in interpreting the model (pilot) plant data produced. This also aids to study process options at different operating conditions. Comparing these model equations, equation 3 of these three equations is the most accurate as indicated by it R-squared (correlations coefficient) value of 100 %, then followed by equations 2 and 4 of R squared values of 99 % and 91 %, respectively.

$$X_{C_2H_2} = 56.27012 - 0.38320\,A + 1.16349\,B + 0.016015\,AB - 7.72955\,x\,10^{-3}A^2 - 0.012677\,B^2 \quad (2)$$

$$X_{HCl} = 56.92611 + 1.41842\,A - 0.74074\,B + 1.3849\,x10^{-2}\,AB - 1.1909\,x\,10^{-2}A^2 - 5.61325\,x\,10^{-3}B^2 \quad (3)$$

$$Y_{C_2H_3Cl} = 31.97047 + 6.6790\,x\,10^{-2}\,A + 0.22451\,B + 1.0587\,x10^{-2}\,AB - 5.34844\,x\,10^{-3}A^2 - 6.79166\,x\,10^{-3}B^2 \quad (4)$$

III. RESULTS AND DISCUSSION

The results generated from the computer simulation of the process are presented below:

Table 2.0: Simulation Results for the Vinyl chloride synthesis

Run	Flow rate of C_2H_2 (kgmole/hr)	Flow rate of HCl (kgmole/hr)	C_2H_2 Conversion (%)		HCl Conversion (%)		Yield of C_2H_3Cl (%)	
	A	B	Hysys Sim.	R.S.M Model	Hysys Sim.	R.S.M Model	Hysys Sim.	R.S.M Model
1	50	50	90.0899	84.3069	90.0859	84.6259	45.08	42.652
2	50	100	90.094	87.4437	45.5525	40.1107	30.36	29.4067
3	100	50	50.05	47.2133	100	100.852	33.3333	32.3448
4	100	100	90.0919	90.3879	90.0879	90.9581	45.08	45.5663
5	39.6447	75	90.0902	92.5036	48.1088	51.4879	31.4624	36.3253
6	39.6447	75	90.0902	92.5036	48.1088	51.4879	39.1994	36.3253
7	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
8	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
9	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
10	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
11	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
12	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
13	110.355	75	68.0263	68.3564	100	98.9159	40.4898	40.4636
14	110.355	75	68.0263	68.3564	100	98.9159	40.4844	40.4636
15	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
16	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
17	75	75	90.0919	90.0919	90.0879	90.0879	45.08	45.08
18	75	110.355	90.0912	90.6195	61.5528	63.8349	36.6539	36.582
19	75	39.6447	52.9138	57.8724	100	102.308	34.5851	36.5988

3.1 Statistical Analysis and Optimization

The Analysis of variance of the second order regression model for the conversion of acetylene (%), conversion of HCl (%) and yield of Vinyl (%) revealed the significant level of the model at 99 %, 100 % and 91 % for conversion of acetylene (%), conversion of HCl (%) and yield of Vinyl (%) , respectively as presented in tables 3.0, 4.0 and 5.0, respectively. The statistical results with low P-values in the tables show how the model fits the simulation results. This highly infers that the total variance in the response could be explicated using this model. The statistical correlation is often shown by Regression results and significance between the independent variables and the dependent variables. The correlation coefficient (R^2) is the percentage of responses (%) (conversion of acetylene, conversion of HCl and yield of Vinyl) variation that is described by their relationship with flow rate of acetylene (kgmole/hr) and flow rate of HCl (kgmole/hr). Therefore, the adjusted correlation coefficient is the percentage of responses (%) variation that is explained by its relationship with flow rate of acetylene (kgmole/hr) and flow rate of HCl (kgmole/hr), adjusted for the number of independent variables (predictors) in the model. The importance of this adjustment is because correlation coefficient (R^2) for this model increases when a new predicting variable is added. Hence, for evaluating and analyzing the explanatory strength of models with different numbers of independent variables, the adjusted R^2 is a useful tool. The significance of the P-value for each coefficient is to test the null hypothesis that the coefficient has zero effect (Amodu , Ntwampe, & Ojumu, 2014b).

Table 3.0: Analysis of variance for the conversion of C_2H_2

Source	Term df	Error df	F	p-value
Whole-plot	3	3.92	31.10	0.0034
a-Flow rate of C2H2	*1*	*3.99*	*54.52*	*0.0018*
a^2	*1*	*3.83*	*15.59*	*0.0183*
B^2	*1*	*3.88*	*30.32*	*0.0058*
Subplot	2	8.80	334.14	< 0.0001
B-Flow rate of HCl	*1*	*8.80*	*486.48*	*< 0.0001*
aB	*1*	*8.80*	*181.80*	*< 0.0001*
Variance components				
Source	**Variance**	**Std Err**	**95% CI Low**	**95% CI High**
Group	*6.92*	*5.71*	*-4.27*	*18.11*
Residual	*2.20*	*1.05*	*1.04*	*7.48*
Total	9.12			
-2 Log Likelihood	69.38		BIC	92.94
R-Squared	0.99		AIC	85.38
Adj R-Squared	0.98		AICc	99.78

Table 4.0: Analysis of variance for the conversion of HCl

Source	Termdf	Error df	F	p-value
Whole-plot	3	4.00	54.87	0.0010
a-Flow rate of C2H2	*1*	*4.00*	*139.64*	*0.0003*
a^2	*1*	*4.00*	*24.07*	*0.0080*
B^2	*1*	*4.00*	*3.89*	*0.1199*
Subplot	2	9.00	1.201E+007	< 0.0001
B-Flow rate of HCl	*1*	*9.00*	*1.998E+007*	*< 0.0001*
aB	*1*	*9.00*	*4.046E+006*	*< 0.0001*
Variance components				
Source	**Variance**	**Std Err**	**95% CI Low**	**95% CI High**
Group	*12.08*	*8.55*	*-4.67*	*28.83*
Residual	*7.407E-005*	*3.491E-005*	*3.505E-005*	*2.468E-004*
Total	12.08			
-2 Log Likelihood	-21.59		BIC	1.96
R-Squared	1.00		AIC	-5.59
Adj R-Squared	1.00		AICc	8.81

Table 5.0: Analysis of variance for the conversion of C_2H_3Cl

Source	Term df	Error df	F	p-value
Whole-plot	3	13.00	28.58	< 0.0001
a-Flow rate of C2H2	*1*	*13.00*	*7.59*	*0.0164*
a^2	*1*	*13.00*	*40.60*	*< 0.0001*
B^2	*1*	*13.00*	*45.49*	*< 0.0001*
Subplot	2	13.00	25.88	< 0.0001
B-Flow rate of HCl	*1*	*13.00*	*8.375E-005*	*0.9928*
aB	*1*	*13.00*	*51.76*	*< 0.0001*
Variance Components				
Source	**Variance**	**Std Err**	**95% CI Low**	**95% CI High**
Group	*0.000*	*0.000*	*0.000*	*0.000*
Residual	*3.38*	*1.33*	*1.78*	*8.78*
Total	3.38			
-2 Log Likelihood	66.30		BIC	89.85
R-Squared	0.91		AIC	82.30
Adj R-Squared	0.86		AICc	96.70

Interpretation of the simulated data is easy with graphical representation as well as predicting the optimal conditions. From the statistical optimization with C.C.D of response surface methodology, themaximum conversion for acetylene, maximum conversion for HCl and maximum yield for Vinyl chloride is found to be 89.0238 %, 93.089 % and45.7696 %,respectively. This optimum (maximum) responses is accomplished when the flow rates of acetylene and HCl are 100 kgmole/hr and 95.2863 kgmole/hr respectively. In addition, the interactive effect of the flow rates of acetylene and of HCl on the response of the system was assessed by plotting three-dimensional curves of the response against the predicting variables as shown in figures 3.0, 4.0 and 5.0. The response distribution in this process simulation with respect to the variation of the independent variables shows that higher conversion of 93.089 % for HCl is achieved compared to 89.0238 % for acetylene.

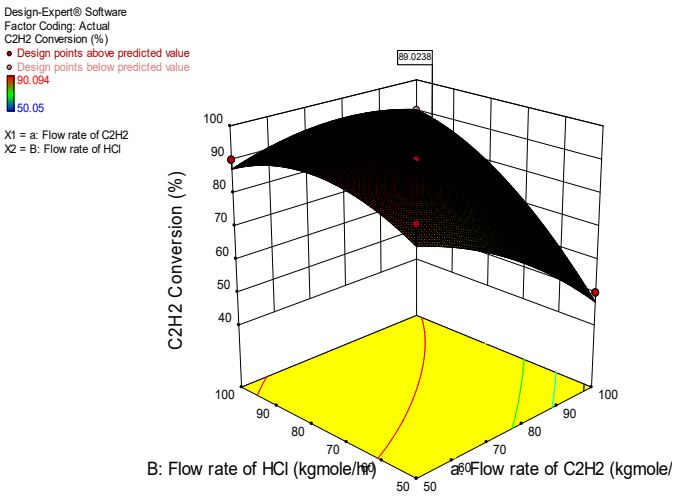

Figure 2.0: Surface plot for the conversion of acetylene

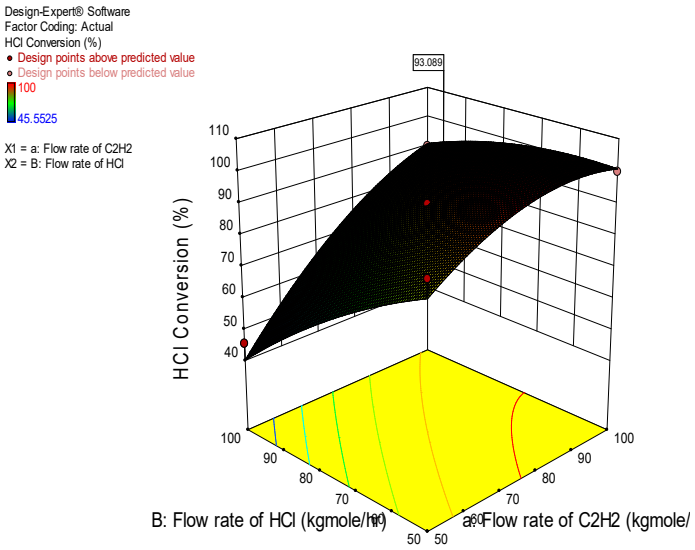

Figure 3.0: Surface plot for the conversion of HCl

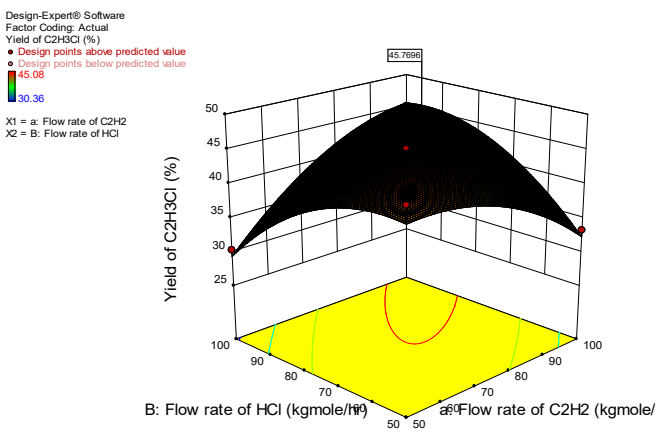

Figure 6.0is the contour plot for the statistical optimization, and it is the two-dimensional (2D) representation of the response variable against combinations of flow rates of acetylene and HCl. It shows the relationship between the responses (conversion of acetylene, conversion of HCl and yield of Vinyl chloride); and predictors(flow rates of acetylene and HCl). Within the limit of statistical optimization as depicted by this contour plot, optimum conversions (%) of acetylene and HCl are found to be 89.0238 % and 93.089 %, respectively; and optimum vinyl chloride yield of 45.7696 %. This optimum responses are found at optimum predicting flow rates of acetylene and HCl are observed to be 100 kgmole/hr and 95.312 kgmole/hr, respectively.

Figure 4.0: Surface plot for the yield of Vinyl chloride

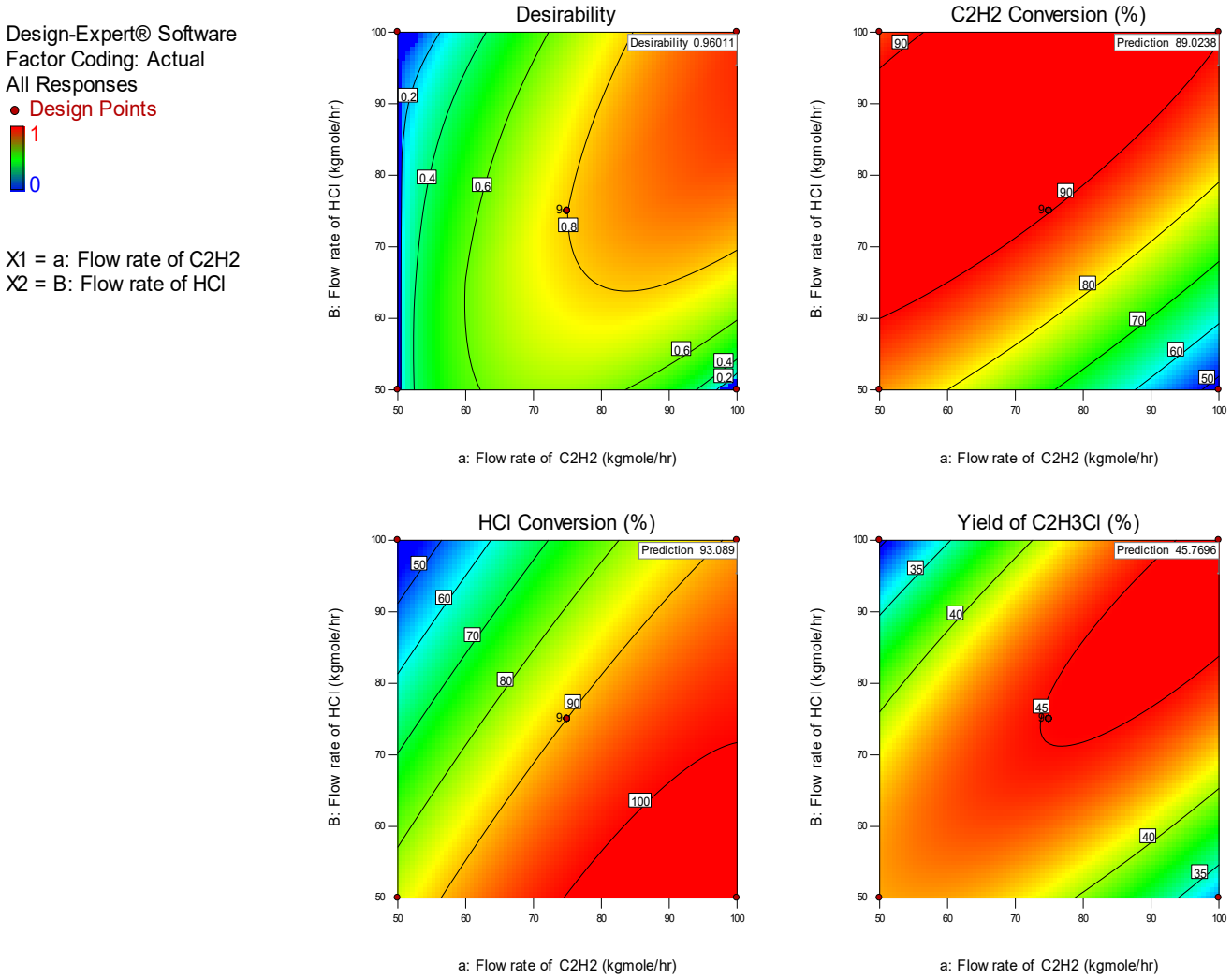

Figure 6.0: Contour plot for the responses, indicating optimum conditions

IV. CONCLUSION

This research paper has examined the statistical analysis of computer simulation for the synthesis of Vinyl chloride from acetylene using Aspen HYSYS 8.8. Here, the influence of flow rates of acetylene and HCl on the conversion of acetylene, conversion of hydrogen chloride and yield of vinyl chloride was examined.The simulation results obtained are found to beroughly equal to design values. The results and further calculationsreveals that approximate value to that of real-time synthesis of vinyl chloride from acetylene (vinylation) can be achieved from computer simulationand the synthesis of vinyl chloride from acetylene is realistic. Moreover, simulation of chemical processes with computerare usually used to curtain the possibility of the reaction and achieve the projected responses of variables or factors under some dominantanalogous conditions. The conversion values of over 90 % of this process shows good closeness and corroboration with the previousdiscovery of (Datanni et al., 2013). The research has shown that the models used can be recommended forsimulation, design and optimization; and could be used as scale up for the pilot synthesis of Vinyl chloride from acetylene.

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