Production of aniline by hydrogenation of nitrobenzene

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***Abstract*—Aniline, an important compound in organic chemistry, is mainly used to synthesize polyurethane and its precursors. Being one of the most important industrial chemicals, it is used to produce other industrial chemicals like methylene diphenyl diisocyanate (MDI), cyclohexylamine, benzoquinone, alkyl anilines, methylene dianiline etc. In this study, production of aniline at 10 tons/h was done by reducing nitrobenzene using hydrogen and this process was simulated using DWSIM open source software. The operating conditions of the different unit operations for this simulation were selected to achieve 75 percent conversion of nitrobenzene to aniline. Heat integrations were done by heating the reactants with the heat liberated from reactor. The property packages used were Lee-Kesler-Plocker and NRTL models. Sensitivity analysis was performed on three of the main units used in the process i.e. on the cooler, heat exchanger and distillation column.**

***Keywords*—Nitrobenzene, Aniline, Hydrogenation, Sensitivity Analysis, Rigorous Distillation**

I. Introduction

Aniline is an organic compound consisting of a phenyl group attached to an amino group, where aniline is the prototypical aromatic amine. The amino group provides unique reactivity which makes it an industrially important intermeditate. [1] It is a flammable liquid chemical and is slightly soluble in water. It is also known as phenylamine or aminobenzene.

Its main applications are in the production of herbicides, dyes, explosives, pigments, pesticides, plastics (polyurethanes) where aniline acts as an important intermediate. In the field of pharmaceuticals, paracetamol (acetaminophen), a widely used antipyretic is also prepared from aniline. [2,3] Polyaniline, an intrinsically conducting polymer is also produced from aniline.

Aniline is formed by the reduction of nitrobenzene using hydrogen. This process was proposed by Haber and his initial scheme was published in 1898. The scheme proposed that the transformation of nitrobenzene to aniline is a three-step process in which the intermediates nitrosobenzene and phenylhydroxylamine are formed. In addition to this, it was suggested that the by-products azobenzene, azoxybenzene, and hydrazobenzene could be formed via a side reaction of the above intermediate species. Hydrogenation can also be done using a catalyst to enhance the rate of reaction but the transformation is extremely superficial and needs to be done under relatively mild conditions. [4] However, in this paper, the side reactions and formation of intermediates have been neglected. Hence, simulation has been performed accordingly. These assumptions were made due to lack of literature or existing papers available for the simulation of the process. Basic knowledge from scientific papers was taken into consideration to create the DWSIM flowsheet and simulation.

The non-random two-liquid model (NRTL) is an activity coefficient model used to calculate phase equilibria and mainly applied for processes involving polar compounds. In this process, there are 3 polar chemicals, namely, nitrobenzene, aniline and water. Hence, the NRTL property package was selected. Lee-Kesler-Plocker (LKP) model is applied for systems with high Hydrogen content. Since the production of aniline is done by hydrogenation of nitrobenzene it was necessary to apply this property package.

II. Process description

The main process for aniline production is hydrogenation of nitrobenzene, given by the reaction equation:

$$\mathrm{C}_6H_5NO_2(g) + 3H_2(g) \rightarrow C_2H_5NH_2(g) + 2H_2O(g)$$

The process flowsheet designed for the production of aniline from nitrobenzene and hydrogen is shown in Fig.1.

Nitrobenzene (MSTR-NB) at room temperature of 24°C is sent to a heat exchanger (HE-1) where it is heated to 214.93°C. The heated nitrobenzene (MSTR-NB1) is then sent to the heater (HEAT-1) and further heated to 450°C. Gaseous nitrobenzene (MSTR-NB2) gets mixed with gaseous hydrogen (MSTR-H2) in a mixer (MIX-1). This reactants mixture stream (MSTR-1) is sent to the conversion reactor (RCTR) where the reaction takes place at 330°C. [5]

Standard Gibbs free energy was calculated using enthalpy and entropy data from the literature for every compound. Further, the reaction's equilibrium constant was found and equilibrium conversion was calculated. For this process, an approximate of 75 percent conversion with respect to nitrobenzene was obtained. This value was entered in the conversion reactor (RCTR) to obtain the desired yield of aniline.

The heat of reaction from the reactor is used to heat the feed nitrobenzene in the heat exchanger (HE-1). After heat

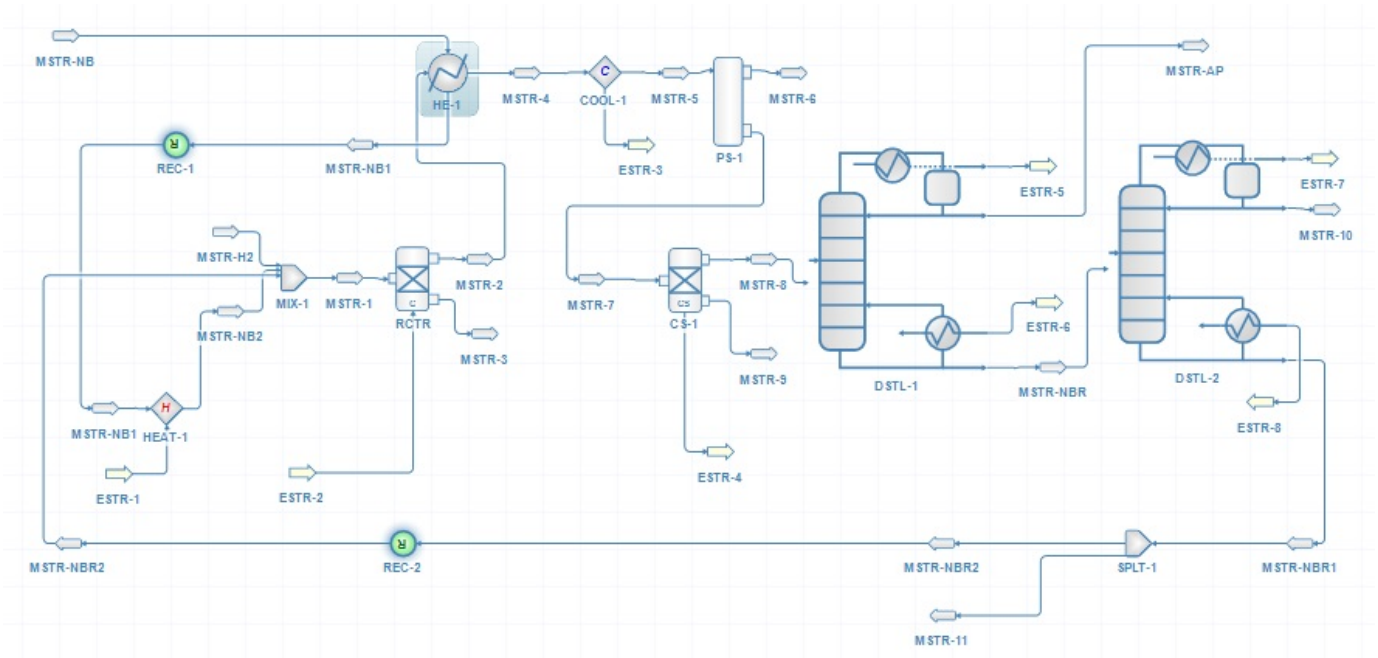

Fig. 1. DWSIM flow sheet

exchange the mixture is at 163°C and is now sent to a cooler (COOL-1) to further reduce its temperature to 50°C. The cooled mixture (MSTR-5) contains only hydrogen in the vapor phase which is removed using a phase separator (PS-1).The liquid stream (MSTR-7) from the phase separator is sent to a compound separator (CS-1) (which has been assumed to be a decanter) where water is completely separated from the organic mixture.

This organic mixture of nitrobenzene and aniline (MSTR-8) is sent to a distillation column (DSTL) to separate aniline and nitrobenzene based on their boiling points. Rigorous distillation column model of DWSIM has been used to simulate the distialltion column. The preliminary data required for the rigorous distillation column (DSTL-1) was generated using a short cut distillation column assuming the top product composition (MSTR-AP) to be 98.1 percent aniline.

Nitrobenzene coming in the residue (MSTR-NBR) consists of traces of aniline which is further purified using another distillation column (DSTL-2). The recovered nitrobenzene stream (MSTR-NBR1) is recycled and a part of the recycle stream is purged.

III. Results and Discussion

The simulation results of main streams in the process, i.e. of the reactor and distillation column-1 are given below.

As shown in table 1, it was observed that at a temperature and pressure of 311.17°C and 1.4 bar, the product stream from reactor contained aniline in large quantity of around 11 tons/h. Even though large amount of aniline was produced, it was a diluted stream with mole fraction of about 0.246. Its purity was improved using two distillation columns.

Since aniline is more volatile than nitrobenzene, it was obtained as distillate product from distillation column 1 (refer first half of table 2). The less volatile component, nitrobenzene, was observed in residue with a mole fraction of about 0.843 (refer second half of table 2) which is further purified in distillation column 2. Again in the other distillation column, nitrobenzene was obtained as residue product which could be reused again by recycling. To avoid accumulation of reactants, a part of the recycled stream was removed as purge.

TABLE I

Products from reactor

Species	Mass Flows (kg/h)	Mole Fraction
Aniline	11482	0.246
Water	4411.99	0.488
Nitrobenzene	4936.18	0.08
Hydrogen	187.11	0.185

TABLE II

Products from distillation column 1 (Distillate and Residue)

Species	Mass Flows (kg/h)	Mole Fraction
Aniline	10818.11	0.981
Nitrobenzene	273.57	0.018
Aniline	653.96	0.156
Nitrobenzene	4659.29	0.843

Flowsheet | Spreadsheet | Material Streams | Sensitivity Analysis

Sensitivity Studies | Independent Variables | Dependent Variables | Results | Chart

Start Sensitivity Analysis | Break Calculation | Send Data to Regression Plugin

Results

COOL-1 - Outlet Temperature (C)	MSTR-5 - Mass Flow (Vapor Phase) / Aniline (kg/h)	MSTR-5 - Mass Flow (Vapor Phase) / Nitrobenzene (kg/h)	MSTR-5 - Mass Flow (Vapor Phase) / Water (kg/h)	MSTR-5 - Mass Flow (Vapor Phase) / Hydrogen (kg/h)
50	13.1149	2.46115	154.058	233.823
60	24.78	4.85046	259.659	233.823
70	46.4779	9.44285	430.993	233.826
80	88.3566	18.5348	710.197	233.83
90	174.712	37.6299	1161.59	233.837
100	363.419	80.0889	1824.76	233.853
110	751.645	170.721	2554.72	233.886
120	1427.3	341.353	3124.22	234.153
130	2467.83	640.038	3505.41	234.691
140	3981.58	1160.25	3753.12	236.604
150	6114.87	2093.97	3894.06	243.405

Fig. 2. Sensitivity Analysis Table for Cooler

A. *Sensitivity Analysis for Cooler*

Hydrogenation of nitrobenzene to aniline is an exothermic reaction occurring at 330°C. The reactor product stream contains aniline, water and unreacted reactants nitrobenzene, hydrogen. After being sent to the heat exchanger, the products attain a temperature of 163.69°C. They were further cooled by the cooler to facilitate the formation of two phases. The vapor phase after cooling mainly consisted of unreacted hydrogen which was separated using a gas-liquid separator. In order to determine the temperature at which maximum phase separation occurs, a sensitivity analysis was performed on the coolers output stream (MSTR-5). Change in mass flow of each of the species, in vapor phase, was studied for a temperature range of 50°C to 150°C. The tabulated and graphical results are shown in Fig. 2 and Fig. 3 respectively. At 50°C, aniline was

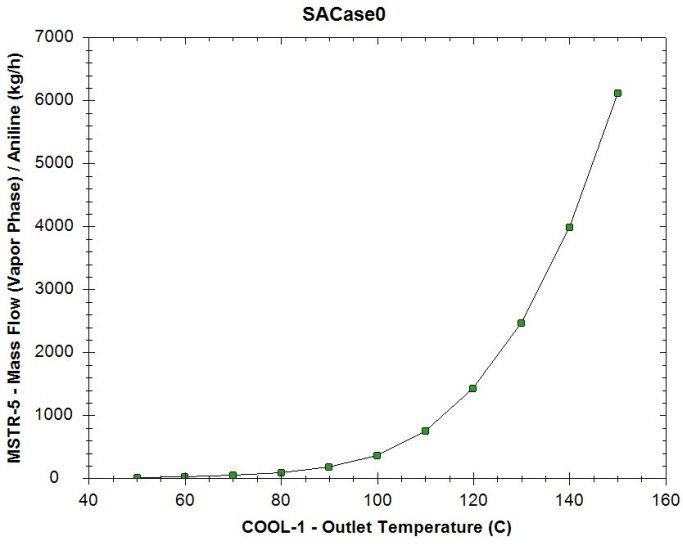

Fig. 3. Sensitivity Analysis Chart for Cooler

completely in liquid in liquid phase. Hence the reactor product was cooled to 50°C to separate the unreacted hydrogen. The water present along with the aniline and nitrobenzene forms a two phase liquid mixture which could be separated using a decanter.

B. *Effect of reflux ratio*

For the Distillation Column (DSTL-1), where a mixture of aniline and nitrobenzene (MSTR-8) is separated, sensitivity analysis was done by varying the reflux ratio from 1 to 6 and its effect on condenser duty, distillate molar flow, reboiler duty and number of stages was analyzed. However, no effect on any of the above parameters was observed by the software (refer Fig.4). Hence, a manual analysis was performed by changing the number of stages and noting the effect on the distillate and residue compositions. These results have been mentioned below in Table 3.

Results

DSTL-1 - Reflux Ratio	DSTL-1 - Condenser Duty (kW)	DSTL-1 - Distillate Molar Flow (kmol/h)	DSTL-1 - Reboiler Duty (kW)	DSTL-1 - Number of Stages ()
1	8700.12	118.386	-10038.1	10
2.25	8700.12	118.386	-10038.1	10
3.5	8700.12	118.386	-10038.1	10
4.75	8700.12	118.386	-10038.1	10
6	8700.12	118.386	-10038.1	10

Fig. 4. Sensitivity Analysis Table for Distillation Column 1

TABLE III

Analysis on upstream and downstream aniline composition (Mole fractions)

No. of stages	Upstream	Downstream
8	0.95	0.24
9	0.97	0.18
10	0.98	0.16

C. *Sensitivity Analysis for Heat Exchanger*

Sensitivity analysis was performed on the heat exchanger (HE-1). Here, the hot fluid outlet temperature (i.e. MSTR-4, containing reaction mixture) was varied from 50°C to 170°C

and its effect on cold fluid outlet temperature (i.e. MSTR-NB1, containing nitrobenzene) was recorded. No variation was shown by the software (refer fig.5). However, when the analysis was done manually by inputting the values of heat to be exchanged between the two fluids (in calculation parameters section), the results were obtained as shown in Table 4 and it can be concluded that as the amount of heat exchanged between the fluids increases the cold fluid outlet temperature increases and that of hot fluid decreases.

Results

HE-1 - Hot fluid outlet temperature (C)	HE-1 - Cold fluid outlet temperature (C)
50	214.943
60.9091	214.943
71.8182	214.943
82.7273	214.943
93.6364	214.943
104.545	214.943
115.455	214.943
126.364	214.943
137.273	214.943
148.182	214.943
159.091	214.943
170	214.943

Fig. 5. Sensitivity Analysis Table for Heat Exchanger

TABLE IV

Analysis on Cold and Hot fluid outlet temperatures

Heat exchanged (kW)	Cold Fluid Outlet temperature (°C)	Hot Fluid Outlet temperature (°C)
1000	132.22	224.26
1500	181.83	178.11
2000	224.04	162.04
2500	224.05	156.20
3000	224.05	149.51
4000	237.33	133.34

IV. Conclusion

Process simulation for the production of aniline by reduction of nitrobenzene was done using DWSIM. The various thermodynamic data were entered for each unit operation after thorough research and calculation for its feasibility. The simulation yielded good results providing with better knowledge relating the thermodynamics and kinetics of the reaction. Number of separation units were included based on the different separation principles to obtain considerable purity of the final aniline product. Sensitivity analysis was performed on the cooler and it showed that as the outlet temperature of the cooler increases, mass flow of aniline in vapor phase also increases. Hence, lower temperature condition is preferred in order to get higher mass flow of liquid aniline which is the desired product.

While working with DWSIM, the team felt that the sensitivity analysis parameters could be improved i.e. more number of dependent and independent variable combinations could be added in the software, because, even after trying to perform different types of analysis on the process, the desired results were not obtained from the software. It was possible only after manually changing the specifications of the unit. Also, the software could include other objects like decanter, crystalliser, extractor, dryer etc. to improve the simulation and flowhsheet design.

V. Acknowledgment

We would like to extend our hearty gratitude to Dr. Archna, Head of Department of Chemical Engineering, Ramaiah Institute of Technology, for giving us the opportunity to work on this project. We would also like to thank our professors Dr. Mahendra Chintala, Mrs. Sravanthi Veluturla and Mr. Neelesh Singhal, for their kind guidance and help throughout the making of this paper and also in designing the simulation process.

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