Production of Chlorobenzene from Benzene and Chlorine

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Background

Monochlorobenzene is an important derivative of benzene which acts as a precusor to such chemicals as nitrochlorobenzenes and phenols. Even though the use of monochlorobenzene in agrochemicals is declining due to environmental concerns and its carcinogenic nature, it enjoys wide applications in rubber, plastics, pharmaceuticals, dyes and pigments.[1]

Controlled chlorination of benzene with chlorine in liquid phase in 20-40 deg. C gives selective conversion to monochlorobenzene in presence of a suitable metal catalyst. Commonly, Ferric Chloride and Iron raschig rings are used as the catalyst. In that case, the reported conversion (per-pass) is 75% monochlorobenzene and 22% dichlorobenzene with para and ortho derivatives in the ratio 3:2.[2] This information is used in the conversion reactor data. NRTL is the most preferred themodynamic model used in the flowsheet.

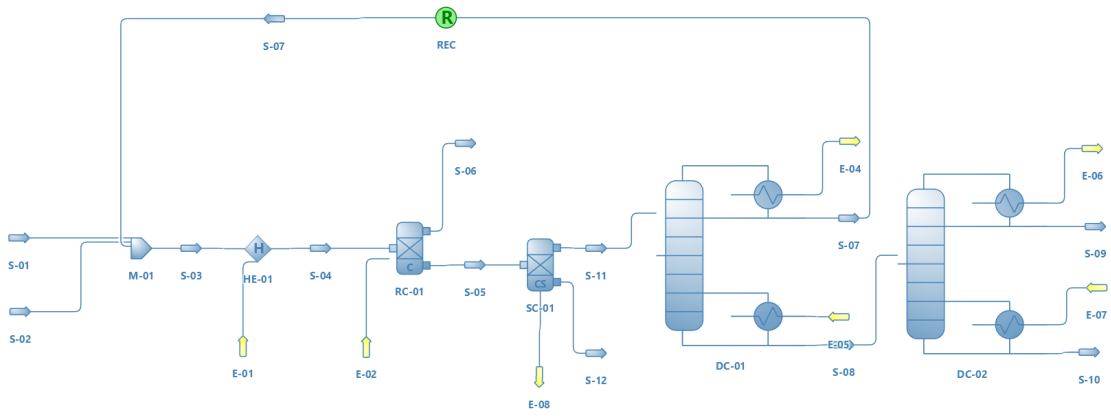

Figure 1: Flowsheet for Production of Chlorobenzene from Benzene and Chlorine

Process Description

Dry Benzene (S-01) and Chlorine (S-02) feeds along with the recycle feed (S-07) are mixed in M-01 and heated to the reactor temperature in HE-01. They are fed to a chlorinator reactor (RC-01) which operates at 40 deg. C and maintained at atmospheric pressure. The product mixture leaving the reactor is flashed into a vapour stream (S-06) rich in hydrochloric acid (94% mol) and a liquid stream (S-05) rich in monochlorobenzene. Hydrochloric acid from S-06 is recovered with the help of a suitable solvent in an absorber and that from S-05 is scrubbed in another tower SC-01.

The liquid stream (S-11) leaving SC-01 is sent to benzene recovery column (DC-01) operated at atmospheric pressure where 99% of unreacted benzene is recovered in the distillate and recycled back to the chlorinator feed. The bottoms of DC-01 (S-08) are fed to chlorobenzene column (DC-02) operated at atmospheric pressure where at least 94% pure monochlorobenzene is recovered in the distillate (S-09). The bottoms (S-10) contain a mixture of dichlorobenzenes which is either subjected to higher degree of chlorination or purified depending on the process requirements.

Results

Stream	S-01	S-02	S-06	S-07	S-09	S-10
Temperature (K)	313.15	313.15	313.15	246.614	406.54	440.74
Pressure (Pa)	101325	101325	101325	101325	101325	101325
Mass Flow (kg/s)	1	1	0.594	0.135	1.196	0.209
Density (kg/m3)	857.8	2.8	1.5	932.2	987.0	865.6
Phase	Liquid	Vapour	Vapour	Liquid	Liquid	Mixed
Molar Composition						
Benzene	1.000	0.000	0.031	0.902	0.001	0.000
Chlorine	0.000	1.000	0.000	0.000	0.000	0.000
Hydrogen chloride	0.000	0.000	0.943	0.088	0.000	0.000
Monochlorobenzene	0.000	0.000	0.025	0.010	0.946	0.182
o-dichlorobenzene	0.000	0.000	0.000	0.000	0.015	0.354
p-dichlorobenzene	0.000	0.000	0.000	0.000	0.039	0.464

Conclusion and Comments

1. A flowsheet for continuous production of Chlorobenzene was built with a product purity of at least 94%

2. Since kinetic data related to catalytic chlorination reaction is not available in the open-source literature, we have used a conversion reactor model in the flowsheet.

3. Hydrochloric Acid from S-07 is absorbed with the help of a suitable solvent such as water and that from S-05 is scrubbed in SC-01. The scrubber is replaced with a compound separator SC-01 with complete recovery for hydrochloric acid to avoid calculation error in downstream blocks (DC-01)

References

[1] Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, *Emissions from Chlorobenzene Production*, Chapter 4 in **LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF CHLOROBENZENES (REVISED)**, March 1994.

[2] Uwe Beck and Eckhard Loser, *Chlorinated Benzenes and other Nucleus-Chlorinated Aromatic Hydrocarbons* in **Ullmann's Encyclopedia of Industrial Chemistry**, Vol. 8 (2010), pp. 488-491.