Styrene Production Process with Ethylbenzene Recycling

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Background:

Styrene, C_6H_5-C_2H_5, is a monocyclic aromatic hydrocarbon mainly used in the polymer industries to manufacture resins, synthetic rubber, and plastics. Also, it is a colorless oily liquid with sweet smell. Currently, more than 90% of styrene is produced through catalytic dehydrogenation of ethylbenzene at temperatures starting from 630°C and pressures slightly above atmospheric pressure in the presence of water steam. However, two side reactions take place in this process: (1) Pyrolysis of Ethylbenzene to benzene and ethylene and (2) Ethylbenzene hydro alkylation where toluene and methane are produced.

Chemistry:

Main Reaction: $C_6H_5 - C_2H_{5(g)} \leftrightarrow C_6H_5 - C_2H_{3(g)} + H_{2(g)}$

Side Reactions: (1) $C_6H_5 - C_2H_{5(g)} \rightarrow C_6H_{6(g)} + C_2H_{4(g)}$

(2) $C_6H_5 - C_2H_{5(g)} + H_{2(g)} \rightarrow C_6H_5 - CH_{3(g)} + CH_{4(g)}$

In the said reactions, it is modeled with 50% conversion at the main reaction, while negligible and 2% with the 1st and 2nd side reactions, respectively.

Description of Process:

A 20 kmol/hr fresh ethylbenzene feed (S-01) at 20°C, 180 kPa mixed with 100 kmol/hr steam (S-02) at 120°C, 180 kPa and recycled ethylbenzene (S-48) to enter an evaporator (HE-01). After the evaporation, the mixed feed is further preheated in a heat exchanger (HE-02). The energy of hot reaction products is used for heating the reactor feed. Raw materials (S-05), before entering the reactor (RC-01), is mixed with superheated steam (S-43) to meet a mass ratio of steam to ethylbenzene vapor around 3:1 and the temperature of the reactor feed (S-06) is above 630°C. This will enter the first adiabatic reactor (RC-01), where catalytic dehydrogenation of ethylbenzene to styrene occurs. The reaction products (S-07) will again be heated

using superheated steam (S-40) at 750°C and 250 kPa before entering the second reactor (RC-02). The reactor products (S-10) will be used as heating medium for HE-01 and HE-02 and will pass through series of Cooling Water Heat Exchanger (HE-04 & HE-05) and a cooler (HE-06) to reduce the temperature to 25°C at 100 kPa. The cooled stream (S-18) will enter a 1st separator (V-01) in which condensate (S-20) is collected. The vapor (S-19) from the separator is further cooled in a brine cooler (HE-07) to 5°C and enter another separator (V-02). In the second separator (V-02), hydrogen is obtained and condensates (S-23, S-24) is mixed with the 1st condensate stream (S-20) from V-01. This mixture (S-25) enters the liquid-liquid phase separator (V-03) where the organic (S-28) and the aqueous phases (S-27) are separated. The crude organic stream is carried out by distillation under reduced pressure of about 5 kPa in two columns. In the 1st partial condenser column (DC-01), components of benzene, toluene, and a portion of ethylbenzene are distilled off (S-30) while bottoms (S-31) will enter the 2nd column (DC-02) to distill off the available ethylbenzenes (S-32). Another distillation column (DC-03) is provided to separate the styrene from the stream as final products. The overhead of the last column (S-34) is pumped and recycled back to the feed stream as ethylbenzene is abundant at around 95.5% purity. Lastly, the bottom products (S-33, S-35) of DC-02 & DC-03 are collected to form stream with 99.9% mol styrene.

Results:

Thermodynamic Package

Peng-Robinsons (PR) is selected for process fluids while Steam Tables (IAPWS-IF97) is for pure water streams/utilities.

Reaction Yield

From 20 kmol/hr (2123.3 kg/hr) ethylbenzene feed, a produced 19.12 kmol/hr (1,991.36 kg/hr) of 99.9% styrene is calculated. This shows a yield of 95.6%.

The results below show the material and component balances with conditions within the process.

Table 1. Streamwise Results for the Styrene Production with Ethylbenzene Recycling

Object	S-01	S-02	S-03	S-04	S-05	S-06	S-07	S-08	
Temperature	20	120	65.167	101.907	400	659.003	622.268	622.268	C
Pressure	180	180	180	170	160	160	120	120	kPa
Mass Flow	2123.3	1801.53	4576.56	4576.56	4576.56	18649.7	18649.7	0	kg/h
Molar Flow	20	100	126.158	126.158	126.158	907.338	920.279	0	kmol/h
Volumetric Flow	2.4419	1791.44	1431.14	2264.53	4397.87	43917.7	57056.5	0	m3/h
Molar Fraction (Vapor)	0	1	0.740639	0.999996	1	1	1	0	
Molar Fraction (Liquid 1)	1	0	0.259361	4.34033E-06	0	0	0	0	
Molar Fraction (Vapor) / Ethylbenzene	1	0	0.0418156	0.20514	0.205143	0.0285236	0.0134988	0	
Molar Fraction (Liquid 1) / Ethylbenzene	1	0	0.671545	0.907829	0.488565	0.0280426	0.0178812	0	
Molar Fraction (Vapor) / Styrene	0	0	0.00017624	0.00120081	0.00120083	0.000166967	0.0142259	0	
Molar Fraction (Liquid 1) / Styrene	0	0	0.00412669	0.00700237	1.01463E-05	6.19447E-14	1.28856E-10	0	
Molar Fraction (Vapor) / Hydrogen	0	0	7.95066E-35	5.89059E-35	5.89057E-35	8.19038E-36	0.0134988	0	
Molar Fraction (Liquid 1) / Hydrogen	0	0	7.69779E-38	7.44511E-38	7.95945E-99	4.48193E-156	1.09129E-113	0	
Molar Fraction (Vapor) / Benzene	0	0	1.02151E-25	1.47362E-25	1.47362E-25	2.04895E-26	2.81214E-22	0	
Molar Fraction (Liquid 1) / Benzene	0	0	2.76466E-25	1.25958E-25	1.68302E-25	2.60057E-26	4.00986E-22	0	
Molar Fraction (Vapor) / Ethylene	0	0	4.98556E-44	3.71168E-44	3.71166E-44	5.16078E-45	2.81194E-22	0	
Molar Fraction (Liquid 1) / Ethylene	0	0	7.38842E-46	4.0701E-46	8.58369E-47	1.41758E-49	1.88405E-26	0	
Molar Fraction (Vapor) / Toluene	0	0	0.000382176	0.00100217	0.00100217	0.000139344	0.000699835	0	
Molar Fraction (Liquid 1) / Toluene	0	0	0.00277265	0.00210261	0.00254701	0.00251418	0.00981677	0	
Molar Fraction (Vapor) / Methane	0	0	1.52691E-30	1.13256E-30	1.13256E-30	1.57473E-31	0.00056245	0	
Molar Fraction (Liquid 1) / Methane	0	0	6.41068E-33	4.46655E-33	4.35569E-36	3.01574E-41	6.35755E-13	0	
Molar Fraction (Vapor) / Water	0	1	0.957626	0.792657	0.792654	0.97117	0.957514	0	
Molar Fraction (Liquid 1) / Water	0	1	0.321556	0.0830662	0.508878	0.969443	0.972302	0	

Object	S-09	S-10	S-11	S-12	S-13	S-14	S-15	S-16	
Temperature	600	582.136	582.136	582.136	517.11	517.11	483.513	183.51	C
Pressure	120	120	120	120	120	120	120	120	kPa
Mass Flow	18649.7	18649.7	-4.14107E-12	18649.7	18649.7	18649.7	18650.8	18650.8	kg/h
Molar Flow	920.279	926.49	-∞	926.49	926.49	926.49	926.507	926.507	kmol/h
Volumetric Flow	55633.6	54860.3	0	54860.3	50675.3	50675.3	48512.9	29138	m3/h
Molar Fraction (Vapor)	1	1	0	1	1	1	1	1	
Molar Fraction (Liquid 1)	0	0	0	0	0	0	0	0	
Molar Fraction (Vapor) / Ethylbenzene	0.0134988	0.00643598	0	0.00643598	0.00643598	0.00643598	0.00643824	0.00643824	
Molar Fraction (Liquid 1) / Ethylbenzene	0.0208574	0.0113375	0	0.0113375	0.0162792	0.0162792	0.0188882	1.43382E-07	
Molar Fraction (Vapor) / Styrene	0.0142259	0.0208346	0	0.0208346	0.0208346	0.0208346	0.0208421	0.0208421	
Molar Fraction (Liquid 1) / Styrene	7.8859E-10	4.71567E-09	0	4.71567E-09	4.67637E-07	4.67637E-07	3.75697E-06	1.50178E-06	
Molar Fraction (Vapor) / Hydrogen	0.0134988	0.0198443	0	0.0198443	0.0198443	0.0198443	0.0198512	0.0198512	
Molar Fraction (Liquid 1) / Hydrogen	2.56597E-108	6.209E-104	0	6.209E-104	2.33733E-89	2.33733E-89	2.73534E-82	4.52266E-06	
Molar Fraction (Vapor) / Benzene	2.81214E-22	4.12536E-22	0	4.12536E-22	4.12536E-22	4.12536E-22	4.10967E-22	4.10967E-22	
Molar Fraction (Liquid 1) / Benzene	4.21953E-22	6.5225E-22	0	6.5225E-22	7.22908E-22	7.22908E-22	7.42652E-22	4.89119E-25	
Molar Fraction (Vapor) / Ethylene	2.81194E-22	4.12516E-22	0	4.12516E-22	4.12516E-22	4.12516E-22	4.10947E-22	4.10947E-22	
Molar Fraction (Liquid 1) / Ethylene	3.11056E-26	6.82619E-26	0	6.82619E-26	2.48733E-25	2.48733E-25	4.47255E-25	2.0453E-25	
Molar Fraction (Vapor) / Toluene	0.000699835	0.000963309	0	0.000963309	0.000963309	0.000963309	0.000963823	0.000963823	
Molar Fraction (Liquid 1) / Toluene	0.0084017	0.010419	0	0.010419	0.00699686	0.00699686	0.00581839	1.5879E-07	
Molar Fraction (Vapor) / Methane	0.00056245	0.000826845	0	0.000826845	0.000826845	0.000826845	0.000827135	0.000827135	
Molar Fraction (Liquid 1) / Methane	1.76319E-12	5.82394E-12	0	5.82394E-12	8.69519E-11	8.69519E-11	3.11423E-10	3.02411E-07	
Molar Fraction (Vapor) / Water	0.957514	0.951095	0	0.951095	0.951095	0.951095	0.951077	0.951077	
Molar Fraction (Liquid 1) / Water	0.970741	0.978243	0	0.978243	0.976724	0.976724	0.97529	0.999993	

Object	S-17	S-18	S-19	S-20	S-21	S-22	S-23	S-24	
Temperature	174.366	25	25	25	5	5	5	5	C
Pressure	120	100	100	100	100	100	100	100	kPa
Mass Flow	18650.8	18650.8	2798.81	15852	2798.81	58.538	2722.72	17.552	kg/h
Molar Flow	926.507	926.507	46.5883	879.919	46.5883	19.3479	26.2661	0.974283	kmol/h
Volumetric Flow	28544.4	1138.21	1122.3	15.9104	450.511	447.496	2.99699	0.0175501	m3/h
Molar Fraction (Vapor)	1	0.0502838	1	0	0.415295	1	0	0	
Molar Fraction (Liquid 1)	0	0.949716	0	1	0.563792	0	1	1	
Molar Fraction (Vapor) / Ethylbenzene	0.00643824	0.128038	0.128038	0	0.000953551	0.000953551	0	0	
Molar Fraction (Liquid 1) / Ethylbenzene	7.16561E-08	8.49141E-13	0	8.49141E-13	0.226399	0	0.226399	4.66256E-16	
Molar Fraction (Vapor) / Styrene	0.0208421	0.41449	0.41449	0	0.00198132	0.00198132	0	0	
Molar Fraction (Liquid 1) / Styrene	7.93052E-07	3.7077E-11	0	3.7077E-11	0.733723	0	0.733723	1.76576E-14	
Molar Fraction (Vapor) / Hydrogen	0.0198512	0.394782	0.394782	0	0.950086	0.950086	0	0	
Molar Fraction (Liquid 1) / Hydrogen	3.09991E-06	1.20014E-07	0	1.20014E-07	0.000386015	0	0.000386015	1.17019E-07	
Molar Fraction (Vapor) / Benzene	4.10967E-22	8.17292E-21	8.17292E-21	0	8.09877E-22	8.09877E-22	0	0	
Molar Fraction (Liquid 1) / Benzene	3.14568E-25	2.28377E-27	0	2.28377E-27	1.38998E-20	0	1.38998E-20	6.75687E-29	
Molar Fraction (Vapor) / Ethylene	4.10947E-22	8.17242E-21	8.17242E-21	0	1.92487E-20	1.92487E-20	0	0	
Molar Fraction (Liquid 1) / Ethylene	1.41065E-25	7.49799E-27	0	7.49799E-27	3.16735E-22	0	3.16735E-22	8.07848E-27	
Molar Fraction (Vapor) / Toluene	0.000963823	0.0191677	0.0191677	0	0.000461045	0.000461045	0	0	
Molar Fraction (Liquid 1) / Toluene	9.00027E-08	2.6473E-11	0	2.6473E-11	0.0336581	0	0.0336581	9.47511E-14	
Molar Fraction (Vapor) / Methane	0.000827135	0.0164491	0.0164491	0	0.039446	0.039446	0	0	
Molar Fraction (Liquid 1) / Methane	2.10011E-07	1.31819E-08	0	1.31819E-08	0.000119561	0	0.000119561	1.4806E-08	
Molar Fraction (Vapor) / Water	0.951077	0.027073	0.027073	0	0.00707242	0.00707242	0	0	
Molar Fraction (Liquid 1) / Water	0.999996	1	0	1	0.00571449	0	0.00571449	1	

Object	S-25	S-26	S-27	S-28	S-29	S-30	S-31	S-32	
Temperature	9.28685	24.97	24.97	24.97	24.9729	32.0962	55.8203	52.2365	C
Pressure	100	100	100	100	95	5	5	5	kPa
Mass Flow	18592.3	18592.3	15872.2	2720.02	2720.02	76.2052	2643.81	951.682	kg/h
Molar Flow	907.159	907.159	881.043	26.1161	26.1161	0.830895	25.2852	9.03806	kmol/h
Volumetric Flow	573.197	624.974	15.9306	3.05281	3.05283	420.354	4.35652	1.21503	m3/h
Molar Fraction (Vapor)	0.029058	0.0295624	0	0	0	0.999614	9.41148E-05	2.02561E-05	
Molar Fraction (Liquid 1)	0.970942	0.970438	1	1	1	0.000385988	0.999906	0.99998	
Molar Fraction (Vapor) / Ethylbenzene	0.225591	0.221741	0	0.00348819	0.00348666	0.0568712	0.298539	0.703752	
Molar Fraction (Liquid 1) / Ethylbenzene	1.85148E-13	1.44232E-12	0	0.227699	0.227699	0.137697	0.233305	0.650923	
Molar Fraction (Vapor) / Styrene	0.731104	0.718628	0	0.00754741	0.00754412	0.0151202	0.685405	0.257158	
Molar Fraction (Liquid 1) / Styrene	1.02089E-11	6.3058E-11	0	0.737937	0.737937	0.0543915	0.761696	0.33509	
Molar Fraction (Vapor) / Hydrogen	0.000388646	0.000382012	0	0.938714	0.938722	0.0123346	2.42621E-30	1.70089E-29	
Molar Fraction (Liquid 1) / Hydrogen	6.44376E-11	1.227E-10	0	0.00039228	0.00039228	3.05348E-07	6.55537E-35	4.77671E-34	
Molar Fraction (Vapor) / Benzene	1.38502E-20	1.36137E-20	0	2.29158E-21	2.29087E-21	4.39503E-19	7.23076E-24	1.81582E-23	
Molar Fraction (Liquid 1) / Benzene	1.47886E-27	3.8142E-27	0	1.39797E-20	1.39797E-20	1.12817E-19	7.34563E-25	2.05643E-24	
Molar Fraction (Vapor) / Ethylene	3.15849E-22	3.10455E-22	0	2.81981E-20	2.8195E-20	1.00244E-20	3.47404E-40	1.06285E-39	
Molar Fraction (Liquid 1) / Ethylene	1.66481E-28	2.95696E-28	0	3.18807E-22	3.18807E-22	6.03153E-24	1.5249E-43	4.96524E-43	
Molar Fraction (Vapor) / Toluene	0.033538	0.0329657	0	0.00150597	0.00150541	0.911879	0.016056	0.0390903	
Molar Fraction (Liquid 1) / Toluene	1.00799E-11	4.51211E-11	0	0.0338514	0.0338514	0.807911	0.00499895	0.0139877	
Molar Fraction (Vapor) / Methane	0.000119573	0.000117531	0	0.0487449	0.0487422	0.00379499	2.6415E-26	1.07974E-25	
Molar Fraction (Liquid 1) / Methane	5.71528E-11	9.85951E-11	0	0.000120693	0.000120693	5.25818E-07	3.16476E-30	1.36212E-29	
Molar Fraction (Vapor) / Water	0.00925953	0.0261659	1	1.07212E-14	1.07199E-14	1.23189E-13	6.28534E-25	1.72584E-24	
Molar Fraction (Liquid 1) / Water	1	1	1	3.91781E-15	3.91781E-15	2.18013E-15	5.25879E-27	1.48416E-26	

Object	S-33	S-34	S-35	S-36	S-37	S-38	S-39	S-40	
Temperature	58.1633	49.9997	58.1634	58.1634	50.4556	20	133.525	750	C
Pressure	5	5	5	5	180	180	300	250	kPa
Mass Flow	1692.16	651.732	299.959	1992.12	651.732	651.732	14073.2	14073.2	kg/h
Molar Flow	16.2475	6.15835	2.87981	19.1272	6.15835	6.15835	781.18	781.18	kmol/h
Volumetric Flow	179.944	6.52965	28.8557	208.766	0.772473	0.748833	8525.33	26566.7	m3/h
Molar Fraction (Vapor)	0.0199527	0.00174593	0.0180309	0.0196603	0	0	1	1	
Molar Fraction (Liquid 1)	0.980047	0.998254	0.981969	0.98034	1	1	0	0	
Molar Fraction (Vapor) / Ethylbenzene	0.00141615	0.93029	0.00141717	0.00141631	0.931844	0.925312	0	0	
Molar Fraction (Liquid 1) / Ethylbenzene	0.000991546	0.954913	0.000992258	0.000991654	0.954885	0.954885	0	0	
Molar Fraction (Vapor) / Styrene	0.998584	0.0171429	0.998583	0.998584	0.0171927	0.0162517	0	0	
Molar Fraction (Liquid 1) / Styrene	0.999008	0.0246127	0.999008	0.999008	0.0246	0.0246	0	0	
Molar Fraction (Vapor) / Hydrogen	7.4822E-131	6.79979E-31	3.80137E-174	6.44998E-131	3.16078E-29	1.62084E-28	0	0	
Molar Fraction (Liquid 1) / Hydrogen	1.98084E-135	1.96568E-35	1.00638E-178	1.70757E-135	1.20673E-33	1.20673E-33	0	0	
Molar Fraction (Vapor) / Benzene	2.48781E-45	2.46649E-23	2.18376E-54	2.1182E-45	2.31912E-23	3.18601E-23	0	0	
Molar Fraction (Liquid 1) / Benzene	2.34957E-46	2.98077E-24	2.06242E-55	2.00049E-46	3.01867E-24	3.01867E-24	0	0	
Molar Fraction (Vapor) / Ethylene	4.99614E-114	3.40732E-40	1.02367E-145	4.30564E-114	1.26914E-39	3.97077E-39	0	0	
Molar Fraction (Liquid 1) / Ethylene	2.10984E-117	1.65764E-43	4.3229E-149	1.81825E-117	7.60325E-43	7.60325E-43	0	0	
Molar Fraction (Vapor) / Toluene	1.83464E-13	0.0525674	1.39887E-17	1.55951E-13	0.0509633	0.0584365	0	0	
Molar Fraction (Liquid 1) / Toluene	5.21044E-14	0.0204739	3.97284E-18	4.42906E-14	0.0205303	0.0205303	0	0	
Molar Fraction (Vapor) / Methane	1.15914E-112	1.23658E-26	9.42958E-150	9.99165E-113	1.39569E-25	5.40572E-25	0	0	
Molar Fraction (Liquid 1) / Methane	1.34707E-116	1.61582E-30	1.09583E-153	1.16116E-116	2.32013E-29	2.32013E-29	0	0	
Molar Fraction (Vapor) / Water	3.50928E-70	2.09492E-24	2.06353E-90	3.01212E-70	2.10181E-24	3.94683E-24	1	1	
Molar Fraction (Liquid 1) / Water	2.8668E-72	1.8208E-26	1.68573E-92	2.46066E-72	2.18338E-26	2.18338E-26	0	0	

Object	S-41	S-42	S-43	S-44	S-45	S-46	S-47	S-48	
Temperature	778.989	750	750	20	133.525	20	116.87	20	C
Pressure	160	160	160	300	300	180	180	180	kPa
Mass Flow	14073.2	14073.2	14073.2	16410.4	16410.4	811.048	811.048	651.732	kg/h
Molar Flow	781.18	781.18	781.18	230	230	45.02	45.02	6.15835	kmol/h
Volumetric Flow	42697.4	41513.5	41513.5	16.4384	1052.63	0.812476	0.8577	0.748833	m3/h
Molar Fraction (Vapor)	1	1	1	0	0.104299	0	0	0	
Molar Fraction (Liquid 1)	0	0	0	1	0.895701	1	1	1	
Molar Fraction (Vapor) / Ethylbenzene	0	0	0	0	0	0	0	0.925312	
Molar Fraction (Liquid 1) / Ethylbenzene	0	0	0	0	0	0	0	0.954885	
Molar Fraction (Vapor) / Styrene	0	0	0	0	0	0	0	0.0162517	
Molar Fraction (Liquid 1) / Styrene	0	0	0	0	0	0	0	0.0246	
Molar Fraction (Vapor) / Hydrogen	0	0	0	0	0	0	0	1.62084E-28	
Molar Fraction (Liquid 1) / Hydrogen	0	0	0	0	0	0	0	1.20673E-33	
Molar Fraction (Vapor) / Benzene	0	0	0	0	0	0	0	3.18601E-23	
Molar Fraction (Liquid 1) / Benzene	0	0	0	0	0	0	0	3.01867E-24	
Molar Fraction (Vapor) / Ethylene	0	0	0	0	0	0	0	3.97077E-39	
Molar Fraction (Liquid 1) / Ethylene	0	0	0	0	0	0	0	7.60325E-43	
Molar Fraction (Vapor) / Toluene	0	0	0	0	0	0	0	0.0584365	
Molar Fraction (Liquid 1) / Toluene	0	0	0	0	0	0	0	0.0205303	
Molar Fraction (Vapor) / Methane	0	0	0	0	0	0	0	5.40572E-25	
Molar Fraction (Liquid 1) / Methane	0	0	0	0	0	0	0	2.32013E-29	
Molar Fraction (Vapor) / Water	1	1	1	0	1	0	0	3.94683E-24	
Molar Fraction (Liquid 1) / Water	0	1	1	1	1	1	1	2.18338E-26	

Conclusions and Recommendations

DWSIMv.8 is used for modeling for this project. The topic is adopted from Section 8.5.2 Styrene Process of Chemical Process Design and Simulation (Aspen Plus and Aspen HYSYS Applications) by Juma Haydary. Results show that the calculated yield of 95.6% is near the reference value of 96.5%. Thus, DWSIM shows that it can run simulations on par with the results from licensed software like ASPEN HYSYS.