Methanol Alkylation of Toluene to produce Styrene Monomer

The process flow diagram or flowsheet for the conversion of toluene and methanol into styrene monomer and ethylbenzene is given below. Pure toluene enters the flowsheet through Stream S1, while pure methanol enters via Stream S4. The styrene product leaves via Stream S33, while the ethylbenzene byproduct leaves through Stream S31. Four other streams leave the flowsheet—S36, S17g, S23g, and S35. Stream S36 vents mostly hydrogen. Stream S17g and S23g are smaller vents from the partial condensers of two distillation columns. Stream S35 is the wastewater produced by the flowsheet. Stream S1, S4, S31, S33, and S35 exist at 25°C and 1 atm. Streams S17g, S23g, and S36 exist as vapors at 1 atm and are to be used as fuels. The two vent streams—S17g and S23g—represent only two percent of the total molar flow of these three vapor streams.

The chemical process simulation for the material and energy requirements of this HYSYS flowsheet is mathematically modeled by the set of algebraic equations on the next two pages. The general descriptions of the process variables appearing in these equations are provided on the fourth page. The HYSYS recycle operation labeled “RCY” in the above flowsheet is not part of the mathematical model, since Streams S9 and S10 are physically the same stream. In the mathematical model, Stream S9 is represented as Stream S10.

Each of the 32 functional equations in the mathematical model represent the process simulation for a physical process unit—a mixer, heater, cooler, valve, reactor, decanter, distillation column, pump, or compressor—in the flowsheet. Each functional equation states that knowing the process state—temperature, pressure, molar flow rate, and component mole fractions—of each incoming material stream to a process unit along with any of its design parameters, the process states of all outgoing material streams along with any heat duty or work requirement(s) can be determined. Basically, knowing the incoming material stream conditions and the design parameters, HYSYS will calculated the outgoing material streams plus any heat duties or work requirement for a process unit.

The mathematical algorithm that indicates how the equations in the mathematical model are to be solved is given in the last two pages. The functional equation “styrene” for the mathematical algorithm states that knowing the conditions of the pure toluene stream, the pure methanol stream, and all of the design parameters, the HYSYS flowsheet simulation will calculated the conditions for the styrene stream, the ethylbenzene stream, and all of the heat duties and work energies; that is the material and energy requirements for that flowsheet. As indicated in the mathematical algorithm, an iteration must be done on the conditions of the reactor inlet (S10) using a numerical technique call successive substitution. Basically, the stream conditions of the reactor inlet (S10) are continually assumed until the calculated conditions of the outlet leaving fired Heater FH1 (S10') match those of the assumed conditions (S10) within a set of tolerances on pressure, molar flow rate, molar enthalpy, and component mole fractions.
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Flowsheet Mathematical Model

Toluene/Methanol Feed Preparation Section:

1. \[ \Psi_{S2}, \dot{W}_{P1} = \text{pumpP1}[\Psi_{S1}, \epsilon_{P1}, P_{outP1}] \]
2. \[ \Psi_{S3}, \dot{Q}_{E1} = \text{heaterE1}[\Psi_{S2}, V_{f, outE1} = 1, \Delta P_{E1}] \]
3. \[ \Psi_{S5}, \dot{W}_{P2} = \text{pumpP2}[\Psi_{S4}, \epsilon_{P2}, P_{outP2}] \]
4. \[ \Psi_{S6}, \dot{Q}_{E2} = \text{heaterE2}[\Psi_{S5}, V_{f, outE2} = 1, \Delta P_{E2}] \]
5. \[ \Psi_{S7} = \text{mixerM1}[\Psi_{S3}, \Psi_{S6}] \]

Recycle Mixing and Preheating Section:

6. \[ \Psi_{S8} = \text{mixerM2}[\Psi_{S26}, \Psi_{S7}, \Psi_{S21}] \]
7. \[ \Psi_{S9}, \dot{Q}_{FH1} = \text{heaterFH1}[\Psi_{S8}, T_{outFH1}, \Delta P_{FH1}] \]

Styrene Monomer Reaction Section:

8. \[ \Psi_{S11} = \text{reactorR1}[\Psi_{S10}, CT_{R1, SM}, CT_{R1, EB}, \Delta P_{R1}] \]

Reactor Effluent Cooling/Decanting Section

9. \[ \Psi_{S12}, \dot{Q}_{E3} = \text{coolerE3}[\Psi_{S11}, T_{outE3}, \Delta P_{E3}] \]
10. \[ \Psi_{S13}, \Psi_{S14}, \Psi_{S15} = \text{decanterF3}[\Psi_{S12}, \Delta P_{F3}] \]
11. \[ \Psi_{S36} = \text{valveV5}[\Psi_{S13}, P_{outV5}] \]

Methanol Recycle Purification Section:

12. \[ \Psi_{S15B} = \text{valveV3}[\Psi_{S15}, P_{outV3}] \]
13. \[ \Psi_{S16}, \dot{Q}_{EC3} = \text{heaterEC3}[\Psi_{S15B}, V_{f, outEC3} = 0, \Delta P_{EC3}] \]
14. \[ \Psi_{S17}, \Psi_{S17}, \Psi_{S18}, \dot{Q}_{C3}, \dot{Q}_{R,C3} = \text{columnC3}[\Psi_{S16}, CP_{C3}, W_{S18, LK}, VR_{C3}] \]
15. \[ \Psi_{S17g} = \text{valveV6}[\Psi_{S17g}, P_{outV6}] \]
16. \[ \Psi_{S20}, \dot{W}_{P3} = \text{pumpP3}[\Psi_{S17}, \epsilon_{P3}, P_{outP3}] \]
17. \[ \Psi_{S21}, \dot{Q}_{E4} = \text{heaterE4}[\Psi_{S20}, V_{f, outE4} = 1, \Delta P_{E4}] \]
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(18) \[ \Psi_{S34} = \text{valve} V4 \Psi_{S18}, \quad P_{\text{out}V4} \]

(19) \[ \Psi_{S35}, \quad \dot{Q}_{E8} = \text{cooler} E8 \Psi_{S34}, \quad T_{\text{out}E8}, \quad \Delta P_{E8} \]

Toluene Recycle Purification Section:

(20) \[ \Psi_{S14B} = \text{valve} V1 \Psi_{S14}, \quad P_{\text{out}V1} \]

(21) \[ \Psi_{S22}, \quad \dot{Q}_{EC1} = \text{heater} E1 \Psi_{S14B}, \quad V_{f, \text{out}EC1} = 0.01, \quad \Delta P_{EC1} \]

(22) \[ \Psi_{S23v}, \Psi_{S23}, \Psi_{S24}, \quad \dot{Q}_{C,C1}, \quad \dot{Q}_{R,C1} = \text{column} C1 \Psi_{S22}, \quad \overline{CP}_{C1}, \quad w_{S23,HK}, \quad V_{R_{C1}} \]

(23) \[ \Psi_{S23g}, \quad \dot{W}_{K1} = \text{compressor} K1 \Psi_{S23v}, \quad \epsilon_{K1}, \quad P_{\text{out}K1} \]

(24) \[ \Psi_{S25}, \quad \dot{W}_{P4} = \text{pump} P4 \Psi_{S23}, \quad \epsilon_{P4}, \quad P_{\text{out}P4} \]

(25) \[ \Psi_{S26}, \quad \dot{Q}_{E5} = \text{heater} E5 \Psi_{S25}, \quad V_{f, \text{out}E5} = 1, \quad \Delta P_{E5} \]

Styrene Monomer Purification Section:

(26) \[ \Psi_{S24B} = \text{valve} V2 \Psi_{S24}, \quad P_{\text{out}V2} \]

(27) \[ \Psi_{S27}, \quad \dot{Q}_{EC2} = \text{cooler} E2 \Psi_{S24B}, \quad V_{f, \text{out}EC2} = 0, \quad \Delta P_{EC2} \]

(28) \[ \Psi_{S28}, \Psi_{S29}, \quad \dot{Q}_{C,C2}, \quad \dot{Q}_{R,C2} = \text{column} C2 \Psi_{S27}, \quad \overline{CP}_{C2}, \quad w_{S29,LK} \]

(29) \[ \Psi_{S30}, \quad \dot{W}_{P5} = \text{pump} P5 \Psi_{S28}, \quad \epsilon_{P5}, \quad P_{\text{out}P5} \]

(30) \[ \Psi_{S31}, \quad \dot{Q}_{E6} = \text{cooler} E6 \Psi_{S30}, \quad T_{\text{out}E6}, \quad \Delta P_{E6} \]

(31) \[ \Psi_{S32}, \quad \dot{W}_{P6} = \text{pump} P6 \Psi_{S29}, \quad \epsilon_{P6}, \quad P_{\text{out}P6} \]

(32) \[ \Psi_{S33}, \quad \dot{Q}_{E7} = \text{cooler} E7 \Psi_{S32}, \quad T_{\text{out}E7}, \quad \Delta P_{E7} \]

General Mathematical Notation:

\[
\begin{bmatrix}
\text{output\_stream(s)}, \quad \dot{Q}'s \text{ or } \dot{W}
\end{bmatrix} = \text{process\_unit}\begin{bmatrix}
\text{input\_stream(s)}, \quad \text{design\_parameters}
\end{bmatrix}
\]

\(\overline{CP}_u\) means \(P_{C,u}, \Delta P_{C,u}, P_{R,u}, \Delta P_{R,u}, N_{S,u}, N_{FS,u}, \) and \(R_u\) for Column \(u\)
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Flowsheet Variable Descriptions

Material Process Streams:

\[ \Psi_i \]

is short notation for \( T_i, P_i, \dot{n}_i, \) and \( Z_i \), the process state of stream \( i \).

\( T_i \)

is temperature of process stream \( i \), °C.

\( P_i \)

is pressure of process stream \( i \), kPa.

\( \dot{n}_i \)

is bulk molar flow rate of process stream \( i \), kgmol/h.

\( nc \)

is number of chemical components or compounds in the mixture.

\( Z_i \)

is bulk mole fractions of all \( nc \)-components in stream \( i \).

\( z_{i,j} \)

is bulk mole fraction of component \( j \) in process stream \( i \);

vector \( \mathbf{Z}_i \) means all elements \( z_{i,1}, z_{i,2}, \ldots, z_{i,nc} \).

Heaters, Coolers, Valves, Pumps, and Compressor Units:

\( T_{\text{out}U} \)

is outlet temperature for process unit “\( U \)”, °C.

\( P_{\text{out}U} \)

is outlet pressure for process unit “\( U \)”, kPa.

\( V_{f,\text{out}U} \)

is outlet molar vapor fraction for process unit “\( U \)”. 

\( \Delta P_u \)

is pressure drop across process unit “\( u \)”, kPa.

\( Q_u \)

is energy or heat duty required for process unit “\( u \)”, kJ/h.

\( W_u \)

is amount of work required for process unit “\( u \)”, kJ/h.

\( \varepsilon_u \)

is efficiency for pump or compressor unit “\( u \)”, unitless.

Reactor and Decanter Units:

\( CT_{u,SM} \)

is molar conversion of toluene to styrene monomer in reactor unit “\( u \)”. 

\( CT_{u,EB} \)

is molar conversion of toluene to ethylbenzene in reactor unit “\( u \)”. 

\( \Delta P_u \)

is the pressure drop across process unit “\( u \)”, kPa.

Distillation Column Units:

\( \dot{Q}_{e,u} \)

is heat duty of condenser or reboiler unit “\( e \)” in column “\( u \)”, kJ/h.

\( P_{e,u} \)

is exit pressure of condenser or reboiler unit “\( e \)” in column “\( u \)”, kPa.

\( \Delta P_{e,u} \)

is pressure drop thru condenser or reboiler unit “\( e \)” in column “\( u \)”, kPa.

\( N_{S,u} \)

is number of equilibrium stages or trays in column “\( u \)”. 

\( N_{FS,u} \)

is feed-stage location counting from the top of column “\( u \)”. 

\( R_u \)

is molar reflux ratio from the condenser in column “\( u \)”. 

\( W_{L,K} \)

is mass fraction of the light-key component in process stream \( i \). 

\( W_{H,K} \)

is mass fraction of the heavy-key component in process stream \( i \). 

\( VR_u \)

is molar vent ratio of the condenser vapor for column “\( u \)”. 

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Flowsheet Mathematical Algorithm

Stream S1 is pure toluene.  Stream S33 is mostly styrene monomer product.
Stream S4 is pure methanol.  Stream S31 is mostly ethylbenzene byproduct.

\[
\begin{bmatrix}
\Psi_{S33}, \Psi_{S31}, \text{all } \dot{Q}'s, \text{ all } \dot{W}'s
\end{bmatrix}
= \text{styrene}\begin{bmatrix}
\Psi_{S1}, \Psi_{S4}, \text{all design parameters}
\end{bmatrix}
\]

Toluene/Methanol Feed Preparation Section

(1) \[
\begin{bmatrix}
\Psi_{S2}, \dot{W}_p_1
\end{bmatrix}
\leftarrow \text{pumpP1}\begin{bmatrix}
\Psi_{S1}, \epsilon_{P1}, P_{\text{outP1}}
\end{bmatrix}
\]

(2) \[
\begin{bmatrix}
\Psi_{S3}, \dot{Q}_{E1}
\end{bmatrix}
\leftarrow \text{heaterE1}\begin{bmatrix}
\Psi_{S2}, V_{f,\text{outE1}} = 1, \Delta P_{E1}
\end{bmatrix}
\]

(3) \[
\begin{bmatrix}
\Psi_{S5}, \dot{W}_{p_2}
\end{bmatrix}
\leftarrow \text{pumpP2}\begin{bmatrix}
\Psi_{S4}, \epsilon_{P2}, P_{\text{outP2}}
\end{bmatrix}
\]

(4) \[
\begin{bmatrix}
\Psi_{S6}, \dot{Q}_{E2}
\end{bmatrix}
\leftarrow \text{heaterE2}\begin{bmatrix}
\Psi_{S5}, V_{f,\text{outE2}} = 1, \Delta P_{E2}
\end{bmatrix}
\]

(5) \[
\begin{bmatrix}
\Psi_{S7}
\end{bmatrix}
\leftarrow \text{mixerM1}\begin{bmatrix}
\Psi_{S3}, \Psi_{S6}
\end{bmatrix}
\]

ITERATE \[\Psi_{S10}\] in

Styrene Monomer Reaction Section

(8) \[
\begin{bmatrix}
\Psi_{S11}
\end{bmatrix}
\leftarrow \text{reactorR1}\begin{bmatrix}
\Psi_{S10}, CT_{R1,\text{SM}}, CT_{R1,\text{EB}}, \Delta P_{R1}
\end{bmatrix}
\]

Reactor Effluent Cooling/Decanting Section

(9) \[
\begin{bmatrix}
\Psi_{S12}, \dot{Q}_{E3}
\end{bmatrix}
\leftarrow \text{coolerE3}\begin{bmatrix}
\Psi_{S11}, T_{\text{outE3}}, \Delta P_{E3}
\end{bmatrix}
\]

(10) \[
\begin{bmatrix}
\Psi_{S13}, \Psi_{S14}, \Psi_{S15}
\end{bmatrix}
\leftarrow \text{decanterF3}\begin{bmatrix}
\Psi_{S12}, \Delta P_{F3}
\end{bmatrix}
\]

(11) \[
\begin{bmatrix}
\Psi_{S36}
\end{bmatrix}
\leftarrow \text{valveV5}\begin{bmatrix}
\Psi_{S13}, P_{\text{outV5}}
\end{bmatrix}
\]

Methanol Recycle Purification Section

(12) \[
\begin{bmatrix}
\Psi_{S15B}
\end{bmatrix}
\leftarrow \text{valveV3}\begin{bmatrix}
\Psi_{S15}, P_{\text{outV3}}
\end{bmatrix}
\]

(13) \[
\begin{bmatrix}
\Psi_{S16}, \dot{Q}_{EC3}
\end{bmatrix}
\leftarrow \text{heaterEC3}\begin{bmatrix}
\Psi_{S15B}, V_{f,\text{outEC3}} = 0, \Delta P_{EC3}
\end{bmatrix}
\]

(14) \[
\begin{bmatrix}
\Psi_{S17v}, \Psi_{S17}, \Psi_{S18}, \dot{Q}_{C3,\text{C}}, \dot{Q}_{R,\text{C}}
\end{bmatrix}
\leftarrow \text{columnC3}\begin{bmatrix}
\Psi_{S16}, CP_{C3}, w_{S18,\text{LK}}, VR_{C3}
\end{bmatrix}
\]

(15) \[
\begin{bmatrix}
\Psi_{S17g}
\end{bmatrix}
\leftarrow \text{valveV6}\begin{bmatrix}
\Psi_{S17v}, P_{\text{outV6}}
\end{bmatrix}
\]

(16) \[
\begin{bmatrix}
\Psi_{S20}, \dot{W}_p_3
\end{bmatrix}
\leftarrow \text{pumpP3}\begin{bmatrix}
\Psi_{S17}, \epsilon_{P3}, P_{\text{outP3}}
\end{bmatrix}
\]

(17) \[
\begin{bmatrix}
\Psi_{S21}, \dot{Q}_{E4}
\end{bmatrix}
\leftarrow \text{heaterE4}\begin{bmatrix}
\Psi_{S20}, V_{f,\text{outE4}} = 1, \Delta P_{E4}
\end{bmatrix}
\]
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(18) \[
\begin{bmatrix}
\bar{\Psi}_{S34} \\
\end{bmatrix} \iff \text{valve} V4 \begin{bmatrix}
\bar{\Psi}_{S18}, \\
P_{\text{out}V4}
\end{bmatrix}
\]

(19) \[
\begin{bmatrix}
\bar{\Psi}_{S35}, \\
\dot{Q}_{E8}
\end{bmatrix} \iff \text{cooler} E8 \begin{bmatrix}
\bar{\Psi}_{S34}, \\
T_{\text{out}E8}, \Delta P_{E8}
\end{bmatrix}
\]

Toluene Recycle Purification Section

(20) \[
\begin{bmatrix}
\bar{\Psi}_{S14B}
\end{bmatrix} \iff \text{valve} V1 \begin{bmatrix}
\bar{\Psi}_{S14}, \\
P_{\text{out}V1}
\end{bmatrix}
\]

(21) \[
\begin{bmatrix}
\bar{\Psi}_{S22}, \\
\dot{Q}_{EC1}
\end{bmatrix} \iff \text{heater} EC1 \begin{bmatrix}
\bar{\Psi}_{S14B}, \\
V_{f, \text{out}EC1} = 0.01, \Delta P_{EC1}
\end{bmatrix}
\]

(22) \[
\begin{bmatrix}
\bar{\Psi}_{S23v}, \\
\bar{\Psi}_{S23}, \\
\bar{\Psi}_{S24}, \\
\dot{Q}_{C,C1}, \\
\dot{Q}_{R,C1}
\end{bmatrix} \iff \text{column} C1 \begin{bmatrix}
\bar{\Psi}_{S22}, \\
\bar{CP}_{C1}, \\
w_{S23, HK}, \\
VR_{C1}
\end{bmatrix}
\]

(23) \[
\begin{bmatrix}
\bar{\Psi}_{S23v}, \\
W_{K1}
\end{bmatrix} \iff \text{compressor} K1 \begin{bmatrix}
\bar{\Psi}_{S23v}, \\
\bar{\Psi}_{S23}, \\
\dot{Q}_{K1}, \\
P_{\text{out}K1}
\end{bmatrix}
\]

(24) \[
\begin{bmatrix}
\bar{\Psi}_{S25}, \\
W_{P4}
\end{bmatrix} \iff \text{pump} P4 \begin{bmatrix}
\bar{\Psi}_{S23}, \\
\bar{\Psi}_{S23}, \\
\dot{Q}_{P4}, \\
P_{\text{out}P4}
\end{bmatrix}
\]

(25) \[
\begin{bmatrix}
\bar{\Psi}_{S26}, \\
\dot{Q}_{E5}
\end{bmatrix} \iff \text{heater} E5 \begin{bmatrix}
\bar{\Psi}_{S25}, \\
V_{f, \text{out}E5} = 1, \Delta P_{E5}
\end{bmatrix}
\]

Recycle Mixing and Preheating Section

(6) \[
\begin{bmatrix}
\bar{\Psi}_{S8}
\end{bmatrix} \iff \text{mixer} M2 \begin{bmatrix}
\bar{\Psi}_{S26}, \\
\bar{\Psi}_{S7}, \\
\bar{\Psi}_{S21}
\end{bmatrix}
\]

(7) \[
\begin{bmatrix}
\bar{\Psi}_{S10}, \\
\dot{Q}_{FH1}
\end{bmatrix} \iff \text{heater} FH1 \begin{bmatrix}
\bar{\Psi}_{S8}, \\
\bar{\Psi}_{S8}, \\
T_{\text{out}FH1}, \Delta P_{FH1}
\end{bmatrix}
\]

UNTIL \[
\bar{\Psi}_{S10} = \bar{\Psi}_{S10}
\]

Styrene Monomer Purification Section

(26) \[
\begin{bmatrix}
\bar{\Psi}_{S24B}
\end{bmatrix} \iff \text{valve} V2 \begin{bmatrix}
\bar{\Psi}_{S24}, \\
P_{\text{out}V2}
\end{bmatrix}
\]

(27) \[
\begin{bmatrix}
\bar{\Psi}_{S27}, \\
\dot{Q}_{EC2}
\end{bmatrix} \iff \text{cooler} EC2 \begin{bmatrix}
\bar{\Psi}_{S24B}, \\
V_{f, \text{out}EC2} = 0, \Delta P_{EC2}
\end{bmatrix}
\]

(28) \[
\begin{bmatrix}
\bar{\Psi}_{S28}, \\
\bar{\Psi}_{S29}, \\
\bar{\Psi}_{S29}, \\
\dot{Q}_{C,C2}, \\
\dot{Q}_{R,C2}
\end{bmatrix} \iff \text{column} C2 \begin{bmatrix}
\bar{\Psi}_{S27}, \\
\bar{\Psi}_{S27}, \\
\bar{\Psi}_{S27}, \\
\bar{CP}_{C2}, \\
w_{S29, HK}
\end{bmatrix}
\]

(29) \[
\begin{bmatrix}
\bar{\Psi}_{S30}, \\
W_{P5}
\end{bmatrix} \iff \text{pump} P5 \begin{bmatrix}
\bar{\Psi}_{S28}, \\
\bar{\Psi}_{S28}, \\
\dot{Q}_{P5}, \\
P_{\text{out}P5}
\end{bmatrix}
\]

(30) \[
\begin{bmatrix}
\bar{\Psi}_{S31}, \\
\dot{Q}_{E6}
\end{bmatrix} \iff \text{cooler} E6 \begin{bmatrix}
\bar{\Psi}_{S30}, \\
\bar{\Psi}_{S30}, \\
T_{\text{out}E6}, \Delta P_{E6}
\end{bmatrix}
\]

(31) \[
\begin{bmatrix}
\bar{\Psi}_{S32}, \\
W_{P6}
\end{bmatrix} \iff \text{pump} P6 \begin{bmatrix}
\bar{\Psi}_{S29}, \\
\bar{\Psi}_{S29}, \\
\dot{Q}_{P6}, \\
P_{\text{out}P6}
\end{bmatrix}
\]

(32) \[
\begin{bmatrix}
\bar{\Psi}_{S33}, \\
\dot{Q}_{E7}
\end{bmatrix} \iff \text{cooler} E7 \begin{bmatrix}
\bar{\Psi}_{S32}, \\
\bar{\Psi}_{S32}, \\
T_{\text{out}E7}, \Delta P_{E7}
\end{bmatrix}
\]