Dynamic simulation of manufacture of styrene by the catalytic dehydrogenation of ethyl benzene

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Abstract. Styrene is an important chemical compound derived from benzene. It is produced conventionally by the catalytic dehydrogenation of ethyl benzene in the presence of iron oxide catalyst. The reaction is reversible endothermic and is carried out in a series of adiabatic packed bed reactors. The present study deals with the dynamic simulation of the process of styrene manufacture using the Honeywell UniSim design suite. The control parameters of various controllers in the process have been derived using the auto-tune feature of the software. Various scenarios of servo problems were studied. The dynamic behaviour of the process parameters during various scenarios in the operating chemical plant is also studied. The results are very much useful for conducting the hazard analysis of the plant and thereby designing the trip systems of the plant.

1. Introduction

Styrene is a versatile organic compound with molecular formula C₈H₈. The chemical compound has characteristics like colourless, pungent odour, viscous, and has a tendency to polymerize. It is also known as vinyl benzene, phenyl ethane, or ethyl benzene. Styrene is used as monomer for the production of polystyrene. It is also used for the preparation of latex, synthetic rubber, etc. polystyrene polymer is well known for its strength, durability, and low cost, it is used to make plastic packaging, disposable cups, containers insulation, fiberglass, automobile, bat parts, and carpet making [4].

Industrial production of styrene is carried out by dehydrogenation reaction of ethyl benzene in the presence of an iron-based catalyst in packed bed reactors. The molecular reaction of dehydrogenation of ethyl benzene is given by,

\[ C_6H_5C_2H_5 \leftrightarrow C_6H_5CH=CH_2 + H_2 \]  

(1)

The catalytic reaction is endothermic so that steam is also given along with the reactants as a heat source for the reaction. The reversible reaction is done in a series of adiabatic packed bed reactors. Along with the desired product styrene, benzene and toluene are also produced by side reactions. These side reactions can affect the yield of the desired product styrene[5].

\[ C_6H_5C_2H_5 \leftrightarrow C_6H_6 + C_2H_4 \]  

(2)

\[ C_6H_5C_2H_5 + H_2 \leftrightarrow C_6H_5CH_3 + CH_4 \]  

(3)

The major issue based on the dehydrogenation reaction is side reactions. The other one is catalyst poisoning. As long as the reaction proceeds there may be a chance of clogging of the active sites of the
catalyst by carbon particles. But this problem can be overcome to some extent by using a high concentration of steam in the reaction mixture.

\[ \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \rightarrow 8\text{C} + 5 \text{H}_2 \quad (4) \]

Dehydrogenation of ethylbenzene gives products like styrene, hydrogen, benzene, and toluene. The product after the reaction needs to be separated. For this often separators are used for separating products in different phases and distillation columns to separate components in a similar phase. This brings the need for simulation for better control and maintenance of the processing system. Process simulation is used for process mapping, design and assessment, and cost analysis. A simulator is computer software used to develop an accurate mathematical model for the process in order to understand its actual behaviour of the system during regular plant operations. Simulators are able to analyse the performance of the system both at steady-state and dynamic conditions. By steady-state analysis, the behaviour of the system at any instant can be found out. It performs mass and energy balance of a stationary process (a process in an equilibrium state) but any changes over time had to be ignored[7]. The ultimate objective of the present investigation is to simulate the steady-state and dynamic performance of the process plant to analyse the behaviour of the system based on real-time data in a better way.

2. Materials and methods
Honeywell UniSim design software is used to simulate the styrene production plant. Both the steady-state and dynamic analysis of catalytic dehydrogenation reaction of ethylbenzene is done using the software. It is an emerging process simulation tool. The simulation tool provides various build-in thermodynamic package for the precise prediction of thermodynamic behaviour, physical and transport property of the hydrocarbon, non-hydrocarbon, petrochemical, and chemical fluids. The software also helps to find out the optimum process operating conditions, the number of heat exchange components, and flow equipment specifications for minimising the total cost of the process.

The draft process is described as follows: 100% pure ethylbenzene at a temperature of 30°C and pressure about 101.3 kPa is used as the reactant. Initially, the feed is mixed with steam (800°C and 200kPa) in the ratio 1:20 to obtain a temperature of 620°C. Two packed bed reactors in series with a heater in between the reactor are used. The output from the reactors contains styrene, hydrogen, unreacted ethylbenzene, and side products benzene, toluene, ethylene, methane, and water by condensation of steam. The high-temperature product stream is cooled to 65°C and is fed to a series of separators. The vapour from the top of the separator contains ethylene and hydrogen. The bottom product is allowed to pass through the series of two distillation columns. By removing the by-products formed (benzene and toluene) from the stream, the purity of the styrene increases. The unreacted feed is then recycled back to the feed from the top of the second distillation column [7].

The fluid package Peng- Robinson gives the vapour-liquid equilibrium data for the dehydrogenation reaction. The main dehydrogenation reactor is a kinetic plug flow reactor (Volume - 283 m³, No. of tubes – 5, Void fraction – 0.454) with the kinetic parameters as given in table-1[6].

| Table 1. Kinetic parameters |
|----------------------------|
| Kinetic parameters | Reaction 1 | Reaction 2 | Reaction 3 |
| Forward | Backward | Forward | Backward | Forward | Backward |
| A | 7.217e+007 | -5.476 | 9.924e+012 | - | 8.209e+007 | - |
| E | 9.132e+004 | - | 2.08e+005 | - | 9.15e+004 | - |
| B | - | - | - | - | - | - |
| C | - | 3.152 | - | - | - | - |
| D | - | -0.00237- | - | - | - | - |
\[ k = A \exp(-E/RT) \times T^{\beta} \]

where, \( A \) – Pre-exponential factor, \( E \) – Activation energy, \( \beta = B, C, D \) – adsorption constants.

The modeling of fired heater provided at the inlet of the dehydrogenation reactor using Gibbs reactor with methane as fuel. The steady-state mode of the draft process has been simulated and the performance of the process is analysed for varying process conditions such as temperature, pressure, and feed concentration other design parameters. The exercise gave the best set of operating parameters and design parameters as an outcome. The Optimised steady state-process is further converted to suit the requirement to derive a pressure-flow relation to developing the dynamic model.

3. Results and Discussion

3.1. Steady state simulation

![Steady state simulation of styrene plant](image)

The steady-state process simulation in presented in Figure 1. The equipment parameters and process conditions are presented in tables 2 and 3 respectively.

| Equipment          | Type         | Diameter/Length(mm) | Capped End     |
|--------------------|--------------|---------------------|----------------|
| Reactor 1          | Horizontal   | 3800/25000          | -              |
| Reactor 2          | Horizontal   | 3800/25000          | -              |
| Separator          | Horizontal   | 1676/5876           | Hemispherical  |
| Distillation column 1 | Trayed     | 1500/6100           | Hemispherical  |
| Distillation column 2 | Trayed     | 1500/6100           | Hemispherical  |
Table 3. Process conditions

| Name                  | Feed | R₁- in | R₂- out | Product Styrene |
|-----------------------|------|--------|---------|-----------------|
| Vapour fraction       | 0    | 1      | 1       | 0               |
| Temperature, °C       | 30   | 620    | 610     | 30              |
| Pressure, kPa         | 101  | 20     | 20      | 189             |
| Molar flow, kmol/hr   | 150  | 3,318  | 3,450   | 102             |
| Mass flow, kg/hr      | 15,920 | 73,590  | 73,590  | 10,580          |

3.2. Dynamic simulation

3.2.1. Control of flowrate of steam. The flow rate of steam to the process is controlled using a flow controller system. The steam flow rate is maintained at 3000 kmol/hr. Here, the molar flow rate of steam is given as process variable and the actuator desired position is taken as OP. The valve mode is taken as a first-order transfer function with a time constant of a few seconds, which means that first-order lag can be modelled in the response of the actuator position to changes in the desired actuator position. The controller tuning parameters are selected by using auto-tuning section using fine-tuning controllers.

Figure 1 shows the dynamic response of the controlled process to a set point disturbance caused by a positive step change in SP from the default initial value (SP = 3000 kmol/hr) to new value (3500 kmol/hr), followed by a later positive step change from latter to initial value 3000 kmol/hr. The PID tuning parameters are; $K_c = 0.0517$, integral time constant $T_i = 0.0218$min, and derivative time constant $T_d = 0.00485$ min.
3.2.2. Ethyl benzene feed flow control. The flow controller is used to control the feed (Ethylbenzene) flow into the system. The feed flow rate is 150 kmol/hr. A valve VLV – feed is introduced to control the flow of feed, required pressure-flow specifications are given. Here, the molar flow rate of feed is given as process variable, and actuator desired position of valve VLV -steam is taken as OP. The valve mode is taken as a first-order transfer function with a time constant of a few seconds, which means that first-order lag can be modelled in the response of the actuator position to changes in the desired actuator position. The controller tuning parameters are selected by using the auto-tuning section using fine-tuning controllers.

The PID tuning parameters are; \(K_c = 0.0661\) integral time constant \(T_i = 0.0435\) min, and derivative time constant \(T_d = 0.00966\) min.

Figure 4 shows the dynamic response of the controlled process to a set point disturbance caused by a negative step change in SP from the default initial value (SP = 150 kmol/hr) to a new value (180 kmol/hr), followed by a later positive step-change from latter to initial value 150 kmol/hr.

3.2.3. Reactor inlet stream temperature control. It is necessary to keep the inlet temperature of the first bed at 620°C for optimum conversion. Beyond this temperature, styrene can get polymerized. The temperature controller is used to control the temperature at the inlet of the reactor at which the reaction takes place. A valve VLV – TIC 101 introduced to control the flow of methane whose combustion results in the generation of heat, required pressure-flow specifications are given. Here, the temperature at the inlet of the reactor is given as a process variable, and the actuator desired position of valve VLV -TIC 101 is taken as OP. The valve mode is taken as a first-order transfer function with a time constant
of a few seconds. The controller tuning parameters are selected by using the auto-tuning section using fine-tuning controllers.

The PID tuning parameters are; \( K_c = 5.75 \) integral time constant \( Ti = 0.219 \text{ min} \), and derivative time constant \( T_d = 0.0488 \text{ min} \).

Figure 7 shows the dynamic response of the controlled process to a set point disturbance caused by a negative step change in SP from the default initial value (SP = 620°C) to a new value (610°C), followed by a later positive step-change from latter to initial value 620°C.

3.2.4. Ratio control of methane to airflow. The ratio of methane flow rate to air flow rate was maintained at 1:25 in the fired heater. A ratio controller is used for this purpose. A combination of selector and PI controllers are used for this purpose. The methane to air ratio in the Quotient mode of the selector block is used as the PV for a PI Controller. Here the desired controller mode action is given which is direct in this case. The controller tuning parameters are selected by using the auto-tuning section using fine-tuning controllers. The first case represents the PI control with tuning parameters; \( K_c = 0.136 \) integral time constant \( Ti = 0.00386 \text{ min} \). Figure 8 shows the dynamic response of the controlled process to a set point disturbance caused by a positive step-change in SP from the default initial value (SP = 0.4) to a new value (0.398), followed by a later positive step-change from latter to initial value 0.4.

Figure 6. The PI controlled dynamic response of IC 100 due to the step change in SP.
3.3. Interaction between the control units

3.3.1. Effect of change in feed flow rate with change in steam flow rate. Here, the feed flow is changed and simultaneously the steam flow. The flow rate of feed is changed. Here, the methane flow to the reactor is increased by increasing the opening of valve V-100, and the corresponding IC 100 ratio controller will increase the opening of valve VLV 101 to increase the airflow thereby maintaining the required methane-air ratio.

![Figure 7. The controlled dynamic response of FIC 101 due to step change in set point](image)

![Figure 8. The controlled dynamic response of FIC 100 due to step change in set point](image)

![Figure 9. The interaction response of IC 100 due to step change in FIC 100 and FIC 101](image)
3.3.2. Effect of change in feed flow rate without change in steam flow rate. The feed flow rate is changed from 150 to 155 kmol/hr. Since the steam is not enough to heat the feed to the temperature of the feed entering the reactor decreases. This activates TIC 101 which increases the valve opening which increases the flow of methane. The change in the flow of methane affects the ratio controller. The ratio controller tries to maintain the ratio between methane and air by increasing the opening of the valve.

Figure 10. The interaction response of TIC 101 due to step change in FIC 100 and FIC 101

Figure 11. The controlled dynamic response of FIC 101 due to step change in set point

Figure 12. The interaction response of IC 100 due to step change in FIC 101
3.3.3 Effect of change in feed flow rate of steam without change in feed flow rate. Steam increases the temperature of the feed to 470⁰C. But when the flow of steam increases with no change in the flow of feed, the steam will heat the feed to more than 470⁰C. Here, steam flow is changed from 3000 to 3025 kmol/hr. Hence the temperature of the feed of the reactor inlet is more than 620⁰C. This causes a reduction in the requirement of methane. Hence the opening of the valve is reduced by the action of the temperature controller TIC 101. The reduction in the flow of methane actuates the ratio controller IC which will reduce the opening of the valve also to maintain the ratio of methane and air in the set point.

Figure 13. The interaction response of TIC 101 due to step change in FIC 100.

Figure 14. The controlled dynamic response of FIC 100 due to step change in set point
3.3.4. Effect of change in temperature. The temperature controller TIC 101 controls the temperature of the reactor using the valve which regulates the flow of methane. Here the temperature is reduced from 620 to 615°C. The set-point temperature has decreased the flow of methane to the reactor therefore
decreases to make the change possible. So the valve opening is reduced by the controller. But the reduction in the flow rate of methane will change the ratio between methane and air. So the ratio controller will adjust the opening of the valve. By decreasing the opening of the valve, the airflow is reduced thereby bringing back the ratio in the set point.

**Figure 18.** The interaction response of IC 100 due to step change in TIC 100

4. Conclusion
The styrene production from ethyl benzene has been simulated using UniSim Design R460. The dynamic simulation of the plant has been studied with the installation of the different types of controllers. The interaction between various controllers is studied. The controller behaviour has been studied for servo problems and also the interaction between the controllers also been studied. The dynamic behaviour of the process parameters in the complete plant during various scenarios in the operating chemical plant is also studied. The results are very much useful for conducting the hazard analysis of the plant and thereby designing the trip systems of the plant.

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