A dynamic simulation of a styrene production process

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Abstract. Dynamic simulation plays a crucial role in process engineering, especially in designing control systems. As the interest in dynamic simulation for effective control and operation rises, the goal of the paper is to study and improve the dynamic performance of a styrene production process using simulation software to tackle various process design problems. The simulation process is carried out in four stages. In the first stage, flowsheet topology and process parameters are selected to meet the requirement of the main product. Control systems are designed for each piece of equipment in the process in the second stage. Both of the stages mentioned earlier are conducted in a steady-state environment. After finishing the second stage, steady-state simulation is complete. The third stage involves tuning control parameters of control loops in a dynamic environment. In the final stage, the performance of the system is tested by introducing disturbances in the form of pulse inputs. The results of the dynamic simulation illustrate that the control system is significantly influenced by the ethylbenzene feed flowrate disturbance. The production rate is heavily affected by the disturbance, while the production quality is assured. The average settling time of the process is 270 minutes.

1. Introduction
Styrene (molecular formula: C₆H₅CH=CH₂), also known as phenylethylene; vinylbenzene, is an important monomer in the chemical industry. It is a clear and colorless liquid that has a characteristic pungent odor [8]. The styrene monomer is produced at a massive scale for polymerization. Several applications of the styrene monomer include [6], [8]:

• Polystyrene (PS) is used extensively in packaging applications. The molded polystyrene is used in items such as automobile interior parts, furniture, and home appliances.

• Styrene Acrylonitrile (SAN) is used in articles that do not require optical clarity, such as appliances and houseware materials.

• Acrylonitrile Butadiene Styrene (ABS) is used increasingly in the construction of motor vehicles.
Styrene Butadiene latex (SB latex) is used in coatings of paper and cartoons as well as in carpet backing.

There are several industrial styrene production processes. Among them, the most important and well-known one is catalytic dehydrogenation of ethylbenzene in the presence of various metal oxides as catalysts in packed bed reactors. The direct dehydrogenation of ethylbenzene to styrene accounts for 85% of commercial production [3]. Due to its widespread application in practice, the catalytic dehydrogenation of ethylbenzene is chosen for the simulation in the paper.

Over the years, process simulation holds a vital role in process engineering. The need for simulation for better control and maintenance of the processing system is increasing due to various operational constraints, regulations as well as market competition. A simulator is a computer software which is used to develop an accurate mathematical model for the process in order to understand the actual behaviour of the system during regular plant operations [1]. A large number of simulation softwares have been developed and used widely today, such as Aspen HYSYS, Aspen Plus, DWSIM and CHEMCAD. HYSYS is a powerful engineering simulation tool that has been uniquely created with respect to the program architecture, interface design, engineering capabilities, and interactive operation. It is widely applied in universities and colleges for introductory and advanced courses, especially in chemical engineering. In the industry, this software is used in research, development, modeling, and design [2].

HYSYS is capable of analysing the behaviour and performance of a process in both static and dynamic states. The steady-state analysis comprises performing mass and energy balances of a stationary process (a process in an equilibrium state) but any changes over time are ignored [1]. The dynamic state, however, deals with process behaviour in real time. The dynamic analysis of a process can provide insight into the process system, which is not possible with the steady-state analysis. The main focus of the paper is to simulate the steady-state and dynamic performance of the styrene production process and eventually evaluate the process dynamic response by adding disturbances to the system. Particularly, HYSYS is used throughout the simulation process in this study.

2. Methodology

2.1. Ethylbenzene dehydrogenation to styrene process

The catalytic dehydrogenation of ethylbenzene process consists of the following reactions:

\[ C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH=CH_2 + H_2 \]  
\[ C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4 \]  
\[ C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \]

The main reaction (1) producing the main product styrene and hydrogen is highly endothermic, while reactions (2) and (3) give undesirable by-products. The reactions occur in gas phase and in the presence of steam. Thermodynamic and kinetic properties of reactions (1), (2), and (3) are modeled by the Peng-Robinson equation of state in the simulation.

The ethylbenzene dehydrogenation process can be accomplished either adiabatically or isothermally. The adiabatic process occurs in multiple reactors operated in series. Over 75% of all operating styrene plants carry out the dehydrogenation reaction adiabatically [3]. Therefore, the adiabatic dehydrogenation of ethylbenzene is chosen for the simulation.

For the process to achieve high conversion, the following operational constraints need to be considered [9]:

- The reactor temperature should be kept at 530°C or higher to ensure a desirable reaction rate. If the temperature is too high, more undesirable by-products are generated. Also, high temperature favors coking formation, which reduces the efficiency of the catalytic process.
- The operating pressure for reactors should be from 1.2 to 3 bar.
3. Results

3.1. Process description
The case model was simulated in HYSYS software. The Peng-Robinson fluid package was chosen for the simulation because of its ability to calculate the properties of hydrocarbon precisely. The styrene process can be briefly described as follows: pure ethylbenzene feed stream at 30°C and 150 kPa is the reactant of the process. The ethylbenzene stream is pressurized through a pump, while steam is pressurized in a compressor. The two streams are then mixed with the ethylbenzene recycle stream at mixer MIX-100. The outlet stream obtained is heated to 530°C. The ratio between steam and ethylbenzene before proceeding to reactors is 13. The reactor section comprises three plug flow reactors operating in series. Prior to each reactor is a heater with the objective of providing energy for the reaction. The effluent which contains various components including the unreacted ethylbenzene, the main product styrene, hydrogen, by-products methane, ethylene, benzene, toluene and water, is at a high temperature and needs cooling. It is cooled to 30°C before proceeding to the three-phase
separator. At the three-phase separator, a majority of gas and water is eliminated. The remaining components are then separated through a series of distillation columns. Column T-100 operates at ambient pressure has two purposes: purifying the remaining gas and water and separating benzene and toluene. The bottom product containing styrene and ethylbenzene is then separated in column T-101 at vacuum pressure. The separation process is difficult due to the relative volatility of ethylbenzene to styrene is low, resulting in a high number of trays is required in column T-101. The bottom product is the main product styrene, while the distillate contains mainly unreacted ethylbenzene is recycled back to the mixer. The overall production process diagram is demonstrated in the following Figure 2.

![Styrene production process diagram](image)

**Figure 2.** Styrene production process diagram

### 3.2. Steady-state simulation

After the steady-state simulation (which is after finishing stage 2), all thermodynamic parameters in the process are fixed. The sizing of equipment is determined. For reactors and the three-phase separator, the significant sizing parameters are their volumes. In terms of distillation columns, the sizing parameters such as diameter, type of tray and number of trays need to be known. The following Table 1 contains information about the main thermodynamic parameters of the process as well as the sizing parameters of the equipment obtained after the steady-state simulation.

**Table 1.** Main process parameters

| Sub-system | Process Parameters |
|------------|--------------------|
| Reactors   |                    |
| Reactor PFR-100: P=760 kPa, T=530°C, V=2 m³, Conversion: 48.16% |
| Reactor PFR-101: P=586.4 kPa, T=530°C, V=2 m³, Conversion: 53.1% |
| Reactor PFR-102: P=338.3 kPa, T=530°C, V=2 m³, Conversion: 35.28% |
| Molar flow of the inlet ethylbenzene feed: 58 kmole/h |
| Molar flow of steam: 721.6 kmole/h |
Overall conversion: 84.26%

Three-phase separator V-100

- P=134.6 kPa, T=30°C, V=19.5 m³
- Molar flow of the separated gas: 43.53 kmole/h
- Molar flow of the separated water: 720.2 kmole/h
- Styrene loss: 0.3 kmole/h

Column T-100

- Molar flow of the overhead vapor stream: 0.09 kmole/h
- Molar flow of the overhead liquid stream: 6.703 kmole/h
- Styrene loss: 0.12 kmole/h
- Rectifying section diameter: 0.85 m
- Stripping section diameter: 1.2 m
- Type of tray: Bubble cap, Number of trays: 26
- Reboiler: P=180 kPa, V=6 m³
- Condenser: P=133.8 kPa, V=5.2 m³

Column T-101

- Molar flow of the recycle ethylbenzene: 8.2 kmole/h
- Column diameter: 2.8 m
- Type of tray: Bubble cap, Number of trays: 100
- Reboiler: P=30 kPa, V=5 m³
- Condenser: P=60 kPa, V=21.2 m³

3.3. Dynamic simulation

The performance and sustainability of the system were tested by introducing disturbances to the system as pulse inputs. The disturbances lasted from 30 to 60 minutes before being eliminated. Process variables are expected to fluctuate during the existence of the disturbances. After eliminating the disturbances, the response of the system should settle back to the setpoints. The disturbances introduced in the study were the ethylbenzene feed flow rate disturbance of ±10% and ethylbenzene feed flow rate disturbance of ±30%. Table 2 summarizes all the disturbances used in this study.

Table 2. Performance results of the control system with different disturbances

| Disturbance type | Duration of disturbances introduced to the system |
|------------------|-----------------------------------------------|
|                  | 30 minutes | 60 minutes |
| +10% ethylbenzene feed flowrate | Stable     | Stable     |
| -10% ethylbenzene feed flowrate  | Stable     | Stable     |
| +30% ethylbenzene feed flowrate  | Stable     | Stable     |
| -30% ethylbenzene feed flowrate  | Stable     | Stable     |

The results show that the system was able to tolerate all the disturbances used in the study. The settling time, which is defined as the time to reach the set point with an error of less than 5% [4], varies in each case. The settling time for the +10% ethylbenzene feed flow rate case in 30 minutes and 60 minutes is 340 minutes and 400 minutes respectively. The dynamic response of the control system in the case of +10% ethylbenzene feed flowrate disturbance in 60 minutes was introduced is similar to the 30 minutes case. However, because the disturbance existed longer, the control system needed more time to settle back to the initial setpoint. A similar trend can be seen in the +30% ethylbenzene feed flowrate disturbance. The intensity of the disturbance increased, which led to a higher impact on the
system, resulting in a higher settling time. Figure 3 demonstrates the performance of the system under the effect of +10% ethylbenzene feed flowrate in 30 minutes.

![Figure 3](image)

**Figure 3.** The performances of the control system under the effect of the +10% ethylbenzene feed flowrate in 30 minutes: (a) ethylbenzene feed disturbance in 30 minutes, (b) Dynamic response of the liquid percent level of the reboiler, (c) The fluctuation of styrene production rate, (d) Dynamic response of styrene product quality.

In all of the cases, the molar flow of the styrene product was heavily influenced by the disturbances. In a typical case of +30% ethylbenzene feed flowrate in 60 minutes, after the disturbance was introduced, the styrene molar flow skyrocketed to 79.36 kmole/h then suddenly plummeted to only 13.35 kmole/h when the disturbance was eliminated before eventually reaching the original setpoint. The ethylbenzene feed flow rate disturbances caused the stream to fluctuate, which affected the ratio between steam and ethylbenzene directly and eventually had a slight effect on the product quality, in particular, the styrene composition output.

4. Conclusions and recommendations

In this study, a styrene production process was designed along with the control system. Dynamic simulation was conducted by introducing the molar ethylbenzene feed stream flowrate disturbance. The system show positive results as it was capable of withstanding the disturbance and returning to its original setpoints. The molar flowrate of the main product styrene fluctuated the most, while the product quality was assured as styrene composition was still maintained at 99.9%, while the styrene used for polymerization should have a purity greater than 99.6% [7]. Overall, the average time for the process to recover from the disturbances is 270 minutes, which is calculated from all of the settling times of each disturbance case.

Several modifications should be made in future works in order to further improve the production process. First, heat integration should be applied using pinch analysis to take advantage of the available process heat instead of relying on purely heat from utilities. Additionally, an in-depth cost
analysis should be made to evaluate the economic potential and effectiveness of the production process.

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