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Technical Chemistry A
(Chemical Process Development)
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Experiment

Styrene Production from Ethylbenzene

Objective:

- **A “Mini-plant” which represents the main parts of the entire industrial process, including recycle streams, has to be operated:**
 - **isothermally operated reactor for dehydrogenation of ethylbenzene to styrene (catalyst bed 30 mm diameter, 1.5 m length, about 600 °C)**
 - **distillation column (200 mbar, 30 mm diameter, Sulzer CY packing, 3 m height, equivalent to about 36 theoretical plates)**
 - **feed rate about 250 g/h ethylbenzene**
 - **about 50 % ethylbenzene conversion, recycling of the unconverted ethylbenzene into the reactor**
- **Experimental task:**
 - **start up of reactor, distillation column and all recycle streams**
 - **operating of the plant in order to reach a stationary state**
 - **controlling the produced styrene and the recycled ethylbenzene, including the by-products benzene and toluene, using gas-chromatography**

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1. Mini-Plant Technique

To establish a new process in chemical process development some decades before very expensive pilot plants have been necessary on the way to an industrial scale production plant. Scale-up factors of about 10 usually not have been exceeded. In consequence the realization of a new process needs many years.

Today the progress of chemical engineering enables large scale-up factors. It may be possible to design a production plant on base of laboratory scale experiments. But nevertheless experimental data of the process under real conditions are unavoidable. Therefore, it is a usual technique to build up a so called “mini-plant” in a laboratory scale which includes all essential parts and especially all recycle loops of the intended industrial plant. This is a relatively inexpensive method and above all it needs not too much time which is today a very important criterion during industrial process development.

The mini-plant has to be operated continuously during a sufficient time period in order to get mainly information about:

- stability of catalysts, solvents, construction and sealing materials etc.
- enrichment of by-products, impurities – e.g. from the reactants – etc. in recycle loops
- special necessities of the process, e.g. analysis and controlling.

The mini-plant of this experiment shows – as an example in a simplified configuration – the well known styrene production process from ethylbenzene which is realized in very large plants all over the world. The reactor section is designed according to [1]. The entire mini-plant consists only of the reactor and one distillation column for separating the product styrene and recycling of the unconverted ethylbenzene. It allows to demonstrate the start-up procedure and the enrichment of the by-products benzene and toluene in the recycle loop during longer periods of operation. Principally, also the influence on the process by changing various operation parameters can be investigated.

2. Styrene Production from Ethylbenzene

The following text in this section is taken from [2] (shortened) and is **permitted for personal use only !**

2.1 Data of Styrene and Ethylbenzene

Styrene, also known as phenylethylene, vinylbenzene, styrol, or cinnamene, $C_6H_5-CH=CH_2$, is an important industrial unsaturated aromatic monomer. It occurs naturally in small quantities in some plants and foods. In the nineteenth century, styrene was isolated by distillation of the natural balsam storax. It has been identified in cinnamon, coffee beans, and peanuts, and it is also found in coal tar.

The development of commercial processes for the manufacture of styrene based on the dehydrogenation of ethylbenzene was achieved in the 1930s. The need for synthetic styrene – butadiene rubber (Styrene – Butadiene Rubber (E-SBR)) during World War II provided the impetus for large-scale production. After 1946, this capacity became available for the manufacture of a high-purity monomer that could be polymerized to a stable, clear, colorless, and cheap plastic (Polystyrene and Styrene Copolymers). Peacetime uses of styrene-based plastics expanded rapidly, and polystyrene is now one of the least expensive thermoplastics on a cost-per-volume basis. Styrene itself is a liquid that can be handled easily and safely. The activity of the vinyl group makes styrene easy to polymerize and copolymerize. When the appropriate technology became available through licensors styrene was quickly transformed into a bulk-commodity chemical, growing to a world-wide capacity estimated at 17×10^6 t/a in 1993.

Styrene is a colorless liquid with a distinctive, sweetish odor. Some physical properties of styrene are summarized on the right.

Vapor pressure is a key property in the design of styrene distillation equipment.

Temperature [°C]	Vapor pressure [kPa]
20	0.6
50	3.2
80	12.2
100	25.7
145.2	101.3

Antoine equation:

$$\log_{10} P = [6.08201 - 1445.58 / (209.43 + T)]$$

Styrene is miscible with most organic solvents in any ratio. It is a good solvent for synthetic rubber, polystyrene, and other non- cross-linked high polymers. Styrene and water are sparingly soluble in each other. The composition of the azeotropic mixture at standard pressure is ca. 66 wt-% styrene and 34 wt-% water, and the minimum boiling point is 94.8 °C.

Ethylbenzene is almost exclusively (>99 %) used as an intermediate for the manufacture of styrene monomer. 50 % of the world's benzene production is consumed for this purpose. Less than 1 % of the ethylbenzene produced is used as a paint solvent or as an intermediate for other chemicals. Currently, almost all ethylbenzene is produced commercially by alkylating benzene with ethylene, primarily via two routes: in the liquid phase with aluminum chloride catalyst (Friedel-Crafts reaction), or in the vapor phase with a fixed bed of either a Lewis acid or a synthetic zeolite catalyst developed by Mobil Corporation.

Under ordinary conditions, ethylbenzene is a clear, colorless liquid with a characteristic aromatic odor. Ethylbenzene is an irritant to the skin and eyes and is moderately toxic by ingestion, inhalation, and skin adsorption. Some physical properties of ethylbenzene are summarized on the right.

The vapor-liquid equilibrium of the ethylbenzene / styrene mixture shows a nearly ideal behavior. Due to the small difference of the boiling points the separation factor (relative volatility) is low at about 1.35 .

M_r , Styrene $C_6H_5-CH=CH_2$	104.153
bp (101.3 kPa)	145.15 °C
mp	-30.6 °C
Flammable limits in air	1.1 – 6.1 vol %
Flash point, Tag Closed Cup (TCC)	31.1 °C
Autoignition point	490 °C
Heat of formation, ΔH_f	
gas (25 °C)	147.4 kJ/mol
liquid (25 °C)	103.4 kJ/mol
Heat of vaporization, ΔH_v	
(25 °C)	421.7 J/g
(145 °C)	356.7 J/g
Heat of polymerization, ΔH_p (25 °C)	-69.8 kJ/mol
Volume shrinkage on polymerization, typical	17.0 %
Refractive index, n_D (20 °C)	1.54682
Density, g/mL (20 °C)	0.9050

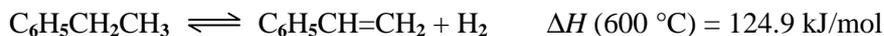
M_r , Ethylbenzene $C_6H_5-CH_2-CH_3$	106.168
bp (101.3 kPa)	136.186 °C
mp	-94.949 °C
Heat of vaporization, ΔH_v	335 J/g
Flash point, Tag Closed Cup (TCC)	15 °C
Autoignition point	460 °C
Refractive index, n_D (20 °C)	1.49588
Density, g/mL (20 °C)	0.8669

2.2 Catalytic Dehydrogenation of Ethylbenzene

2.2.1 Main Reactions

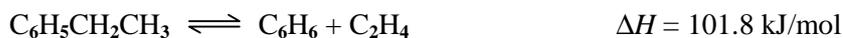
Direct dehydrogenation of ethylbenzene to styrene accounts for 85 % of commercial production. The reaction is carried out in the vapor phase with steam over a catalyst consisting primarily of iron oxide. The reaction is endothermic, and can be accomplished either adiabatically or isothermally. Both methods are used in practice.

The major reaction is the reversible, endothermic conversion of ethylbenzene to styrene and hydrogen:

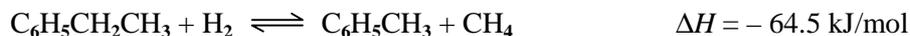


This reaction proceeds thermally with low yield and catalytically with high yield. As it is a reversible gas-phase reaction producing 2 mol of product from 1 mol of starting material, low pressure favors the forward reaction.

Competing thermal reactions degrade ethylbenzene to benzene, and also to carbon:



Styrene also reacts catalytically to toluene:



The problem with carbon production is that carbon is a catalyst poison. When potassium is incorporated into the iron oxide catalyst, the catalyst becomes self-cleaning (through enhancement of the reaction of carbon with steam to give carbon dioxide, which is removed in the reactor vent gas).



Typical operating conditions in commercial reactors are ca. 620 °C and as low a pressure as practicable. The overall yield depends on the relative amounts of catalytic conversion to styrene and thermal cracking to byproducts. At equilibrium under typical conditions, the reversible reaction results in about 80 % conversion of ethylbenzene. However, the time and temperature necessary to achieve equilibrium give rise to excessive thermal cracking and reduced yield, so most commercial units operate at conversion levels of 50 – 70 wt %, with yields of 88 – 95 mol %.

Dehydrogenation of ethylbenzene is carried out in the presence of steam, which has a threefold role:

- 1) It lowers the partial pressure of ethylbenzene, shifting the equilibrium toward styrene and minimizing the loss to thermal cracking
- 2) It supplies the necessary heat of reaction
- 3) It cleans the catalyst by reacting with carbon to produce carbon dioxide and hydrogen.

Many catalysts have been described for this reaction. One catalyst – Shell 105, also used in this experiment – dominated the market for many years, and was the first to include potassium as a promoter for the water-gas reaction. This catalyst is typically 84.3 % iron as Fe_2O_3 , 2.4 % chromium as Cr_2O_3 , and 13.3 % potassium as K_2CO_3 . It has good physical properties and good activity, and it gives fair yields.

In recent years, the situation has become more complex. The market has become more competitive, causing manufacturers to seek new catalysts that produce higher yields without compromising activity or physical properties, or catalysts that meet specific requirements. A catalyst life of ca. two years is claimed.

2.2.2 Adiabatic Dehydrogenation

Over 75 % of all operating styrene plants carry out the dehydrogenation reaction adiabatically in multiple reactors or reactor beds operated in series (Fig. (1)). The necessary heat of reaction is applied at the inlet to each stage, either by injection of superheated steam or by indirect heat transfer.

Fresh ethylbenzene feed is mixed with recycled ethylbenzene and vaporized. Dilution steam must be added to prevent the ethylbenzene from forming coke. This stream is further heated by heat exchange, superheated steam is added to bring the system up to reaction temperature (ca. 640 °C), and the stream is

passed through catalyst in the first reactor. Adiabatic reaction drops the temperature, so the outlet stream is reheated prior to passage through the second reactor. Conversion of ethylbenzene can vary with the system, but is often about 35 % in the first reactor and 65 % overall. The reactors are run at the lowest pressure that is safe and practicable. Some units operate under vacuum, while others operate at a low positive pressure. The steam : ethylbenzene ratio fed to the reactors is chosen to give optimum yield with minimum utility cost. The reactor effluent is fed through an efficient heat recovery system to minimize energy consumption, condensed, and separated into vent gas, a crude styrene hydrocarbon stream, and a steam condensate stream.

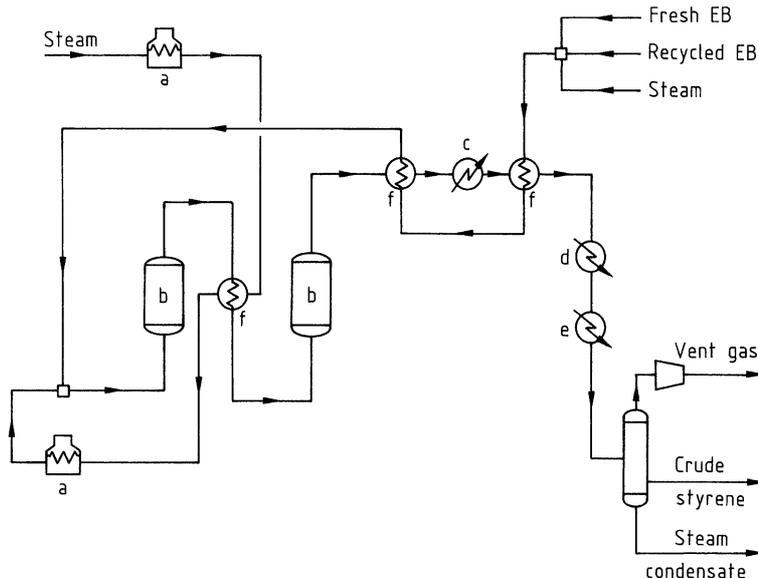


Fig. 1 Adiabatic dehydrogenation of ethylbenzene (EB)

- a) Steam superheater, b) Reactor, c) High-pressure Steam, d) Low-pressure Steam, e) Condenser, f) Heat exchanger

The crude styrene goes to a distillation system. The steam condensate is steam-stripped, treated, and re-used. The vent gas, mainly hydrogen and carbon dioxide, is treated to recover aromatics, after which it can be used as a fuel or a feed stream for chemical hydrogen. The complete technology is for sale from various licensors.

2.2.3 Isothermal Dehydrogenation

Isothermal dehydrogenation (Fig. (2)) was pioneered by BASF and has been used by them for many years. The reactor is built like a shell-and-tube heat exchanger. Ethylbenzene and steam flow through the tubes, which are packed with catalyst. The heat of reaction is supplied by hot flue gas on the shell side of the reactor – exchanger. The steam : oil mass ratio can be lowered to about 1 : 1, and steam temperatures are lower than in the adiabatic process. A disadvantage is the practical size limitation on a reactor – exchanger, which restricts the size of a single-train plant to about 150×10^3 t/a, translating into increased capital for large plants.

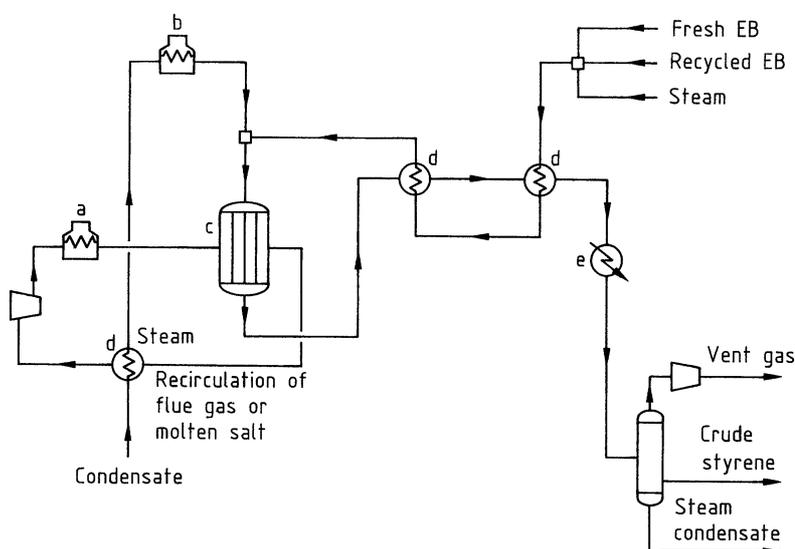


Fig. 2 Isothermal dehydrogenation of ethylbenzene (EB)

- a) Heater, b) Steam superheater, c) Reactor, d) Heat exchanger e) Condenser

Lurgi GmbH operates an isothermal reactor system that uses a molten salt mixture of sodium, lithium, and potassium carbonates as the heating medium. The multitubular reactor is operated at ca. 600 °C under vacuum and a steam : ethylbenzene ratio of 0.6 – 0.9. High conversion and selectivity are claimed. A demonstration plant has been operated since 1985 in Italy, by Montedison. The technology is offered for license, but so far no more units have been built.

Isothermal dehydrogenation is also used in this experiment. The reactor consists of one vertical mounted tube with 30 mm inner diameter and a catalyst bed (Shell 105) of 1.5 m height. The reactor tube is heated by an electrical furnace, according to [1] (see section 3, Fig. 4).

2.2.4 Distillation of Crude Styrene

A typical crude styrene from the dehydrogenation process consists of:

Benzene (<i>bp</i> 80 °C)	1 %
Toluene (<i>bp</i> 110 °C)	2 %
Ethylbenzene (<i>bp</i> 136 °C)	32 %
Styrene (<i>bp</i> 145 °C)	64 %
Others	1 %

The separation of these components is reasonably straightforward, but residence time at elevated temperature needs to be minimized to reduce styrene polymerization. At least three steps are involved. Benzene and toluene are removed first, and either sent to a toluene dehydrogenation plant or further separated into benzene for recycling and toluene for sale. Ethylbenzene is then separated and recycled to the reactors. Finally, styrene is distilled away from the tars and polymers under vacuum to keep the temperature as low as possible. Fig. 3A shows a typical distillation train. The variant shown in Fig. 3B is the Monsanto approach, where the major split is accomplished first, followed by separation of the benzene – toluene mixture.

Ethylbenzene and styrene, having similar boiling points, require 70 – 100 trays for their separation depending on the desired ethylbenzene content of the finished styrene.

If bubble-cap trays are used, as in old plants, a large pressure drop over the trays means that two columns in series are necessary to keep reboiler temperatures low. The most modern plants use packing in place of trays which permits this separation to be achieved in one column. This results in less pressure drop, giving a lower bottom temperature, shorter residence time, and hence less polymer. Sulzer has done pioneering work in the field of packings for distillation.

A polymerization inhibitor (distillation inhibitor) is needed throughout the distillation train. Today usually aromatic compounds with amino, nitro, or hydroxy groups are used (e.g., phenylenediamines, dinitrophenols, and dinitrocresols). The distillation inhibitor tends to be colored and is thus unacceptable in the final product; finished monomer is usually inhibited instead with *tert*-butylcatechol (TBC) (10 – 50 mg/kg) during storage and transportation.

2.3 Alternative Processes for Styrene Production

The only other route to commercial production of styrene uses also ethylbenzene as starting material, but it involves co-production of propylene oxide (Oxirane process, ca. 15 % of the styrene production). The

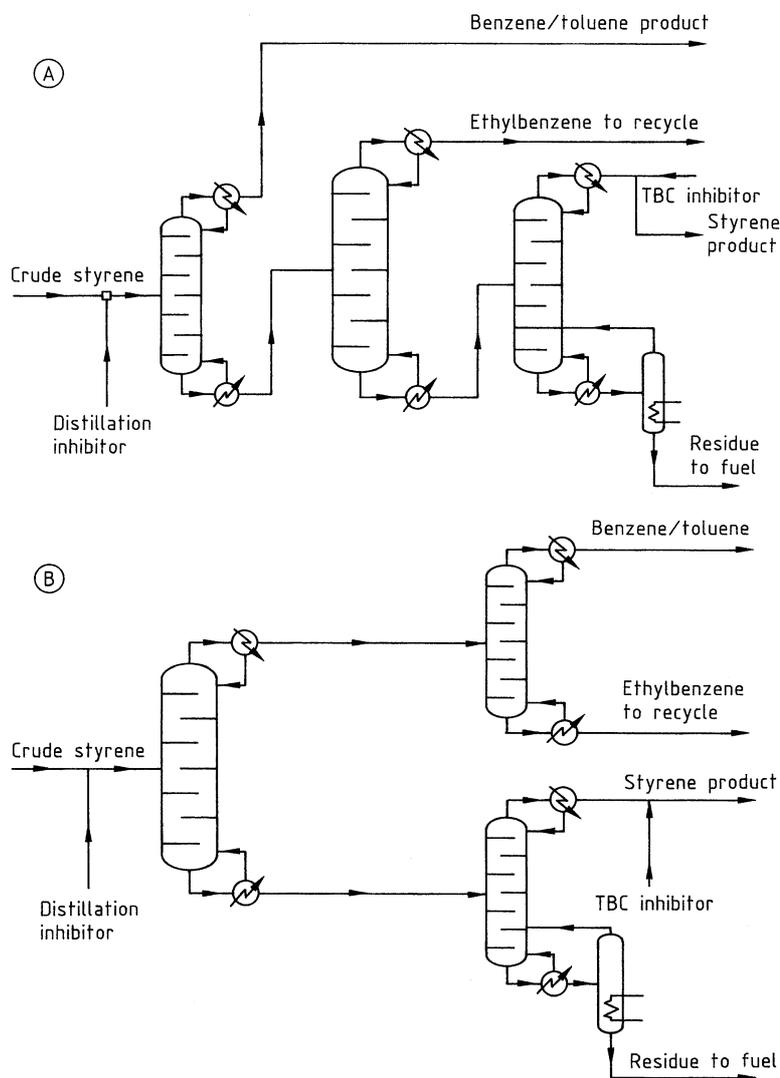


Fig. 3 Distillation of crude styrene

A) Standard approach B) Monsanto approach

first step is direct air oxidation of ethylbenzene at ca. 130 °C and 0.2 MPa to form ethylbenzene hydroperoxide. In the next step this is able to oxidize propylene to propylene oxide in presence of a metallic catalyst (e.g. molybdenum or titanium, 110 °C, 4 MPa). Ethylbenzene hydroperoxide itself is reduced to α -methylbenzyl alcohol (methyl phenyl carbinol) which finally is dehydrated to styrene at 250 °C and low pressure over a suitable metal oxide contact (often Al_2O_3).

Furthermore, there are numerous research projects for new processes:

- Oxidative hydrogen removal during the dehydrogenation of ethylbenzene to styrene,
- Styrene from butadiene (via 4-vinylcyclohexane-1 and ethylbenzene),
- Styrene from toluene (via oxidation to stilbene (diphenyl ethylene) and reaction with ethylene to styrene),
- Separation of styrene from pyrolysis gasoline of the steam cracking process.

3. Design of the Mini-Plant

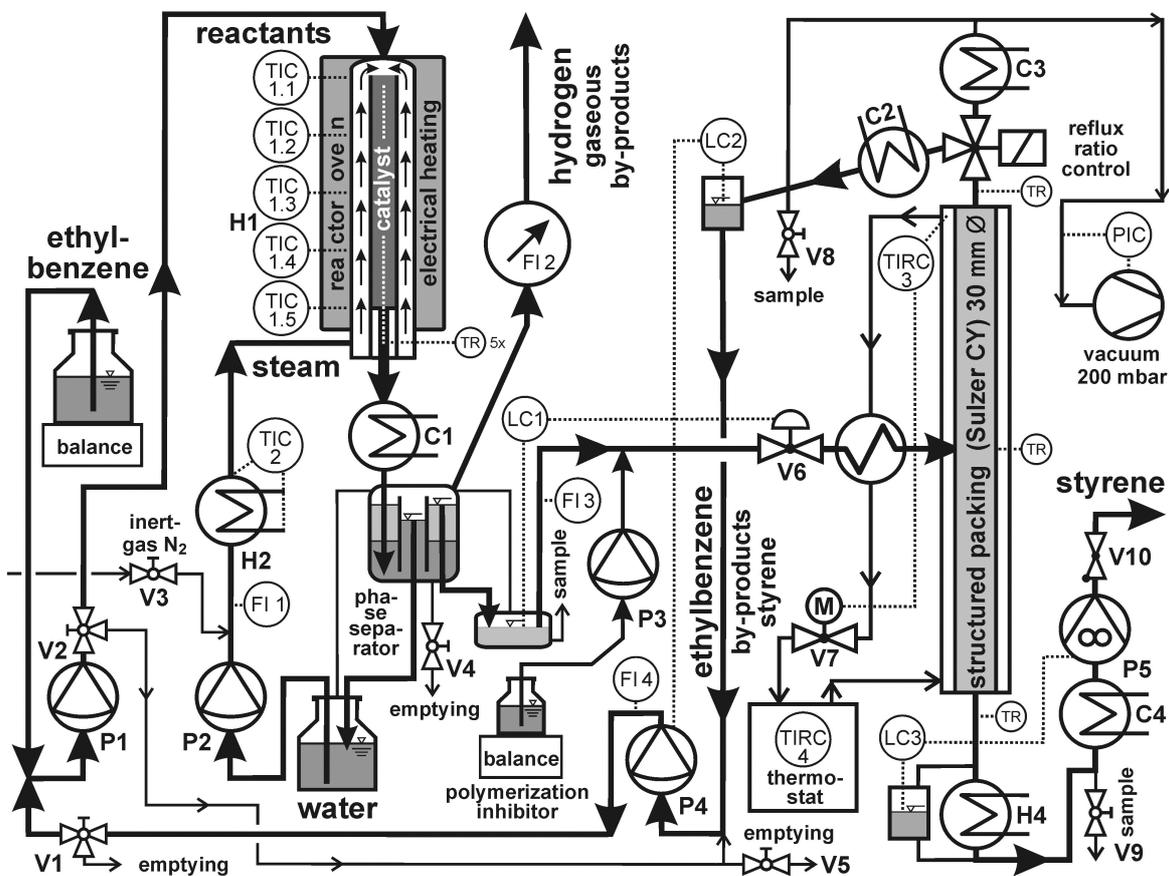


Fig. 4 Flow scheme of the experimental plant

Fresh ethylbenzene from a bottle on a balance, mixed with the recycled ethylbenzene from top of the distillation column, is fed by pump P1 to the top of the electrically heated reactor furnace H1. Water is pumped by P2 through the flow indicator FI1 (rotameter) to the electric heater H2, where it is evaporated and superheated. The steam enters the outer tube (44.3 mm inner diameter) in the reactor furnace H1 and is further heated during up-streaming. At the top of the reactor furnace the steam is mixed with the evaporating ethyl benzene and enters the inner tube which contains the catalyst (30.5 mm inner diameter, additionally in the center a tube of 6 mm outer diameter is included for the thermo-couples (see below), height of the catalyst packing 1.5 m). This design [1] guarantees an uniform heating of catalyst and down-streaming gases during the endothermic dehydrogenation reaction. The products are cooled and condensed in the cooler C1 and arrive at the phase separator. Here the offgas (mainly hydrogen, some carbon dioxide from side-reactions) is separated and measured by the flow indicator FI2 (wet gas meter).

The separation of the two liquids in the phase separator is enhanced by a packing of glass wool (bottom: water, top: organic phase of styrene, ethylbenzene and by-products like benzene and toluene). The water spillage flows into the water reservoir. The overflowing organic phase arrives in a small glass vessel, containing two optical sensors of the level control LC1. The gas phase (warning: hydrogen !) of these three containers is connected in order to avoid pressure differences.

The organic phase has to be transferred completely and continuously into the distillation column which works at a vacuum of about 200 mbar. Due to the pressure difference this can be realized using the motor driven control valve V1 which is adjusted automatically by LC1 or by manual control. The flow is indicated by FI3 (rotameter). By pump P3 a small amount of polymerisation inhibitor *tert*-butylcatechol (TBC: 1,2-dihydroxy-4-*tert*-butylbenzene), solved in ethylbenzene is added.

The distillation column has an inner diameter of 30 mm and a height of 3 m. It contains a structured packing of stainless steel mesh (Sulzer CY) which is equivalent to about 36 theoretical plates. This can demonstrate the process for the production of a styrene with a purity better than 99 % at a reflux ratio of ca.10 (the commercial process for the production of a high purity styrene suitable for polymerization needs about 70 – 100 theoretical plates). The reboiler is the electric heater H4 (manually adjusted). The product (mainly styrene) is cooled by the cooler C4 and pumped out of the vacuum by the geared pump P5 which is controlled by an optical sensor in the level control LC3. On top of the distillation column a solenoid valve guides the vapor stream either to the reflux condenser C3 or to the distillate outlet through the cooler C2. The reflux ratio is manually adjusted using a time controller. The gas phase behind the coolers C2 and C3 is connected with a membrane vacuum pump, including a pressure controller (about 200 mbar). In order to avoid undesired condensation inside the distillation column it is provided with a heating jacket. Hot water from a thermostat is pumped up-streaming through it, controlled by the temperature control TIRC3 at the upper end of the heating jacket, using the motor driven control valve V2. This hot water stream is also used for preheating of the distillation feed in the heat exchanger H3.

The distillate, mainly containing ethylbenzene, has to be pumped completely out of the vacuum by P4 through the flow indicator FI4 (rotameter) back to the ethylbenzene feed pump P1. P4 is controlled by an optical sensor in the level control LC2 on top of the distillation column.

The continuous monitoring of the temperatures in the reactor furnace and in the distillation column gives first important information on the recorder about the proper functioning of the plant:

- temperature controller of the reactor furnace H1 (TIRC1)
- temperature controller of the water heater H2 (TIRC2)
- two additional thermo couples TR in the heating jacket of the reactor furnace H1 (top and bottom)
- three thermo couples TR in the central tube of the catalyst bed in the reactor furnace H1: top (inlet), middle and bottom (outlet)
- three temperature sensors TR (Pt-100 resistors) in the distillation column top (distillate), middle (feed position) and bottom (waste product)
- thermostat for the distillation column (TIRC4)
- temperature controller on top of the heating jacket of the distillation column (TIRC3)

The reaction rate in the reactor furnace continuously has to be observed by balancing the feed stream of ethylbenzene and the offgas stream in the wet gas meter FI2 (hydrogen, carbon dioxide can be neglected).

In order to supervise the functions of the plant additionally samples of the following product streams should be analyzed by gas-chromatography (see section 5.3) at regular intervals:

- organic phase of the reactor furnace
= feed of the distillation column (before adding the polymerization inhibitor), available in the glass vessel of level control LC1 via a septum using an injection syringe,
- distillate, available at the ball valve behind the distillate cooler C2:
to get a sample out of the vacuum a small special glass vessel has to be screwed tightly into the thread below the ball valve; by slowly opening of the ball valve the vacuum can be adapted in the vessel and sampling is possible (a baffle in the tube above the ball valve guarantees that always the actual distillate concentration is present in the sample); after closing the ball valve the glass vessel can slowly be removed (adaptation to atmosphere pressure),
- distillation waste outlet (getting an actual sample at the outlet of the geared pump P5).

4. Task of the experiment

- start up of reactor, distillation column and all recycle streams
- operating of the plant in order to reach a stationary state
- controlling the produced styrene and the recycled ethylbenzene, including the by-products benzene and toluene, using gas-chromatography

Principally – if sufficient time available – also the influence on the process by changing various operation parameters can be investigated, e.g.:

- reactor temperature
- ethylbenzene feed rate into the plant
- ethylbenzene / water ratio in the reactor feed
- reflux ratio in the distillation column
- evaporation rate in the distillation column

5. Start up and operation of the experiment

5.1 Safety instructions

All used chemicals – ethylbenzene, styrene, toluene and benzene – are at least irritant to the skin and eyes and are moderately toxic by ingestion, inhalation, and skin adsorption. Benzene is highly toxic, but is involved only as a by-product of very low concentrations. All substances are inflammable, especially hydrogen gas is highly inflammable.

The safety information about the used chemicals is available at the experimental plant at has to be considered !

The following safety regulations inevitably are to be observed:

- continuously safety glasses have to be used,
- any contact of substances with the skin has to be avoided,
- the doors at the experimental plant have to be closed as far as possible,
- any ignition source has to be avoided,
- the plant has to be rinsed with nitrogen before and behind the experiment.

5.2 Operating instructions

- a) rinse the plant with nitrogen via the ball valve behind pump P2 (the nitrogen amount of 40 liters has to be measured with the wet gas meter FI2),
- b) open of all cooling water streams,
- c) switch on the recorder,
- d) switch on the electric heating of the reactor furnace H1 at TIRC1 (adjust to 750 °C),
- e) switch on the vacuum pump of the distillation column, adjust the pressure control PC to 200 mbar,
- f) switch on the thermostat of the heating jacket of the distillation column (90 °C),
- g) switch on the temperature controller TIRC3 of the heating jacket of the distillation column (85 °C),
- h) switch on the electric heater of the reboiler H4 (control current 9 mA).

The following steps are carried out not before constant temperatures in the reactor furnace H1 are reached (observe on the recorder) :

- i) switch on the evaporator / superheater for water H2 (manual control 70 %),
- j) switch on the water pump P2,
- k) as soon as the water loop is running – i.e. water spills out of the phase separator into the water reservoir – switch on the ethylbenzene pump P1
- l) for the mass balance: note the time and the data of the balance an the wet gas meter FI2,

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- m) switch on the pump P3 for the polymerization inhibitor,
- n) switch on the motor driven valve V1 (manual control about 50 %).

5.3 Analysis methods

The instructions for the analysis using the gas-chromatograph is given by the assistant.

6. Literature

- [1] Patat, F.; Kirchner, K.: "Praktikum der technischen Chemie" (in German), 4th Edition, page 237 – 244, de Gruyter, Berlin 1986
- [2] Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A25, chapter "Styrene", page 329 – 344, VCH, Weinheim 1994, 6th edition as electronic release (available from the University of Dortmund via the homepage of the university library); also printed as: "Industrial organic chemicals: starting materials and intermediates, an Ullmann's encyclopedia" 1st Edition, Vol. 7, chapter "Styrene", page 4417 – 4441, Vol. 4, chapter "Ethylbenzene", page 2207 – 2220, Wiley-VCH, Weinheim 1999
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