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CHAPTER 2

THE THEORY OF STYRENE SYNTHESIS

2.1 Choice of reaction

In the styrene monomer producing plants, there are several methods. The following ones have been used for the commercial production of styrene.

1. Dehydrogenation of ethylbenzene.
2. Oxidation conversion of ethylbenzene to α- phenyl ethanol via acetophonone and subsequent dehydration of the alcohol.
3. Side chain chlorination of ethylbenzene followed by dehydrogenation.
4. Side chain chlorination of ethylbenzene hydrolysis to the corresponding alcohols followed by dehydration.
5. Pyrolysis of petroleun and recovery from various petroleum process.
6. Oxidation of ethylbenzene to ethylbenzene hydroperoxide which is reacted with propylene to give α-phenyl ethanol and propylene oxide. The alcohol is dehydrated to styrene.

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At present, all of the styrene are commercially manufactured by the dehydrogenation of ethylbenzene. The oxidation precess (process#2) has been practices for a number of years but has been abandoned on favor of dehydrogenation. Process (3) and (4) involving chlorine have generally suffered from the high cost of raw materials and the chlorinated contaminante in the monomer. Manufacture of styrene directly from petroleum stream (process #5) is difficult and costly. Lastly, the Halcon process (process#6) is a recent innovation in chemical technology (10).

2.2 The dehydrogenation of ethylbenzene

It is known that, in most industrial, the dehydrogenation of ethylbenzene process is used. Here we will study this process which can be categorized into 3 steps as follows.

1. Alkylation of benzene with ethylene in the present of aluminium chloride to form ethylbenzene.
2. Catalytic dehydrogenation of purified ethylbenzene in the presence of steam to give styrene.
3. Purification of styrene monomer.

The flow diagram of this 3 steps are shown in figure 2.1

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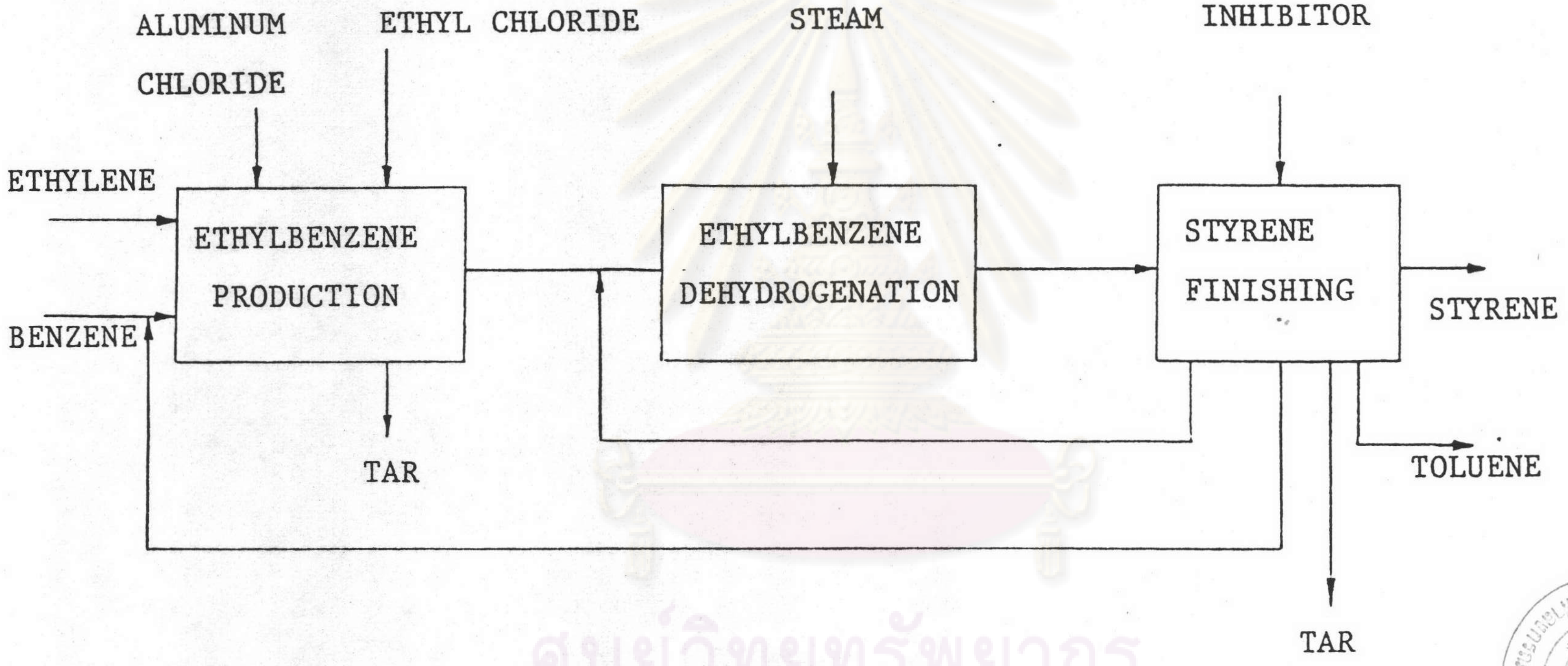

FIG 2.1 FLOW DIAGRAM OF PRODUCTION STYRENE MONOMER

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2.2.1 Ethylbenzene production step

When ethylene and benzene react in the presence of aluminium chloride and hydrogen chloride in anhydrous system, alkylation of benzene ring occurs to produce ethylbenzene and higher ethylated benzenes. Ethylene purity is not critical on this system as long as impurities are hydrogen, light parafin hydrocarbon, or other inert materials. Acetylene is to be avoided because it increases catalyst consumption. Benzene used is classified as ¨Styrene Grade¨. This term defines a benzene with a boiling range of 1°C and a minimum freezing point of 4.85°C. This corresponds to a purity slightly above 99%. Total sulfur should be below 0.1% and aluminium chloride with a minimum purity of 97.5%

In order to operate with high catalyst efficiencies hydrogen chloride must be added as a promoter. This is accomplished by furnishing the reaction mixture with ethylchloride which in turn provides the desired HCl as well as ethylene.

If ethylene comes to equilibrium with benzene at 95°C, the products are shown in figure 2.2

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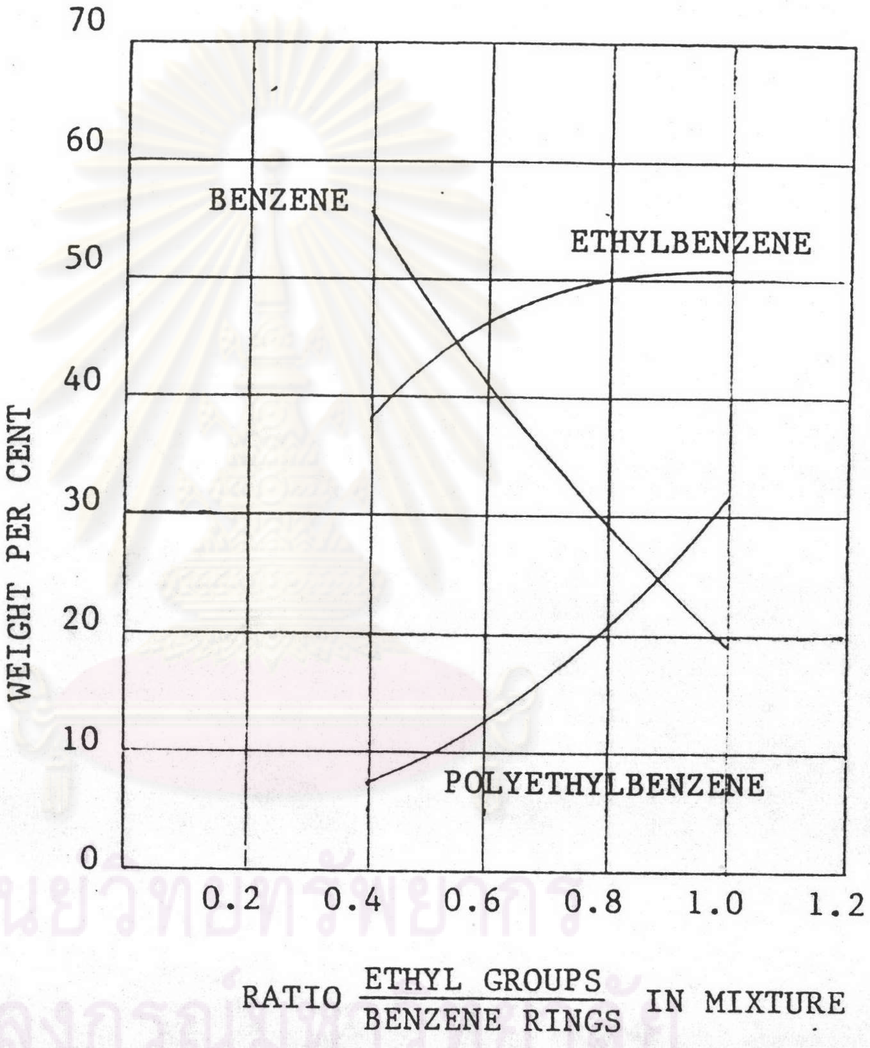

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FIG 2.2 EQUILIBRIUM RELATIONS IN THE ETHYLATION OF BENZENE

Obviously, satisfactory ethylbenzene can be obtained only when the quantity of polyethyl is cut down. This is accomplished in two ways: firstly, by reducing the ratio of ethyl groups to benzene rings in the mixture, thus creates a more favorable equlibrium, and secondly, by recycling the polyethyls formed. We may then consider two simultaneous reactions, the forward one of alkalation and the backward one of dealkylation. Benzene in the alkylated product is recycled and polyethylbenzenes are sent back to the reactor for dealkylation. Experiment production substantiates the optimun operating point as predicted by theory that

$$.58C_2H_4 + C_6H_6 \underset{95\ C}{\overset{AlCl_3}{\rightleftharpoons}} .51C_6H_6 + .41\text{Ethylbenzene} + .08\text{Polyethylbenzene}$$

The alkylation process consists of the following steps.

1. Feed preparation
2. Reaction
3. Removal of heat of reaction
4. Reactor off-gas treatment
5. Catalyst preparation
6. Catalytic hydrolysis
7. Separation
8. Washing

The alkylation process is shown in figure 2.3

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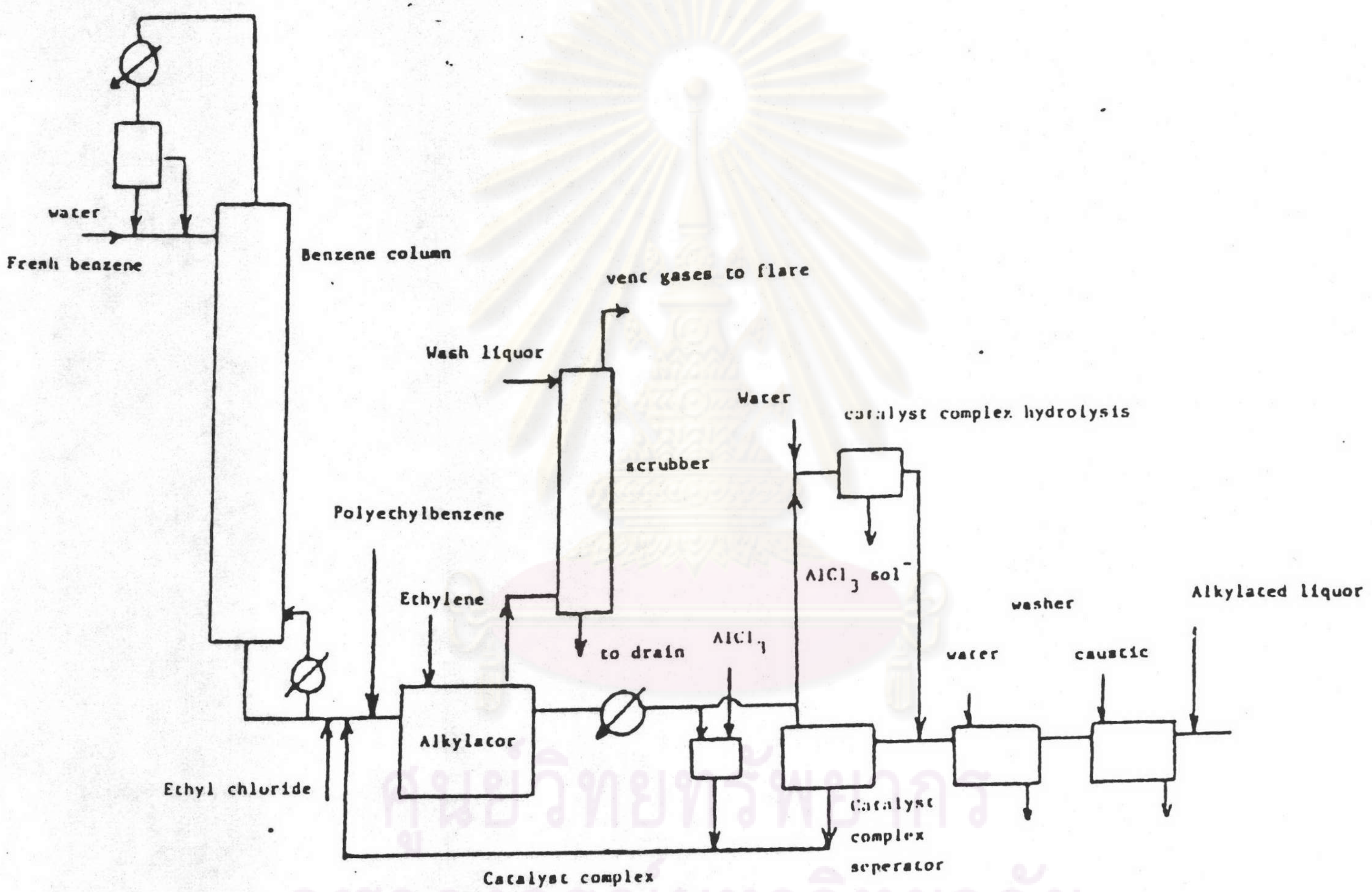

FIG 2.3 ALKYLATION OF BENZENE WITH ETHYLENE

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The last unit of this step is the purification of ethylbenzene. The operation is carried out conventionally in three separation towers, toping the benzene out first, then the ethylbenzene and finally the polyethylbenzene. The ethylbenzene purification process is shown in figure 2.4

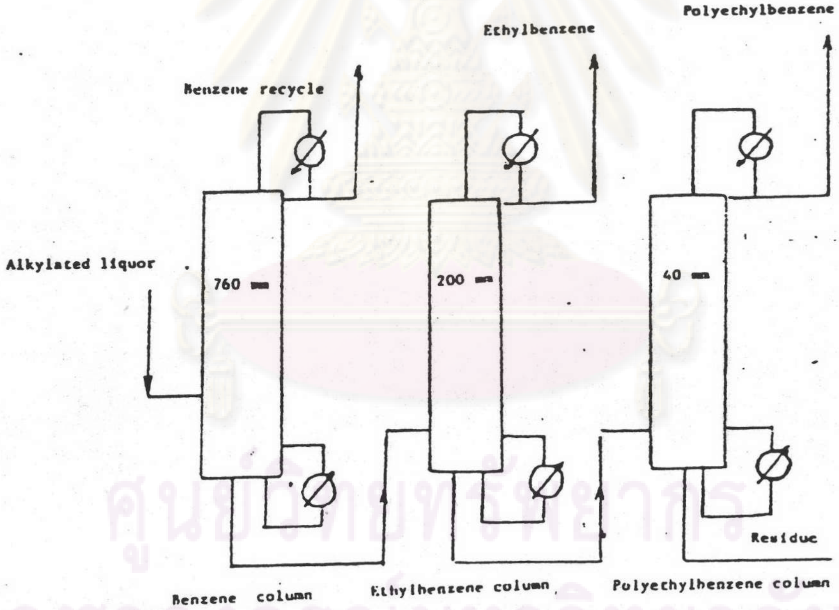

FIG 2.4 ETHYLBENZENE DISTILLATION

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2.2.2 Ethylbenzene dehydrogenation step

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CHCH_2 + H_2$$

Ethylbenzene Styrene Hydrogen

The dehydrogenation of ethylbenzene is an endothermic reaction. Consequently, the increase in volume encourages the dehydrogenation and hence, according to Le Chateliers' principle, the pressure will decrease while the temperature rises. In stead of running this high temperature reaction under a partial vacuum, steam is used as diluent to reduce the partial pressure of the reactants. At the total operating pressure, the process, whose theoretical equilibrium is at 630°C, will give only 25 - 30% styrene in the liquid product. The addition of steam shifts the equilibrium point along the pressure axis and makes possible a theoretical styrene concentration of 70 - 80%. Although the equilibrium relation is favorable at this temperature, the reaction rate is too slow for practical application. As the result, at higher temperature where the reaction rate is adequate and the equilibrium is more favorable, simultaneous cracking reactions are also favored. So, there will be large amount of by products (benzene,toluene). The need for a selective dehydrogenation catalyst is apparent. The catalyst is chosen to specifically catalyze the dehydrogenation reaction, reduce the side reaction and permit a high reaction rate at a temperature low enough that the cracking reactions are minimized. Nowaday, many industries try to improve the activities of the catalyst for

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higher conversion and selectivity.

The dehydrogenation process is shown in figure 2.5

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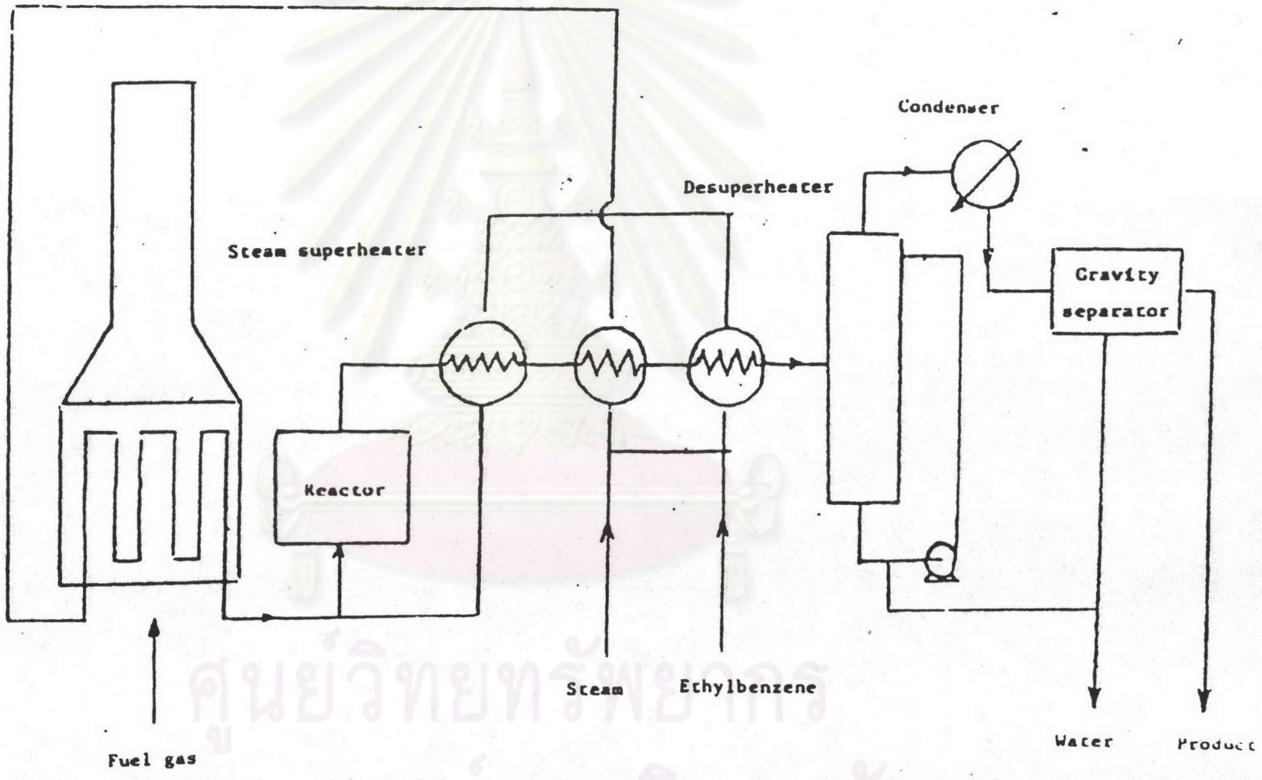

FIG 2.5 DEHYDROGENATION OF ETHYLBENZENE

2.2.3 Purification of styrene monomer

The final step is the purification of the crude dehydrogenater material which contains (styrene, ethylbenzene,benzene and toluene). The fractionation requirements are rather strict. Not only the styrene product but also recycled benzene and toluene must be of very high purity. There are two major problems that encounter in styrene purification.

1. Styrene polymerizes rapidly when it is heated and will firstly form a viscous liquid and, finally, yield a sokid polymer. The rate of polymerization increases remarkably with temperature as shown in figure 2.6

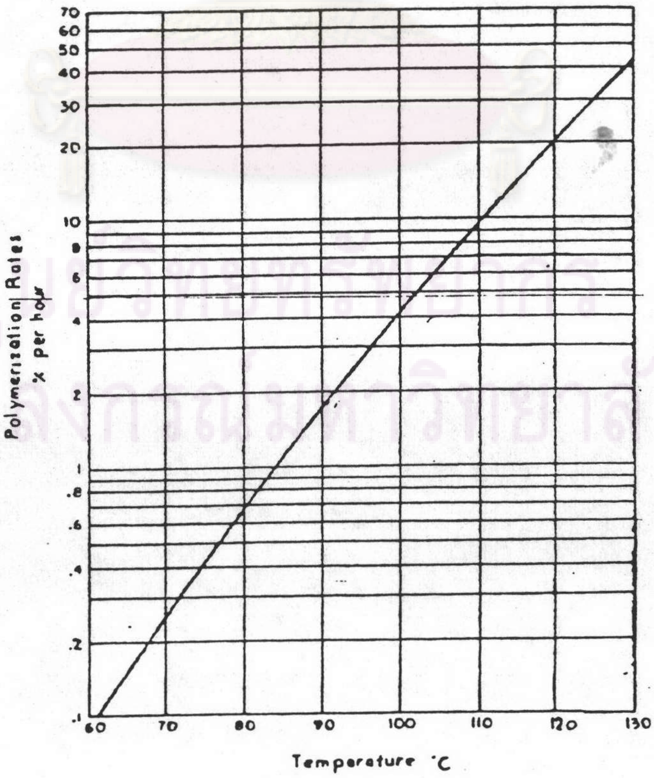

FIG 2.6 STYRENE POLYMERIZATION RATE AT VARYING TEMPERATURE

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2. The boiling points of ethylbenzene (136°C) and styrene (145°C) are very close to one another. This necessitates a large number of theoretical plates for the desired separation.

At 30 mm Hg absolute, the boiling point of styrene is 54°C and the polymerization rate has dropped to less than 0.1% per hour. To run the process under vacuum, then, appears to be necessary. However, the ethylbenzene-styrene separation requires 70 actual plates with the pressure drop of 4 mm Hg per plate throughout such a column, the bottom temperature at 310 mm Hg will cause excessive polymer formation. Even though a low distillation temperature is achieved, the normal irregularities of operation still necessitates further pre-caution. As very small quantities of certain foreign materials catalyze the polymerization reaction greatly. To act against such possibities, elemental surfur is dissolved in styrene to act as a polymerization inhibitor. Only by a combination of vacuum operation, suitable inhibitor of styrene and special column design make styrene be distilled sucessfully. The styrene purification process is shown in figure 2.7 (5,7,8)

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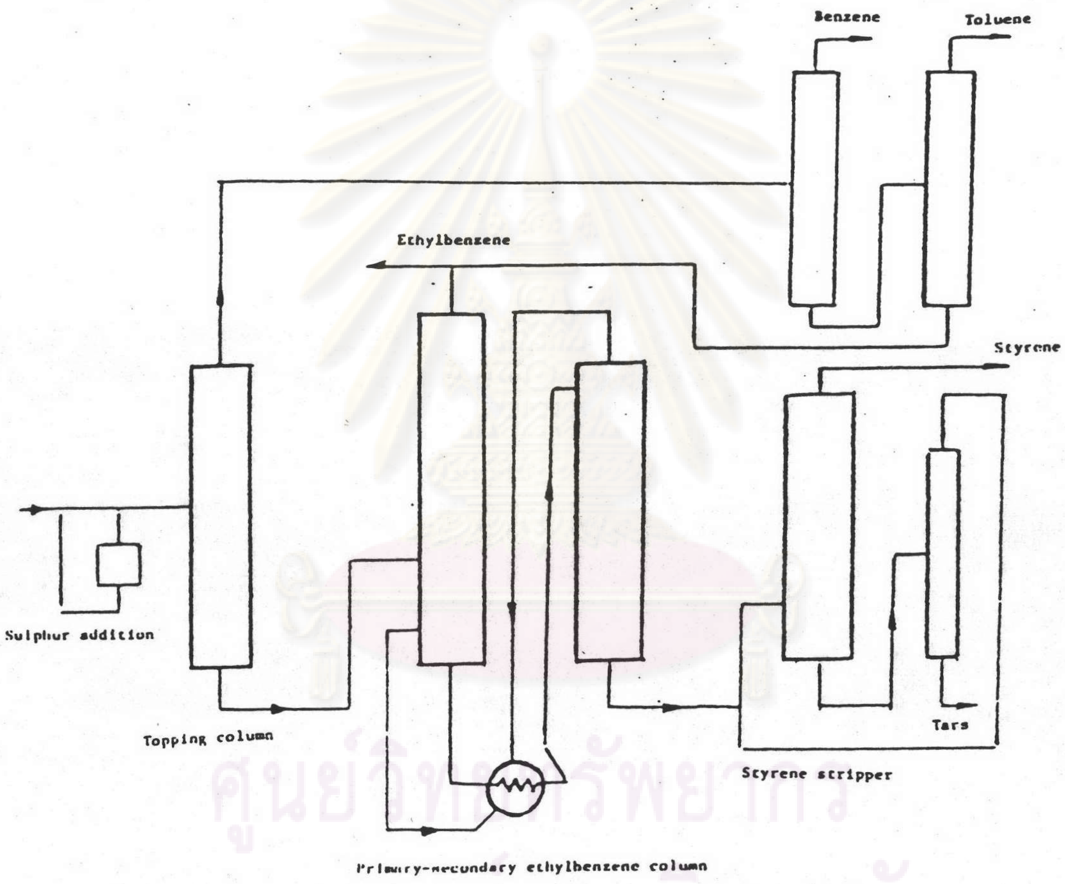

FIG 2.7 PURIFICATION OF STYRENE

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2.3 Catalyst for dehydrogenation

Various catalysts have been used, but in most case, the main constituent is iron oxide to which a promoter and an inert support may be added. One of the most inportant catalyst was Standard Oil 1707 (18.4per cent of ferric oxide, 4.6 per cent potassium oxide, 4.6 per cent cupric oxide and the rest inert), but this has been superceded by Shell 105 and 205 catalyst which are largely iron oxide containing varying quantities of potassium carbonate and chromium oxide promoters. In Germany a non-regenerative catalyst, such as zinc phosphate has been used, this type of catalyst has normal life about one to two years. As mentioned earlier, one reason for gradual loss of activity is that the trace quantities of chloride ion in ethylbenzene react with the potassium of the catalyst forming potassium chloride which volatilizes and is carried down-stream by the hot gases. As the gas stream cools, the potassium chloride is deposited, eventually forming restriction which must be cleared up.

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When ethylbenzene is heated to temperature above 500°C, it is pyrolysed where styrene, benzene, toluene, hydrogen, methane, ethylene and tar are formed. The styrene yields is understandably, poor, and it was found that by using an iron oxide catalyst, the rate of reaction to styrene could be selectively increased (using temperature at which the by-product reactions were comparatively slow). Table 2.1 show some of the dehydrogenation of tehylbenzene to styrene catalysts.

Table 2.1

Principal catalyst using in the dehydrogenation of ethylbenzene to styrene

Composition	Condition of reaction	Name or company	Year
Al_2O_3	Without steam		1973
Al_2O_3, Cr_2O_3	Without steam		1973
	Benzene		1946
Al_2O_3(85), Cr_2O_3(15)	Steam		1972
Al_2O_3(15), Cr_2O_3(70), Cu(15)	CO_2		1947
Al_2O_3(83), Cr_2O_3(15), K_2O(2)	Steam		1974
Al_2O_3(90), MoO_3(10)	Steam	HARSHAW 1201	1972
Al_2O_3,UO_{225}	CO_2/N_2		1974
Al_2O_3,V_2O_5	Steam		1973
Al_2O_3(60), CuO(22), Cr_2O_3(18)	Ethylene/Steam	GIRDLER T 531	1972
Al_2O_3,MgO,V_2O_5	Steam	DISTILLERS	1971
Bi_2UO_6,UO_3	Steam		1974
Sb_2O_3(40),UO_3(20), K_2CO_3(20)	Steam		1972
SnO_2,(80), K_2CO_3(20)	Steam		1972
TiO_2(80), K_2CO_3(20)	Steam		1972
TiO_2(60), CuO(20), K_2CO_3(20)	Steam		1972
Tio_2(60), K_2CO_3(20), ZnO(20)	Steam		1972

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The catalyst that use in this study is chromium alumina CR-0211. It specification is in table 2.2

Table 2.2

Specification of chromiun alumina CR-0211

Surface area	57.1	m^2/gm
Lose due to ignite at 700°C	3.95	%
% Cr_2O_3 at 700°C	20.33	
Average crush strength	14.9	lbs
Average bulk density loose	1.2	gm/cc
Average bulk density packed	1.25	gm/cc
Average length	0.16	inch
Average diameter	0.16	inch

2.4 Effect of variable on dehydrogenation of ethylbenzene

The known variables which effect on the yield of styrene are

1. Reactor pressure
2. Reaction temperature
3. Steam to ethylbenzene ratio
4. Catalyst to ethylbenzene ratio
5. Catalyst particle size
6. Ethylbenzene feed purity

2.4.1 Reactor pressure

From the equilibrium constant, it is obvious that lower pressure favours higher equilibrium conversions

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to styrene. Over the normal operating range, we found that an increasing in the reaction pressure of 1 psi will decrease in conversion of styrene to 0.5%(10) while all other conditions are kept constant. The by-product reactions are considered to be independent of pressure in the reactor and, hence, the result of increasing reactor pressure at constant temperature will increase the ratio of by-product to styrene which reduce the ultimate styrene yield. In the commercial plant, we also found that an increasing in reaction pressure of 1 psi will decreases the styrene yield by 0.3 - 0.5%(10).

2.4.2 Reactor temperature

Remembering that the styrene reaction is limited by a chemical equilibrium while the side reaction are not. Now consider the following equation.

rate of formation for the by-products due to the catalytic reaction(7)

$$\frac{d(B,T)}{dt} = k_{B,T}P_E\Delta V \qquad (1)$$

rate of formation for styrene by catalytic reaction(7)

$$\frac{d(S)}{dt} = k_S(P_E-P_HP_S)\Delta V/K_p \qquad (2)$$

where B,S,T,H = benzene, styrene monomer, toluene, hydrogen respectively

$k_{B,T}$ = velocity co-efficient for production of by product (benzene, toluene)

k_S = velocity co-efficient for production of styrene monomer

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K_p = equilibrium constant

P_i = partial pressure of component i

ΔV = small volume of catalyst

$$\frac{d(B,T)}{d(S)} = \frac{k_{B,T}P_E}{k_S(P_E-P_HP_S/K_p)} \qquad (3)$$

$k_{B,T}/k_S$ and K_p are increased with temperature, while the partial pressures of ethylbenzene, styrene monomer and hydrogen are constant. It will be found that there is a unique temperature at which the production of by-product per unit production of styrene is a minimum(7).

At low temperature K_p is decreased, $P_E-P_HP_S/K_p$ is also reduced to zero as quickly as chemical equilibrium is approach. The ratio of by-product to styrene production then tends to be an infinity. As the temperature increases, the value of K_p is increased which causes the value of P_HP_S/K_p approaching to zero. The ratio of by-product to styrene production is approached to ratio $k_{B,T}/k_S$. Using the reasoning set out above together with experimentally derived value of $K_p, k_S, k_{B,T}$ it is possible to calculate the optimum temperature for any concentration of ethylbenzene, hydrogen, styrene monomer and by-product if the ratio of steam to ethylbenzene and reaction pressure are assumed.

Ethylbenzene is relatively easily cracked to give benzene, toluene, styrene and tar and the rate of the various reaction increase rapidly with increasing temperature. The highest temperature occurs in the adiabatic reactor, and thus the yield loss due to cracking will be greatest

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in this case. In fact, loss due to cracking at around 660°C is too high, thus, reactors are normally operated at below 650°C.

2.4.3 Steam to ethylbenzene ratio

The quantity of steam added to the ethylbenzene feed to the reactor sets the partial pressure of the reactants, while its temperature sets the temperature at which the reaction takes place, Low partial pressure favours high conversion and styrene yields, thus indication that the ratio of steam to ethylbenzene used should be high.

However steam is a costly material and a balance must be attained between styrene yield and excessive steam cost. In addition, an increasing in steam to ethylbenzene ratio will effect on the volume of gas to be handled and condensed. The cost of processing equipment for a constant production of styrene is, therefore, increased by increasing this ratio

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2.4.4 Catalyst to ethylbenzene ratio

In adiabatic type reactor, the condition of the main reaction is in the equilibrium state. At the same time, the catalytic side reactions are still proceeding and, therefore, the ratio of by-product to styrene production is approaching to infinity. This will occur if the great amount of catalyst in relative to ethylbenzene is used. On the other hand if a little amount is used, the equilibrium condition will not be attained and either conversion to styrene will below with consequently high distillation cost or reactor temperature will be increased and gives the desired conversion at a lower yield. The optimum quantity of catalyst will depend on the conversion level required, reactor pressure, the age and type of catalyst.

2.4.5 Catalyst particle size

The smaller the catalyst particle size the greater will be the surface area exposed to the reactants and therefore the faster the reaction. Increasing number of commercial plant are using particle size down to 1.5 mm diameter, although cylindrical catalyst pellets measuring 5 x 5 mm are probably the most commonly used at present(7).

2.4.6 Ethylbenzene purity

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The styrene in the feed stream has a slightly effect of reducing the net conversion to styrene while benzene and toluene act only as diluents. Some of the diethylbenzene present may be dehydrogenated to divinybenzene which even in trace quantities can cause serious problem due to the formation of insoluble cross-linked polymer. Cumene is partially dehydrogenated to α-methylstyrene and its subsequent removal from styrene product is difficult. Chloride, if the concentration is high (100 ppm), can poison the dehydrogenation catalyst. The level is normally about 1-5 ppm, and at this level, chloride appears to cause few problem except that potassium salt used as promoters in the catalyst tend to be converted to pottassium chlorides, volatised and deposited in the heat exchanger down stream of the catalyst bed(7).

2.5 Role of diluent

From the dehydrogenation of ethylbenzene to styrene

$$C_6H_5C_2H_5 \rightleftharpoons C_6H_5CHCH_2 + H_2$$

According to Le Chateliers' priciple, an increasing in volume of the reaction will be accompany the decrease in pressure while increasing the temperature will favour the reaction. However, there are some disadvantages in operating the process at sub-atmospheric pressure, such as if there any leaks, the air will flow through the system and cause the explosion. A better solution is to reduce the partial pressure by diluting the ethylbenzene with diluent while maintaining the total pressure slightly above the atmospheric pressure. As the result, if we use the appropriate diluent, there are many advantage as follows

1. It lower the partial pressure of ethylbenzene without the need to operate at sub-atmospheric pressure.
2. It provides an internal heat source for the endothermic heat of reaction making adiabatic operation possible.
3. It prevents the deactivation of the catalyst.

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4. It controls the temperature.
5. It reduces the undesirable side reactions.
6. It increases the yield(14).

2.6 By-product of the reaction

In the dehydrogenation of ethylbenzene to styrene, there are several reactions occur as follows.

(1)

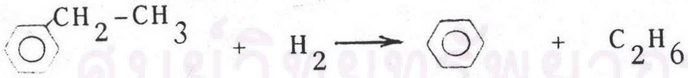
(2)

(3)

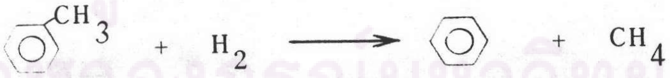
$$0.5C_2H_4 + H_2O \longrightarrow CO + 2H_2 \qquad (4)$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (5)$$

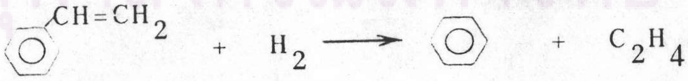
$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (6)$$



(7)

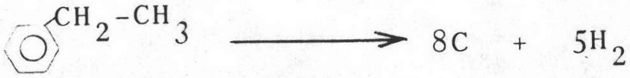


(8)



(9)

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \qquad (10)$$



(11)

$$8C + 16H_2O \longrightarrow 8CO_2 + 16H_2 \qquad (12)$$

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When we use only ethylbenzene, equation (1), (2) and (3) can be used to describe the dehydrogenation of ethylbenzene to styrene. In the case that ew use steam as diluent, equations (1) to (5) can be used to describe the dehydrogenation of ethylbenzene to styrene. Equations (7) to (12) can be ignored(3,4,9).

2.7 Kinetic of reaction

Catalytic dehydrogenation reactions may be interpreted employing a kinetic model which is assumed that surface reaction is rate controlling step: that is the adsorption and desorption are nearly in equilibrium and mass transfer is not the rate limiting step. Application of Langmuir's model to kinetic reaction for the complex system can be derived as following(4,15).

$$r_i = \frac{kb_iP_i}{1+\sum_j b_jP_j} \qquad (4)$$

By applying this equation to the dehydrogenation of ethylbenzene, the rate of equation is shown below.

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$$r_i = \frac{kb_E(P_E-P_HP_S/K_1)}{1+b_EP_E+b_SP_S+b_HP_H+b_IP_I} \qquad (5)$$

where r = rate of dehydrogenation of ethylbenzene to styrene

k = rate constant of ethylbenzene dehydrogenation

K_1 = equilibrium constant for styrene monomer reaction

b_i = adsorption constant of component i

P_i = partial pressure of component i

subscript E = ethylbenzene
H = hydrogen
S = styrene
I = inert

The detail has shown in appendix D

Because of the high operation temperature, the equilibrium adsorption constant of hydrogen should have a considerably lower value than the corresponding constant for hydrocarbons. So, the term $b_H P_H$ can be eliminated from the rate equation(4,7,16).

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