# Pyrolytic Dehydrogenation of Ethylbenzene to Styrene

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The efficiency of the pyrolytic dehydrogenation of ethylbenzene to styrene was determined at  $700^{\circ}$ ,  $750^{\circ}$ , and  $800^{\circ}$  C. at atmospheric pressure in the absence and presence of steam as diluent. Operating with a 20% per pass yield of styrene, an ultimate yield of 55-60% was obtained, both in the absence and presence of steam.

**I** N 1869 Berthelot (1) reported that ethylbenzene yielded styrene uponpyrolysis. Hepassedgaseous ethylbenzene through an empty porcelain tube maintained at moderate red heat, and the conditions were such that the ethylbenzene was practically all decomposed. From the fraction boiling up to  $250^{\circ}$  C, he isolated benzene, toluene, styrene, and a xylene-ethylbenzene fraction which was mainly *p*-xylene. Although Berthelot gave no actual figures, he stated that the yield of benzene was slightly less than that of styrene, that the yield of toluene was about one third that of styrene, and that the yield of the xylene-ethylbenzene fraction was about one third that of toluene.

Numerous patents have been issued on the pyrolysis of ethylbenzene (5, 6, 7, 11-15). Among the various means claimed for increasing the yield of styrene are pyrolysis under reduced pressure (15) and in the presence of inert diluents (12, 13), disturbing the equilibrium by the use of hydrogen acceptors (7, 11, 14), and operation in the presence of undesirable by-products in order to suppress their formation (14), in the presence of steam at high temperature and short contact time (5, 6), and in the presence of organic chlorides and nitrogen bases (13). In this last case part

of the styrene yield is due to chlorination followed by dehydrochlorination.

Relatively few studies have been made on the noncatalytic dehydrogenation of ethylbenzene to styrene. There are a few papers on the thermodynamics and mechanism of the reaction (8, 9), but most of the information is found in the claims of the patent literature. Berthelot's data (1) are only qualitative with respect to temperature and yield, and the two reports by Dobryanskii and coworkers (3, 4) cover only

the relatively low pyrolytic temperatures of  $600\,^\circ$  and  $650\,^\circ$  C.

Feed Reservoirs

This paper presents data on the relation of styrene yield to contact time and temperature in the absence and presence of steam. These noncatalytic data were obtained in order to have a measure for evaluating catalysis in the conversion of ethylbenzene to styrene.

### APPARATUS AND PROCEDURE

Figure 1 is the flow diagram, and Figure 2 shows the details of the furnace and preheater. The quartz pyrolysis tube (12-mm.

inside diameter, 15-mm, outside diameter, 105 cm, long, and packed with 4-mesh quartz chips) was connected to the recovery system by a metal-to-quartz adapter (Figure 3) developed by Robert Johnson of this laboratory. Ethylbenzene and water were pumped by bellows pumps (2) from graduated cylinders to a vaporizer-preheater, from which the gaseous mixture passed to the pyrolysis tube. The temperature of the pyrolysis was given by a thermocouple wired to the outside of the quartz tube at the experimentally determined point of average temperature. The pyrolyzate passed through a gas separator (a brass condenser with internal cooling coil), which retained the greater portion of the liquid product. The exit gas from the separator passed through two wet ice traps, a sampling manifold, a bubbler for visual observation of rate, and, finally, a gas meter. All runs were made at essentially atmospheric pressure.

#### ANALYSIS OF PYROLYZATE

The styrene content of the liquid pyrolyzate was calculated from its bromine number. This method was checked against ethylbenzene-styrene mixtures of known composition and was found to be reliable. The amount of high boiling residue in the pyrolyzate was determined by topping a 25-gram sample under an absolute pressure of 2 mm, with the distilling tube at 30 ° C. and the condensing tube at -78 ° C. For the few cases in which the crude pyrolyzate was too darkly colored to permit bromometric titration, the bromine numbers were determined on the distillates from the vacuum topping. Benzene and toluene in

> the pyrolyzate were determined by distillation at ordinary pressure through a microcolumn, and the fractions boiling up to  $85^{\circ}$  C. and from  $85^{\circ}$  to  $125^{\circ}$  C. were assumed to be benzene and toluene, respectively. Vacuum fractionation of a 2500-cc. composite sample of pyrolyzate had previously shown that these two distillation fractions were essentially ( $95 \pm \%$ ) benzene and tolucne,

# Figure 1. Flow Diagram



Vaporizer

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Bellows

Pumps

Pyrolysis

Furnace



Figure 2. Details of Furnace and Preheater

respectively. The recovery of styrene from this fractionation agreed with that calculated from the bromine number of the original pyrolyzate, and the purity of the styrene fraction was 98.1% by freezing point. Gas samples were collected continuously during the pyrolyses and were analyzed by conventional absorption and combustion methods.

#### CALCULATION OF YIELD AND CONTACT TIME

The styrene percentage yield per pass was defined as the grams of styrene produced per 100 grams of ethylbenzene pyrolyzed; the ultimate percentage yield of styrene, as the grams of styrene produced per 100 grams of ethylbenzene consumed. The amount of nonconsumed ethylbenzene was obtained by subtracting from the liquid hydrocarbon pyrolyzate the sum of the benzene, toluene, styrene, and residue produced; this method assumed the absence of xylenes and of materials boiling between styrene and the residue. The assumption of a negligible amount of material boiling between styrene and the residue from vacuum topping was confirmed by the close agreement between the amount of bottoms obtained in the vacuum distillation and the amount of residue obtained in vacuum topping.

This method of analysis was employed rather than that of Mavity, Zetterholm, and Hervert (10), who assumed the benzene and toluene productions to be stoichiometrically equivalent to the ethylene and methane contents, respectively, of the gas. This assumption is satisfactory for evaluating catalytic dehydrogenation of ethylbenzene where the ultimate yield of styrene is 90% and better, but it was found to be quite inadequate for evaluating the pyrolytic dehydrogenation of ethylbenzene where the ultimate yield is relatively low. In other words, if the reaction is not cleancut, as is the case with pyrolytic dehydrogenation, the stoichiometric relation fails.

The contact time in seconds at the temperature of pyrolysis was calculated as free space (41 cc.) divided by gas rate per second. The gas volume was arbitrarily taken as the gas volume of the total feed.

## **DISCUSSION OF RESULTS**

GAS COMPOSITION AND PRODUCTION. The gas consisted of hydrogen, paraffins, and ethylene (Table I). The paraffin index was 1.3-1.4 for operation in the absence of steam and 1.2 for operation in the presence of steam. The presence of steam favored the production of ethylene at the expense of paraffin. The total weight of gas produced at 700° C. was essentially independent of the presence or absence of steam (Figure 5). At 750 °C. the presence of steam increased the gas production slightly (Figure 6); at 800° C, the experimental data show a minimum in gas production at a steamethylbenzene ratio of 5 (Figure 7). At 0.2-second contact time the gas production ranged approximately from 2% at 700°C. to 9% at 800°C.

PYROLYSIS IN ABSENCE OF STEAM. Exploratory experiments established the fact that the temperature of pyrolysis must be above 600° C. in order to produce styrene at a commercially practical rate. A 12% yield per pass of styrene was obtained at 650° C. with a contact time of 2.3 seconds. The yields of styrene, per pass and ultimate, are plotted in Figure 4. The plots of the per pass yields show maxima at 700° C. (1-second contact time)

TABLE I. EFFECT OF OPERATING CONDITIONS ON GAS COMPOSITION AT 0.2-SECOND CONTACT TIME						
° C.	Mole Ratio, H2O/EBª	Gas H1	Compn., M C <sub>2</sub> H <sub>4</sub>	ole % CnH2n+2	Paraffin Index	
700 750 800 700 750 800	0 0 5 5 5	67.8 60.6 58.0 66.8 60.5 56.3	$\begin{array}{c} 14.0\\ 18.6\\ 21.1\\ 20.1\\ 26.1\\ 28.1 \end{array}$	$     18.2 \\     20.8 \\     20.9 \\     13.1 \\     13.4 \\     15.6   $	1.4 1.3 1.3 1.2 1.2 1.2	
$^{a}$ EB =	= ethylbenzene.					



and at 750  $^{\circ}$  C. (0.7-second contact time), but not at 800  $^{\circ}$  C. ~ The maximum at 800°C. presumably occurs at a shorter contact time than the one experimentally employed. The ultimate yield increased with decrease in contact time and with increase in temperature. The following table lists the required contact times at 700°, 750°, and 800° C. for maximum styrene yields per pass in the absence of steam:

Temp	Contact Time.	Styrene Yield, %		
° C.	Sec.	Per pass	Ultimate	
700	1.0	21	35	
750	0.7	28	48	
800	0.1	30	48	

According to Ostromislensky and Shepard (12, 13) the ultimate percentage yield of styrene obtainable by the pyrolysis of ethylbenzene in the absence of steam is dependent on K in the equation

$$\frac{0.64 \ V/R + T}{633} = K$$



- $R \\ T$ =
- ethylbenzene rate, g./min. interior temperature of tube at longitudinal center Κ parameter varying between 0.8 and 1.2, optimum -

efficiency being attained at K = 1

The maximum yield of styrene should therefore be obtained at a temperature below  $633 \degree C$ , which is completely in disagreement with our data.

PYROLYSIS IN PRESENCE OF STEAM. Pyrolysis at 700 ° C. in the presence of steam was studied at contact times ranging from 0.1 to 0.6 second and pyrolysis at  $750\,^\circ$  and  $800\,^\circ\,\mathrm{C}.$  was studied at contact times ranging from 0.1 to 0.4 second. Figures 5, 6, and 7 compare data for pyrolysis in the absence and presence of steam at these three temperatures. These plots include per pass weight yields of gas, benzene, toluene, styrene, and residue,

TABLE II. EFFECT OF STEAM-ETHYLBENZENE RATIO ON STYRENE YIELD AT 750° C.				
Contact Time,	Mole Ratio,	Styrene Yield, %		
Sec.	$H_{2}O/EB$	Per pass	Ultimate	
0.2	10	23	53	
0.2	7.5	25	52	
0.2	õ	29	55	
0.2	2.5	17	60	
0.2	0	20	55	
0.1	50	21	52	
0.1	10	21	49	
0.1	7.5	16	59	
0.1	5	20	60	
0.1	2.5	14	63	
0.1	0	12	58	

Operating Conditions and Ultimate Yields of Styrene at 20% Yield Per Pass TABLE III.

Mole Ratio, H2O/EB	Temp., °C.	Contact Time, Sec.	Ultimate Styrene Yield, %
0	700	$\begin{array}{c} 0.8 \\ 0.2 \\ 0.8 \\ 0.1 \end{array}$	38
0	750		55
5	700		52
5	750		60







Figure 5. Pyrolysis of Ethylbenzene at 700° C.



Figure 6. Pyrolysis of Ethylbenzene at 750° C.



Tigure 7. Pyrolysis of Ethylbenzene at 800° C.

based on the ethylbenzene charged. The ultimate vield of styrene is readily calculated from these data by dividing the once-through percentage yield of styrene by the corresponding percentage consumption of ethylbenzene. Steam-ethylbenzene ratios as high as 50 were tested, but there was no advantage in raising the ratio above 10. Table II presents data for pyrolysis at 750° C, with several steamethylbenzene ratios and at contact times of 0.2 and 0.1 second. The material balances for all the pyrolyses averaged 98%. The duplicability of the ultimate yield values was  $\pm 2\%$ .

COMPARISON OF PYROLYSIS IN PRES-ENCE AND ABSENCE OF STEAM. The data in Table II show little if any advantage for steam. However, Table III, which lists the operating conditions and ultimate yields obtained at a fixed per pass yield of 20%, shows that steam is beneficial. For example, operation

at 700° C.and 0.8 second gave an ultimate yield of 38% in the absence of steam and a 52% ultimate yield in the presence of steam. Operation at  $750\degree$  C, and 0.1 second in the presence of steam gave essentially the same yield as obtained with twice the contact time in the absence of steam.

### GENERAL CONCLUSIONS

Within the experimental range studied, steam Within the experimental range studied, steam was beneficial at  $700^{\circ}$  and  $750^{\circ}$ , but not at  $800^{\circ}$  C. In general, the presence of steam represed the production of toluene. The formation of high boiling residue was favored by increase in temperature and contact time. Carbon formation  $(0.01 \text{ to } 0.05\% \text{ of the hydrocarbon feed) was too$ small under all conditions to be correlated withthe effect of steam.

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