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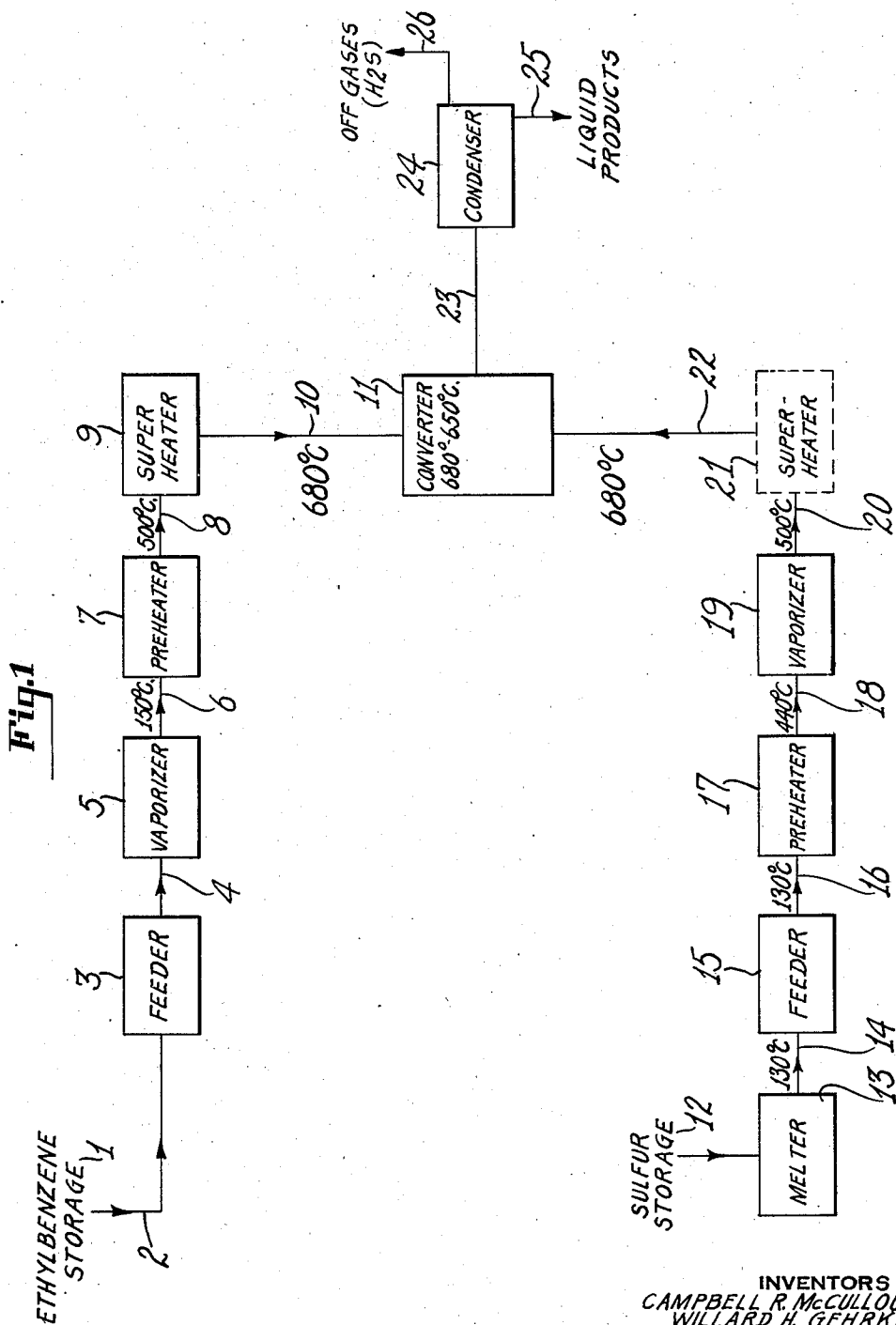
C. R. McCULLOUGH ET AL

2,392,289

PROCESS FOR PRODUCING STYRENE

Filed Sept. 8, 1943

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

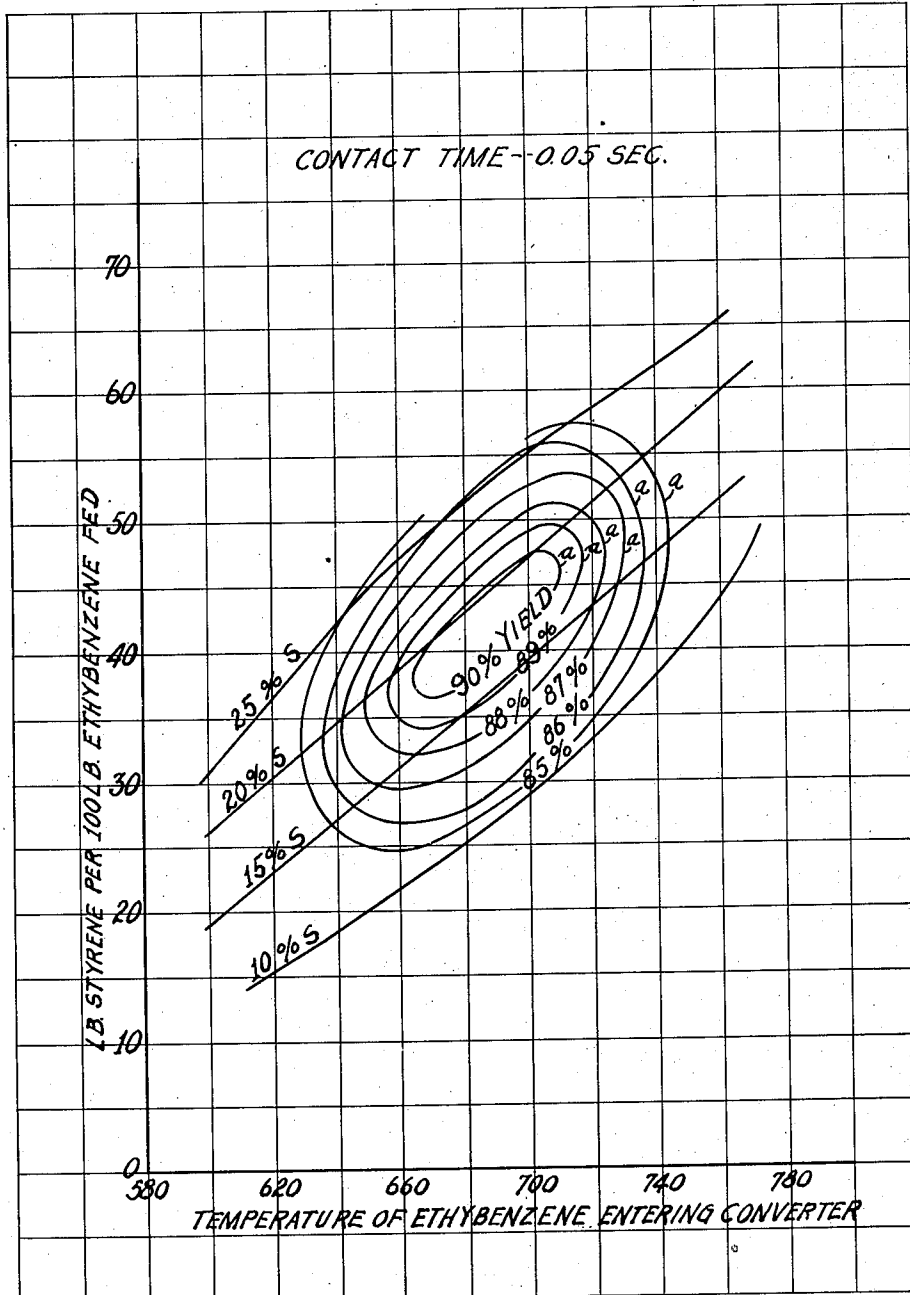


Fig. 2

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3 Sheets-Sheet 3

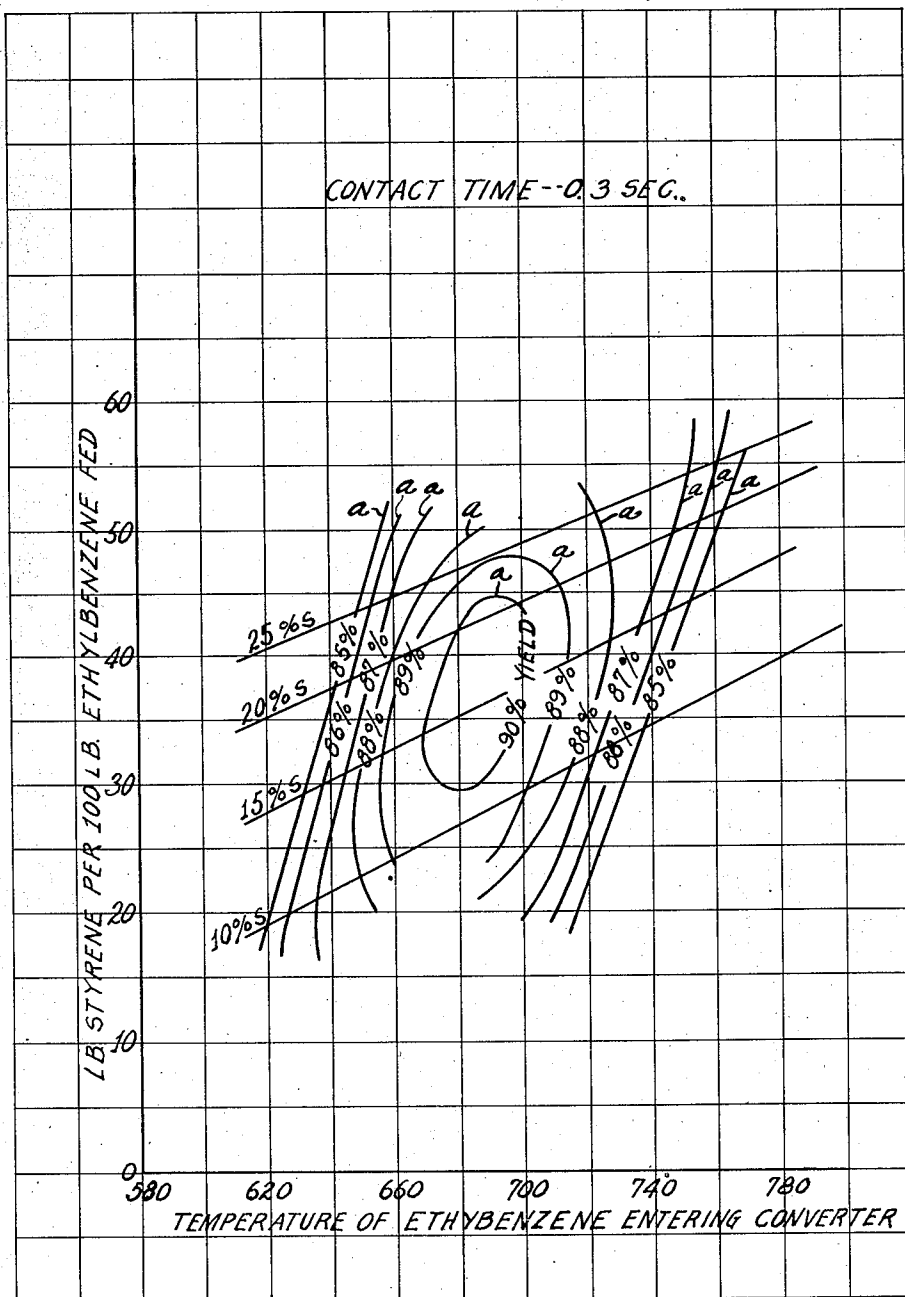


Fig. 3

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2,392,289

PROCESS FOR PRODUCING STYRENE

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8 Claims. (Cl. 260—669)

This invention provides an improved process for producing styrene by the dehydrogenation of ethylbenzene.

When ethylbenzene is subjected to dehydrogenation temperatures in the absence of a catalyst as described in Ostromislensky U. S. Patent 1,541,175, or in Harris U. S. Patent 2,253,934, it is usual under certain conditions to obtain yields of styrene of the order of from 40% to 55%, together with conversions varying upwardly to 33%. A careful determination of the relationship between yield and conversion shows that the highest yield obtained by the strictly thermal dehydrogenation of ethylbenzene is about 55% and is obtained when the conversion is quite low, i. e., up to 25%. It has been found that conversion is a function of time and temperature. Thus for a temperature of 600° C. and a contact time of 3 seconds, 10% conversion is obtained, whereas at a temperature of 740° C. a conversion of 10% is also obtained in 0.03 second. Within these limits the yield is dependent entirely upon conversion, as far as can be determined.

In prior attempts to increase the yield and conversion of styrene, various addition materials (hydrogen acceptors) have been added to the ethylbenzene, which addition materials are designed to combine with the hydrogen liberated and hence to increase the equilibrium concentration of styrene obtained in the process. These addition materials constitute various carbon compounds and elements such as sulfur, chlorine and compounds containing these and other elements. Thus in U. S. Patent 1,870,876, Smith advocates the use of benzol, ethylene chloride and sulfur. It is recommended in this patent that approximately 2% of sulfur based on the total mixture, or 4% of sulfur based upon the ethylbenzene in the mixture undergoing pyrolysis be employed.

In U. S. Patent 1,997,967 to Gibbons and Smith additional studies on the effect of various addition agents to the pyrolysis mixture are reported. As much as 6 parts of sulfur per 100 parts of ethylbenzene were employed by Gibbons and Smith and a conversion called "productivity" of 30.4% together with a yield called "efficiency" of 42.6% is reported when this amount of sulfur is employed.

Somewhat more favorable yields and conversions are reported when smaller quantities of sulfur were used. For example, when three parts of sulfur per 100 parts of ethylbenzene were employed the conversion was 31.6% and the yield was 41.6%, with two parts of sulfur the conversion was 27.9% and the yield was 43.1%, while

with one part of sulfur the conversion and yield were respectively 24.2% and 36.0%. As a whole, however, the work reported by Gibbons and Smith using sulfur or, for that matter, any other addition agent does not show any better yields and conversions than may be obtained using strictly thermal methods.

The experimental work of Gibbons and Smith as well as Smith, mentioned above, was carried out by heating ethylbenzene vapor in an electrically heated iron or Chromel tube 3 feet long and $\frac{3}{4}$ inch in internal diameter. The rate of flow of ethylbenzene into the furnace was approximately 100 grams per hour through the above tube. This rate of flow will give a contact time of approximately 16 seconds.

It is obvious from the above discussion of the prior art that such prior art processes were limited to the addition of sulfur in amount up to 6%, based upon the ethylbenzene, while contact times were relatively long.

We have now found that if the dehydrogenation of ethylbenzene to styrene be carried out in the presence of much larger amounts of sulfur than was employed in the prior art, and under conditions such that the time of exposure, at reaction temperatures, of the ethylbenzene to the sulfur vapor be relatively short, that much higher yields and conversions of styrene may be obtained. We have also determined that the greatest effectiveness of sulfur employed in these larger quantities is realized if the sulfur be first vaporized and the vapors thereof be then mixed with the hot ethylbenzene vapors. Thus in the preferred mode of operation, according to our invention, the sulfur and ethylbenzene are separately vaporized, the ethylbenzene vapors being heated to temperatures sufficiently high to cause incipient dehydrogenation, and the sulfur and ethylbenzene vapors then mixed together. The mixture of vapors so formed is maintained at reaction temperatures for 0.03 second to 2.5 seconds, at the end of which period the reaction is quenched by sharply cooling the gases. A liquid condensate containing the styrene is obtained from the cooled gases.

The sulfur vapor, prior to mixing with the ethylbenzene should be heated to a temperature of at least 500° C. and may even be heated to temperatures as high as the reaction temperatures which temperatures may be between 600° C. and 780° C. The proportion of sulfur employed with respect to the ethylbenzene has been found to be critical and high yields of styrene may be obtained when sulfur is employed in

amounts ranging from 10 lbs. to 25 lbs. per 100 lbs. of ethylbenzene, i. e., 10% to 25% based upon the ethylbenzene with which it is to be mixed for the reaction.

The ethylbenzene vapor should be heated prior to mixing with the sulfur vapor, to temperatures within the range of from 600° C. to 780° C. The vapors of sulfur and ethylbenzene are then combined and the resulting mixture of vapors allowed to interact at the reaction temperature for a period of time prior to cooling, the length of such period being advantageously proportioned to the reaction temperature. Thus higher temperatures within this range are preferably employed with the short contact times, and the lower temperatures in this range with the higher contact times. The relationship between contact time and temperature of reaction will be somewhat as follows:

Contact time, seconds	Temperature, °C.
0.03 to 0.1	630-780
0.1 to 0.5	620-740
0.5 to 2.5	600-660

Our preferred process may be carried out as indicated on the diagrammatic flow sheet constituting Figure 1 of the drawings. In Figure 1, numeral 1 represents a source of liquid ethylbenzene. Pipe 2 provides a means for conveying the ethylbenzene from the storage vessel to a flow measuring device or feeder 3, wherein the flow of liquid ethylbenzene is measured and controlled. The measured ethylbenzene then passes by pipe 4 to vaporizer 5 in which, by the application of heat, the liquid ethylbenzene is converted to vapor at a temperature of about 150° C., which temperature represents a superheat of about 15° C. above the normal boiling point of this material. The vapor then flows by pipe 6 to preheater 7, where additional heat is added and the vapor attains a temperature of, say, 500° C. At this point the preheated vapors are conveyed by pipe 8 to a superheater 9 where the temperature is further raised to the temperature at which pyrolysis begins. Because of the thermal instability of ethylbenzene at temperatures above 600° C. a superheater is employed wherein a short contact time may be obtained which permits the ethylbenzene to be heated well within the temperature range, at which it will normally undergo dehydrogenation. However, because of the short contact time employed the heating of the ethylbenzene may be effected without substantial dehydrogenation in the superheater. A preferred temperature for the operation of our process is within the range of from 650° C. to 680° C., although the overall workable range of temperature for our process is within the limits of 600° C. to 780° C.

The superheater ethylbenzene vapors produced in superheater 9 pass by means of pipe 10 into converter 11, where the reaction with sulfur takes place.

The sulfur supplied to our process originates at a source indicated in the flow sheet by numeral 12. It passes thence to sulfur melter 13 and the molten sulfur then passes by pipe 14 to sulfur feeder 15. The sulfur feeder measures and controls the flow of molten sulfur passing by means of pipe 16 into preheater 17. Here the temperature of the molten sulfur is raised to about 440° C. or to a temperature just short of the boiling point, after which the liquid sulfur

passes by means of pipe 18 into vaporizer 19. At this point the molten sulfur is vaporized and a slight degree of superheat imparted thereto, after which the sulfur vapors pass by means of pipe 20 into a further superheater 21. In some cases, which are explained more fully below, it may not be necessary to employ superheater 21 and for this reason it is indicated in the flow sheet by dotted lines. If, however, the superheater 21 is employed the temperature of the sulfur is raised thereby to a temperature approximating the temperature of the converter and passed into the converter 11 by means of pipe 22. In case superheater 21 is not employed, the temperature of the sulfur vapor is raised by the vaporizer to at least in excess of 500° C.

Converter 11 is merely an empty chamber which may be constructed of stainless steel and provided with a brick or other refractory lining in order to protect the steel from the action of the heated sulfur vapors within the chamber. It may be provided with external heating means, or if adiabatic operation is contemplated, with heat insulation so as to enable it to be maintained at the reaction temperature.

The size of the reaction chamber is proportioned to the amount of gases being processed so as to afford an average time of sojourn of the gases in the chamber within the range given above.

The gases leaving converter 11 by means of pipe 23 pass into condenser 24 wherein they are cooled by contact with cold surfaces which are in turn cooled by means of a cooling fluid such as water. While it is not necessary that the cooling be sufficiently effective to cool the gases, in the first instance to temperatures low enough to cause condensation of the condensable vapors, it should be sufficiently drastic so that further reactions in the hot gases are quenched. Such quenching of the reaction represents the termination of the contact period. The initiation of the reaction is, of course, caused by the mixing together of the hot vapors in the converter. The condenser 24 produces a liquid condensate which leaves the condenser by pipe 25, which condensate is then treated by conventional means, not shown, for recovery of contained styrene. The gaseous products consisting mainly of hydrogen sulfide and hydrogen pass out of the system by pipe 26 to recovery or disposal means, not shown in the drawings.

Considerable latitude is possible in the operation of our process. Because of the separate feeding means provided, an adjustment and control of the desired amounts of ethylbenzene and sulfur processed in the converter may be made and we have accordingly found that the best results are obtained when the amount of sulfur employed is maintained within the range of from 10 lbs. to 25 lbs. of sulfur per 100 lbs. of ethylbenzene flowing to the converter. Within this range of sulfur content the reaction produces styrene at a yield of from 85% to 87% and even as high as 90%, with a conversion of from 25% to 50%.

Without limiting ourselves to a precise theory, a simple conception of the reaction is as follows:

The reaction taking place in the converter consists in the dehydrogenation of ethylbenzene forming styrene and hydrogen. The sulfur reacts with hydrogen forming hydrogen sulfide and to some extent other organic sulfur compounds such as carbon disulfide and traces of mercap-

tans. As a result of the combination of sulfur with the hydrogen the equilibrium is displaced in the direction of greater concentrations of styrene in the reacted gases, without forming increased amounts of by-products.

The beneficial results of separately heating the ethylbenzene and sulfur are two-fold. One advantage is to permit higher preheating temperatures for the ethylbenzene to be attained outside of the converter than is possible when the ethylbenzene and sulfur are first mixed and then heated together. A second result is to substantially decrease the formation of by-product tarry bodies which represent a material loss to the process.

Because of the first advantage mentioned above, it is possible by means of the higher preheat which may thus be obtained to operate the converter without supplying additional heat to the converter itself. In other words the operation of the converter approaches a substantially adiabatic state. When this condition is reached (or approached) the operation of the converter proceeds solely by means of the heat present in the reacting gases supplied thereto. Since the overall reaction heat change of the reaction taking place in the converter is to some extent endothermic, it is desirable that the gases be introduced into the converter at a sufficiently elevated temperature so that the final temperature of the gases leaving the converter is still well within the reaction range, i. e., above 600° C. Thus the possibility of supplying a large proportion of the necessary heat to the converter by means of super-heated ethylbenzene vapor may, under some conditions of operation, make unnecessary the supplying of further additional preheat to the sulfur above about 500° C. by means of sulfur preheater 21 in Figure 1 of the drawings. The supply of some additional heat from an external source to converter 11 is, of course, not precluded.

By separately vaporizing and preheating the ethylbenzene and the sulfur prior to mixing in the converter a substantial decrease of the by-products tars is obtained over that which is obtained when vaporizing and preheating a mixture thereof. This effect is illustrated in the following tabulation in which the percentage of tar in the condensate is given for certain amounts of styrene in the condensate obtained by each method of operation. The figures were obtained by averaging the results obtained from a large number of runs and are grouped according to the ranges of styrene concentration in the condensate:

Percentage of styrene in condensate	Vaporizing and preheating the mixture of sulfur and ethylbenzene	Vaporizing and preheating the sulfur and ethylbenzene separately before mixing
10-20	5.1	3.0
20-30	5.1	4.1
30-40	7.0	5.1
40-50	13.2	6.0
50-60	16.0	9.4

The heat required by the converter 11 of Figure 1 after it has reached a steady state, and neglecting heat losses to its surroundings, is, of course, the algebraic sum of the several heats of reaction for the reactions taking place therein. The principal reaction is, of course, the dehydrogenation of ethylbenzene forming styrene and

hydrogen. This reaction is an endothermic one. The second important reaction is the formation of hydrogen sulfide by reaction of the liberated hydrogen and the sulfur present. This reaction is exothermic, although it is not sufficiently so to supply all of the heat absorbed or required in the principal endothermic reaction. In addition to the main reactions there are various minor secondary reactions which take place with respect to which the thermal characteristics are unknown. On the whole, however, it may be said that the net overall thermal effect of the reactions in the converter is a slightly endothermic one. This means that the temperature of the gases leaving the converter will generally be lower than the temperature of the gases entering the converter.

As pointed out above, by carefully controlling the various factors of our process, it is possible to obtain yields of styrene from ethylbenzene better than 85% and even somewhat over 90%.

Figures 2 and 3 illustrate the results obtained at contact times of 0.05 and 0.3 second, and illustrate the critical effect obtained by employing between 10 pounds and 25 pounds of sulfur per 100 pounds of ethylbenzene. A similar effect is obtained over the range of contact times from 0.03 second to 2.5 seconds.

In Figures 2 and 3 the abscissae give a temperature of the ethylbenzene vapor entering the converter, while the ordinates give the pounds of styrene per 100 pounds of ethylbenzene charged. In other words, the ordinates correspond to the conversions obtained. The lines of the figure labeled, respectively, 10% S, 15% S, 20% S and 25% S represent the per cent of sulfur charged based on the ethylbenzene, that is, the pounds of sulfur per 100 pounds of ethylbenzene charged. The lines in the diagram marked "a" define the approximate fields wherein the yield of styrene obtained is within the stated yield figure.

Figure 2 illustrates specifically the performance of a converter utilizing a contact time of 0.05 second. In order to obtain maximum yields of styrene from ethylbenzene, heating of the ethylbenzene entering the converter should be carried to a temperature between about 664° C. and 710° C. The sulfur vapor is heated to a temperature within the range of 500° C. to 710° C. The amount of sulfur mixed with the ethylbenzene should be between about 16 pounds and 20.5 pounds (16% and 20.5% based upon the ethylbenzene), preferably about 18 pounds of sulfur per 100 pounds of ethylbenzene.

Figure 3 illustrates the performance of the converter utilizing the somewhat longer contact time of 0.3 second. Ethylbenzene vapor should be heated to a temperature of from about 648° C. to 684° C. and then mixed with heated sulfur vapor in amount varying between about 11 pounds to about 22 pounds (11% to 22% of sulfur based upon the ethylbenzene), preferably about 16.5 pounds of sulfur per 100 pounds of ethylbenzene.

What we claim is:

1. The process which comprises separately heating a stream of sulfur vapor and a stream of ethylbenzene vapor, said ethylbenzene being heated to a temperature at which a dehydrogenation reaction occurs, mixing said sulfur and ethylbenzene together in the proportions of between 10% and 25% sulfur based on said ethylbenzene maintaining the resulting mixture at a temperature of from 600° C. to 780° C. for a period of

from 0.03 second to 2.5 seconds and then cooling said mixture.

2. The process which comprises heating a stream of ethylbenzene vapor to a temperature between 600° C. and 780° C. and then mixing said ethylbenzene vapor with sulfur vapor in the proportion of more than 10% but less than 25% by weight of sulfur based on said ethylbenzene, maintaining the resulting mixture at a temperature of between 600° C. and 780° C. for a period of at least 0.03 second, cooling said mixture of ethylbenzene and sulfur after an interval of less than 2.5 seconds contact therebetween, and recovering a condensate from said mixed vapors.

3. The process defined in claim 2, in which the temperature of said mixture of ethylbenzene and sulfur is maintained within the limits of 650° C. to 680° C.

4. The process for producing styrene which comprises heating a stream of ethylbenzene vapor to a temperature between 650° C. and 680° C., separately heating a stream of sulfur vapor to a temperature above 500° C. but below 680° C., mixing said ethylbenzene and said sulfur vapor in the proportions of 10 pounds to 25 pounds of sulfur per 100 pounds of ethylbenzene, and thereby initiating a dehydrogenation reaction of said ethylbenzene to produce styrene, and after a period of between 0.03 second and 0.5 second after initiation of said reaction, quenching said reaction by cooling the vapors, and thereafter recovering styrene from said cooled vapors.

5. The process for producing styrene which comprises heating a stream of ethylbenzene vapor to a temperature between about 664° C. and 710° C., separately heating a stream of sulfur vapor to a temperature above 500° C., mixing said

sulfur vapor with said ethylbenzene vapor in the proportions of between 16 pounds and 20.5 pounds of sulfur per 100 pounds of ethylbenzene, and after a period of about 0.05 second cooling said vapors and thereafter recovering styrene from said cooled vapors.

6. In the process for producing styrene by the dehydrogenation of ethylbenzene, the step which comprises heating together at a temperature between 600° C. and 780° C., and for an interval of more than 0.03 second, but less than 2.5 seconds a mixture of ethylbenzene vapor and sulfur vapor, the amount of sulfur comprising between 10% and 25% by weight of the ethylbenzene in said mixture.

7. The process defined in claim 6, in which the mixture of vapors is maintained at a temperature between 630° C. and 780° C. for a period of between 0.03 and 0.1 second.

8. The process which comprises heating a stream of ethylbenzene vapor to a temperature between 600° C. and 780° C., separately heating a stream of sulfur vapor to a temperature in excess of 500° C., but below a temperature such that when mixed together with said ethylbenzene the temperature of said mixture will be below 780° C., mixing together said ethylbenzene vapor and sulfur vapor streams in the proportion of between 10% and 25% by weight of sulfur based on said ethylbenzene and after an interval of more than 0.03 second but less than 2.5 seconds, during which interval the mixture is maintained in a thermally insulated reaction zone, cooling said mixture and recovering a condensate from said vapor.

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