

UNITED STATES PATENT OFFICE

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PROCESS OF MAKING STYROLS

No Drawing.

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This invention relates to a process for making styrols, more particularly to a process for making them from alkyl benzols.

Styrol and its homologues have been made by cracking ethyl benzol or other alkyl benzols at elevated temperatures, which causes the splitting off of hydrogen and the formation of styrol or an alkyl styrol depending upon the starting material. This dehydrogenation process has also been carried out in the presence of inert gases, such as nitrogen and carbon dioxide. The reaction which takes place during the cracking is reversible to a certain extent, depending upon the temperature, the concentration of the styrol in the reaction products and upon the presence of catalysts or catalytic material such as might constitute or form part of the reaction furnace. Hence, where the reaction is carried out with the alkyl benzol alone or in the presence of inert gases, there is a tendency for the hydrogen to recombine at least in part with the styrol and regenerate an alkyl benzol, with a consequent reduction in the yield of styrol. Furthermore, other hydrocarbons are formed during the dehydrogenation process and some of these tend to combine with the styrol. One by-product which is formed during the cracking is benzol.

Among the objects of the invention are to provide a method for increasing the yield of styrol or its homologues obtained by the pyrogenic dehydrogenation of ethyl or other alkyl benzols, to increase the concentration of the styrol in the reaction products thus obtained, to carry out the dehydrogenation of the alkyl benzol in the presence of substances which favorably influence the reaction and minimize its reversibility, and to increase both the productivity and efficiency of the process. A further object is to reduce the formation of benzol as a by-product in the process.

In carrying out the invention, benzol is mixed with an alkyl benzol, such as ethyl benzol, and the mixture is then subjected to a cracking temperature in an ordinary form of cracking tube or furnace, but preferably there is also added to the mixture a dehydro-

genating compound or mixture. It has already been found that certain materials when present during the reaction act chemically by combining with the hydrogen set free from the alkyl benzol to form substances which are stable under reaction conditions and thus prevent reversal of the reaction by which the hydrogen would recombine with the styrol formed and regenerate an alkyl benzol. Some of the dehydrogenating compounds not only act chemically in this manner but they also release or form a gas which further assists the process by reducing the partial pressure of the alkyl benzol. Other materials are known which act only physically to reduce the partial pressure of the alkyl benzol but have no chemical effect. By the use of a proper dehydrogenating compound or mixture, the cracking process may be favorably affected by increasing the productivity, efficiency and the concentration of styrol in the steam distillate. It has been found that when benzol is added to an alkyl benzol such as ethyl benzol, and the mixture then subjected to cracking conditions, the benzol favorably affects the reaction by reducing the partial pressure of the ethyl benzol. As before pointed out, one of the by-products of the cracking of an alkyl benzol is benzol, and it appears that by mixing benzol with the alkyl benzol prior to the cracking operation, the presence of this added benzol also minimizes the production of benzol as a by-product from the alkyl benzol and increases the production of styrol.

Among substances which act wholly or mainly chemically are carbon disulphide, carbon tetrachloride, ethylene and sulphur; among those acting wholly or largely physically are ethyl alcohol, acetone, nitrogen, ammonia and carbon dioxide; and among those acting both chemically and physically are ethylene chloride, sulphur monochloride, sulphur dichloride, sulphur dioxide. While in carrying out the present invention a mixture of alkyl benzol and benzol alone may be cracked, it is preferred, as before stated, to carry out the cracking operation in the presence of material which acts chemically or chemically and physically as well. This may

be accomplished by mixing with the alkyl benzol and benzol one or more of the above substances. For instance, a combination of 100 parts ethyl benzol, 80 parts benzol, 15 parts ethylene chloride and 4 parts sulphur, has given excellent results, and almost equally good results have been obtained from a mixture of 100 parts ethyl benzol, 80 parts benzol, 15 parts acetone and 4 parts sulphur. In carrying out the process an iron or a chromel tube furnace may be used and it may be heated electrically or in any other suitable way. It should be provided with the usual accessory apparatus, such as containers for the ingredients used, temperature measuring devices, the usual flow meters, pressure recording instruments, condensers, receivers, etc. In the examples given in the present application, an electrically heated tube furnace, either iron or chromel, 3' long and $\frac{3}{4}$ " inside diameter was used. The rate of flow of ethyl benzol into the furnace was approximately 100 grams per hour for this size of tube. The temperature in the tube in the reaction zone may lie between about 600—750° C. and preferably between 675—720° C.

The products of cracking were purified by a steam distillation followed by a fractionation using a four bulb pear column. When cracking ethyl benzol, the fraction distilling off below 105° C. may be considered benzol; the fraction coming over 105° C. may be considered as a mixture of styrol and ethyl benzol. The proportion of styrol in the latter fraction is determined by heating a portion of the fraction in a sealed tube at 180° C. over night and recovering the styrol resin so formed by steam distillation. The styrol resin is then dried and weighed.

As showing the improved results obtained by adding benzol to the mixture before cracking, the following data is given using in one case a mixture of 100 parts ethyl benzol, 80 parts benzol, 15 parts ethylene chloride and 4 parts sulphur, this mixture being passed through a cracking tube and purified as above described. There were obtained from the reaction products 31 parts styrol, 40 parts recovered ethyl benzol and 62 parts recovered benzol. The concentration of the styrol fraction was 44%, the productivity was 31% and the efficiency 51.7%.

Using the same mixture but omitting the 80 parts benzol, the recovery from the reaction products was 27.6 parts styrol, 37 parts recovered ethyl benzol and 1.5 parts recovered benzol. The concentration of the styrol fraction was 42.9%, the productivity was 27.6% and the efficiency was 44%.

In the present application, the term "productivity" is used to designate the ratio between the styrol produced and the ethyl benzol passed through the cracking furnace. The term "efficiency" is used to designate the ratio between the styrol produced and the

ethyl benzol consumed during the dehydrogenation. The productivity, efficiency and concentration of styrol in the resulting steam distillate are all of importance for the best results with the process. Inert gases exert a favorable influence on efficiency but have only a moderate effect on productivity and concentration. On the other hand, the dehydrogenating compounds which react chemically readily give high concentrations of styrol. Dehydrogenating mixtures properly selected as to ingredients and proportions so as to both reduce the partial pressure of the ethyl benzol and also chemically react, exert an extremely favorable influence on all three factors. When ethyl benzol is used as the starting material, the resulting material is ordinary styrol, while when alkyl benzois are used containing one or more higher alkyl radicals in the side chain, various homologues of styrol are produced.

By mixing benzol with the alkyl benzol according to the present invention, the partial pressure of the alkyl benzol is reduced and the formation of benzol as a by-product during the cracking is minimized, with consequent increase in the production of styrol. The bulk of the styrol can be isolated easily in a concentrated solution and the recovered hydrocarbons including the unchanged benzol turned back into the process without further purification.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A method of producing a styrol which comprises heating a preformed mixture of benzol and alkyl benzol to approximately 600 to 750° C. to thereby split the latter into a styrol and hydrogen, continuously reacting upon the hydrogen with a material capable of forming a stable compound therewith under reaction conditions, and separating the styrol from the products.

2. The method of producing a styrol which comprises heating a preformed mixture of benzol and alkyl benzol to approximately 600 to 750° C. to thereby split the latter into a styrol and hydrogen while lowering the partial pressure of the alkyl benzol by the benzol, continuously reacting upon the hydrogen by a material comprising sulphur and separating the styrol from the products.

3. The method of producing styrol which comprises heating a preformed mixture of benzol and ethyl benzol to about 600 to 750° C. in the presence of a material comprising sulphur, and separating styrol from the reaction products.

4. The method of producing styrol which comprises heating a preformed mixture of benzol and ethyl benzol to about 675 to 720° C. in the presence of sulphur and a volatile organic compound capable of reducing the

partial pressure of the ethyl benzol, and separating styrol from the reaction products.

5 5. The method of producing styrol which comprises heating a preformed mixture of benzol and ethyl benzol to 600-750° C. in the presence of a dehydrogenating mixture comprising ethylene chloride and sulphur, and recovering styrol from the reaction products.

10 Signed at Passaic, county of Passaic, State of New Jersey, this 17th day of April, 1929.
OMAR H. SMITH.

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