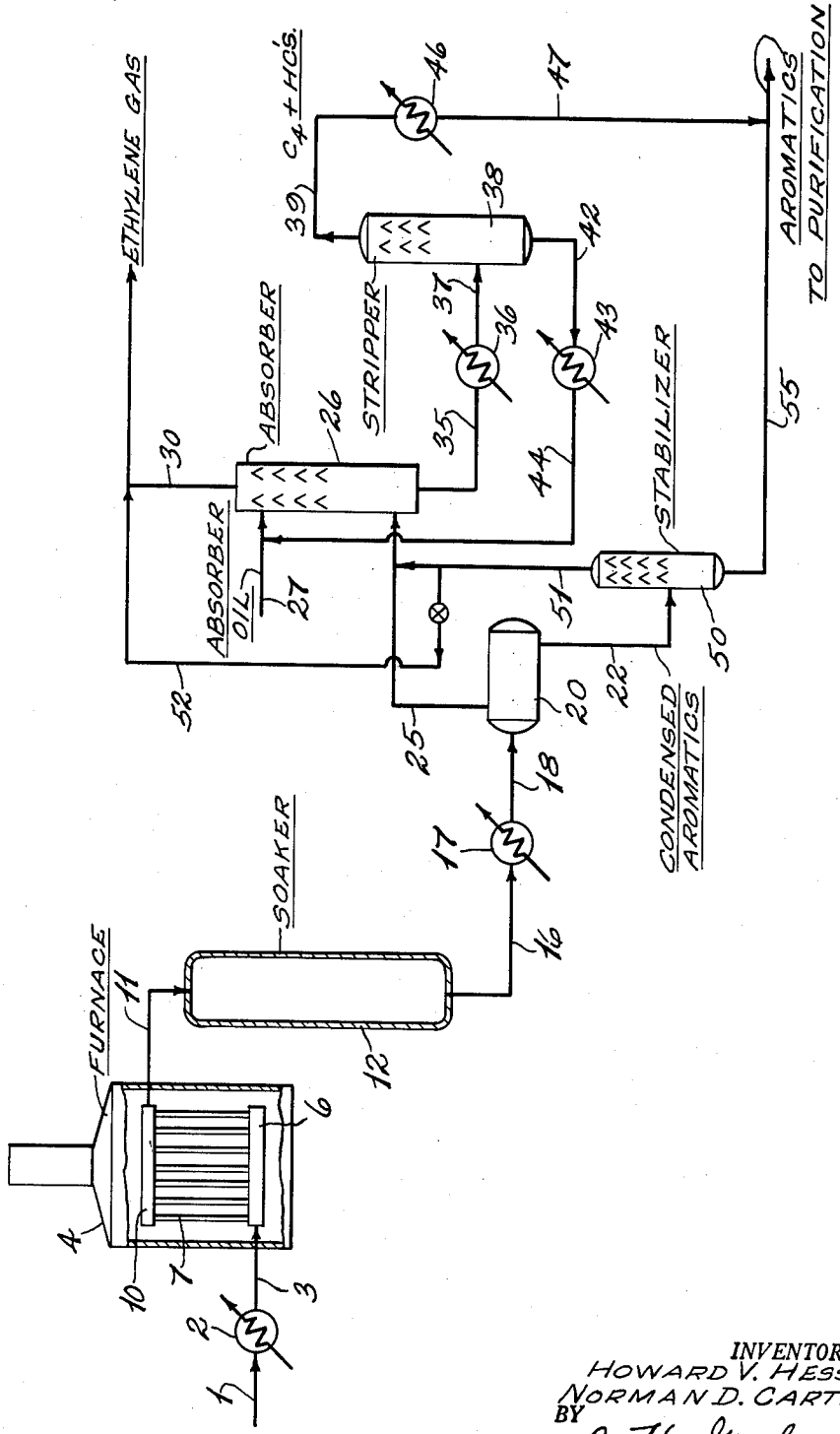
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CONVERSION OF GASEOUS HYDROCARBONS INTO ETHYLENE AND AROMATICS

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CONVERSION OF GASEOUS HYDROCARBONS INTO ETHYLENE AND AROMATICS

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This invention relates to an improved process for pyrolyzing ethane and C_3 hydrocarbons to form a mixture of ethylene and a liquid aromatic fraction containing substantial quantities of benzene, toluene and naphthalenes. More specifically, this invention discloses a process whereby a substantial quantity of aromatic hydrocarbons is produced as a byproduct of ethylene manufacture by the pyrolysis of C_3 hydrocarbons.

It has been known in the past that aromatics can be produced as a byproduct of ethylene production by pyrolysis of C_3 hydrocarbons. However, previous processes for concomitantly producing ethylene and aromatics from propane or propane-propylene mixtures have had the disadvantages that increased aromatic production has always been at the expense of the ethylene content of the product mixture and that the aromatic byproducts have had a substantial diolefin content. Moreover, in the known processes, conversion of propane or propane-propylene mixtures has been held below 75 per cent per pass in order to minimize coke formation. As a consequence it has been necessary in conventional processes to resort to recycle of hydrocarbons in order to realize economic utilization of the charge hydrocarbon. Recycle requires a substantial investment in gas separation equipment such as oil adsorbers and strippers to separate unconverted hydrocarbons from the gaseous reaction product comprising ethylene, methane hydrogen etc. In contrast to former pyrolysis methods for gaseous hydrocarbons, the process of this invention effects better than 97 per cent conversion of hydrocarbons per pass so that a once-through operation is realized and recycle is eliminated. In addition, the production of aromatics at the expense of ethylene is minimized with the consequence that good yields of both ethylene and aromatics are obtained. The aromatic product is of high quality and possesses a low diolefin content; nitration grade benzene and toluene are simply prepared from the aromatic product by acid treatment followed by fractional distillation.

The once-through ethane or C_3 hydrocarbon pyrolysis process of this invention is a combination of cracking and soaking operations, each of which is effected under prescribed critical conditions. Ethane can be used in the process of the invention, but since the charge is normally a C_3 hydrocarbon, the invention will hereafter be described as involving C_3 hydrocarbon conversion. The C_3 hydrocarbon, which may be propane, propylene or a mixture of the two, is introduced at an inlet temperature from atmospheric to 800° F. into a cracking zone at a pressure below 50 p. s. i. g. and is raised to a temperature between 1350 and 1550° F. by indirect heat exchange in a period of 0.5 to 2 seconds, which is the residence time, calculated on the basis of charge gas, prescribed for the cracking zone. The residence time in the cracking section varies within the prescribed limits with the composition of the C_3 hydrocarbon charge mixture and with the amount of preheat imparted to the C_3 hydrocarbon mixture, that is the temperature between atmospheric and 800° F. selected for introduction of the gas mixture into the cracking zone. Better than 90 per cent conversion of the charge C_3 hydrocarbon mixture is effected in the cracking section which is, of necessity, constructed of a nickel-free chrome steel, and which possesses a critical amount of surface area per volume of free space; in order to effect better than 90 per cent conversion in the cracking zone, it is necessary that the amount of surface area per volume of free space be maintained above 200 square feet per cubic foot. The effluent gas from the cracking zone which is at a temperature between 1350 and 1550° F., is immediately passed into an adiabatic or isothermal soaker which is also constructed of nickel-free chrome steel. The gas is passed through the soaking section at a rate such that a residence time of 10 to 40 seconds is realized therein, and issues from the soaker at a temperature in the range of 1100 to 1350° F. In the soaking zone, additional conversion of C_3 hydrocarbons takes place so that better than 97 per cent conversion of charge is effected in the combined cracking and soaking operations. In addition, aromatic production is raised to a level higher than 15 per cent of the charge hydrocarbon gas and the diene content of the aromatic fraction is substantially reduced by the soaking operation.

It is necessary that the cracking and soaking operations be effected within the precise limits defined above in order to obtain high yields of both ethylene and aromatics. The production of high yields of both ethylene and aromatics and the prevention of excessive carbon deposition are also dependent on observance of the prescribed conditions in both the cracking and soaking zones. The critical conditions in the cracking zone are pressure, temperatures of charge introduction and of product withdrawal, residence time and amount of surface area per volume of free space in the cracking zone which is constructed of nickel-free chrome steel. The critical conditions in the soaking zone are the material of construction, the inlet and outlet temperatures, pressure and the residence time.

Ethane, propane, propylene or a mixture of these hydrocarbons can be employed in the process of this invention for producing ethylene and a high-quality aromatic-rich fraction. Since pure ethane, propane and propylene are high cost products, they are not usually employed in commercial adaptations of this process. Excellent results have been obtained with pure propane and propylene in small-scale pilot units. The most commonly used charge is a mixture comprising 70 to 95 per cent propane and 5 to 30 per cent propylene which is available as a refinery byproduct.

In order to prevent coking in the cracking zone, it is necessary that pressures below 50 p. s. i. g. be employed therein. The operational pressure should be as close as possible to atmospheric as is compatible with flow of the gases through the process equipment. Since the pressure limitation of 50 p. s. i. g. is also to avoid excessive pressure drop throughout the equipment, it is recommended that a bundle of relatively short cracking tubes be used in the cracking section rather than a long cracking coil. The construction of the cracking section out of a bundle of short tubes minimizes pressure drop and, in addition, is helpful in obtaining the required surface to volume relationship.

The C_3 hydrocarbon mixture may be introduced into the cracking zone at temperatures in the range of atmospheric to 800° F., but it is desirable to impart as much preheat as possible into the C_3 hydrocarbon mixture. Accordingly, the charge mixture is ordinarily introduced into the cracking zone at a temperature between 500 and 800° F. Sufficient heat is applied to the cracking zone so that the product mixture is raised by indirect

heat exchange to a temperature between 1350 and 1550° F. and preferably between 1450 and 1550° F. in a period of 0.5 to 2 seconds. The necessity of supplying sufficient heat to the cracking zone to supply the necessary sensible heat and endothermic heat of reaction in the prescribed contact time is the basis for the requirement that the amount of surface area per volume in the cracking zone be maintained at a high level.

A residence time of 0.5 to 2 seconds based on the charge gas fed to the cracking zone is essential for effecting better than 90 per cent conversion of C_3 hydrocarbon mixture in the cracking zone. As would be expected, the residence time is dependent in part on the amount of preheat that has been imparted to the C_3 hydrocarbon mixture prior to its introduction into the cracking zone, on the composition of the C_3 hydrocarbon mixture and on the amount of surface area per volume of free space. Regardless of the variation in these conditions, the residence time must fall within the prescribed limits of 0.5 to 2 seconds. In the preferred modification wherein the C_3 hydrocarbon mixture is preheated to a temperature between 500 and 800° F., contact times between 0.7 and 1.5 seconds are preferred in the cracking zone.

The tubes comprising the cracking zone must be constructed of steel which is free from carbon formers such as nickel and vanadium in order to prevent excessive carbon formation during the higher than 90 per cent C_3 conversion effected therein. Chrome steel comprising 27 per cent chromium and 73 per cent steel, is a preferred material for the cracking tubes.

The transmission of sufficient heat to effect better than 90 per cent conversion of C_3 hydrocarbons per pass in the cracking zone requires a large amount of heat exchange surface. It has been discovered that a minimum amount of 200 square feet per cubic foot of free space is necessary in the cracking tubes in order to effect better than 90 per cent conversion of C_3 hydrocarbons per pass at the conditions prescribed in this invention. While the minimum amount of surface area per volume above 200 square feet per cubic foot must be maintained in the cracking zone, it is recommended that the cracking zone be so constructed that the amount of surface area per volume of free space be in the neighborhood of 225 to 350 square feet per cubic foot.

There are two general means of constructing the cracking zone so that the necessary surface to volume ratio is realized. The cracking zone can be constructed of a plurality of small diameter tubes which are, of necessity, of limited length because the pressure drop allowable in the cracking section is limited to a maximum of 50 p. s. i. g. The other alternative involves using larger diameter tubes which are packed with material of the same type employed in constructing the cracking tubes; for example, large diameter tubes can be packed with small diameter tubes or chrome steel wool. The necessary packing to give the required surface to volume ratio can also be obtained by inserting a honeycomb framework within larger diameter tubes.

The gas issuing from the cracking zone is immediately introduced into the adiabatic soaker. The adiabatic soaker contains a large volume of free space in comparison with surface area and is essentially a large insulated drum wherein the effluent from the cracking section cools adiabatically. The inlet temperature to the soaking section is the outlet temperature from the cracking zone and falls in the range of 1350 to 1550° F., and preferably in the upper half of this range. After the product gas has been in the soaker for a period of 10–40 seconds it issues from the soaking section at an outlet temperature in the range of 1100 to 1350° F. A residence time of 12 to 25 seconds and an outlet temperature of 1200° F. have been found to be the preferred conditions for withdrawing an effluent from the soaking section. The prescribed residence times in the soaking section are also based on the gas charged to the cracking section.

During its passage through the soaking section, the conversion of C_3 hydrocarbons is raised to higher than 97 per cent. There is also effected a substantial increase in the liquid aromatic product which is primarily realized from additional C_3 conversion rather than from ethylene utilization. The third important result achieved during the soaking operation is that the diene content of the liquid aromatic product is substantially destroyed so that a high quality liquid aromatic fraction is obtained by the prescribed cracking and soaking operations of this invention.

As a result of passage through the cracking and soaking zones under the above-described conditions, better than 97 per cent conversion of the C_3 hydrocarbon mixture is effected. The yield of ethylene, basis the weight of propane converted, is between 30 and 35 per cent. The yield of high-quality aromatic-rich fraction obtained by the process of the invention is between 23 and 30 per cent; the aromatic fraction comprises condensed liquid fraction and liquids recovered from the gas stream by absorption.

The high-quality of the aromatic product is indicated by the bromine number and diene number of the product prior to further refining such as acid treatment. The bromine numbers of the untreated aromatic fraction are in the neighborhood of 25 to 40, and the diene numbers vary from 5 to 15. The aromatic fraction comprises approximately 5 per cent non-aromatic fraction lighter than benzene, 45 per cent benzene, 10 per cent toluene, 10 per cent naphthalene and 30 per cent higher boiling aromatics. The benzene fraction obtained on fractional distillation of the aromatic product generally contains less than 0.6 weight per cent diolefins and can be converted to nitration grade benzene by acid treatment.

The process of the invention is diagrammatically illustrated in the accompanying drawing.

Propane is introduced through a pipe **1** into a preheater **2** wherein it is raised to a temperature of about 750° F. A C_3 hydrocarbon mixture at a temperature of 750° F. is then introduced through a pipe **3** into a manifold **6** which is located in a furnace **4** and which communicates with the tube bundle **7** comprising the cracking zone. The cracking zone possesses a ratio of surface area to volume of free space above 200.

During passage through the cracking section in a period of about 1.3 seconds, more than 90 per cent of the C_3 hydrocarbon mixture is converted to product. The product from the cracking section issues at a temperature of about 1500° F. into a header **10** and immediately passes through the conduit **11** into a soaker **12** wherein the product from the cracking section is cooled adiabatically to a temperature of about 1200° F.

During passage through the soaker **12**, the C_3 hydrocarbon conversion is raised above 98 per cent and the yield of liquid aromatic fraction is raised from about 5 to 25 per cent. Increased aromatic production is obtained primarily from increased C_3 hydrocarbon conversion. The soaker **12** may contain some packing which is not shown on the drawing.

The product gas from the cracking section is cooled to a temperature of about 1200° F. during its 20 second residence time therein. In addition to effecting increased conversion of C_3 hydrocarbon mixture and a manifold increase in yield of liquid aromatic fraction, the passage of the product from the cracking section through the soaker substantially destroys all the acetylene in the product from the cracker and converts the dienes present in the cracker product to aromatics. As a consequence, the aromatic product obtained by the process of this invention is a high-quality product substantially free of acetylenes and containing a very low content of dienes.

There issues from the soaker **12** at a temperature of about 1200° F. a product containing a high concentration of ethylene and a high-quality aromatic fraction. The gaseous portion of the product comprises mainly ethylene,

hydrogen and methane. Further treatment of the product is by conventional procedures for separating liquid product from gaseous product. A representative procedure for separating the ethylene gas from the liquid aromatic fraction is shown in the drawing.

The effluent from the soaker **12** is introduced through a pipe **16** into the heat exchanger **17** wherein it is cooled and is then passed through a pipe **18** into a gas-liquid separator **20**. In the separator **20**, the condensed aromatic fraction is separated from the gaseous fraction of the product. Further treatment of the condensed aromatic fraction which is removed from the separator **20** through a pipe **22** will be described hereafter.

The gaseous portion of the product is withdrawn from the separator **20** through a pipe **25** and is introduced into an absorber **26** wherein it is subjected to countercurrent contact with an absorber oil such as mineral seal oil which is introduced into the absorber **26** through a pipe **27**. Contact of the gaseous fraction of the product removes heavier hydrocarbons from the product gas.

The effluent which is removed from the absorber **26** through a pipe **30** comprises approximately 37.2 weight per cent ethylene, 48.8 weight per cent methane, 9.0 per cent ethane, 2.3 weight per cent hydrogen and 2.5 weight per cent C_3 hydrocarbons. Since this product gas comprises such a low concentration of propylene, it may be used directly in a hydrochlorinator to prepare ethylene chlorohydrin, an intermediate in the preparation of ethylene oxide and ethylene glycol. If a pure ethylene stream is desired, the effluent from the absorber **26** is passed to a conventional separation system for recovering ethylene from lighter gases. Separation of the pure ethylene fraction from the product gas obtained through the pipe **30** is not shown, since separation does not constitute any part of the process of this invention. It is noteworthy that the C_3 hydrocarbon content of the product gas is so low that the necessity of recycle to the cracking section is eliminated.

Returning to the treatment of the absorber oil, there is withdrawn from the bottom portion of the absorber **26** through a pipe **35** absorber oil saturated with the fraction comprising C_4 hydrocarbons and benzene removed from the product gas. The saturated absorber oil is introduced into a heat exchanger **36** wherein it is raised to a temperature sufficient to free the absorbed C_4 plus fraction. The heated absorber oil is introduced through a pipe **37** into a stripper **38** wherein the C_4 plus hydrocarbon fraction is removed as an overhead through a pipe **39**. The lean absorber oil is removed from the bottom of the stripper **38** through a pipe **42**, is cooled in a heat exchanger **43** and is recycled through a pipe **44** to the absorber **26**.

The C_4 plus hydrocarbon fraction from the stripper **38** is cooled in a heat exchanger **46** and is then combined through a pipe **47** with the condensed aromatic fraction which was obtained from the separator **20**.

The condensed aromatic fraction which is separated from the gaseous portion of the product in the separator **20** is introduced into a stabilizer **50** wherein absorbed gases are separated from the condensed aromatics. The gas fraction stripped from the condensed aromatic is removed from the upper portion of the stabilizer **50** through a pipe **51** and is normally combined with the product gas in the pipe **25** prior to the latter's introduction into the absorber **26** for the removal of C_4 plus hydrocarbon fraction.

If the gas removed from the condensed aromatic fraction of the stabilizer **50** does not contain C_4 plus hydrocarbons, it is possible to bypass the absorber **26** and recombine the gas from the stabilizer **50** directly with the product gas from the absorber **26**. The alternate line **52** provides for direct combination of the gas from the stabilizer **50** with the product gas from the absorber **26**.

The condensed aromatic fraction free of absorbed gases is withdrawn from the bottom portion of the stabilizer **50** through a pipe **55** for combination with the C_4 plus hydrocarbon fraction.

The following example illustrates the process of this invention for obtaining high yields of ethylene and of high quality aromatic fraction by pyrolyzing propane in a combination of cracking and soaking operations at prescribed conditions:

Propane was passed at room temperature to a cracking coil where there was 281.6 sq. ft. of surface per cubic foot of free volume. The cracking coil outlet temperature was 1500° F. and the contact time in the cracker was 1.2 seconds. The effluent from the cracker contained 9.4 per cent of propane and 11.7 per cent of propylene. This cracker effluent was passed immediately to a soaker where it was held for 34.4 seconds. The products were removed from the soaker at 1200° F. Yields of 27.9 weight per cent ethylene and 24.73 weight per cent aromatic liquids were obtained. No propane and only 1.9 weight per cent propylene appeared in the outlet from the soaker.

The product obtained in this run had the composition shown in Table I wherein the yields are shown on the basis of weight per cent charge.

Table I

	Weight per cent
Hydrogen	1.7
Methane	36.6
Ethylene	27.9
Ethane	7.0
Propylene	1.9
Total liquids including C_4 plus hydrocarbon fraction and condensed liquids	24.73

In Table II there is shown the approximate composition on a volume per cent basis of the total liquid product.

Table II

	Volume per cent
Butadiene	5
Pentadiene	1
Cyclopentadiene	12
Benzene prerun	4
Benzene	38
Toluene	8
Naphthalene	8
Heavy aromatics	24

The benzene fraction obtained by straight distillation of the liquid product had a bromine number of about 1.0, a diene number of about 0.7 and a specific gravity of 0.8840; after acid treatment, the benzene fraction had a specific gravity of 0.8847, a R. I. at 68° F. of 1.5009 and an acid wash color between 0 and 1. Acid treatment of the toluene fraction gave a product having a specific gravity of 0.8723, a R. I. at 68° F. of 1.4981 and an acid wash color between 1 and 2. The high quality of the aromatic products of the process of this invention is well demonstrated by these properties.

Although the combined cracking-soaking operation of this invention for producing ethylene and aromatics has been described using C_3 hydrocarbons as the charge material, it is reiterated that the process of the invention is applicable to the conversion of ethane into a product comprising ethylene and aromatics. As long as the cracking and soaking operations are effected at the prescribed critical conditions, a high yield of ethylene and aromatics are obtained by cracking ethane, propane, propylene or a mixture thereof.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for converting a gaseous hydrocarbon

selected from the group consisting of ethane, propane, propylene and mixtures thereof to ethylene and a liquid aromatic fraction which comprises introducing said hydrocarbon at a temperature from atmospheric to 800° F. into cracking tubes constructed of nickel-free chrome steel and having a relationship of surface area to volume of free space above 200 square feet per cubic foot, passing said hydrocarbon through said tubes at a pressure below 50 p. s. i. g. and at a rate such that a contact time of 0.5 to 2 seconds is obtained, raising said gaseous hydrocarbon to a temperature level of 1350 to 1550° F. during passage through said cracking tubes, removing an effluent gas from said cracking tubes at a temperature between 1350 and 1550° F., passing said effluent gas immediately through a soaker at a rate such that a residence time of 10 to 40 seconds is maintained and in said soaker allowing said effluent to cool essentially adiabatically, whereby more than 97 per cent hydrocarbon conversion is effected and the yield and quality of the liquid aromatic fraction are substantially improved, issuing a product gas from said soaker at a temperature in the range of 1100 to 1350° F. and separating said product gas into an ethylene-rich fraction and into a liquid aromatic fraction.

2. A process according to claim 1 in which the residence time of the cracker effluent in the soaker is between 12 and 25 seconds.

3. A process according to claim 1 in which the gaseous hydrocarbon comprises 70 to 95 per cent propane and 5 to 30 per cent propylene.

4. The process according to claim 1 wherein gaseous hydrocarbon is introduced into the cracking tubes at a temperature between 500–800° F.; the cracking tubes have between 225 and 350 square feet of surface area per cubic foot of free space therein; said gaseous hydrocarbon is present in the cracking tubes for a contact time between 0.7 and 0.5 seconds; and the effluent gas is removed from the cracking tubes at temperatures between 1450–1550° F.

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