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[54] **BENZENE FROM PYROLYSIS GASOLINE**
17 Claims, 1 Drawing Fig.

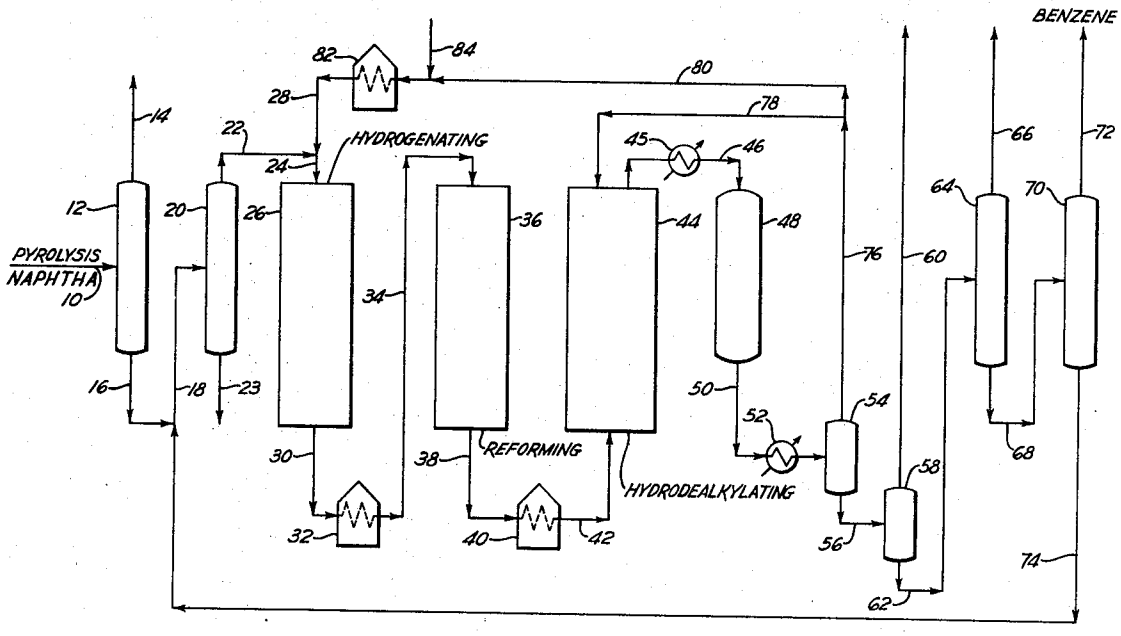
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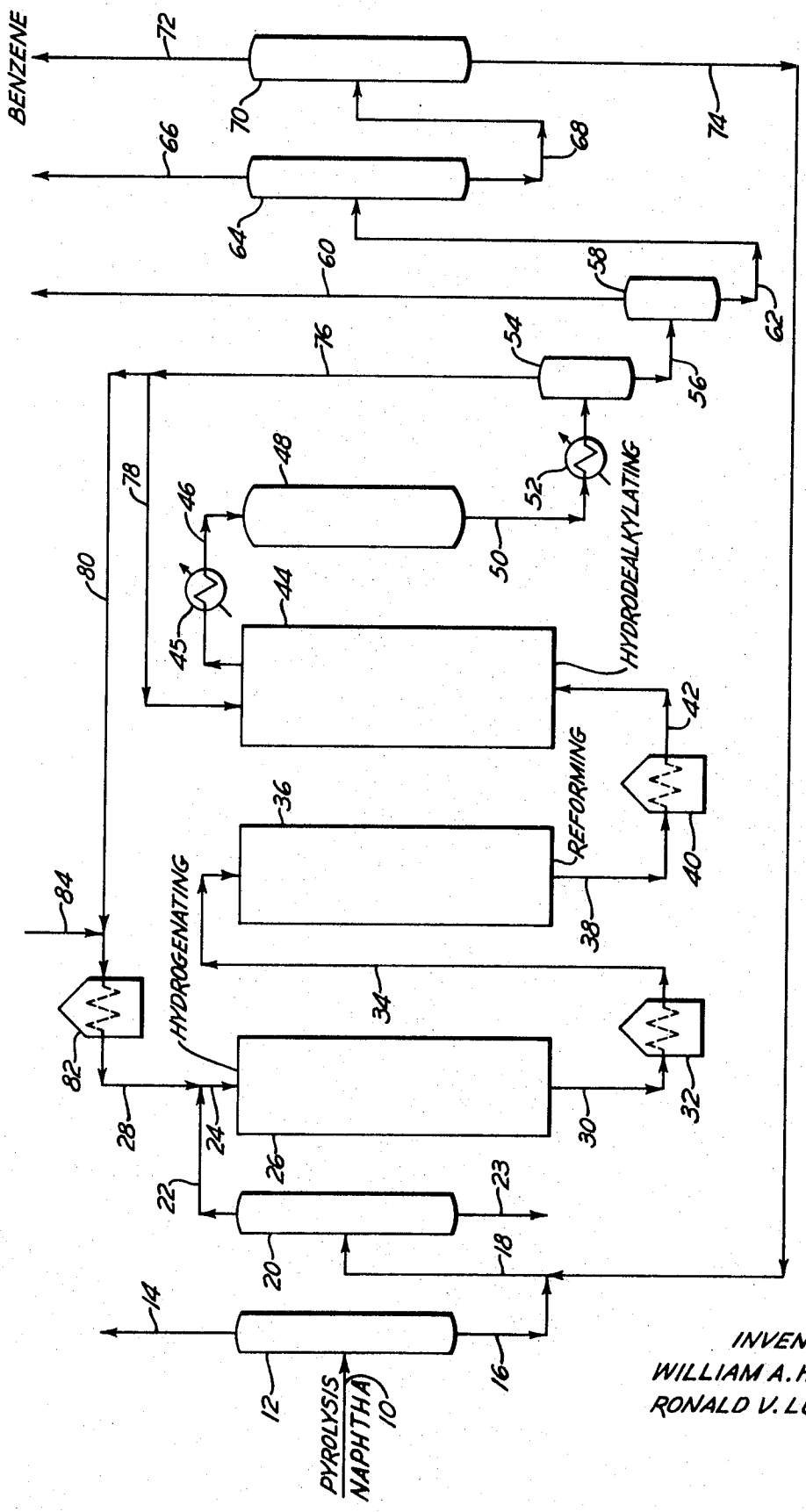
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ABSTRACT: A process for the production and recovery of benzene from pyrolysis naphtha produced by high-temperature cracking of ethane, propane, naphtha or gas oil to produce ethylene. The process comprises the steps of hydrogenating a selected cut of pyrolysis naphtha to saturate olefins, reforming the hydrocarbon product from the hydrogenation step to convert benzene precursors to aromatic compounds and partially crack the nonaromatic hydrocarbons present and thereafter hydrodealkylating the hydrocarbon product from the reforming step to convert the alkyl aromatics to benzene and further crack nonaromatic compounds including those boiling at about the benzene boiling point, so that benzene may then be separated from the hydrodealkylation effluent by conventional distillation.





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BENZENE FROM PYROLYSIS GASOLINE

BACKGROUND OF THE INVENTION

This invention relates to a process for the production of benzene from pyrolysis naphtha by hydrogenating a selected cut of pyrolysis naphtha, reforming the hydrogenated product and hydrodealkylating the reformed product. The benzene thus produced and the benzene originally contained in the pyrolysis naptha feed to the process can then be separated from the hydrodealkylated product by conventional fractional distillation, thereby eliminating the step of solvent extraction normally employed in recovering benzene from pyrolysis naphtha.

The increased demand for ethylene and changes in ethylene manufacturing technology has produced an increased amount of pyrolysis naphtha which is a byproduct of ethylene manufacturing. Only a small quantity of pyrolysis gasoline byproduct is produced when ethane is used as the sole starting material for the production of ethylene. However, when propane is used as the starting material approximately 25 pounds of pyrolysis naphtha is produced for each 100 pounds of ethylene product. When naphtha is used as a starting material about 45 pounds of byproduct material is produced for each 100 pounds of ethylene product. The modern trend in ethylene manufacturing technology indicates that it is more desirable to use mixtures of ethane and propane, naphtha or gas oil as a starting material and this trend coupled with the increased demand for ethylene obviously increases the amount of byproduct pyrolysis naphtha the ethylene manufacturer has available.

One of the problems encountered in the utilization of the byproduct is that the byproduct contains an amount of highly unsaturated hydrocarbon compounds, such as acetylenes, aliphatic diolefins, vinyl substituted aromatics, and cyclic diolefins and these compounds polymerize readily at temperatures above about 260° F. or at ambient temperatures over a long period of time. The highly unsaturated hydrocarbons also readily polymerize when contacted with air and/or light. The polymeric compounds thus formed are termed gums and render the pyrolysis naphtha unsuitable as a motor fuel blending component and make additional processing of the byproduct difficult. The acetylene produced in the ethylene product is usually removed under mild hydrogenating conditions before the ethylene is separated from the product. The mild hydrogenating conditions do not, however, remove higher molecular weight acetylenes or other gum-forming compounds and these remain in the pyrolysis naphtha byproduct. The prior art solution to making the pyrolysis naphtha a suitable motor fuel blending component is to hydrogenate under conditions that will saturate the gum-forming compounds but will not saturate the monoolefin or aromatic compounds. It is not desirable to saturate the monoolefin compounds because these are valuable as motor fuel blending agents and the aromatic compounds present are also valuable in motor fuel. The prior art hydrogenation obviously requires extraneous hydrogen. As benzene and the other aromatics contained in the pyrolysis naphtha became more valuable as petrochemicals than as motor fuel blending agents, the aromatics were separated from the completely hydrogenated pyrolysis naphtha by selective distillation, adsorption or solvent extraction.

Although selective distillation can be employed to separate compounds boiling very closely to each other, it is usually expensive and of little commercial importance. Adsorption and solvent extraction as applied to the recovery of benzene from pyrolysis naphtha both suffer from essentially the same inherent defects and therefore will be discussed together as solvent extraction. To separate the aromatics by solvent extraction, it is necessary to first saturate not only the gum-forming compounds but also to saturate the monoolefins, again increasing in the extraneous hydrogen requirements. In addition to saturating the monoolefins the sulfur containing hydrocarbons must be removed, again increasing the extraneous

hydrogen requirements. The olefins must be saturated and sulfur containing hydrocarbons removed because the order of solubility of hydrocarbon material in a solvent that is selective for aromatics is as follows: the least soluble material is the paraffinic material followed in order of increasing solubility by naphthenes, olefins, diolefins, acetylenes, sulfur bearing molecules, and aromatics. After solvent extraction, the impure benzene could be separated by distillation, but it is noted that this process only recovers the indigenous benzene and does not produce more benzene than was contained in the original pyrolysis naphtha starting material. The reason that solvent extraction was employed rather than simple distillation is that the pyrolysis naphtha contains nonaromatic compounds boiling close to benzene and they are not removed by the hydrogenation step. Further, hydrogenation conditions employed by the prior art in some cases were of such severity that when monoolefins were saturated some aromatics were saturated to produce compounds boiling close to benzene, for example, benzene was converted to cyclohexane.

In the process of this invention, by selecting certain sequential processing steps and operating conditions for each step, the need for solvent extraction is eliminated and high purity benzene can be separated from the product by simple distillation.

Therefore, an object of this invention is to eliminate solvent extraction from the process for producing benzene from pyrolysis naphtha. Another object of this invention is to increase the yield of benzene from pyrolysis naphtha over and above the quantity of benzene inherently contained in the pyrolysis naphtha starting material. Another object of this invention is to effect substantial heat savings by performing the sequence of process steps at ascending temperature levels so that no intermediate cooling is required between the steps. Another object of this invention is to operate the sequence of process steps at attenuating pressure levels so that compression is not required between the processing steps. A further object of this invention is to minimize the total hydrogen consumption and minimize the amount of extraneous hydrogen required while increasing the yield of benzene from pyrolysis naphtha.

SUMMARY OF THE INVENTION

A process is described for increasing the yield of benzene from a feed stock of pyrolysis naphtha. Pyrolysis naphtha is a byproduct in the manufacture of ethylene where ethane, ethane and propane, naphtha or gas oil is dehydrogenated or cracked at high temperatures to produce ethylene. The process initially comprises the hydrogenation of a selected cut of pyrolysis naphtha comprising from about six to 12 carbon atoms per molecule or about six to 10 carbon atoms per molecule to saturate olefins. Hydrogen sulfide formed from the sulfur compounds in the hydrogenation step can be removed from the hydrogenation effluent if the quantity is of sufficient magnitude to impair the life of the catalyst in the subsequent reformer stage. The hydrogenation effluent is then reformed at a temperature higher than the hydrogenation temperature and a pressure slightly less than the hydrogenation pressure to convert benzene precursors to aromatic compounds and to partially crack the nonaromatic compounds. The reformer effluent is then charged to a hydrodealkylation stage maintained at a temperature higher than the reformer temperature and a pressure slightly less than the reformer pressure to further convert alkyl aromatics to benzene and crack all remaining nonaromatic compounds including those boiling close to benzene, such as thiophene, isoheptanes, 2,2-dimethylpentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, etc. The effluent from the hydrodealkylation unit can by hydrogenated to saturate trace olefins produced in the hydrodealkylation step or passed directly to a hydrocarbon recovery section where benzene is separated from the other hydrocarbons by distillation. Reforming conditions are selected so that hydrogen production is maximized and the

need for extraneous hydrogen in the hydrogenation and hydrodealkylation steps is minimized.

BRIEF DESCRIPTION OF THE DRAWING

The drawing discloses one preferred embodiment of the process to maximize the yield of benzene from pyrolysis naphtha.

DETAILED DESCRIPTION OF THE INVENTION

The subject yields a maximum amount of high purity benzene from pyrolysis naphtha by conserving the amount of benzene contained in the original pyrolysis naphtha feed and further by converting precursors of benzene to aromatic and/or alkyl aromatic compounds in the reforming step and further by converting the alkyl aromatic compounds to benzene in the hydrodealkylation step. Thereby the quantity of benzene contained in the original feed is not only retained but also enhanced by the quantity of benzene produced in the processing steps of this invention. Further, nonaromatic compounds including those boiling at about the benzene boiling point are cracked to lower boiling hydrocarbons and/or converted to aromatic compounds which allows the recovery of benzene substantially free of close-boiling materials by conventional distillation.

Another novel feature of the process of this invention is that each of the sequential processing steps, that is, hydrogenation reforming and hydrodealkylation, are carried out at progressively higher temperatures so that no intermediate cooling between steps is required. Nor is intermediate cooling followed by subsequent reheating required. In one embodiment of this invention, it is necessary to cool the effluent from the hydrodealkylation step before a final hydrotreating operation to saturate trace olefinic compounds produced in the hydrodealkylation step, but then it is not necessary to heat the effluent from the subsequent hydrotreating step prior to product distillation. If a final hydrotreating is not employed, the effluent from the hydrodealkylation step would normally be cooled before distillation, so it can be seen that even with the employment of a final hydrogenation step, the overall thesis of heat savings is valid.

Still another advantage of the process of this invention is that the pressure employed in each of the steps is selected so that each process step performs its intended function at a higher pressure level than its subsequent step so that no depressurizing and repressurizing are necessary. By careful selection of other process conditions, the appropriate descending pressure levels can be maintained notwithstanding pressure drops normally occurring between process steps and in each process step.

The need for extraneous hydrogen is reduced by incorporation of reforming within the sequence of processing steps. Since reforming results in a net production of hydrogen via dehydrocyclization and dehydrogenation reactions, hydrogen is produced in the reforming step which is utilized in the hydrodealkylating and hydrogenation steps. By proper selection of process conditions in the reforming step, partial cracking of nonaromatic hydrocarbons can be accomplished and the cracking of aromatic hydrocarbons can be eliminated. Further, reforming conditions are controlled so that aromatics are not saturated, thereby conserving hydrogen. For example, if benzene were saturated to cyclohexane in the reformer step the cyclohexane would be cracked in the hydrodealkylation step requiring additional hydrogen to saturate the cracked cyclohexane. It should be understood at this point that aromatic rings are not hydrogenated in any of the processing steps, thereby conserving the aromatics present in the original pyrolysis naphtha feed.

Total hydrogen requirements are minimized by selecting proper operating conditions for the reforming unit as pointed out above and also by selecting proper hydrogenating conditions so that all gum-forming compounds and most but not necessarily all of the monoolefins are saturated in the hydrogenation step and not the aromatic rings.

Complete saturation of monoolefins would be necessary if the pyrolysis naphtha were first hydrogenated and then solvent extracted. But it is an advantage of our invention that complete saturation of the monoolefins is not necessary. By not completely saturating monoolefins, although we saturate monoolefins to a low level of about 0.5 weight percent, we prevent saturation of aromatic rings and thereby minimize hydrogen required as well as conserve the hydrogen that would be consumed by saturating the monoolefins.

Three distinctive process steps are employed to accomplish the advantages outlined above, and though distinctive, the steps are not exclusive as a great deal of cooperation exists among the steps to accomplish desired objectives. To begin with, the hydrogenation step is necessary to saturate gum-forming hydrocarbons that would make additional processing difficult. In addition, most but not necessarily all of the monoolefin hydrocarbons are saturated as these hydrocarbons would tend to cause coke formation or rapid catalyst aging in the reforming step. Further, sulfur containing hydrocarbons are converted to hydrogen sulfide and hydrocarbon and the hydrogen sulfide, if present in a quantity sufficient to impair the reformer catalyst like, may be removed before the hydrogenation effluent is fed to the reformer. It is important that under the conditions employed in the hydrogenation step aromatic rings are not hydrogenated. Therefore, the quantity of aromatics indigenous to the pyrolysis naphtha feed pass unreacted to the reformer and hence to the hydrodealkylation step and the naphthenes contained in the pyrolysis naphtha and produced in the hydrogenation step are converted to aromatics in the reforming step. The reforming step performs the additional functions of: converting normal paraffins containing six or more carbon atoms per molecule, to naphthenes by isomerization and dehydrocyclization, and the naphthenes thus formed to aromatics, cracking and dehydrogenating dicyclic naphthenes to form aromatics, and partially cracking nonaromatic hydrocarbons. The hydrodealkylation step not only converts to benzene the alkyl aromatics formed in the reforming step and the alkyl aromatics inherent in the pyrolysis naphtha feed but also further cracks remaining nonaromatic materials including those that boil close to benzene.

The starting material for this process, pyrolysis naphtha, is produced as a byproduct from the manufacture of ethylene. For example ethane and propane are fed to thermal cracker or pyrolysis furnace and heated to a temperature of about 1,200° F. to about 1,800° F., preferably between about 1,350° F. and 1,550° F. Low pressures up to about 200 p.s.i.a. are normally employed, a pressure below about 35 p.s.i.a. being satisfactory. The time of exposure to the high temperatures is usually about 0.5 to 5 seconds, contact times of 0.1 to 1 second being preferred. The effluent from the pyrolysis step contains hydrogen, normally gaseous hydrocarbons, normally liquid hydrocarbons, carbon dioxide, varying amounts of sulfur containing hydrocarbons and trace quantities of nitrogen and oxygen containing hydrocarbons. The high temperature pyrolysis product is rapidly cooled, usually by quenching with water or oil to a temperature of about 400° F. The gaseous product from the quenching step is then from and caustic washed to remove the carbon dioxide present. The caustic washed gases are then preheated to a temperature normally between 150° F. and 325° F. and then introduced into a catalytic hydrogenation zone which is operated at mild hydrogenation conditions to selectively hydrogenate acetylenes. The mild hydrogenation conditions comprise a temperature of between 150° F. and 325° F. and a flow rate of between 1,000 and 2,500 $ft.^3/hr./ft.^3$ of catalyst bed. The hydrogen and normally gaseous hydrocarbons comprising fuel gas, ethane, ethylene, propane, propylene, butane and butylenes are separated from the normally liquid byproduct pyrolysis naphtha also known as aromatic distillate. The thus obtained aromatic distillate forms the starting material for the process of our invention.

The aromatic distillate has a boiling range of about 100° F. to about 700° F. and preferably between about 100° F. and 375° F. The amount and composition of the distillate is dependent upon the type of feed selected for pyrolysis, the pyrolysis

temperature, contact time and pressure. The normally liquid distillate is of such complexity that accurate and complete analyses are difficult. It is felt that the complexity of this material has, in part at least, obscured the feasibility of producing benzene from it by the particular sequence of steps employed in this invention.

The charge stock for the process of this invention comprises a mixture of compounds comprising between about 6 and about 30 percent by weight of unsaturated compounds which readily thermally polymerize. By an unsaturated compound which readily thermally polymerizes is meant a compound which has a potential gum value of over 500 milligrams per 100 milliliters of compound after 5 hours as determined by ASTM test D–873. Examples of compounds that readily thermally polymerize include unsaturated hydrocarbons, such as vinyl substituted aromatics, aliphatic di- and triolefins, and cyclic diolefins. Specific examples of these compounds are styrene, isoprene, cyclopentadiene, etc. The charge stock also comprises between about 20 and 30 percent by weight of benzene and many precursors of benzene when the process steps of the subject invention are employed. Precursors of benzene include substituted dicyclopentadienes, toluene, styrene, indene, naphthenes, six to 10 carbon atom paraffins, olefins and diolefins, etc. Included in the charge stock there may be small amounts of sulfur, nitrogen and oxygen containing hydrocarbons, such as for example thiophenes, pyrroles, pyridines and phenols. Normally, the amounts of nitrogen and oxygen-containing compounds are negligible and the sulfur-containing compounds are less than 0.1 percent and usually between 0.05 and 0.005 weight percent of the charge stock. It is one advantage of the process of this invention that these sulfur compounds are converted to hydrogen sulfide and hydrocarbon during the hydrogenation step, and if the hydrogen sulfide in the effluent stream is of sufficiently high concentration to poison the reformer catalyst it may be removed prior to reforming.

Referring now to the drawing, the aromatic distillate or pyrolysis naphtha is introduced to the process system through line **10** where it is depentanized in distillate tower **12**, the overhead removed via line **14** which after finishing can be added to the gasoline blending pool. The bottoms from tower **12** are removed via line **16** to line **18** and introduced into tower **20** wherein the aromatic distillate is cut to remove the hydrocarbons having **11** or more carbon atoms per molecule. This cut corresponds to an end point of about 350° F. to about 400° F. and preferably between about 360° F. to about 375° F. The hydrocarbons having 11 or more carbon atoms per molecule are removed via line **23** and are suitable for use as a fuel oil cutter stock. The overhead from tower **20** is removed via line **22** to line **24** to the hydrogenating section **26**. The product contained in line **22** can be heated to the desired hydrogenation temperature by conventional means, not shown. The hydrogenating step can comprise any hydrogenating process that will saturate the readily polymerizable unsaturated compounds and prevent their conversion to gums and further saturate most monoolefins but does not saturate aromatic rings. A process as described in McKinney et al., U.S. Pat. No. 3,216,924, is satisfactory. In general, satisfactory hydrogenation processes fall into two broad classes and the choice of the hydrogenation process to be employed will depend to some extent on the amount of sulfur contained in the feed stock and other factors apparent to one skilled in the art. The particular hydrotreating process selected is not critical as long as the results outlined above are obtained. The first class of satisfactory hydrogenating processes are those employing catalysts comprising metals selected from Group VI*a* and/or the iron group metals of Group VIII, their oxides and/or sulfides unsupported or supported upon a noncracking support such as clay, kieselguhr, alumina, etc. This class of process is operated at a temperature of about 260° F. to about 800° F. and preferably about 400° F. to about 600° F. The process is not seriously affected by sulfur in the feed stock, however, the catalyst is more active in the sulfided state and therefore some sulfur in the feed stock is desirable. Usually about 100 to 500 p.p.m. of sulfur in charge stock is preferred. The second class of hydrogenation processes utilizes a noble metal catalyst and generally operates at temperatures of about 125° F. to about 250° F. At such temperatures, the feed is in the liquid phase and the tendency for the gum-forming compounds to polymerize is minimized. The catalyst, however, is subject to partial deactivation when relatively high sulfur content feeds are hydrogenated. In one embodiment of the process of this invention the hydrogen sulfide produced in the hydrogenation step is above about 10 p.p.m. of the hydrocarbon effluent and preferably above about 1 p.p.m. can be removed in a hydrogen sulfide removal zone (not shown) by any suitable separation process including adsorption, extraction, chemical combination, etc. A preferred method of removing the hydrogen sulfide is to employ a porous adsorbent such as zinc oxide. Additional hydrogenating conditions include a total reaction pressure of about 300 to about 1,000 p.s.i.g., and preferably about 400 to about 800 p.s.i.g. The space velocity can range from 0.5 to 8 LHSV and preferably about 1 to 6 LHSV. The hydrogen purity is not critical and can range from about 40 to 100 percent, preferably about 70 to 95 percent. A hydrogen to hydrocarbon mol ratio of 1:1 to 10:1 is satisfactory with a ratio of 1.5:1 to 6:1 being preferred. The hydrogenated product prior to reforming should have a bromine number of about 0 to about 5, and preferably the bromine number is about 0 to about 2.

The hydrotreating section effluent exists from the hydrotreating section via line **30**. The temperature of the product is raised by heating means **32** to a reforming temperature higher than the hydrogenation temperature and enters a reforming section **36** via line **34** at a pressure slightly lower than the hydrogenation pressure. Proper selection of reforming conditions is of upmost importance to the successful practice of this invention. Reforming conditions are mild enough so that aromatics are not saturated but severe enough to crack some of the nonaromatic hydrocarbons. The main purpose of the reforming step is to dehydrogenate naphthenes present, isomerize and dehydrocyclize normal paraffins to produce hydrogen, aromatics and alkyl aromatics. The hydrogen produced is utilized in the other processing steps of this invention and the alkyl aromatics produced are dealkylated in the hydrodealkylation step and recovered as benzene. Some naphthenes such as methylcyclopentane and cyclohexane boil near the benzene boiling point and are converted to aromatics in the reforming step and, therefore, are not cracked in the thermal hydrodealkylation step. Some isomerization of normal paraffins occurs in the reforming step and some of these isomers boil close to benzene so they must be cracked in the hydrodealkylation step. Examples of isomers formed would be isopentanes, 2,2-dimethylpentane, etc. All monoolefins need not be saturated in the hydrogenation step prior to reforming, however, it is a preferred practice to saturate most or substantially all of the monoolefins as the monoolefins tend to suppress the activity of the reformer catalyst. It is permissible to leave unsaturated about 0 to 1 weight percent of the monoolefins prior to reforming and preferably 0 to 0.5 weight percent. Not saturating all monoolefins in the hydrogenation step conserves some hydrogen when compared to prior art processes. It is essential to the overall conversion of hydrogen that naphthenes such as cyclohexane are dehydrogenated in the reforming step as these compounds if fed to the hydrodealkylation step would crack and therefore additional hydrogen would be consumed.

The reforming system **36** can be of a fixed or moving bed type and employ a suitable reforming catalyst such as platinum group metals on a support such as alumina with or without rhenium activation or Group VI*a* oxides on a support such as clay, kieselguhr, alumina, etc. and preferably promoted with halides such as chlorine or fluorine. The reforming temperature can be from about 850° F. to about 1,100° F. and preferably is from about 900° F. to 1,000° F. The desired reforming pressure is from about 150 p.s.i.g. to about

700 p.s.i.g. and preferably from about 300 p.s.i.g. to about 700 p.s.i.g. Space velocity can be from 1.0 to 5.0 LHSV or a more preferred range is from 1.5 to 4.0 LHSV. Hydrogen purity is not critical but should be above 40 percent and preferably about 70 percent. The hydrogen to hydrocarbon ratio can be from 1:1 to about 10:1 and preferably from 5:1 to 10:1. A single bed reforming unit can be employed but it is more desirable to employ a plurality of beds with heating means between each bed to supply the endothermic reaction heat and to raise the reforming temperature level as the hydrocarbon progresses through the reforming unit. Higher reforming temperatures in the later reforming stages promotes cracking.

The reformer effluent exits from the reforming section **36** via line **38** and is raised in temperature by heating means **40** to a temperature higher than the reforming temperature. The reforming effluent enters the hydrodealkylation section **44** through line **42** at a pressure slightly less than the reformer pressure. The hydrodealkylation section converts alkyl aromatics formed in the reformer section and contained in the pyrolysis naphtha feed to benzene. Examples of alkyl aromatics originally present or formed in the reformer section include toluene, xylene, ethylbenzene, mesitylene, etc. The pyrolysis feed contains a significant percentage of alkyl aromatics and a substantial additional amount is formed in the reforming section. The hydrodealkylation step performs the additional function of cracking remaining nonaromatic hydrocarbons including those boiling close to the boiling point of benzene, such as isoheptanes, cyclohexane, thiophene, etc. The hydrodealkylation system can be operated in one, two, or more stages to control the exothermic heat of reaction. Recycled cooled hydrogen can enter a second stage from vessel **54** through line **76** to line **78** and hence into a second stage of system **44** to maintain the initial temperature of stage **2** at about the same temperature as stage **1**. At the inlet of each stage or a single stage of section **44** the temperature of the mixture is about 1,100° F. to about 1,400° F., preferably about 1,140° F. to about 1,350° F. and the pressure is about 300 to 1,000 pounds per square inch gauge, preferably about 350 to 600 pounds per square inch gauge, while at the outlet of each stage or a single stage the temperature of the mixture is about 1,325° F. to about 1,400° F. and the pressure is about 300 to 1,000 pounds per square inch gauge, preferably about 350 to 600 pounds per square inch gauge. The molar ratio of hydrogen to hydrocarbon in each stage or a single stage is about 3:1 to 10:1, preferably about 4:1 to 7:1. Calculated on the basis of plug flow through each stage the residence time of the mixture therein is about 20 to about 200 seconds, preferably about 25 to about 100 seconds.

The hydrodealkylation effluent exits section **44** via line **46** and enters a hydrotreating finishing section **48** wherein small amounts of olefins which are generated in the thermal hydrodealkylation section are saturated. The olefins are usually present in amounts of 10 to about 1,000 p.p.m. of total hydrocarbon. The hydrotreating finishing section is only a preferred embodiment of this invention and is not an essential step. The effluent from section **44** is cooled prior to entering section **48** by heat exchange **45** to a temperature of about 200° F. to about 700° F. preferably about 250° F. to about 600° F. Section **48** contains a suitable hydrogenating catalyst such as metals selected from Group VI and/or Group VIII supported on a support such as alumina. The pressure of section **48** is only slightly less than the pressure of section **44**.

The finished hydrocarbon exits section **48** via line **50** through heat exchanger **52** to vessel **54** where hydrogen is separated from the hydrocarbon product and recycled after compression (compressor means not shown) via line **76** to section **44** through line **78** and to section **26** via line **80**. Fresh externally supplied hydrogen such as purified hydrogen produced in the pyrolysis step, enters line **80** via line **84** and is heated with recycle hydrogen in heater **82** before entering section **26**. The temperature of the product entering vessel **54** is about 100° F. to about 150° F., preferably about 100° F. to about 120° F. Hydrocarbon product exits vessel **54** via line **56** to vessel **58** wherein dissolved light gases such as hydrogen and methane are separated from the product via line **60**. The bottoms from vessel **58** enters fractionator **64** via line **62** and is stripped of hydrocarbons boiling below benzene the overhead removed via line **66** and the bottoms via line **68**. The product benzene is separated from the remaining hydrocarbons in fractionator **70** and removed via line **72**. The benzene product has a purity of about 99.8 percent to 100.0 percent benzene. The bottoms from tower **70** are recycled to line **18** via line **74**.

We claim:

1. A process for increasing the benzene yield from a hydrocarbon material comprising generally from about six to about 12 carbon atoms per molecule obtained as the byproduct from the pyrolysis cracking of hydrocarbons to produce primarily ethylene which comprises:

hydrogenating said hydrocarbon material in the presence of hydrogen generated within said process under hydrogenating conditions including a hydrogenating temperature and a hydrogenation pressure in the presence of a hydrogenation catalyst to saturate olefinic hydrocarbons;

reforming said hydrocarbon material under reforming conditions including a reforming temperature higher than said hydrogenating temperature and a reforming pressure lower than said hydrogenating pressure in the presence of a reforming catalyst to increase aromatic content of said hydrocarbon material and to produce hydrogen;

hydrodealkylating said hydrocarbon material in the presence of hydrogen from said reforming step under hydrodealkylating conditions including a temperature higher than said reforming temperature and a pressure lower than said reforming pressure to hydrodealkylate aromatic compounds and also crack remaining nonaromatic hydrocarbons to obtain an effluent comprising benzene and hydrogen;

recycling said hydrogen to said hydrogenation step; and

recovering benzene from said effluent by distillation.

2. A process in accordance with claim **1** wherein said hydrogenating temperature is from about 125° F. to about 800° F.; said reform temperature is from about 850° F. to about 1,100° F.; and said hydrodealkylating temperature is from about 1,100° F. to about 1,400° F.

3. A process in accordance with claim **1** wherein

said hydrogenating total pressure is from about 300 to about 1,000 p.s.i.g.; said reforming total pressure is from about 150 to about 700 p.s.i.g.; and said hydrodealkylating total pressure is from about 300 to about 1,000 p.s.i.g.

4. A process in accordance with claim **1** wherein

said hydrogenating conditions includes a hydrogen to hydrocarbon mol ratio of about 1:1 to about 10:1; said reforming conditions includes a hydrogen to hydrocarbon mol ratio of about 1:1 to about 10:1; and said hydrodealkylating conditions includes a hydrogen to hydrocarbon mol ratio of about 3:1 to about 10:1.

5. A process in accordance with claim **1** wherein

said hydrogenating temperature is from about 200° F. to about 600° F. and said hydrogenating total pressure is from about 400 to about 800 p.s.i.g.; said reforming temperature is from about 900° F. to about 1,000° F. and said reforming total pressure is from about 300 about 700 p.s.i.g.; and said hydrodealkylating temperature is from about 1,140° F. to about 1,350° F. and said hydrodealkylating total pressure is from about 350 to about 600 p.s.i.g.

6. A process in accordance with claim **1** which includes separating hydrogen sulfide formed in the hydrogenating step from the effluent of said hydrogenating step by contacting said effluent with a material selective for the removal of hydrogen sulfide.

7. A process in accordance with claim **1** which includes hydrogenating said effluent from a hydrodealkylating step under hydrogenating conditions including a temperature of

about 200° F. to about 700° F. in the presence of a hydrogenating catalyst to saturate olefins produced in said hydrodealkylation step.

8. A process for increasing the benzene yield from a hydrocarbon material comprising generally from about six to about 10 carbon atoms per molecule obtained as the byproduct from the pyrolysis cracking of hydrocarbons to produce primarily ethylene which comprises:

hydrogenating said hydrocarbon material in the presence of hydrogen generated within said process under hydrogenating conditions including a hydrogenating temperature and a hydrogenation pressure in the presence of a hydrogenation catalyst to saturate olefinic hydrocarbons;

reforming said hydrocarbon material under reforming conditions including a reforming temperature higher than said hydrogenating temperature and a reforming pressure lower than said hydrogenating pressure in the presence of a reforming catalyst to increase aromatic content of said hydrocarbon material and to produce hydrogen;

hydrodealkylating said hydrocarbon material in the presence of hydrogen from said reforming step under hydrodealkylating conditions including a temperature higher than said reforming temperature and a pressure lower than said reforming pressure to hydrodealkylate aromatic compounds and also crack remaining nonaromatic hydrocarbons including those boiling close to benzene to obtain an effluent comprising benzene and hydrogen;

recycling said hydrogen to said hydrogenation step; and

recovering benzene from said effluent by distillation.

9. A process in accordance with claim 8 wherein

said hydrogenating temperature is from about 125° F. to about 800° F; said reform temperature is from about 850° F. to about 1,100° F.; and said hydrodealkylating temperature is from about 1,100° F. to about 1,400° F.

10. A process in accordance with claim 8 wherein

said hydrogenating total pressure is from about 300 to about 1,000 p.s.i.g.; said reforming total pressure is from about 150 to about 700 p.s.i.g.; and said hydrodealkylating total pressure is from about 300 to about 1,000 p.s.i.g.

11. A process in accordance with claim 8 wherein

said hydrocarbon mol ratio of about 1:1 to about 10:1; said reforming conditions includes a hydrogen to hydrocarbon mol ratio of about 1:1 to abut 10:1; and said hydrodealkylating conditions includes a hydrogen to hydrocarbon mol ratio of about 3:1 to about 10:1.

12. A process in accordance with claim 8 wherein

said hydrogenating temperature is from about 200° F. to about 600° F. and said hydrogenating total pressure is from about 400 to about 800 p.s.i.g.; said reforming temperature is from about 900° F. to abut 1,000° F. and said reforming total pressure is from about 300 to about 700 p.s.i.g.; and said hydrodealkylating temperature is from about 1,140° F. to about 1,350° F. and said hydrodealkylating total pressure is from about 350 to about 600 p.s.i.g.

13. A process in accordance with claim 8 which includes separating hydrogen sulfide formed in the hydrogenating step from the effluent of said hydrogenating step by contacting said effluent with a material selective for the removal of hydrogen sulfide.

14. A process in accordance with claim 8 which includes hydrogenating said effluent from the hydrodealkylating step under hydrogenating conditions including a temperature of about 200° F. to about 700° F. in the presence of a hydrogenating catalyst to saturate olefins produced in said hydrodealkylation step.

15. A process for increasing the benzene yield from a hydrocarbon material comprising generally about six to 10 carbon atoms per molecule obtained from a byproduct of the pyrolysis cracking of hydrocarbon to produce primarily ethylene which comprises:

hydrogenating said hydrocarbon material in the presence of hydrogen generated within said process under hydrogenating conditions including an average hydrogenating temperature of about 650° F. and a hydrogenating pressure of about 800 p.s.i.g. in the presence of a supported hydrogenating catalyst selected from the group consisting of metal from Group VI and the Iron Group metals from Group VIII of the Periodic table, their oxides and sulfides to saturate olefinic hydrocarbons;

reforming aid hydrocarbon material reforming conditions including an average reforming temperature of about 925° F. and a reforming pressure of about 500 p.s.i.g. in the presence of a reforming catalyst selected from the group consisting of metals from Group VI and metals from Group VIII of the Periodic table, their oxides and sulfides supported on a base to increase aromatic content of said hydrocarbon material and to produce hydrogen;

hydrodealkylating said hydrocarbon material in the presence of hydrogen from said reforming step under hydrodealkylating conditions including an average temperature of about 1,250° F. and a pressure of about 450 p.s.i.g. to hydrodealkylate aromatic hydrocarbons and also crack remaining nonaromatic hydrocarbons including those boiling close to benzene to obtain an effluent comprising benzene and hydrogen;

recycling said hydrogen to said hydrogenating step; and

removing benzene from said effluent by distillation.

16. A process in accordance with claim 15 which includes separating hydrogen sulfide formed in the hydrogenating step from the effluent of said step by contacting said effluent with an adsorbent comprising zinc oxide.

17. A process in accordance with claim 15 which includes hydrogenating said effluent from the hydrodealkylating step under hydrogenating conditions including a temperature of about 200° F. to about 700° F. and in the presence of a hydrogenating catalyst selected from the group consisting of metals from Group VI and the Iron Group metals from Group VIII of the Periodic table, their oxides and sulfides supported on a base to saturate olefins produced in said hydrodealkylating step.

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(5/69) UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,625,879 Dated December 7, 1971

Inventor(s) William A. Horne and Ronald V. Luzar

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 11, after "subject" insert --process-- .

Column 4, line 58, after "then" delete "from" and insert --compressed-- .

Column 9, line 44, claim 11, after first "said" insert --hydrogenating conditions includes a hydrogen to-- .

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents