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CONVERSION OF HYDROCARBONS

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This invention relates particularly to the conversion of olefinic hydrocarbons into aromatic hydrocarbons.

It is especially concerned with the use of composite catalytic materials which foster simultaneously two types of reactions so that a conversion ordinarily requiring two operations is effected in a single operation.

The present invention is closely related to the motor fuel problem in that it makes possible the conversion of normally gaseous olefin hydrocarbons into substantial yields of gasoline boiling range liquids which have a relatively high antiknock value, chiefly on account of their high content of aromatics although other liquid products concurrently produced also contribute to this property.

Extensive researches have shown that the property of a hydrocarbon which permits it to burn in an internal combustion engine cylinder without detonation effects under conditions of relatively heavy loads and low engine speeds is definitely associated with its molecular structure. To recount briefly the results of these researches it has been shown that in general hydrocarbons of "more condensed" structure show less tendency to detonate or "knock," and that in general compounds of any structure show lower knocking tendencies when there are double bonds between carbon atoms than when the compound is completely saturated with hydrogen. Thus the hydrocarbons with greatest knocking tendencies are the straight chain paraffin hydrocarbons of normal structure. The isomeric forms have less tendency to knock and in general the mono-olefins and di-olefins knock less than the corresponding paraffins. Cycling of aliphatic chains also reduces knocking tendencies, and according to this rule hexamethylene shows less tendency to knock than hexene which has the same carbon to hydrogen ratio. The progressive dehydrogenation of hexamethylene (or cyclohexane) results in increasing antiknock rating until benzol is reached. In general then the compounds of highest antiknock rating are the isomeric aliphatic hydrocarbons of condensed structure and the aromatic.

In the cracking of hydrocarbon oils such as petroleum fractions for the production of gasoline there is a considerable incidental production of fixed gases which include ethylene, propylene, and the butylenes as constituents thereof. Processes are in vogue at the present time for the utilization of the three and four carbon atom olefins to produce increased yields of gasoline boiling range liquids by polymerizing these so-called higher olefins either thermally or catalytically and either in admixture with the other less reactive gases or after segregation of the higher olefins by fractionation or solvent extraction. It is to be noted, however, that very little use has been made of the ethylene production for the manufacture of gasoline even though this compound is generally produced in an amount equalling the total production of propylene and butylenes. As a rule when ethylene polymerizes under heat or a combination of heat and catalyst, it has a tendency to form high molecular weight compounds of the nature of lubricating oils rather than to yield polymers of lower molecular weight boiling within the gasoline range. In other words the reaction is difficult to control and at the present time the ethylene content of cracked gases is utilized principally as a fuel along with the other less reactive constituents of the gas mixtures.

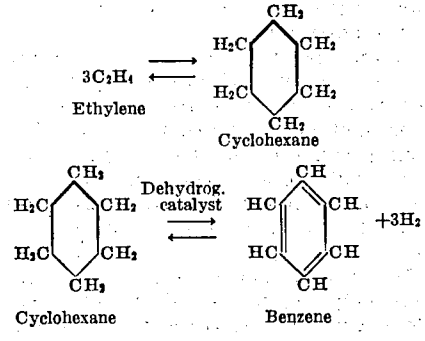
In one specific embodiment the invention comprises simultaneous polymerization and dehydrogenation of ethylene and/or other normally gaseous olefin hydrocarbons to produce gasoline boiling range liquids having relatively high antiknock value due to their high aromatic content, while utilizing catalysts which are active in splitting off hydrogen from saturated cyclic hydrocarbons.

In a further specific embodiment of the invention polymerizing catalysts may be employed along with the dehydrogenating catalysts to accelerate the polymerization reaction.

As already intimated in the preceding paragraph, the present invention has for its principal feature the utilization of concurrent polymerization and dehydrogenation reactions to effect the production of aromatics and other high antiknock cyclic hydrocarbons from normally gaseous olefins and particularly ethylene. Effective dehydrogenating catalysts which may be employed include the metals of the eighth group of the periodic table including iron, nickel, and cobalt, and the noble metals platinum, and palladium, although it is within the scope of the invention to utilize any catalyst which has been found effective in splitting off hydrogen from naphthenes or other saturated cyclic hydrocarbons to form corresponding aromatics without substantial change in configuration of the molecules. Those familiar with catalysis will realize that not all dehydrogenation catalysts which may be employed alternatively will be exactly equivalent in their actions. As a rule nickel is

a cheap and readily available catalyst and one which is succiently effective as will be shown in later examples. The process may be operated under temperature and pressure conditions favoring polymerization without the employment of polymerizing catalysts in connection with the dehydrogenating catalysts, although the invention also includes the use of polymerization catalysts which are found to operate effectively in conjunction with certain of the dehydrogenation catalysts. For example, heavy metal salts such as aluminum chloride and zinc chloride may be employed with the majority of the dehydrogenating catalysts already mentioned and also phosphoric acid either as a liquid or as a constituent of solid granular masses produced by primarily incorporating a liquid phosphoric acid with an inert carrier and then calcining to effect partial dehydration. It is to be noted again that different combinations of polymerizing and dehydrogenating catalysts will have different effects upon the course of the joint reactions which are not exactly predictable from the separate effects of the two types of catalysts on the same reaction. It is again within the scope of the reaction to employ any polymerizing catalyst along with any dehydrogenating catalyst when the combination produces beneficial results in the production of aromatics from the normally gaseous olefins.

The type of reaction which is brought about according to the present process is typified by the following structural equations although it is not intended to infer that the reaction mechanism indicated is a complete explanation of the observed results since the difficulties of proving reaction mechanisms are well-known to chemists and sufficient analytical work has not been done in the present instance to entirely substantiate the suggested equations.



In the above equation two molecules of propylene may be substituted for three of ethylene, and a similar equation can be developed wherein butylenes are employed as starting material. In other words, the ethylene shown typifies any other of the normally gaseous olefins and the cyclo-hexane and benzene typify various cycloparaffins and homologs of benzene respectively.

The process may be employed on ethylene or individual gaseous olefins produced from any source in the pure state or admixed with other hydrocarbons. Thus the reactions may be brought about on the relatively light gas mixtures separated as overhead during the fractionation of cracking plant gases to produce so-called stabilizer overhead fractions consisting principally of three and four carbon atom hydrocarbons. Obviously the reactions will be more definite when relatively pure compounds are employed so that the equations correspond more nearly to that shown above. However, with suitable modifications of temperature, pressure and time of reaction along with selection of more or less active catalyst composites, substantial yields of aromatics may be produced from any olefin-containing gas mixture.

The process may be operated by batch or continuous methods with adjustment of operating conditions to produce the best results. In batch operations the mixed catalytic materials may be placed in pressure vessels and normally gaseous olefins alone or in admixture with other hydrocarbons or relatively inert gases may be introduced under suitable pressure and temperature conditions for effecting the reactions. Continuous operations may be effected by passing special compounds as ethylene or olefin-containing gas mixtures through granular catalytic materials containing dehydrogenating catalysts or if found desirable, combinations of polymerizing and dehydrogenating catalysts, at rates corresponding to the best production of aromatics and other compounds of high antiknock value.

The temperatures employed in the present process are of relatively low order and in general do not exceed 350° C. The pressure employed will depend upon whether polymerization is effected thermally or catalytically. In the case of strictly thermal polymerization, pressures as high as 100 atmospheres may be employed while considerably lower pressures may suffice in cases where polymerizing catalysts are used such as the solid phosphoric acid catalyst mentioned.

The following examples are given to indicate the character of the results produced in the operation of the process of the invention although its generally broad scope is not to be subjected to corresponding limitations.

Example I

In this case ethylene was converted into substantial yields of aromatic hydrocarbons in two ways to show the effect of the joint use of polymerizing and dehydrogenating catalysts. In a primary run liquid orthophosphoric acid was placed in a steel pressure vessel and ethylene was introduced at a temperature of 300° C. until a pressure of approximately 60 atmospheres was attained. The reaction temperature was maintained at 300° C. by proper cooling, but the pressure rose to about 100 atmospheres before the reaction was complete and then fell as the ethylene was polymerized. In this run there was a production of 80% of liquid hydrocarbon material by weight of the ethylene produced, this liquid containing 62% of hydrocarbons boiling up to 225° C. Analyses indicated that there was less than 1% aromatic hydrocarbons in this gasoline fraction.

In a second run conditions and amounts were duplicated except that a mixture of nickel and nickel oxide in powdered form was added to the liquid phosphoric acid. In this case the 80% liquid yield contained 65% by volume of gasoline boiling range fraction up to 225° C. and analyses indicated the presence of 23% of aromatic hydrocarbons in this gasoline.

Example II

Ethylene was added to a pressure vessel maintained at a temperature of 320° C. in the absence of any catalytic material. There was a 50% yield of liquid which contained 24% of gasoline boiling range fractions, these fractions being completely free from aromatics. When nickel was added to the pressure vessel and the experiment repeated the 50% liquid yield was 35% gasoline boiling

range fractions and contained 32% of aromatics.

I claim as my invention:

1. A process for the production of substantial yields of benzene from ethylene which comprises subjecting said ethylene to simultaneous contact with granular catalytic material comprising essentially a phosphoric acid and a metal of the eighth group of the periodic table at a polymerizing temperature.

2. A process for the production of aromatic hydrocarbons which comprises contacting normally gaseous olefins at polymerizing temperature with a granular catalyst comprising a phosphoric acid and a metal of the eighth group of the periodic table.

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