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**CATALYTIC DISPROPORTIONATION OF  
PARAFFINIC HYDROCARBONS**

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4 Claims

**ABSTRACT OF THE DISCLOSURE**

A Group VIII catalytic composite, preferably nickel, is utilized in disproportionating paraffinic hydrocarbons. Products of the reaction, effected at a temperature of from 150° C. to about 300° C., include aromatic hydrocarbons and paraffins having at least one more carbon atom per molecule than the paraffin employed as the charge stock.

**APPLICABILITY OF INVENTION**

Disproportionation of relatively low molecular weight paraffinic hydrocarbon, having no more than five carbon atoms in a single chain per molecule, in accordance with the present invention, results in the production of heavier paraffins, aromatics and some lighter paraffins. Thus, normal pentane can be disproportionated to produce n-hexane, n-heptane, benzene, toluene and C<sub>8</sub> aromatics, as well as butanes. Where the charge stock predominates in higher molecular weight paraffins, the product will, correspondingly, contain significant quantities of alkyl-substituted aromatics—i.e. xylenes and ethylbenzene from dimethylpentanes.

Thus, the present invention provides a relatively simple catalytic route to the production of valuable hydrocarbons from less valuable hydrocarbons. As will be recognized by those cognizant of petroleum refining techniques, and the various products derived therefrom, butanes find widespread utility as the starting material for isobutylene, whereas aromatics, especially benzene, toluene and the mixed xylenes, are often employed for their motor fuel blending value, as industrial solvents and petrochemical intermediates. Since there currently exists an overabundance of relatively low molecular weight normally liquid paraffins having from five to seven carbon atoms per molecule, the conversion thereof to aromatics and butanes affords an additional tool for further enhancing the value of products derived from petroleum oils.

The mechanism by which these reactions occur appears to be one in which fragments are removed from adsorbed reactant molecules, which fragments add to other adsorbed reactant molecules to yield larger molecules. The reactive fragments are readily scavenged by adsorbed co-reactants such as hydrogen, hydrazine, hydrogen peroxide, etc., with resulting formation of other hydrocarbons, amines, and alcohols, respectively. Hence discovery of this ability of hydrocarbons to fragment in the manner described has led to the potential formation of even more valuable organic compounds containing inorganic substituents starting only with hydrocarbons and reactive inorganic reagents.

In the presently disclosed invention, it is observed that as soon as carbon chains of six or more units are formed, the compounds have a strong tendency to dehydrocyclize to form aromatic compounds; the latter tendency increases with carbon chain length.

**OBJECTS AND EMBODIMENTS**

An object of the present invention is to effect the disproportionation of paraffinic hydrocarbons to produce

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paraffins having more and less carbon atoms per molecule.

A corollary objective is to dehydrocyclize normal paraffins containing no carbon chain longer than five carbon atoms to produce aromatic hydrocarbons.

Specifically, the present invention is intended to produce butanes, benzene, toluene, mixed xylenes and normal hexane from normal pentane.

In one embodiment, therefore, the present invention involves a process for disproportionating a paraffinic hydrocarbon which comprises contacting said paraffinic hydrocarbon, at a temperature above about 100° C. with a catalytic composite of at least one Group VIII metallic component containing adsorbed hydrogen, and recovering a hydrocarbon having a greater number of carbon atoms per molecule.

A specific embodiment is directed toward a process for disproportionating pentane which comprises contacting pentane, at a temperature of from about 150° C. to about 300° C. with a catalytic composite containing nickel and adsorbed hydrogen, and recovering a product effluent containing aromatic hydrocarbons and paraffins having more than five carbon atoms per molecule.

Other objects and embodiments will become evident from the following description of the present invention.

**SUMMARY OF INVENTION**

As hereinbefore set forth, the present invention involves disproportionation of paraffinic hydrocarbons, and particularly those with no carbon chain of more than six atoms, and especially of five atoms or less, the latter including butane, pentane, iso-hexanes, and dimethylpentanes. The products of the reaction include paraffins having one less carbon atom per molecule, paraffins having at least one more carbon atom per molecule and, in the case of pentane and/or iso-hexanes, significant quantities of aromatic hydrocarbons. With dimethylpentanes, and higher paraffins, the aromatics formed are alkyl-substituted.

The process is conducted catalytically at a temperature above about 100° C., and preferably at a temperature in the range of from 150° C. to about 300° C. The LHSV (liquid hourly space velocity) is generally above 0.5, and most often in the range of 1.0 to about 5.0. In a specific example which follows, it will be noted that the higher space velocities appear to favor the formation of aromatic hydrocarbons from normal pentane. The preferred catalytic composite contains nickel in amounts of from 25.0% to 75.0% by weight, calculated as the element, combined with a suitable carrier material including kieselguhr, alumina, zirconia, silica, boria, magnesia, other refractory oxide material and mixtures of two or more, etc. Although nickel is particularly preferred, other Group VIII metals may be employed, including cobalt, iron, platinum, osmium, iridium, rhodium, palladium, and ruthenium. These are not, however, as successful in promoting aromatization; that is, the selectivity of conversion with respect to aromatic hydrocarbons is significantly improved through the use of nickel as the active catalytic component.

An advantage of the present process resides in operability at extremely low pressures including atmospheric. However, it is generally advisable, to facilitate flow of material to impose a pressure up to about 100 p.s.i.g. on the system.

An essential feature of the present invention involves the use of a catalyst containing adsorbed hydrogen. That is, while added or recycle hydrogen in small amounts offers no adverse effects, its utilization does not particularly enhance the results obtained. The catalyst is caused to adsorb hydrogen, prior to commencing operation, by pretreatment in an atmosphere thereof, at a temperature

above the maximum process temperature of 300° C. This catalyst pretreatment, to absorb hydrogen, is, therefore, effected at a temperature of from 300° C. to about 500° C.

#### EXAMPLES

The following examples are herein presented for the purpose of illustrating the method of the present invention, as well as the unusual benefits to be afforded through the utilization thereof. In these examples, the use of specific reactants, catalyst, and/or conditions, is not intended to limit the present invention beyond the scope and spirit of the appended claims.

##### Example I

Normal-pentane was injected into a hydrogen peroxide-saturated carrier gas stream over a rhodium-alumina catalyst disposed in a microreactor system coupled to a gas chromatograph. At a temperature of 540° F., analysis indicated about 10.0% conversion to propyl and butyl alcohols in an 18-second residence time.

During a series of operations, in which the charge stock was normal pentane and the carrier gas was either helium or hydrogen, designed to determine the effects of various process variables upon product distribution and conversion, the criteria being the removal of not more than one carbon atom, it was observed that the chromatographic analyses were indicating minute (or trace) quantities of aromatic hydrocarbons. The difficulties attendant duplication of results, in the microreactor-chromatographic system, prompted a "scale-up" to a 50.0-cc. capacity system accompanied by continuous n-pentane flow through the catalyst.

##### Example II

The operations herein described were conducted in a glass reactor contained in a 12-inch vertical swing furnace. The catalyst capacity of 50-cc. was disposed in the center four inches. Charge was pumped downflow over the catalyst by means of a bellows pump, and the effluent collected in a wet-ice trap and gas-collecting bottle. The catalyst bed temperature was obtained through the use of a thermocouple well inserted in the center of the bed. Unless otherwise stated, the catalyst was pretreated with hydrogen at a temperature of 430° C. (806° F.). The normal pentane, and in some instances normal hexane, flowed over the catalyst at a rate which was varied from 0.5 to 2.0 cc./minute; catalyst bed temperatures were varied from 230° C. (446° F.) to 300° C. (572° F.). The effluent from the wet-ice trap and gas-collecting bottle was analyzed by Gas-Liquid Chromatographic techniques; aromatics were more specifically separated by a BTX (benzene-toluene-xylene) GLC analysis.

With a commercially available nickel-kieselguhr catalyst (approximately 60.0% by weight of nickel), charging n-pentane at a rate of 0.5 cc./minute (an LHSV of 0.6) and a temperature of 250° C. (482° F.) resulted in a conversion of 44.7% by weight. The aromatic yield was 3.3% by weight, and n-hexane was 0.3% by weight; increasing the charge rate of 1.6 cc./minute (an LHSV

of 1.9), decreased the conversion to 11.7% by weight, but increased the aromatic yield to 7.5% by weight and the n-hexane yield to 0.6% by weight. The yield of products containing less than five carbon atoms was virtually equally divided, on a mole basis, between methane and butanes.

At a lower temperature for hydrogen pretreatment, 370° C. (698° F.), and an LHSV of 1.8, the nickel-kieselguhr catalyst resulted in a conversion of 10.0% by weight at 250° C. The aromatic yield was 7.3% by weight and n-hexane yield was 0.4% by weight.

A hydrogen pretreated catalyst of 7.0% by weight of nickel on alumina, at a temperature of 249° C. and an LHSV of 1.6, resulted in a conversion of only 0.21 mol percent, of which 86.8% were hydrocarbons containing less than five carbon atoms.

With a charge of n-hexane; at a rate of 1.5 cc./minute and a temperature of 251° C., the conversion was 15.9% by weight, and the aromatic and n-heptane yields were 33.7 and 2.4 mol percent respectively. The aromatic product included substantial amounts of toluene, xylenes and ethylbenzene in addition to a major amount of benzene.

The foregoing specification, and the illustrative examples, is believed to indicate the means by which our invention is conducted and the benefits to be afforded through the use thereof.

We claim as our invention:

1. A process which comprises contacting a paraffinic hydrocarbon feedstock whose longest carbon chain contains no more than five carbon atoms, at a temperature below about 300° C. with a catalytic composite containing at least one Group VIII metallic component, said catalytic composite containing adsorbed hydrogen, whereby a paraffinic hydrocarbon containing a greater number of carbon atoms per molecule than said feedstock is obtained.

2. A process according to claim 1 in which the Group VIII metallic component is nickel.

3. The process of claim 1 further characterized in that said temperature is from about 150° C. to about 300° C.

4. A process for disproportionating pentane which comprises contacting pentane, at a temperature of from about 150° C. to about 300° C., with a catalytic composite containing nickel and adsorbed hydrogen, and recovering a product effluent containing aromatic hydrocarbons and paraffins having more than five carbon atoms per molecule.

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