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## TREATMENT OF HYDROCARBONS

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This invention relates particularly to the treatment of paraffinic hydrocarbons and may be applied to treatment of individual paraffins, to mixtures of paraffin hydrocarbons, or to hydrocarbon mixtures containing material percentages thereof, such as fractions of petroleum.

It is more specifically concerned with a process whereby paraffinic hydrocarbons may be dehydrogenated to produce mono-olefinic or di-olefinic hydrocarbons of substantially similar structure.

Dehydrogenation of paraffin hydrocarbons is practiced to obtain more reactive compounds which can be used as a basis for making a large number of chemical derivatives useful in the arts. The normally gaseous mono-olefinic hydrocarbons are readily polymerizable either by thermal-catalytic processes to produce liquid mono-olefins of gasoline boiling range having high anti-knock value, and higher molecular weight olefins are similarly polymerizable into synthetic lubricating oils having high viscosities and viscosity indices. Such higher molecular weight olefins can be made by the dehydrogenation of relatively high molecular weight liquid and solid paraffins.

Cracked gases produced incidental to cracking operations with the primary object of producing gasoline contain considerable quantities of three and four carbon atom hydrocarbons both paraffinic and olefinic and it is current practice to polymerize the olefinic content to augment the yield of gasoline from the cracking process, leaving a residue of propane and butane which must be thermally treated at relatively high temperatures and pressures to produce further yields of gasoline unless the compounds are dehydrogenated to their more reactive olefinic counterparts. The present invention is particularly applicable to the treatment of these gaseous residual paraffins remaining after polymerization of the olefins present in cracked gases although it is also applicable to similar paraffinic fractions from natural gases or refinery gases produced incidental to the storage and primary distillation of petroleums.

In one specific embodiment the present invention comprises the manufacture of olefinic hydrocarbons by subjecting the vapors of paraffinic hydrocarbons mixed with regulated amounts of sulfur vapors to elevated temperatures adequate to cause the formation of hydrogen sulfide. Suitable solid catalysts or catalytic materials may be employed if desired such as, for example, those of a relatively refractory character, including silicates, aluminates, etc.

The reaction of dehydrogenation, brought about by the action of sulfur on paraffins, is to some extent an equilibrium reaction although high yields of olefins are obtainable in a single pass through a heating zone with a moderate excess of sulfur over that equivalent to the hydrogen extracted to form hydrogen sulfide. The temperatures preferably employed are within the approximate range of 550–650° C. The pressure has substantially no independent effect on the reaction and any time may be employed which is necessary to dehydrogenate to a desired extent.

In the operation of the process any method may be employed to obtain a mixture of paraffin hydrocarbons and sulfur vapor in the proper proportion. For example, normally gaseous paraffins may be preheated and passed through molten sulfur in order to volatilize a sufficient proportion thereof to accomplish the dehydrogenation reactions in a succeeding reactor. Similarly normally liquid hydrocarbons may be vaporized and the vapors passed through molten sulfur at a temperature and rate corresponding to the volatilization of the required amount of sulfur. If desired preheated paraffinic hydrocarbons and sulfur vapor may be injected into a reaction zone which may comprise any series of tubes or chambers which will provide time for and expedite the desired reactions.

The hydrogen sulfide produced in the reaction may be removed from the products by absorption by any of the accepted methods such as, for example, those using sodium bicarbonate or those employing selective solvents, and in a completely cyclic process, hydrogen sulfide may be processed for the recovery of the sulfur and the sulfur reused. The well-known reaction between hydrogen sulfide and sulfur dioxide may be employed to regenerate the sulfur. With proper proportioning very little sulfur is fixed as mercaptans or other hydrocarbon sulfur derivatives, but when this occurs any liquid products of the dehydrogenating reactions may be washed with suitable reagents to purify them before they are used.

The following examples are given to show the type of results obtainable when utilizing the

process in practice, although the data given are not intended to unduly limit the invention's proper scope.

*Example I*

N-butane was bubbled through molten sulfur maintained at about 450° C. (boiling point of sulfur is 444.6° C., corrected). The n-butane was thus saturated with sulfur vapor at this temperature and was then passed over a catalyst consisting of alumina promoted by sodium aluminate at a temperature of 600° C. and atmospheric pressure. The products were cooled and passed through caustic soda solution to remove hydrogen sulfide and the following table shows the composition of the gas mixture with respect to its unsaturated content in the run described and in a single blank run made without the addition of sulfur:

| | Run with sulfur (temp. of molten sulfur, 450° C.) | Run without sulfur (blank) |
|---|---|---|
| Propene and butenes percent by volume | 16.3 | 11.2 |
| Ethylene do | 4.9 | 4.8 |
| Total unsaturated hydrocarbons by bromine percent by volume | 22.0 | 17.3 |

*Example II*

N-butane was again bubbled through sulfur maintained at a temperature of 475° C. and the gas saturated with sulfur vapor at this temperature was passed through a tube containing no catalyst at a temperature of 600° C. The products of the reaction were again scrubbed with caustic soda solution to remove hydrogen sulfide and the composition of the gaseous products with respect to olefins is shown in the following table:

| | Run with sulfur (temp. of molten sulfur, 475° C.) | Run without sulfur (blank) |
|---|---|---|
| Propene and butenes percent by volume | 26.2 | 12.2 |
| Ethylene do | 8.0 | 7.4 |
| Total unsaturated hydrocarbons by bromine percent by volume | 34.0 | 19.6 |

It will be seen from the above data that there is a distinct increase in the yield of olefins when sulfur vapor is present as compared with the yields obtained under the same conditions in the absence of sulfur vapor. The most noticeable increases are observed in yields of three and four carbon atom olefins, the amount of ethylene produced remaining approximately constant in both runs.

We claim as our invention:

1. A process for producing olefins from paraffins which comprises passing the paraffins with sulfur vapor and under dehydrogenating conditions over a catalyst comprising alumina promoted by sodium aluminate.

2. A process for converting normally gaseous paraffins into their corresponding olefins which comprises passing the paraffins with sulfur vapor and under dehydrogenating conditions over a catalyst comprising alumina promoted by sodium aluminate.

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