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PRODUCTION OF HYDROCARBONS OF THE GASOLINE TYPE

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The present invention relates to the manufacture and production of saturated hydrocarbons of the gasoline type by catalytic hydrogenation of hydrocarbons having a boiling range similar to that of gasoline and which are obtained by polymerisation of unsaturated hydrocarbons.

The term "polymerisation" when herein employed is intended to include both normal polymerisation and interpolymerisation. Normal polymerisation means the formation of more complex molecules from simple molecules of one substance, the polymerisation product having the same percentage composition as that of the initial material. Interpolymerisation means the formation of more complex molecules from simple molecules of two or more substances, the interpolymerised molecules having the same percentage composition as the sum of the constituent molecules. For example, in the case of isobutylene ($(CH_3)_2C=CH_2$), di-isobutylene and triisobutylene are polymerisation products; on the other hand an interpolymerisation product of isobutylene and of α-butylene may, for example, have the formula

$$(CH_3)_3—C—CH=CH—CH_2—CH_3$$

In the catalytic hydrogenation of unsaturated hydrocarbons having a boiling range similar to that of gasoline, and which are obtained by polymerisation of unsaturated hydrocarbons of low boiling point, the initial materials may be passed together with hydrogen or gases containing sufficient free hydrogen over stationary catalysts. Low yields of the desired saturated hydrocarbons having a boiling range similar to that of gasoline are then, however, frequently obtained when the hydrogenation is carried out at high temperatures, because splitting of bonds between carbon atoms and/or depolymerisation occurs, with the result that hydrocarbons are formed the molecules of which contain a smaller number of carbon atoms than the initial polymerisation products. Moreover, polymerisation and/or condensation products of high molecular weight are sometimes formed during the hydrogenation, the yield in hydrocarbons having a boiling range similar to that of gasoline being thus lowered and the activity of the stationary catalysts weakened, due to the deposition of said products of high molecular weight upon the catalysts.

In order to prevent splitting and depolymerisation, it has been proposed to carry out the catalytic hydrogenation at low temperatures, but in this case products of high molecular weight are sometimes formed in increased amounts which settle on the stationary catalysts, thus diminishing their activity and very considerably lowering the yield of the desired saturated hydrocarbons.

I have now found that the production of saturated hydrocarbons of the gasoline type from hydrocarbons having a boiling range similar to that of gasoline, that means boiling within the range between about 30° and about 210° centigrade, obtained by polymerising unsaturated aliphatic hydrocarbons, which expression when herein employed is intended to include unsaturated aliphatic hydrocarbons containing one or more unsaturated bonds between carbon atoms, more particularly double bonds, especially monoolefines, or mixtures containing such unsaturated hydrocarbons, by catalytic hydrogenation with an added gas comprising free hydrogen in the presence of a stationary hydrogenation catalyst is effected with particularly high yield of the desired products by contacting the catalyst with water vapour.

In said operation the reactants will usually be in the vapour phase.

The water vapour may be present in, or supplied to, the reaction space in the course of the hydrogenation process either continuously or intermittently, or alternately water vapour may be continuously present in the reaction space, if desired in varying amounts and the supply of one or more of the reagents, in particular of polymerised hydrocarbon may be reduced or shut off from time to time.

The water vapour is usually introduced as such into the reaction space either alone or together with one or more of the reagents. Where convenient liquid water may, however, be introduced as such or in addition to steam, which water is converted into water vapour in the course of the process.

When water vapour is present in the reaction space in accordance with the present invention during the hydrogenation reaction proper its amount is usually small, for example, a few per cent by weight of the material to be hydrogenated. Suitable amounts of water are for instance 5, 3, 2 or 1 per cent, although larger amounts up to for example 10 per cent or smaller amounts such as 0.5 per cent may be employed.

When water vapour is intermittently present, the supply of material to be hydrogenated may, if desired, be discontinued and also that of hydrogenating gases during the introduction of water vapour. Such a procedure will be used when, after hydrogenating for some time in the absence of water vapour or in the presence of insufficiently

effective amounts of water vapour, the activity of the catalyst begins to fall below the desired degree. Steam is then passed either alone or together with the hydrogenating gases over the catalyst at elevated temperature, for example, the reaction temperature, the original activity of the catalyst being thus restored. The cycle of operations may be constantly repeated.

The process in accordance with the present invention allows of preparing saturated aliphatic hydrocarbons of a boiling point range similar to that of gasoline and having, more particularly, a high octane number with a very high, and frequently substantially quantitative yield, due to the avoidance of losses occurring by the aforesaid splitting, depolymerisation and/or formation of high molecular compounds or due to the reduction of activity of the catalyst, from polymerisation products obtained, for example, from cracking gases and like mixtures containing unsaturated aliphatic hydrocarbons of low boiling points, if desired in admixture with saturated hydrocarbons which do not participate in the polymerisation.

The present invention is of particular importance for the preparation of iso-octane (trimethylpentane) from di-isobutylene obtained by polymerising isobutylene.

The polymerisation of the unsaturated aliphatic hydrocarbons may be carried out by conventional methods. For example, the initial unsaturated monomolecular aliphatic hydrocarbons such as propylene, α-butylene, β-butylene, isobutylene, amylenes or mixtures thereof, may be absorbed in concentrated inorganic acids such as phosphoric and, more particularly, sulphuric acid, the resulting solution being then heated to effect polymerisation. The polymerisation may also be carried out without absorption agents by heating and/or by silent electric discharges. Also other polymerisation agents such as porous substances, for example, floridin, anhydrous zinc chloride, ferric chloride, aluminum chloride and like metal halides may be employed as polymerising agents, if desired suspended in anhydrous organic solvents, but the use of inorganic acids is preferred. Dimers, trimers or even higher polymers may be formed, the highest polymer employed will, however, usually be a trimer since it is the purpose of the present invention finally to produce saturated aliphatic hydrocarbons of the boiling range of gasoline.

The process in accordance with the present invention is usually carried out by continuously passing the said polymerisation products in the vaporous state together with hydrogen and water vapour at elevated temperatures, preferably below about 350° centigrade, in particular between 200° and 300° centigrade over stationary hydrogenation catalysts, more particularly those which are immune to poisoning by sulphur. Preferred catalysts of this type comprise oxides or sulphides of the metals of group 6 of the periodic table, such as tungsten and molybdenum. Mixtures of catalysts may also be employed, for example, tungsten and/or molybdenum compounds in admixture with zinc oxide, magnesia or salts of phosphoric acid, silicic acid, boron salts and the like. Other hydrogenation catalysts may, however, also be employed in some instances. The catalysts may, when desirable, be supported by carriers and activated by the addition of promoters. Examples of suitable carriers are granulated active carbon, pumice, clay, bleaching earths, such as bentonite and the like.

The hydrogenation is usually carried out under pressure, say pressures of more than 50 atmospheres, for example, pressures of 100, 200, 300, 500 atmospheres or more, but lower pressures for example 40 atmospheres or atmospheric pressure may also be employed.

Pure or technically pure hydrogen may be used as hydrogenating gas in accordance with the present invention; the said gases may contain, in admixture with the free hydrogen, convenient amounts of other gases such as nitrogen, hydrogen sulphide, carbon monoxide, methane and the like.

When working in accordance with the present invention the stationary catalysts are not contaminated by the deposit of polymerisation products of high molecular weight even if the reaction temperature is comparatively low within the given range. On the other hand depolymerisation and splitting are substantially avoided even if the hydrogenation is carried out at comparatively high temperatures.

The following example will further illustrate how the invention may be carried out in practice, but it should be understood that the invention is not limited to said example.

Example

A product obtained by polymerising iso-butylene and substantially consisting of di-isobutylene is continuously passed at 260° centigrade with an addition of 1 per cent by weight of water vapour and an excess of free hydrogen with a throughput of 1.2 litres of di-isobutylene per litre of catalyst per hour under a pressure of 100 atmospheres over a catalyst obtained by impregnating granulated active carbon with an acidified solution of ammonium molybdate and then drying it. A product consisting practically entirely of iso-octane is obtained.

Under identical conditions, but in the absence of water vapour, iso-octane is produced in a yield of only 80 per cent by weight. 9 per cent by weight of di-isobutylene remains unconverted, whilst 11 per cent by weight of iso-butane is formed as a result of depolymerisation.

What I claim is:

1. A process for the non-destructive catalytic hydrogenation of olefins which comprises passing vapors of olefinic hydrocarbons, having a boiling point within the gasoline boiling range and formed by the polymerization of mono-olefins, together with water vapor and a gas containing free hydrogen in contact with a hydrogenation catalyst.

2. A process as in claim 1 wherein the water vapor is present in an amount of between about ½ and about 10% by weight of the polymer to be hydrogenated.

3. A process for the non-destructive catalytic hydrogenation of unsaturated hydrocarbons which comprises passing vapors of unsaturated hydrocarbons, having a boiling point within the gasoline boiling range and formed by the polymerization of unsaturated hydrocarbons, together with water vapor and a gas containing free hydrogen in contact with a hydrogenation catalyst.

4. A process for the non-destructive catalytic hydrogenation of unsaturated hydrocarbons which comprises passing vapors of unsaturated hydrocarbons having a boiling point within the gasoline boiling range and formed by the polymerization of unsaturated hydrocarbons, together with water vapor and a gas containing free hydrogen in contact with a hydrogenation catalyst com-

prising a substance taken from the group consisting of metals of the 6th group of the periodic table, at an elevated temperature but below 350° C.

5. In a process for the non-destructive catalytic hydrogenation of diisobutylene by passing vapors of diisobutylene and a gas containing free hydrogen in contact with a hydrogenation catalyst under non-destructive hydrogenating temperature and pressure conditions, the improvement which comprises adding water vapor to the reaction mixture.

6. A process for the production of iso-octane which comprises continuously reacting vapors of diisobutylene with a gas containing free hydrogen, the mixture of reactants containing about 1% of water vapor by weight of diisobutylene, passing the reaction mixture in contact with a catalyst prepared by impregnating activated carbon with an acidified solution of ammonium molybdate and then drying it, at a pressure of about 100 atmospheres and at a temperature of about 260° C.

7. In a process for the non-destructive catalytic hydrogenation of olefins by passing vapors of olefin polymers with a gas containing free hydrogen over a hydrogenation catalyst under non-destructive hydrogenating conditions of temperature and pressure, the step which comprises adding water vapor to the reaction mixture in an amount of between about ½ and about 10% by weight of the olefin to be hydrogenated.

8. In a process for the non-destructive catalytic hydrogenation of unsaturated hydrocarbons formed by the polymerization of olefins by passing vapors of said polymers with a gas containing free hydrogen over a hydrogenation catalyst under non-destructive hydrogenating conditions of temperature and pressure, the step which comprises adding water vapor to the reaction mixture.

9. A process as in claim 8 in which the water vapor is present in an amount of between about ½ and about 10% by weight of the polymer to be hydrogenated.

10. A process for the non-destructive catalytic hydrogenation of unsaturated hydrocarbons which comprises passing vapors of unsaturated hydrocarbons having a boiling point within the gasoline boiling range and formed by the polymerization of unsaturated hydrocarbons, together with water vapor and a gas containing free hydrogen in contact with a hydrogenation catalyst comprising a substance taken from the group consisting of oxides of metals of the sixth group of the periodic table at an elevated temperature but below 350° C.

11. A process for the non-destructive catalytic hydrogenation of unsaturated hydrocarbons which comprises passing vapors of unsaturated hydrocarbons having a boiling point within the gasoline boiling range and formed by the polymerization of unsaturated hydrocarbons, together with water vapor and a gas containing free hydrogen in contact with a hydrogenation catalyst comprising a substance taken from the group consisting of sulfides of metals of the sixth group of the periodic table at an elevated temperature but below 350° C.

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