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PRODUCTION OF HYDROPOLYMERS

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This invention relates to the production of aviation or motor spirit of high octane number.

Isoparaffinic materials produced in the non-destructive hydrogenation of the product of polymerisation of mixtures of isobutene and normal butenes are valuable components of aviation spirit of high octane number. These isoparaffinic materials have high octane numbers of 91–96 (C. F. R. motor method), depending upon the proportions of isobutenes and normal butenes polymerised, but they have the disadvantage that they boil substanially at or above 100° C. whereas finished aviation spirits are normally required to contain at least 50% boiling below 100° C. Blends of aviation spirit containing such materials must also contain a considerable quantity of volatile constituents that are often of low octane number.

It is among the objects of the invention to produce hydrogenated polymers from an olefinic feedstock consisting of or containing mixtures of isobutene and normal butenes, the hydrogenated polymer products having a considerably increased volatility at 100° C. with no loss in octane number and a range in octane numbers varying according to the operating conditions in polymerisation particularly with respect to temperature and throughput.

According to the invention in a process for the production of isoparaffins by the non-destructive hydrogenation of the polymerisation products of isobutene and normal butenes together or contained in or derived from a butane-butene fraction or other source of isobutane and normal butenes, propene is added to the olefinic feedstock of the polymerization plant or unit in a proportion determined according to the content of isobutene in the olefine feedstock. Thus the butane-butene fraction that may be used may have a normal butenes-isobutene ratio in the range 1.5 to 1 to 2.5:1. To obtain a polymer or hydropolymer distillate to 120° C. which has approximately a 50% volatile content to 100° C. on an A. S. T. M. distillation, the amount of propene to be added for any given content of isobutene is in the range of 60–130% wt. of the isobutene content, and the operating conditions of throughput and temperature are determined to obtain the polymer necessary to yield the desired octane number of the hydropolymer. This temperature should be in the range 130–250° C., but more usually in the narrower range 150–190° C. to obtain an octane number of 90 or higher than 90 for the hydropolymer.

The operating pressure is in the range 250–

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1400 lbs./sq. in. Thus the desired volatile hydropolymer is obtained in one polymerisation operation and is not dependent upon the separate interpolymerisation of propene and isobutene.

The invention comprises the conditions hereinafter described.

In carrying the invention into effect a proportion such for example as 12% of propene may be added to the feed to the catalytic polymerisation plant or unit. This plant or unit may operate for example at 1400 lbs./sq. in., and at a temperature of about 160° C. whereby a suitable polymer and ultimately a hydrogenated polymer may be produced under conditions substantially as hereinafter described.

The following are examples of process conditions as to which the expression S. C. F., as used hereinafter, shall mean standard cubic feet.

Example 1

Feed composition (including added propene):

	Weight per cent
C_2 hydrocarbons	0.2
C_3H_8	8.0
C_3H_6	12.0
C_4H_{10}	30.5
iso-C_4H_8	16.1
n-C_4H_8	32.2
C_5 hydrocarbons	1.0

Operating conditions in polymerisation:

Catalyst	Copper phosphate, cadmium phosphate and phosphoric acid.
Pressure	1400 lbs./sq. in.
Temperature	160° C.
Feed rate S. C. F./lb. catalyst/hour	circa 20
Wt. per cent conversion to polymer on feed	26.5

Polymer composition:

	Volume percent
10–100° C	40.3
100–120° C	48.4
Above 120° C	11.3

This polymer has the same volume per cent. residue above 120° C. (circa 11%) as that produced from a feed consisting solely of C_4 hydrocarbons.

The product of the non-destructive hydrogenation of the 10° C.–120° C. fraction had the following characteristics:

Octane number (C. F. R. motor method) --- 94.0
A. S. T. M. volatility at 100° C.---per cent-- 40

There is thus no substantial loss in octane number of the hydrogenated polymer and the volatility at 100° C. is considerably increased.

Example 2

The yield and quality of the product after non-destructive hydrogenation may be varied at will by change in the operating temperature in polymerisation as shown in the following example:

Feed composition (including added propene):

	Weight per cent
C_3H_8	6.6
C_3H_6	18.2
C_4H_{10}	27.3
iso-C_4H_8	15.8
n-C_4H_8	29.0
C_5 hydrocarbons	3.1

Operating conditions in polymerisation:

Catalyst	As in Example 1
Pressure	1400 lb./sq. in.
Feed rate S. C. F./lb./catalyst/hour	circa 18

The following table indicates yields, composition and characteristics of the products at varying temperatures employed in the polymerisation of the material under the operating conditions indicated.

Temperature, °C	160	190	225
Yields Wt. Percent on Feed:			
Total Polymer	24.1	32.1	43.0
Distillate to 120° C	20.6	25.6	29.0
Hydrogenated Polymer:			
Vol. percent C_7H_{16} and under	36	36	32
Vol. percent C_8H_{18}	53	46	39
Vol. percent C_9H_{20} and over	11	18	29
Vol. percent Distillate to 120° C. on feed	86.2	81.2	69.6
Hydrogenated Distillate to 120° C.:			
Octane No. (C. F. R. M. M.)	92.4	91.2	86.2
A. S. T. M. volatility at 100° C., percent	50	52	50
Octane No. (C. F. R. M. M.):			
C_7H_{16} cut	90.7	88.6	84.5
C_8H_{18} cut	95.8	93.4	87.0

A comparison of Examples 1 and 2 shows that an increase in the propene content from 12% to 18% results in a lower octane number of hydrogenated distillate to 120° C. when operating under the same conditions, i. e. 160° C., 1400 lbs./sq. in. pressure and a throughput of 18–20 S. C. F./lb. catalyst/hour.

Under the conditions set out in the table of Example 2 change in yield of the hydropolymer is obtained by increasing the temperature, but it will be understood that change in yield may also be achieved by change in the feed rate which under the conditions of the table of Example 2 is the same in each case.

Example 2 shows how an increase in operating temperature results in an increased yield of total polymer, a higher percentage of heavy polymer in the total polymer, and a lower octane number of the hydrogenated polymers. Both the C_7H_{16} and C_8H_{18} cuts show reduced octane number with increasing operating temperature. Thus the operating polymerisation temperature must be kept sufficiently low to produce a hydrogenated aviation spirit of the desired octane number.

A suitable feedstock may conveniently be obtained in one operation in the secondary fractionation of the overhead, operating upon cracked petroleum distillates, instead of the butane-butene fractions being used as the source of the olefine feedstock.

Polymerisation catalysts consisting of cadmium di-hydrogen ortho-phosphate or cadmium copper di-hydrogen ortho-phosphate in a solid, hard, dry and porous state respectively prepared from cadmium ortho-phosphate and ortho-phosphoric acid and from copper ortho-phosphate, cadmium ortho-phosphate and ortho-phosphoric acid may be produced and used in the manner described in the specification of the prior United States Patent No. 2,128,126, while polymerisation catalysts prepared from copper ortho-phosphate, calcium ortho-phosphate and ortho-phosphoric acid may be produced in a solid, hard, dry and porous state and used. A proportion of steam is added to the stream of olefine feedstock in a proportion of from 4 to 10% by volume according to known practice to maintain the activity of the catalyst. Any other polymerisation catalysts than those specified may however be used, but those specified are preferred.

In the foregoing examples the polymers were hydrogenated over a catalyst consisting of mixed nickel and tungsten sulphides at a hydrogen pressure of 1000 lbs./sq. in. at a temperature of 250° C. and throughput of about 0.5 volume polymer/volume catalyst/hour.

I claim:

1. A process for the production of isoparaffins from olefins comprising catalytically polymerising an olefinic feedstock at a temperature of from 160° to 190° C. and non-destructively catalytically hydrogenating polymer products of the polymerisation reaction, the said feedstock comprising normal butenes and isobutene in a normal butenes-isobutene ratio in the order of 1.5:1 to 2.5:1 and propene in a proportion in the order of 60% to 130% wt. on the isobutene content of the feedstock.

2. The process of claim 1 in which the polymerising reaction is carried out at a temperature of from 160° to 190° C., and at a pressure in the order of 250 to 1400 lbs. per sq. in., to yield on the hydrogenation of the polymer product a hydropolymer product having an octane number of not less than 90.

3. The process of claim 1 in which the hydrogenation reaction is carried out with a nickel-tungsten sulphide catalyst, under a hydrogen pressure in the order of 1000 lbs. per sq. in., at a temperature of the order of 250° C., and a throughput of the order of 0.5 volume polymer per volume catalyst per hour.

4. A process for the production from C_3 and C_4 olefines of an isoparaffinic hydropolymer distillate to 120° C. having an octane number of at least 90 and a proportion volatile to 100° C. of the order of at least 50% and adapted for use as an aviation or motor spirit comprising catalytically polymerising normal butenes and isobutene in a normal butenes-isobutene ratio in the order of 2:1 together with propene in a proportion in the order of 75 to 115% wt. of the isobutene, at a temperature in the order of 160° C., a pressure in the order of 1400 lbs. per sq. in. and a feed rate in the order of 18 to 20 S. C. F. per lb. catalyst per hour, non-destructively hydrogenating the 10° C.–120° C. fraction of the polymer product and recover-

ing a hydrogenated distillate to 120° C. as the desired product.

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