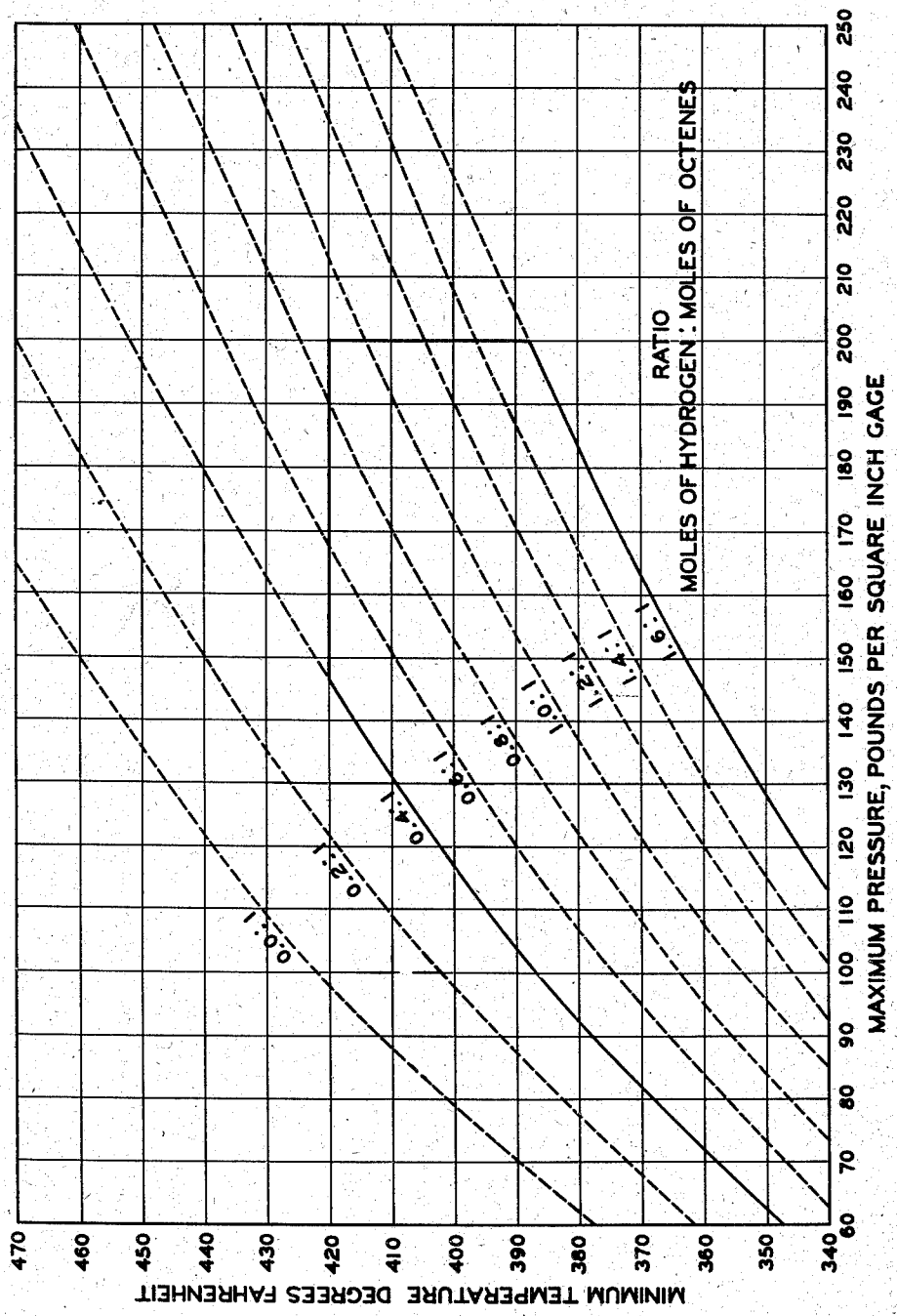
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HYDROGENATION OF HYDROCARBONS

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HYDROGENATION OF HYDROCARBONS

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This invention relates to a special process adapted to the production of octanes by the hydrogenation of octenes and particularly those octenes or octene fractions produced as dimers of butenes.

The process involves the use of very specific conditions of operation which permit the most effective conversion of normally liquid mono-olefinic hydrocarbons boiling within the approximate range of octenes into the corresponding paraffins with substantially no alteration in the structure of the molecules. The conditions which will be later specified have been evolved from a large amount of experimental work and are believed to be optimum.

At the present time great interest is manifested in the production of aviation fuels which must conform to rigid requirements in respect to volatility, stability in respect to gum formation, and high antiknock rating to permit their use under severe conditions of operation encountered at high altitudes including low temperatures and high supercharging pressures. Comparatively few hydrocarbon mixtures have been found to meet all these requirements and at the present time interest is centered around the increased production of iso-octanes, principally 2,2,3-trimethylpentane and 2,2,4-trimethylpentane. These compounds are most readily produced by controllably polymerizing the butenes present in the so-called butane-butene fractions recoverable from cracked gases followed by hydrogenation of the dimer fraction to produce octanes. Owing to the high cost of starting materials and the limited yields at present available, any process which improves the overall efficiency of the hydrogenating step is of immediate interest and the present invention is a contribution to this art.

In one specific embodiment the present invention comprises the manufacture of octanes by hydrogenating octenes in vapor phase in contact with a specially prepared composite catalyst containing reduced nickel while employing definitely limited relationships between temperature, pressure, excess of hydrogen over that required for complete saturation of the olefins, and definite space velocities.

It has been found that the most efficient hydrogenation of octenes under minimum temperature and pressure conditions is brought about by using what may be termed a spaced reduced nickel catalyst of a rather definite composition and produced by a preferred sequence of steps. The overall composition of the catalyst is given below:

	Per cent
Total nickel	62.0
Oxygen in nickel oxide (NiO)	4.0
Graphite	6.0
Kieselguhr	28.0
	100.0

It is obvious that the composition of the catalyst as given above may be varied within reasonable limits without departing from the scope of the invention. However, when the manufacture of the preferred catalytic material is conducted properly, it is generally found that the above analysis represents the composition of the finished material very closely.

The general method of preparation of the catalyst involves the following steps: Kieselguhr is suspended in a relatively dilute aqueous solution of nickel sulfate and a saturated hot solution of sodium carbonate is added gradually with constant agitation, the proportions of kieselguhr, nickel sulfate, and sodium carbonate being chosen so that after washing and drying the precipitate, pelleting in admixture with graphite and reducing with hydrogen, a composition corresponding to that given above is obtained. It is only necessary to employ commercially pure sodium carbonate and nickel sulfate in the primary precipitation although for best results the reactions are brought about in distilled water which can be obtained by the condensation of ordinary plant steam. As a rule a considerable excess of sodium carbonate is employed corresponding to approximately 1.7 moles to 1 mole of anhydrous nickel sulfate. It is important that the temperature of the suspension of kieselguhr and nickel sulfate solution be kept low and therefore the hot saturated sodium carbonate solution is added gradually so as to prevent a noticeable rise in temperature.

The primary precipitate consists of kieselguhr, nickel carbonate, and nickelous hydroxide, the composition of the particles without the silica corresponding to the approximate formula

$$2NiCO_3.7Ni(OH)_2.7H_2O$$

It is probable that some of the water in this formula is associated with the kieselguhr. The relative amounts of carbonate, hydroxide, and water will depend to some extent upon the conditions of drying.

The dry precipitate is now mixed with 4% of its weight of powdered graphite and pelleted into small cylindrical forms of approximately $\frac{7}{32}$'' diameter and $\frac{1}{8}$'' thick in any standard type of pelleting machine. The approximate composition of the material at this point is given below:

	Per cent
Total nickel	40
Carbon dioxide	7
Total water	20
Oxygen in nickel oxide (NiO)	11
Graphite	4
Kieselguhr	18

The formed pellets which still contain the mixture of carbonate and hydroxide are now heated in a stream of air or nitrogen at a temperature of approximately 300° C. (572° F.) to eliminate carbon dioxide. At this temperature it

has been found that there is substantially no oxidation of the graphite. After the requisite amount of carbonate decomposition has been effected, the reduction of the nickel oxides is conducted at increasing temperatures in a stream of hydrogen until a temperature of approximately 425° C. (800° F.) is reached, the reduction being continued until approximately 76% of the oxides have been reduced to nickel which gives a material having the composition shown in the second preceding tabulation. Analyses have indicated that in the formation of the catalyst composite of the preferred composition the following reactions take place in the decarbonizing and reduction steps:

(I) $2NiCO_3.7Ni(OH)_2.7H_2O \rightarrow 9NiO+2CO_2+14H_2O$

(II) $9NiO+7H_2 \rightarrow 7Ni+2NiO+7H_2O$

In the heating and reduction steps the porosity and hence the contact surface of the composite catalyst pellets is greatly increased and the crushing strength of the pellets is reduced to approximately 50% of their original value, this still being sufficiently high enough so that the pellets may be used in beds of reasonable depth in practice without crushing to produce fines.

Using the catalyst prepared as above described it has been found that the best hydrogenating temperatures are within the range of approximately 170–215° C. (338–419° F.) and that for the most effective operation the hydrogenation is conducted by counter-current methods in two stages whereby the octenes are partially hydrogenated in a primary stage using an amount of hydrogen inadequate to effect complete saturation and wherein the partially hydrogenated octene mixture is finally treated with a sufficient excess of hydrogen in the secondary stage. The catalyst is preferably contained in parallel tubes of relatively small diameter between distributing headers, the tubes being surrounded by a cooling medium to maintain the temperature within a close range since the hydrogenating reactions are exothermic and heat must be extracted. It has further been found for most efficient operation that the space velocities (which are defined as the volume of liquid octenes admitted to a given volume of catalyst space per hour) are all in the neighborhood of a value of 4. The attached graph designated as Figure 1 was made up from the data obtained from a series of runs in which temperature, pressure, and ratio of moles of hydrogen to moles of octene vapors were varied. The area included between the full lines represents the preferred area of operating conditions for the two-stage hydrogenation operation mentioned. It will be seen from the indicated limits of this area that for optimum results a temperature of 420° F. should not be exceeded and that no beneficial effects are obtained in utilizing pressures of over 200 lbs. per square inch gauge. In the primary stage of such an operation molal ratios of hydrogen to octenes of from 0.4:1 to 0.8:1 are preferably used and in the second stage wherein final and complete hydrogenation is effected molal ratios of 1:1 to 1.6:1 are preferably employed.

The primary object in inter-relating pressures and temperatures by the use of the graph is to insure completely vapor phase conditions in the mixture of hydrogen and octene vapors entering the catalyst tubes since single phase conditions are necessary for proper distribution and hence accurate temperature control of the entering mixture. For example, if a ratio of hydrogen to octene vapors of 0.6:1 is employed in the primary stage of hydrogenation along with a temperature of 390° F. it will be seen from the graph that a pressure of 120 lbs. per square inch may not be exceeded if completely vapor phase conditions are to be assured. Similarly for a ratio of 1.4:1, which may be employed in the second and final stage of hydrogenation, if the same temperature of 390° F. is used, the pressure can be increased to 188 lbs. without fear of the appearance of liquid and consequent unequal distribution.

The following example is introduced to show the character of the results obtainable in the operation of the process but not with the intention of unduly limiting its scope.

An octene fraction produced by the selective polymerization of iso-butylene to form a mixture of dimers was vaporized and passed over a reduced nickel catalyst of the composition shown in the specification in a two-stage hydrogenation. In the first stage the temperature employed was 330° F., the molal ratio of hydrogen to octene vapors was 0.6:1 and the pressure was 100 lbs. per square inch. In the second stage a temperature of 390° F. was employed with a molal ratio of hydrogen to octene vapors of 1.4:1 and a pressure of 180 lbs. per square inch. As a result of this operation, the octene mixture was 96% hydrogenated to a mixture of octanes consisting principally of 2,2,3-trimethyl pentane and 2,2,4-trimethyl pentane. The octane number of the hydrogenated product as determined by the motor method of testing being 98.

I claim as my invention:

1. A continuous process for the hydrogenation of octenes which comprises subjecting the vapors of said octenes in admixture with a molal excess of free hydrogen of less than 60% to contact with catalytic material comprising approximately 62% nickel, 4% oxygen combined in nickel oxide, 6% graphite, and 28% kieselguhr at temperatures within the range of 170–215° C. under pressure of from atmospheric to 200 lbs. per square inch and times of contact corresponding to liquid space velocities of approximately four per hour.

2. A continuous process for the hydrogenation of octenes which comprises subjecting the vapors of said octenes in admixture with from 40 to 80% of the moles of free hydrogen necessary for their saturation to contact with catalytic material comprising approximately 62% nickel, 4% oxygen combined in nickel oxide, 6% graphite, and 28% kieselguhr at temperatures within the range of 170–215° C. under pressures of the order of 100 lbs. per square inch in a primary stage, subsequently subjecting vapors of the partially hydrogenated products in a secondary stage in admixture with from 100 to 160% of the moles of free hydrogen necessary for their saturation to contact with catalytic material similar to that employed in the first stage at temperatures within the range of 170–215° C. under pressures of approximately 200 lbs. per square inch while maintaining a liquid space velocity of about 4 per hour.

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