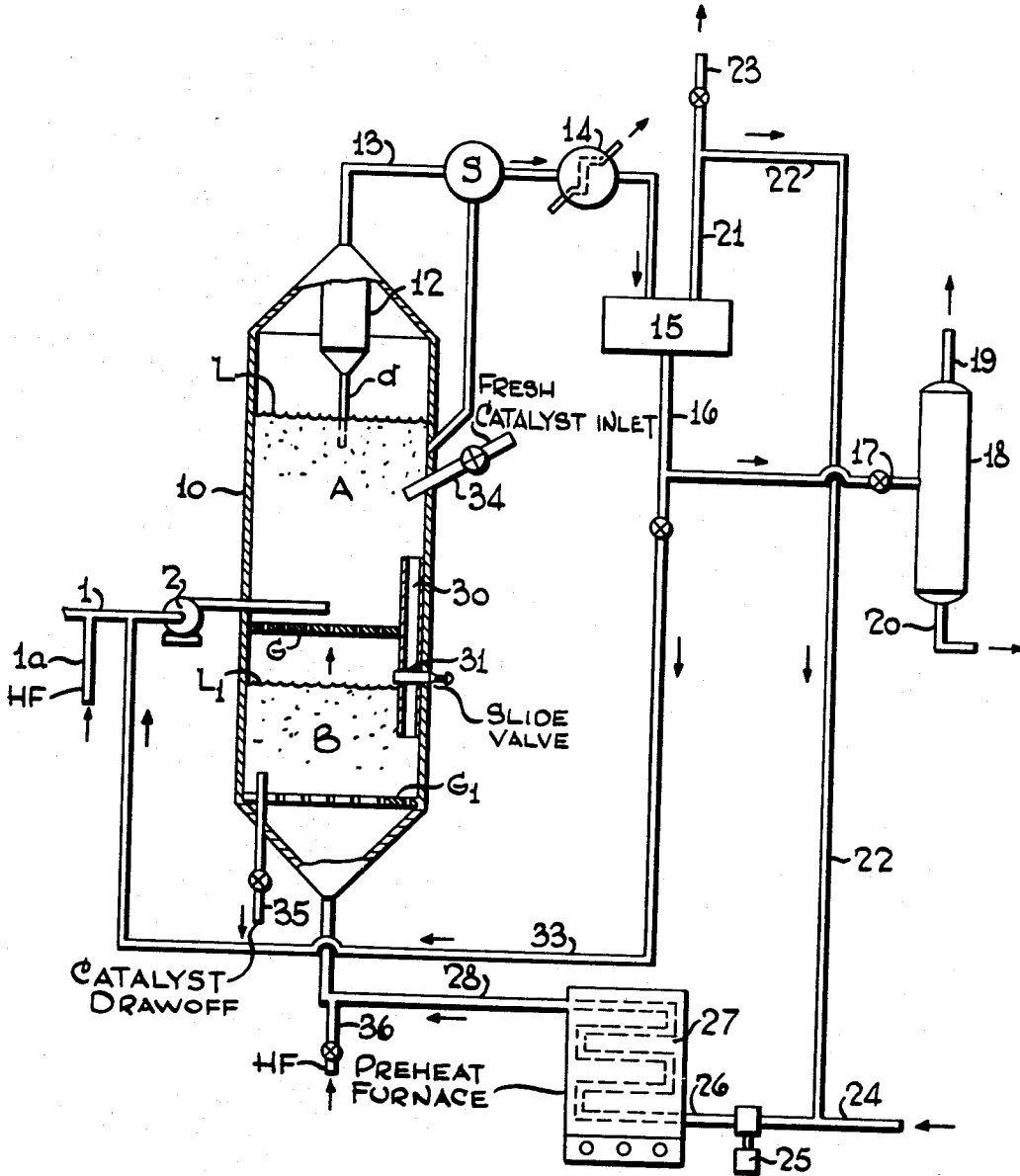


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LOW PRESSURE HYDROGENATION AND HYDROGEN
REGENERATION OF THE CATALYST
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LOW PRESSURE HYDROGENATION AND HYDROGEN REGENERATION OF THE CATALYST

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2 Claims. (Cl. 196—50)

This invention is concerned with the non-destructive hydrogenation of liquid hydrocarbons. More specifically, it relates to the hydrogenation at relatively low pressures of gasoline hydrocarbons for the purposes of improving their lead susceptibility, their stability and to reduce the sulfur content of raw gasoline fractions. It also relates to "hydrofining" kerosenes, heating oils and lubricating oils, thus enhancing their quality for their ultimate uses. It also relates to hydrogenation of oxygenated hydrocarbons, and in fact, to hydrogenation generally.

Hydrogenation of olefins and olefin-containing hydrocarbons at high pressures over suitable catalysts have been well known in the art. The pressures employed have been upward of 30 atmospheres because it was found that the catalyst life was too short for practical use at lower pressures. The catalyst life was impaired by carbon deposition and it was necessary frequently to replace the catalyst used at the lower pressures.

The use of higher pressures in the past art of hydrogenation had the disadvantage of causing excessive cracking of the liquid hydrocarbons. This cracking resulted in the formation of lower molecular weight hydrocarbons which, in general, had low octane numbers and were otherwise undesirable products.

The invention includes means for correcting the prior insufficiencies of low pressure hydrogenation operations by avoiding unfavorable destructive hydrogenation and high yields of the desired products are obtained without substantial production of undesirable lighter hydrocarbons, all of which will appear more fully hereinafter.

The non-destructive hydrogenation process herein described may be used to advantage in processing several types of commercial products from petroleum processing, as previously indicated. One of these types is the hydrogenation of heavy catalytically-cracked naphthas, for example. The conditions of hydrogenation as described below are maintained such that the important reactions are saturation of the olefins and removal of sulfur with little or no formation of light hydrocarbons. Another typical feed to the process is high sulfur kerosene or kerosenes which are high in aromatic content. Here the hydrogenation removes the sulfur, saturates the aromatics and improves the color so that the kerosene has superior burning properties.

A third operation involves hydrofining a heavier fraction of petroleum, that is, one boiling in the 400°-700° F. boiling range for the production of diesel fuel or high grade heating oil. This petroleum fraction may be from crude distillation stills or may be taken from the fractionating tower of catalytic cracking units. Again, saturation of olefins and aromatics, as well as desulfurization, occur. The research cetane number of the diesel oil boiling range material is increased up to 60 or higher by the present invention. The same boiling range hydrocarbons or those boiling in the 500-900° F. range may be similarly processed for the purpose of preparing a recycle feed to a catalytic cracking unit.

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A fourth aspect of the invention relates to the hydrofining of lubricating oil fractions. In this case light lubricating oils are subjected to hydrogenating conditions so that the so-called "viscosity index" is enhanced and the stability of the oil is improved.

In the accompanying drawing, there is shown, diagrammatically, an apparatus layout in which a preferred modification of the invention may be carried into effect.

Referring in detail to the drawing, the liquid feed is introduced in line 1 and pumped by pump 2 into reactor 10. Reactor 10 contains a catalyst having a particle size of from about 100-400 mesh, which is formed into a dense fluidized bed A above a grid member G and fluidized by gasiform material passing through the grid G and into contact with the bed A. The dense phase of fluidized catalyst extends from grid G to level L. Substantially, all of the small amount of catalyst entrained in the vapors leaving the dense phase catalyst bed at level L is separated in one or more "cyclone" separators 12 and returned to the dense phase by one or more dip pipes *d*. The vapors issue from the reactor through line 13 and then pass through an oil scrubber S, or the like, in which the last traces of catalyst is removed and returned to the reactor 10 through line 14. The vapors in line 13 are cooled further in cooler 14 and passed to a high pressure receiver 15. The liquid products are removed from separator 15 through line 16 and passed through a pressure reduction valve 17 to distillation column 18. Normally gaseous hydrocarbons are removed from column 18 through line 19 and the desired liquid products are recovered through line 20.

The gaseous products from separator 15 are removed through line 21 and recycled back to the reactor through line 22. Excessive gaseous products are rejected from the system through line 23. The recycled gas in line 22 is enriched by extraneous hydrogen fed through line 24 and the total hydrogen is fed to a pump 25, then through a reheat furnace 27, withdrawn from said furnace and fed via line 28 to the lower section of reactor 10, in which section the catalyst is regenerated by treatment with a hot hydrogen-containing gas. The lower section of reactor 10 contains a second fluidized catalyst bed supported on grid G₁ and extending to level L₁. The heated recycled gas in line 28 passes upwardly through grid member G₁ and through the dense, fluidized bed B of catalyst, leaving the dense bed at level L₁. This same recycled gas passes up through grid G and mixes with the liquid feed entering the reactor through line 2. The catalyst is circulated from the upper section A of reactor 10 to the lower section B of reactor 10 through a standpipe 30 in which the rate of catalyst flow is controlled by valve 31. Valve 31 is regulated so that the rate of catalyst flow is substantially equivalent to the entrained catalyst in the gases leaving section B and passing upwardly to bed or section A.

The controls for thus maintaining the desired dense phase catalyst levels in beds A and B are as follows: the flow of catalyst from A to B is controlled by manipulating valve 31 in tube 30. Normally, the flow of catalyst from B to A is by elutriation, the distance from L₁ to G being approximately 3-5 ft. in a commercial plant. However, if the upper dense phase level at L₁ becomes, say, too low, the flow of catalyst from bed A may be increased by manipulation of valve 31. Also, excess catalyst may be withdrawn from bed B via valved pipe 35. The quantity of catalyst in bed A may be increased by adding catalyst through valved line 34. Thus, the amount of catalyst (and the upper dense phase levels) in beds A and B may be controlled by manipulation of the indicated controls to add or subtract catalyst from either bed to maintain the desired quantity of catalyst therein.

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An important feature of this invention is the fact that the temperature of the bottom bed B in reactor 10 is higher than the temperature of the upper bed A. This is made possible by heating the gas in line 26 in furnace 27 to a temperature higher than the temperature in the upper bed of reactor 10. The higher temperature in the lower bed B of reactor 10 results in hydrogenation of the carbonaceous material deposited on the catalyst as a result of the reaction in bed A, both because of the higher temperature of the bed and the high partial pressure of the hydrogen in contact with this bed. The hydrogenation reactions in the upper bed of reactor 10 are exothermic, and in order to maintain the temperature of the upper bed less than the temperature of the lower bed at the same time that hot gases and hot catalysts are being carried from the lower bed to the upper bed, the feed is introduced into the upper bed substantially as a relatively cool liquid. Consequently, the sensible heat and latent heat requirements necessary to bring the feed to reaction temperature is sufficient to cool the bed A and the reaction zone to the desired temperature level. To further assist in controlling the temperature of the bed in the upper section, liquid product from separator 15 may be withdrawn through line 33, mixed with the feed in line 1 and fed to the reactor. The recycling of this liquid inert oil will serve to cool the reaction zone by absorbing sensible heat and heat of vaporization.

The operating conditions in this low pressure hydrogenation process will vary with the feed and type of product desired. In general, the total pressure of the system will be in the range of from about 100-500 p. s. i. g. The temperature of the upper bed of the reactor will be from 500°-900° F., and the temperature of the lower bed is in the range of 800°-1100° F. The recycle gas rate, plus the extraneous hydrogen entering the reactor 10 through line 24 is from 500-5,000 cu. ft. per barrel of liquid feed in line 1. The hydrogen gas entering bed B will have a concentration of 85-95 volume per cent.

The catalyst employed in this process may be a known hydrogenation catalyst as described in the prior art, but it is preferred that it be composed of platinum impregnated on alumina, silica-alumina, magnesia, or other suitable carriers or spacing agents. The platinum content should be 0.2-1 wt. per cent of the total catalyst composition. Palladium may be substituted for the platinum in quantities roughly 2-3 times the platinum requirement. As much as 0.5-5 wt. per cent HF (based on the total catalyst weight) may be impregnated on the catalyst to improve its activity. One good method of preparing the catalyst is to impregnate high surface alumina, preferably of the desired particle size with chloroplatinic acid followed by treatment with hydrogen sulfide and then dried at about 50° F. Another desirable catalyst is one with 2-5% (wtg.) V₂O₅ impregnated on active alumina (95-98 wtg. per cent), and promoted with a potassium compound, say, K₂CO₃, KOH etc. to provide a potassium content of 0.2 to 1.0 wtg. per cent based on the total catalyst composition.

As an example of the results obtained from this invention, the following are given:

Feed -----	Heavy catalytic naphtha.
Source -----	Fluid catalytic cracking of 600°-1000° F. cut of mixed crudes.
Boiling range -----	275°-430° F.
Bromine number -----	13 cg./g.
Sulfur—wt. per cent -----	0.38.

Hydrogenation reactor conditions (bed A)

Temperature -----	550° F.
Pressure -----	100 p. s. i. g.
Standard cu. ft. of Hydro- gen/bbl. Feed (85-95% hydrogen)	1000.

Space velocity -----	5 lbs. of oil per lb of cata- lyst per hr.
Catalyst -----	0.2% Pt, on alumina 99.3%, HF 0.5% (per cent by wgt.)

Total product inspection

Boiling range -----	Same as feed.
Butane formation -----	Less than 1%.
Bromine number -----	5.5 cg./g.
Sulfur, wt. per cent -----	0.045.

Conditions in regenerator section (bed B)

Temperature -----	950° F.
Catalyst circulation rate be- tween sections	0.5 lbs./lb. fresh feed.
Pounds of catalyst per pounds of catalyst in re- action section.	1.0.

The above data show an insignificant change in molecular weight of the mixed oil feed during the conversion. The catalyst life is extended, which is an important feature, since in many operations of the character herein described, the initial activity of the catalyst is high but soon tapers off to an unusable level. This is particularly true where, as here, the catalyst is employed in a process where the feed contains sulfur and air is used to regenerate the catalyst. Also, where as here, the hydrogenation is conducted at relatively low pressures, carbonaceous deposits on the catalyst have been excessive. The present technique overcomes this difficulty by treating the catalyst in a zone where the hydrogen concentration is high and at a time when the amount of carbon on the catalyst is relatively small and recently deposited so that removal of this carbon is achieved more easily. The final result of this technique is to permit continuous operation of the system described for several months in a process wherein the feed stock is treated in the presence of a highly active catalyst.

Under similar conditions catalytic cracking recycle stock which contains aromatics may be hydrogenated. These aromatics when cracked form inordinately large quantities of coke on the catalyst. The present hydrogenation process hydrogenates such aromatics to naphthenes which undergo cracking without forming excessive amounts of coke. Also kerosene and heating oil may be "hydrofined" (hydrogenated at low pressure) to saturate olefins and aromatics and also remove sulfur.

An important aspect of this invention is the continuous addition of HF to the system so as to maintain the desired concentration of HF on the catalyst to obtain the optimum results with respect to maintenance of catalyst activity and processing of the hydrocarbons. Normally, HF is lost by volatilization and passes out of the reactor with the effluent vapors. To offset this loss, HF is fed through line 1a to line 1 in the required amount, if not continuously then so as to maintain the desired amount on the catalyst. The HF may be dissolved in the feed and carried into the reactor therewith and deposited on or associated with the catalyst in the reactor. The HF may also be added via line 36 to the recycle gas in line 28 and carried with the latter gas into contact with the catalyst in bed B of reactor 10 to replace the HF which may have been lost by volatilization. The requirement of HF is that necessary to maintain the HF content of the catalyst within the limits previously prescribed, and by periodic examination of the catalyst, the replacement amount may be readily determined.

While this invention describes hydrogen regeneration of the catalyst when the catalyst is employed in hydrogenating hydrocarbons, it is not limited to such an operation. Other types of organic reactions with hydrogen may be carried out in the reactor which include hydrogenation and/or dehydrogenation reactions. For exam-

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ple, unsaturated alcohols may be hydrogenated to form saturated alcohols; aldehydes may be hydrogenated to form corresponding alcohols; and ketones may be hydrogenated to form the corresponding alcohols. Examples of dehydrogenation reactions where the described hydrogenation of catalysts to maintain activity is employed, are:

- Naphthene dehydrogenation... Dehydrogenation and isomerization of methyl cyclopentane to benzene.
- Paraffin dehydrogenation... Dehydrogenation of butane to butene.
- Ethyl benzene... Conversion to styrene.

To recapitulate, briefly, the present improvements go to the matter of hydrogenating organic materials, such as hydrocarbon oils at low pressures and regenerating the platinum type catalyst preferably used with hydrogen, that is to say, the preferred catalyst is from the platinum group including, of course, platinum itself and palladium, usually supported on an adsorbent spacing agent such as active alumina, zirconia, magnesia, activated carbon, silica gel, etc. The catalyst becomes contaminated with carbonaceous deposits and other poisons during, say, a dehydrogenation-hydrogenation operation, such as hydroforming or during the hydrogenation of, say, diolefinic hydrocarbons to remove one double bond, or to saturate branched chain olefins under conditions so that the olefin does not undergo cracking to form corresponding isoparaffins, or to hydrogenate oxygenated hydrocarbons, such as aldehydes and ketones to the corresponding alcohol, or to upgrade lubricating oils by hydrogenation. These catalysts are regenerated with hydrogen rather than air, which means that they do not require a reducing treatment prior to re-use following regeneration as would be the case using air, nor do they require an induction period if following regeneration, these catalysts are placed back on stream.

A disadvantage of low pressure hydrogenation of hydrocarbons and oxygenated hydrocarbons heretofore has been that the deposition of carbonaceous material on the catalyst is excessive. The present invention overcomes this disadvantage by the use of a two zone system in which the catalyst is continuously withdrawn from the reaction zone and treated with hydrogen containing gas in the regeneration zone. The withdrawal of catalyst from the reaction zone for regeneration need not be continuous, but rather may be intermittent or at spaced periods. This withdrawal rate will depend, of course, on the carbon buildup on the catalyst in any specific case. In the drawing the reaction zone and the regeneration zone are shown disposed in a single vessel. It is within the compass of this invention to employ two separate vessels, one to contain the reaction zone and the other, the regeneration zone.

Numerous modifications of the invention may be made by those who are familiar with the art without departing from the spirit thereof.

What is claimed is:

1. The process of treating a material of the class

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consisting of olefins, diolefins, aromatics, alkylated aromatics, and oxygenated hydrocarbons which comprises providing a fluidized bed of hydrogenation-dehydrogenation catalyst consisting essentially of platinum carried on active alumina and also containing a small amount of HF in a treating zone, feeding the said material to said zone, together with a hydrogen containing gas, maintaining a temperature of about 550° F. in said zone, maintaining said zone at a pressure of from about 100-500 p. s. i. g. whereby substantial destructive hydrogenation of said hydrogenatable material is avoided, permitting the hydrogenatable material and the hydrogen to remain resident in said hydrogenation zone for a sufficient period of time to effect the desired conversion, continuously withdrawing catalyst from the said zone by gravity flow and conducting it to a catalyst regeneration zone, disposed below and within the same generally confined space as said hydrogenation zone, treating the catalyst in the said regeneration zone while in the form of a fluidized bed with a hydrogen containing gas at elevated temperatures and pressures for a sufficient period of time to remove carbonaceous deposits acquired by the catalyst in the first-named zone from the said catalyst, returning regenerated catalyst to the first-named zone and recovering product from said first-named zone.

2. The process of nondestructively hydrogenating an unsaturated hydrocarbon at superatmospheric pressures but not exceeding about 500 p. s. i. which comprises feeding the unsaturated hydrocarbon, at least in part in liquid form, and hydrogen gas to a hydrogenation zone containing a fluidized bed of platinum containing catalyst carried on active alumina, contacting the said unsaturated hydrocarbon and the hydrogen with said fluidized bed of catalyst at elevated temperatures, of from about 500° to about 550° F., for a sufficient period of time to effect the desired conversion continuously, withdrawing catalyst containing carbonaceous deposits from the hydrogenation zone by gravity flow, conducting it to a regeneration zone disposed below the said hydrogenation zone but contained within the same generally confined space as said hydrogenation zone, treating said catalyst in said regeneration zone with a hydrogen containing gas while the catalyst is in the form of a fluidized bed at temperatures substantially above those prevailing in said hydrogenation zone, returning regenerated catalyst to the hydrogenation zone by elutriation and recovering from said hydrogenation zone a hydrogenated product.

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