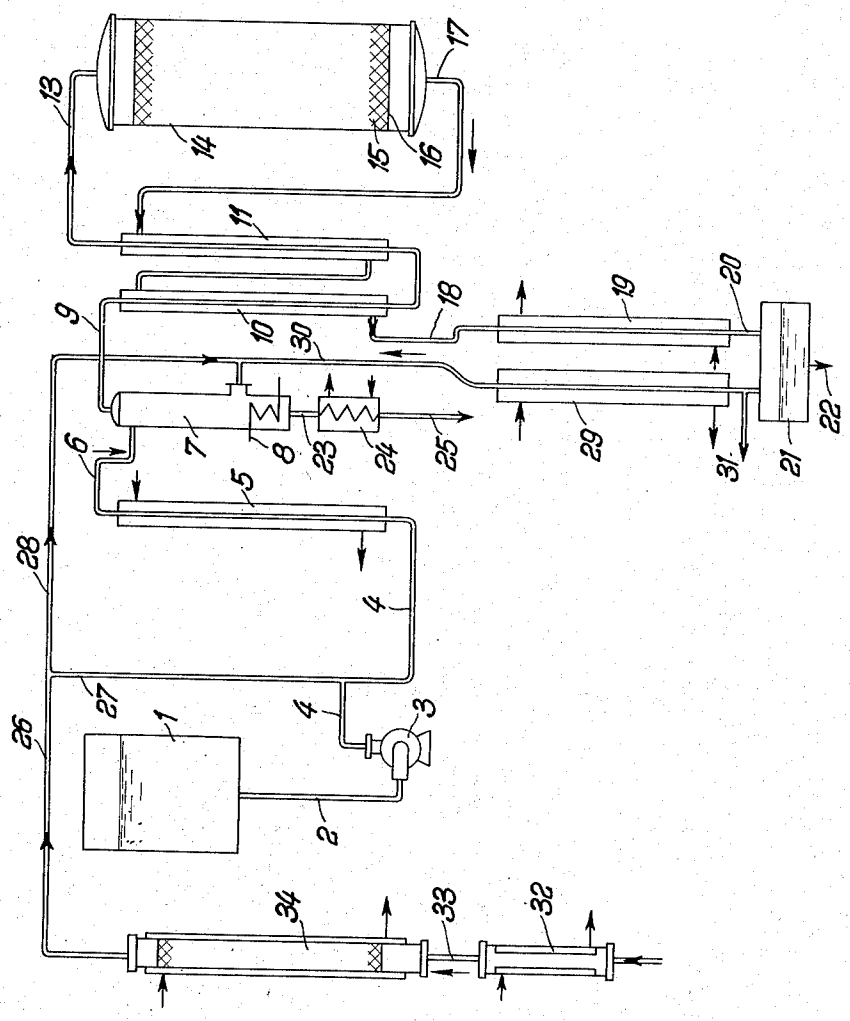
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PROCESS FOR THE HYDROGENATION OF HYDROCARBONS

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PROCESS FOR THE HYDROGENATION OF HYDROCARBONS

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The present invention refers to a process of catalytic hydrogenation of hydrocarbons or hydrocarbon fractions in the presence of hydrogen, in using sulfur resistant catalysts. Such hydrocarbons or hydrocarbons fractions are e.g. obtained from coking, low temperature distillation, or the gasification of coal, lignite, oil shale or other solid fuels, or else in the refining of liquid fuels such as mineral oil, tar, tar oil, or the like. The herein described process is e.g. suited for treating such hydrocarbons as benzol, gasoline, gas oil, middle oils, or fractions of the same and other hydrocarbons, preferably such which are boiling within a range of up to 360 or also 400° C. By means of catalytic hydrogenation, organic sulfur, nitrogen and oxygen compounds, resin formers and similar impurities are eliminated from the hydrocarbons. It is the object of the invention to use for such catalytic hydrogenation hydrogen-containing gases such as town gas, coke oven gas, low temperature distillation gas, water gas, gases obtained from refining or reforming mineral oils and other liquid fuels, synthesis final or recycled gas, or similar gases containing as essential compounds, besides hydrogen, carbon oxide, methane, or other low-boiling, particularly gaseous hydrocarbons, and, in some cases, carbon dioxide, nitrogen, water vapor, or two or several of these substances, and to effect the catalytic hydrogenation in such a way as to eliminate or at least vastly reduce the hitherto unavoidable formation of deposits and incrustations in the used vaporizers, heat exchangers, heaters, lines, and other equipments, as well as on the catalysts.

Moreover, the present invention aims at operating the process in such a way as to impart to the used catalysts a long service life of many months. A further object of the invention is to impart to the gases used for catalytic hydrogenation, by means of a treatment effected prior to refining, such properties which will make those gases specially suitable for refining. A further object of the present invention is to produce in the process proper, by conversion of carbon oxide contained in the hydrogen-containing gas, part of the hydrogen required for catalytic refining, using for the conversion appropriately the same catalyst used for catalytic refining, and carrying out the conversion and catalytic refining simultaneously.

In accordance with the present invention, town gas, coke oven gas, low temperature distillation gas, water gas, gases obtained from refining or reforming mineral oils or other liquid fuels, final or recycled gases from syntheses using hydrogen, e.g. from the Fischer-Tropsch synthesis, or another hydrogen-containing gas, is passed over or through a catalyst at a suitable temperature between 50 and 420° C., appropriately 200–400° C., before being brought into contact with the hydrocarbons to be refined. Only after such pre-treatment, the respective gas is introduced, into the refining process proper. For example, the gas, after such pre-treatment, is passed

through the hydrocarbons to be refined, while the same are completely or partly vaporized, it being at the same time possible to add some gas which was recycled through catalytic refining. The mixture of hydrocarbons to be refined and hydrogen containing gas will then flow through the heat exchangers and heaters into the reactor and from there into the devices provided for separating the refined hydrocarbons from the gas, which latter may then be used for refining—appropriately in branching off a partial flow from the process.

By preparing the hydrogen containing gas in accordance with the present invention, it is possible to effectively prevent a disturbance of hydrogenating refining by the formation of deposits in the vaporizers and heat exchangers or on the catalyst itself and in the connecting lines. The gas treated according to the present invention may be introduced into the hydrogenating treatment of the hydrocarbons at various points. For example, it is possible not only to pass the gas separately or mixed with recycled gas through the vaporizer for the hydrocarbons, but also to add it only before the reactor is entered.

Working temperatures are normally about between 50° C. and the reaction temperature of the subsequent catalytic refining, e.g. the process is operated at temperatures between 160 and 240° C. Appropriately, the temperature of the catalyzer is chosen in such a way that a conversion of carbon oxide into methane will not take place when carbon oxide containing gases are treated. The treatment of the fresh gas according to the present invention is effected with the modification that the treated gas, when passed through a sulfuric acid formaldehyde solution (30 parts by volume 66° sulfuric acid on 1 part by volume 40% formaldehyde) for a period of several minutes will produce only a weak brown coloring. The working temperature, treating period, and quantity of catalyzer may easily be fixed by tests.

In this connection, it will not be necessary to work under pressure. The process will pass off satisfactorily also at normal pressure or, if necessary, at reduced pressure. Thus, it is possible in accordance with the present invention to treat the gas also prior to compression, and to compress it subsequently to the pressure used for catalytic refining, which is usually above atmospheric pressure, e.g. at 20–100 at.

The process according to the present invention offers the further advantage that the catalyzer can be operated with rather varying degrees of efficiency. The load may be reduced down to 10 N m.^{3} gas per 1 m.^{3} catalyzer and 1 hour. On the other hand, it may also be maintained substantially higher, e.g. at up to 1000 N m.^{3} gas and above per m.^{3} catalyzer an hour.

The catalyzer is e.g. applied in extended cylindrical chambers into which the necessary heat may e.g. be introduced from outside. It is for example profitable to operate the process in such a way as to heat the catalyzer, and to introduce the gas into the same at a temperature lower than reaction temperature, so that the gas is brought to reaction temperature when passing the catalyzer. In this case, the necessary heat supply to the catalyzer may be effected by heat exchange between the entry gas and the exit gas, if necessary, with additional heat input, it being possible to use for the heating that heat which is produced by the subsequent catalytic refining. Other methods of heating may also be adopted, e.g. a pre-heating and thus a heating of the gas may be effected by feeding oxygen into the fresh gas at the catalyzer. To achieve this, the process may also be operated with a catalyzer in the form of a fluidized bed or suspension. It is also possible to add the fresh gas to the hydrocarbon vapors emanating from the vaporizer or, as the case may be, to their mixture with recycled gas, and to pass the thus obtained mixture

through the catalyzer, which effects the treatment of the fresh gas in accordance with the present invention, provided that the temperature of the mixture should be kept sufficiently below the temperature of the hydrogenating refining, e.g. at abt. 180–200° C. In this case, the catalyzer is indirectly heated by means of the gas leaving the reactor of the hydrogenating refining, whereby the gas vapor mixture flowing into the reactor is simultaneously heated. There is another method of utilizing the heat produced by catalytic refining for the process according to the present invention, e.g. in such a way as to pass the fresh gas separately or mixed with recycled gas through a catalyzer working by heat exchange with vapors emanating from the reactor of the catalytic refining, conducting such gas from the catalyzer into the vaporizer for the hydrocarbons.

The process according to the present invention is e.g. operated in such a way as to compressing the hydrogenous gas required for the refining hydrogenation to working pressure and to pass the gas over the contact masses, profitably without cooling after compression, i.e. at elevated temperature, appropriately after a second heating.

As catalyzers for preparing the fresh gas for hydrogenating refining in accordance with the present invention, it is possible e.g. to use metal oxides and/or sulfides of the metals of the 6th and 8th groups of the periodic system. Well suitable are in particular the known hydrogenating catalysts which contain as base materials tungsten, molybdenum, vanadium, cobalt, chrome, nickel, or iron, and which may furthermore contain zinc, magnesium, or similar oxide compounds and be deposited on such carrier substances as activated carbon, silicagel, or alumina. These catalyzers may also contain two or several of the said metals.

It has proved specially profitable to use those sulphur resistant catalyzers which are applied for the cracking or hydrogenating refining of hydrocarbons under pressure. But also with alkalized iron catalyzers such as have hitherto been used for the catalytic conversion of organic sulfur compounds in synthesis gases, useful results could be achieved.

For example, molybdic acid on alumina is used as catalyzer, molybdic acid concentrations of abt. 10% being applied. Another highly active catalyzer for the treatment of the fresh gas according to the present invention can e.g. be obtained in such a manner as to intimately mix 70 parts by weight of a commercial aluminum oxide hydrate with bayerite structure, which essentially in the catalyzer serves as a carrier, with 18 parts by weight molybdic acid, 8 parts by weight cobalt hydroxide, and 4 parts by weight graphite. This mixture is pressed into the form of small cylinders. The catalyzers may be introduced into the process in the form of their oxides. Under the action of the present hydrogen sulfide and of the hydrogen sulfide formed by the cracking of organic sulfur compounds respectively, as well as of hydrogen, the metal oxides will in the course of the process gradually change over into a partly sulfiidic and partly metallic form. However, the catalysts can without difficulty be sulfurized or reduced in the known manner before being applied and used in the process in their sulfidic and/or metallic form.

Also precipitating catalyzers have proved to be useful, produced e.g. in such a way that aluminum salts and one of the salts of the said metals or mixtures of such metal salts are precipitated jointly, e.g. in the presence of a carrier, or that alumina or another carrier substance is impregnated with one or several of such metal salts, converting the salts into their oxide form, e.g. by heating.

Also the catalyzer used up in hydrogenating refining may advantageously be used for the process according to the present invention. which process offers in this case the additional advantage of using a specially low-priced catalyst.

It is possible to use for the process according to the present invention starting gases with different hydrogen and carbon oxide contents. A hydrogen partial pressure of under 25 at. and a hydrogen and carbon oxide partial pressure of up to 40 at. have proved specially profitable, the carbon oxide partial pressure being appropriately between 0.1 and 15 at.

It is profitable to use as hydrogen containing gas those gases which emanate from the chambers of coke ovens of conventional structure towards the end of the carbonizing period. Such gases may still be improved by passing methane or methane-containing gases, town gas, or natural gas, through the glowing coke during the last part of the carbonizing period.

A saving of hydrogen required for hydrogenation can be realized by passing water vapor through the catalyzer being used for the catalytic refining of the hydrocarbons. Surprisingly, the presence of water vapor will not interfere with, but frequently favor the refining. Neither will any damages to the contact occur, the sulphur resistant contact being normally used for refining. The present invention offers the great advantage that depositions of carbon on the contact are eliminated, even if the refining takes place at relatively high temperatures of e.g. over 400 to up to 500° C. Moreover, it is possible to avoid a reduction of the octane number in hydrogenating refining. In some cases, even an improvement of the octane number is obtained. The quantities of water vapor required in accordance with the present invention amount to about 5–50% by volume, calculated on the gas freshly entering the process. About 15–35% by volume are profitably used. When working with recycled gas, somewhat larger quantities of water vapor, calculated on the fresh gas, are recommendable.

The water vapor may be introduced into the process at various points. It may be added to the gas flowing into the reactor in which the catalytic refining of the hydrocarbons takes place. It is also possible to introduce the water vapor into the reactor separately from the gas. It will be appropriate in many cases to admix the water vapor already to the hydrogenous gas freshly entering the process, so that the water vapor will pass together with the gas the pre-treatment of the gas. Also in this case, the presence of water vapor will be advantageous; in particular, the water vapor will protect the catalyzer of the pre-treatment against a premature depletion, which may occur in the course of time e.g. by deposits of carbon black or incrustations on the catalyzer. Moreover, the addition of water vapor in the pre-contacting will make the gas better suited for the subsequent catalytic refining. In addition, the conversion of part of the water vapor will effect a certain increase of the hydrogen content of the gas. After the pre-contacting of the gas freshly entering the process, a cooling of the gas which might result in a separation of water vapor will, of course, be avoided. In the case of a two or multiple stage pre-contacting of the gas freshly entering the process, the water vapor may be added either before the first stage or only before one of the subsequent stages.

For example, it is possible to use for the process an apparatus as diagrammatically set up and exemplified in the drawing.

The hydrocarbon fraction to be refined, e.g. benzole, flows from the collector tank 1 through the line 2 to the pump 3, from which it is pumped through the line 4, the pre-heater 5, and the line 6 to the benzole vaporizer 7, which latter is maintained at the desired vaporizing temperature by means of the heater system 8. The vapors leave the vaporizer 7 through the pipe 9 and are heated to the reaction temperature in the heat exchangers 10 and 11. At this temperature, the vapors flow through the pipe 13 into the reactor 14 used for the hydrogenating refining, in which the catalyst 15 is arranged on a

gas-permeable bottom **16**. The vapors leave the reactor through the pipe **17**, pass through the heat exchangers **11** and **10** and leave the latter through the pipe **18**, entering the condenser **19**, in which the refined product is condensed and from which it passes by means of the pipe **20** into the separator **21**. The refined product is discharged from the line **22**.

A small portion of the benzole or the like is passed from the vaporizer **7** through the line **23** and the cooler **24** to the line **25**, through which it may be conducted e.g. to a tar distillation or other distillation plants, in which the higher-boiling substances of the said portion may be returned, if desired, to the refining, e.g. benzole refining.

The hydrogen containing gas required for the catalytic refining may be admixed to the benzole or the like flowing through the line **4** by passage from the line **26**, e.g. through line **27**. This gas in mixture with the benzole into the vaporizer through the heat exchanger **5**. It may also be led—mixed with the recycled gas, if desired—through the line **28** immediately into the vaporizer **7**. The gas which is recycled flows from the separator **21** through the pre-heater **29** and the line **30** into the vaporizer. A portion of the recycled gas is branched off from the process at **31** in order to maintain the composition of the recycled gas constant.

If the hydrogen containing gas would be introduced into the catalytic refining immediately through the line **26**, coke-like deposits would form on the heat exchangers **10** and **11** at the temperature of about 180–240° C. As a result thereof, the difference pressure in the plant caused by the flow resistance, which is 0.5 at. when starting the run, will rise to 2.5 at. and higher within a few days. After about a week of each run, the heat exchangers consisting of nests of boiler tubes lying within the said range of temperature will be clogged with coke-like deposits, so that the plant will have to be shut down. Also in the vaporizer such as constructed and operated e.g. in accordance with the German Patents 930,224 and 930,225, deposits will be found which reduce the passage of the charge to be vaporized and interfere with the vaporization.

In accordance with the present invention, the fresh gas is compressed and first of all passed through a pre-heater **32**, from which it flows through the line **33** into the pressure-resistant container **34**, which is heatable in a known manner. For 100 m.³ fresh gas per hour, about 100 l. catalyst are employed in **34** at a pressure of e.g. 35 at. The fresh gas is heated by means of indirect heating to that temperature which is the optimum for this catalyst. The catalyst consisting of a mixture of molybdic acid, cobalt hydroxide, alumina, and graphite is operated, according to the composition of the fresh gas, within a temperature range of about 100–400° C., appropriately 180–350° C., e.g. at about 200° C.

The gas leaving the catalyst has e.g. the following composition:

CO_2+H_2S	vol. percent	2.0
CnHm	do	0.5
O_2	do	0
CO	do	12.4
H_2	do	55.8
CH_4	do	24.7
N_2	do	4.6

The gas contains abt. 0.1 g. hydrogen sulfide per normal cubic meter, but is free from all other substances which might react with the resin formers contained in the hydrocarbons to be refined. While the untreated coke oven gas causes a black coloration in a formaldehyde/sulfuric acid solution in a few seconds, the gas treated in accordance with the present invention will only color such a solution light brown after being passed therethrough for several minutes.

The gas treated in accordance with the present invention is then admixed, appropriately without cooling, to the recycled gas prior to its entrance into the vaporizer, or introduced already into the hydrocarbons to be vaporized in front of the pre-heater **5**.

After removing the injurious components of the fresh gas in accordance with the present invention, both the separation of elemental sulfur and the formation of resin and coke deposits in the vaporizer and heater systems are suppressed.

Even when the refining is effected in the liquid phase, or when a mixture of liquid and vaporous hydrocarbons is refined, all the injurious deposits and incrustations are eliminated by the process of the invention.

The reactor to be used may advantageously consist of a construction being essentially composed of a pressure bearing outer jacket and an inner jacket in which the catalyst is arranged in such a way as to rest on a perforated bottom. The interior jacket is designed for protecting the pressure bearing jacket in order to withhold overheating temperatures from the pressure bearing jacket and to ensure that occurring corrosions, if any, will only arise in the interior jacket. The space between the pressure bearing jacket and the interior space is connected with the gas chamber of the reactor, so that the interior jacket is essentially not subjected to pressure and may be designed with a very thin wall thickness. The reactor is closed at the top by a lid. On this lid, a gas heater is arranged which is filled with metallic bodies such as Raschig rings, iron balls or the like. Around the said heater, an inductive heating is arranged, which is switched on, if necessary, and will then effect a heating. The gas vapor mixture entering into reaction is introduced through a connection piece into the contact oven and is heated to reaction temperature at the filling bodies by the action of the induction and eddy currents. It will then flow through the contact layer, in which the decomposition of the sulfur, nitrogen and oxygen compounds takes place. The temperature of the gas is thereby increased by abt. 10–50° C., and the gas leaves the catalyst chamber in a purified condition. The reactor is surrounded with a heat insulating coat. When operating the process according to the present invention with addition of water vapor, the latter may already be added to the hydrogenous gas freshly entering the process, and will then be entrained by the said gas through the catalytic pre-contacting for hydrocarbon refining. In the pre-contacting and refining stages, the water vapor effects a substantial reduction of the hydrogen consumption. Moreover, it results in an advantageous equalization of temperature in the catalyzer, which specially accurs during the hydrogenating catalytic refining of the hydrocarbons.

Example

When gasifying a slightly caking long flame gas coal by means of oxygen and water vapor at a pressure of 20 at. for producing long distance gas, tar, tar oil, and gasoline are obtained as byproducts. The substances are obtained in a known manner from the gas produced by the gasification and subjected to pressure, which is in the case of gasoline achieved e.g. by treating the gas with wash oil. Tar and tar oil are jointly subjected to a distillation, during which a fraction extending from the boiling point to a temperature of abt. 210° C. is inter alia take off separately. This light oil fraction containing abt. 25% by volume of phenols may be dephenolized in a known manner, e.g. by extraction with hot dephenolized water or with alkali solution. However, such dephenolization is not absolutely necessary, as the phenols, even if they are contained in the starting material in larger quantities, are converted into hydrocarbons during the hydrogenating refining. The gasoline and the equally dephenolized light oil fraction are combined and subjected to catalytic refining for the purpose of pro-

ducing a satisfactory motor fuel. The mixture shows e.g. the following composition:

Density at 20° C	0.813
Sulfur percent by weight	0.65
Acid oils percent by volume	2
Initial boiling point ° C	64
5% by volume ° C	71
15% by volume ° C	93
Final boiling point ° C	210
Boiling loss percent	2.4

The refining of the crude gasoline is effected at a pressure which should advantageously be somewhat above the pressure of the long distance gas. So e.g. the pressure of the refining plant is maintained at 25 at. in the case of a long distance gas pressure of 20 at. Through the line, 1,000 normal cubic meters fresh gas per hour are conducted to the compressor, which fresh gas is heated up to a temperature of 170–180° C. in the heat exchanger, which is supplemented by an additional heating equipment, if necessary. To this gas, 250 kilos per hour of water vapor being available at a pressure of 36 at. are added through the line 5. The hydrogen containing gas enters the vaporizer together with the water vapor, which vaporizer is maintained at a temperature of 190–220° C. by means of the heater system. 1,000 kilos crude gasoline per hour are introduced into the vaporizer through the line. From the line, 15 kilos vaporizing residues per hour are drawn off, which may be transferred back into the tar obtained in gas production, e.g. prior to the distillation of the former. 1,000 normal cubic meters gas, 250 kilos water vapor and 985 kilos gasoline vapor per hour, which are jointly heated up to a temperature nearly reaching reaction temperature by means of the heat exchangers as well as the heater, are leaving the vaporizer through the line.

The refining loss amounts to 39 kilos per 1,000 kilos crude gasoline. The refined product shows the following composition:

Density at 20° C	0.795
Sulfur percent by weight	0.034
Acid oils percent by volume	0
Initial boiling point ° C	61
5% by volume ° C	74
Final boiling point ° C	203
Boiling loss percent	3.2

As the refined product still contains hydrogen sulfide as well as ammonia, it is washed with caustic solution and water and then dried. In most cases, a further treatment of the refined product may be omitted. In the case of difficult hydrocarbons, particularly gasolines, it may sometimes occur that the refined product is not absolutely stable to light. However, it is possible without difficulty to achieve the desired absolute stability to light by means of a slight after-treatment e.g. by washing with diluted sulfuric acid and/or treating with bleaching earth, alumina, silica, gel, activated carbon, or similar substances in the liquid phase at normal or elevated temperatures or in the gas phase, if necessary, under pressure. Such treatment, which may be effected subsequently to refining by means of the sulfur resistant catalyst, may appropriately be effected in the presence of the hydrogen containing gas and/or the water vapor.

Instead of the said after-treatment, a fractioning of the refined hydrocarbons or hydrocarbon fractions may take place. For it was found that when such fractioning is carried out a distillate stable to light passes over head, whilst those substances which cause the decoloration remain in the distillation residue. The latter may be kept comparatively small, e.g. only at abt. 1–15% of the fractionation feed. It will be appropriate to recycle the distillation residue to the hydrocarbons or hydrocarbon fractions to be refined. In specially difficult cases, such fractioning as well as the after-treatment may be applied—by means of diluted sulfuric acid, bleaching earth, or the like—one after the other, in any desired sequence.

The height of the catalyst bed may be measured at about between 3 and 15 m. In most cases, it will be appropriate to divide the catalyst bed into two or several layers, as the mechanical resistance of the catalyst is sometimes insufficient, if the same is arranged in one single high layer. Moreover, it is advantageous to work with comparatively high flow velocities of e.g. 2 or 3 m. per second. The main effect of such flow velocity consists in that the catalyst is uniformly flown through and heated so as to avoid overheating in places, even if the catalyst cross section is measured comparatively large, e.g. if the catalyst is without any cross section division arranged in a shaft furnace. Also a horizontal division of the catalyst bed into two or several layers will alleviate the danger of over-heating.

It is possible to introduce some of the vapors or gases being in the process according to the present invention, e.g. recycled gas or fresh gas or hydrogen containing gases, between two layers at one or several places of the catalyst bed. The temperature of the introduced gases and/or vapors may be above or below the reaction temperature at which the treated gas/vapor mixture enters the space between two layers. In the first case, the introduced gases or vapors are thus used for introducing heat into the reaction, whilst in the second case they will reduce the reaction temperature at which the treated gas/vapor mixture enters the next layer. Besides this temperature control, it is possible to achieve, e.g. by introducing fresh gas between the catalyst layers, an improvement of the reaction by increasing the hydrogen and/or carbon dioxide concentration. Similar effects may be obtained by introducing water vapor between the layers at one or several places of the catalyst bed resulting in a conversion of water vapor and carbon dioxide into hydrogen.

As already observed, the reaction temperatures may fluctuate within comparatively wide a range; they normally are between abt. 300 and 500° C. Such reaction temperatures may be adjusted by heat exchange with the gas/vapor mixture flowing from the reaction and, if necessary, by additional heating. In case that the gas/vapor mixture leaves the catalyst with comparatively high temperatures and that a comparatively high temperature rise of e.g. 100° C. takes place in the catalyst bed, it is possible also with a heat exchange between the gas/vapor mixture entering the reactor and flowing from the reactor, to easily adjust the desired temperature in such a way that only part of the gas flowing from the reactor is passed through the heat exchange, the heat of the other part being used for other purposes inside or outside the process.

The number of layers into which the catalyst bed is divided in accordance with the present invention may fluctuate within the limits of abt. 2–20. This number is in each separate case chosen with the modification that the mechanical properties of the catalyst should not be overstressed, and that suitable reaction conditions, especially temperature and flow conditions, should be provided. It is also possible to consider the gas quantities to be used in each case, e.g. in such a way as to choose a greater number of catalyst layers when larger quantities of gas are cycled.

When introducing cold gas between the layers, it will be appropriate to introduce more gas for smaller amounts of cycled gas and less gas for higher amounts of cycled gas.

For example, it will be appropriate, for increasing the gas velocity, to work with quantities of abt. 500–2,000 normal cubic meters of gas per ton of starting material put through.

If large amounts of heat are freed during the reaction, it may be appropriate to cool the catalyst. For example, the catalyst may be arranged in vertical tubes which are sprinkled from the outside by a boiling cooling agent.

The vapors of the cooling agent arising thereby are withdrawn from the cooling agent chamber and condensed by utilizing the heat involved, whereupon the condensate can be retransferred into the cooling agent chamber. When arranging the catalyst in the said tubes or in a closed column, this arrangement may also be utilized for keeping the catalyst at constant temperature. In this case, the tubes of the catalyst chamber subdivided in the horizontal plane are surrounded with a high-boiling liquid, e.g. diphenyl oxide. This phase will then effect a heat equalization between the different parts of the catalyst, if such parts will adopt unequal temperatures due to different rates of reaction.

We claim:

1. In the process for the catalytic hydrogenating refining of hydrocarbons in which a hydrocarbon ranging from a normally liquid to solid hydrocarbon is contacted with a hydrogen-containing hydrogenation gas in the presence of a sulfur-resistant hydrogenation catalyst under conditions of elevated temperature and pressure, the improvement which comprises effecting said contacting in the additional presence of 5–50% by volume of water vapor based on the hydrogenation gas.

2. Improvement according to claim 1 in which said contacting is effected in the presence of about 15–35% by volume of water vapor based on said hydrogenation gas.

3. Improvement according to claim 1 in which said hydrogenation gas is a hydrogen containing gas selected from the group consisting of illuminating gas, coke oven gas, low temperature distillation gas, and similar hydrogen-containing gases.

4. Improvement according to claim 1 in which said contacting is effected at a temperature of between 300° and 400° C.

5. Improvement according to claim 1 in which said contacting is effected by passing said hydrocarbon and said hydrogenation gas through a bed of said catalyst and which includes re-cycling the hydrogenation gas after said contacting and introducing fresh hydrogenation gas at an intermediate point in said catalyst bed.

6. Improvement according to claim 1 in which said hydrogenation gas is a member selected from the group consisting of illuminating gas, coke oven gas, low temperature distillation gas, and similar hydrogen-containing gases in which includes passing said hydrogenation gas in contact with said hydrogenation catalyst at a temperature between about 50°–400° C. prior to contact with said hydrogenation gas.

7. Improvement according to claim 1 in which said sulfur-resistant catalyst is a member selected from the group consisting of oxides, sulfides, and mixtures thereof having a base metal selected from the group consisting of metals of the 6th and 8th group of the periodic system.

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