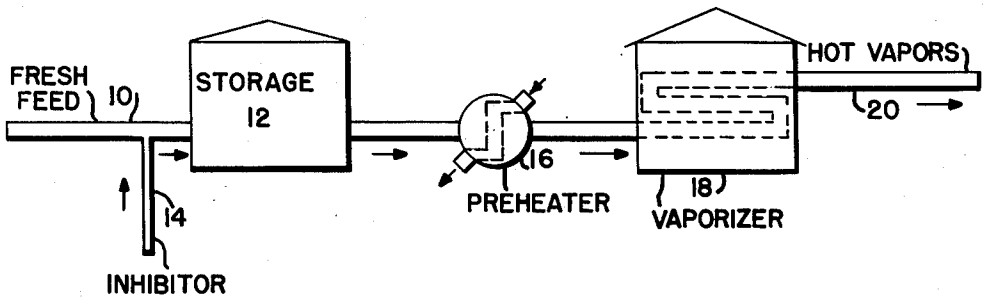
Nov. 27, 1956 J. D. BUSHNELL ET AL 2,772,220

FEED STOCK FOR NAPHTHA REFORMING

Filed Sept. 25, 1952



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United States Patent Office 2,772,220 Patented Nov. 27, 1956

2,772,220

FEED STOCK FOR NAPHTHA REFORMING

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Application September 25, 1952, Serial No. 311,342

5 Claims. (Cl. 196—50)

This invention relates to a process for the heat treatment of hydrocarbons. More particularly, it relates to a process for the thermal or catalytic reforming of a hydrocarbon feed stock consisting essentially of saturated hydrocarbons, i. e., one substantially free of unsaturates.

The usual thermal or catalytic processes for the conversion of hydrocarbon feed stocks into cracked or reformed products of higher octane number all require the supply of large amounts of heat. Heat is required to raise the temperature of the feed stock to the catalytic or thermal conversion range which includes broadly the limits of about 800° F. to 1150° F. for the typical process of this type. In many cases additional heat is required to vaporize the feed stock as a part of the step of raising it to reaction temperature. Furthermore, in most of these catalytic or thermal processes dehydrogenation or cracking reactions play a predominant role so that the process is more or less strongly endothermic. Thus a still further amount of heat must be supplied to furnish the necessary heat of reaction.

In laboratory test runs, and even in some small-scale plant production it is possible to heat the reaction zone externally so that a cold liquid oil can be fed and the necessary heat for vaporization, preheating and reaction all supplied in this way. In present-day commercial practice this is not the preferred method, however, for many reasons. Thus, better results are usually obtained by separating the preheat zone and reaction zone, so that the reaction can take place under more nearly uniform conditions. The recovery of heat from various process streams as preheat to the feed is a particularly important economic advantage, which is to be exploited to the full.

In both the thermal and catalytic types of hydrocarbon conversion, better results are frequently obtained by carrying out the preheating and vaporization steps in such a way that the feed stock is brought rapidly up to the final reaction temperature once it exceeds the limit of about 600–700° F. This is the temperature level above which thermal decomposition begins to take place on longer or shorter exposure, depending of course upon the character of the liquid fed. The amount of preheat which can be usefully recovered from a process stream by indirect heat exchange with the liquid feed is ordinarily below this range. In perhaps more cases than otherwise this limit is not reached, due to a tendency of either the feed stream or the available process streams to form a deposit on the heat exchange surface.

In the usual case where there is some danger of such deposits being formed from unstable or reactive compounds on the feed side of a preheat exchanger, the preheating and vaporization will be carried out in stages, with the first stage limited to a temperature where the feed will remain liquid. Following this initial preheat, the next step is then to pass the preheated feed stock through a second heating section which may be a fired furnace or may involve heat exchange with some higher temperature process stream such as a regeneration gas,

flue gas, or the like. In this heating zone the naphtha feed stock is vaporized. This means, of course, that any non-volatile material present in the naphtha will be deposited on the surface of the heating tubes or other heat exchange surface employed. For this reason it has been well known in petroleum refining that a feed stock to be completely vaporized must be a "clean stock" if frequent shutdowns for tube cleaning are to be avoided.

Although light distillates in the naphtha boiling range are all of them materials which have essentially no non-volatile constituents, petroleum refiners have also appreciated the fact that feed stocks containing olefinic or diolefinic constituents frequently cause trouble in such service. The well-recognized difficulty here is the tendency of such unsaturated materials to form peroxides with any dissolved oxygen, and to polymerize with themselves or other reactive constituents of the blend in a gum- and resin-forming reaction which is itself peroxide-catalyzed.

Accordingly, it has been common practice to give olefin-containing feed stocks special handling to prevent gum-forming reactions before such a complete vaporization step. The addition of oxidation inhibitors or blanketing the processing equipment and storage vessels with an inert gas serves to prevent gum formation, which can be readily detected by standard methods of test. A naphtha taken from intermediate storage may simply be steam stripped to remove dissolved oxygen before further processing, particularly when the storage period is short and little or no gum has actually been formed. In special cases if it is not practical to avoid the formation of such gums and resins, the olefinic naphtha may even be rerun over liquid bottoms to give a clean vapor before it is superheated. Such methods of treating these unsaturated stocks have made it possible in many cases to use an olefinic feed at moderate temperature levels and still approach the clean exchanger conditions found when using a fully saturated or virgin naphtha feed stock.

The cleanliness characteristic of a virgin naphtha feed has ordinarily been taken as the standard in such comparisons. The paraffin, naphthene and aromatic constituents of such a feed stock are nothing like as reactive with oxygen as the olefins and diolefins. They do not form gums and resins on even prolonged exposure to dissolved oxygen, in ordinary storage. In the conventional type of thermal reforming operation where the feed stock has been preheated to a temperature of the order of 300 to 350° F. and then introduced into a heated coil for the reforming reaction, the preheat tubes have remained substantially clean over long periods of time, and the useful onstream period of the reforming process has been limited by coke-forming reactions in the reformer coils.

It has now been found, however, that this same situation does not apply when substantially higher preheat temperatures are employed. In severe thermal reforming, where temperatures well above 1,000° F. are to be employed, the preheat temperature may go as high as 400–500° F., although not ordinarily higher than this. In catalytic reforming processes at high conversion levels, however, such as hydroforming or aromatization the reaction is more strongly endothermic and correspondingly more heat must be supplied. High level heat is available from the product stream, and the highest degree of preheat which can be recovered, such as 600–650° F., becomes economically attractive.

In either type of reforming process, when preheat temperatures of the order of 400–650° F. or higher are employed, it appears that dissolved oxygen in a saturated naphtha feed stock may become sufficiently reactive to cause the formation of appreciable amounts of gummy deposits, at elevated temperatures, on the heat exchange

surfaces in the preheat train. It is particularly surprising to discover that this happens even with feed stocks which are essentially gum-free by standard methods of test, and which contain no constituents commonly regarded as gum formers.

It is an object of the present invention to improve the operation of a heating unit for preheating and vaporizing a virgin naphtha feed stock.

It is another object of this invention to provide a simple means for excluding oxygen from a fully saturated feed stock, free of gum-forming constituents, where this feed stock is to be completely vaporized during preheating for a further processing step at an elevated temperature.

It is a further object to provide a means for excluding oxygen from a saturated hydrocarbon feed stock by the addition of an oxidation inhibitor thereto, which accomplishes this aim without requiring the use of special utilities or processing equipment.

It is a still further object to significantly increase the useful time onstream of a heat exchange unit for preheating and vaporizing a saturated hydrocarbon feed stock in the naphtha boiling range, by adding an oxidation inhibitor to the feed stock in intermediate storage.

According to the present invention a freshly distilled naphtha feed stock, which is being accumulated in storage prior to a subsequent thermal or catalytic reforming process, is treated with from about 0.1 to 1.0 lb. or as much as 5 lbs./5,000 gals. of an oxidation inhibitor. The inhibitor should be added preferably to the freshly distilled naphtha, either before or at the same time as the naphtha feed is introduced into intermediate storage. In this way the possibility of interaction between dissolved oxygen and hydrocarbons during storage is minimized, and the feed stream withdrawn from storage for further processing is essentially free of free oxygen and peroxides. The amount of oxidation inhibitor to be used is substantially the same or somewhat less than that commonly employed for inhibiting an olefinic gasoline with the same inhibitor.

While various gasoline inhibitors may be used according to this invention, the inhibitor should preferably be one having relatively little tendency to form gummy deposits itself on vaporization of the feed containing it. The higher alkyl phenols of the "hindered phenol" type have been found to be satisfactory, such, for example, as 2,6-di-tertiary butyl-4-methyl phenol, or the analogous bis-phenols of the alklated diphenylol propane type. A fraction of petroleum phenols which may be used similarly can be obtained by extracting a heavy cracked distillate boiling within the range of from about 250° to 700° F., with a 30° to 50° Baumé caustic soda solution, and acidifying the resulting extract to release the phenols. The N-alkyl phenylene diamines or alkyl amino types of inhibitor may also be used. All of these phenol type inhibitors belong to the general class of poly-substituted aromatics, including the amine-substituted analogs of the phenols. In any case, the choice of inhibitor will depend upon its tendency to form deposits in the vaporization step, which depends in turn upon the length of time, temperature and degree of exposure to air in storage, as well as on the feed stock and the time at temperature in the preheat equipment.

The invention may be illustrated by referring to the attached drawing, which presents in simplified form a diagrammatic showing of the pertinent parts of a reforming plant. This drawing is constructed so that it may apply either to thermal reforming or to a catalytic reforming process. The operation will be described first with respect to thermal reforming.

The fresh feed to the process, introduced through line **10**, is ordinarily a freshly distilled virgin naphtha of low octane quality. The rate at which this naphtha feed is produced will not necessarily be the same as the rate at which it is to be thermally reformed. Whether this is the case or not a certain amount of the naphtha feed is ordinarily accumulated ahead of the reforming step, so as to insure continuous operation. This accumulation takes place in an intermediate storage tank **12**, which may run at a constant level or a variable level depending upon how well the rate of feed production can be synchronized with the reforming process.

According to the present invention, the fresh feed entering this vessel is combined with the required amount of a gasoline inhibitor, as indicated above, which is equivalent to a concentration of the order of 0.001 weight percent. The inhibitor added through line **14** may be introduced in the feed line before entering the tank or mixed directly in the feed pump feeding into the tank, or otherwise, so as to insure uniform distribution throughout the material in storage.

Naphtha withdrawn from this intermediate storage tank **12** passes through preheater **16**, where it is warmed by heat exchange with any suitable process stream. A typical hot process stream for this use might be a pump-around reflux stream from a product fractionating tower to be externally cooled. While a number or hot liquid or gaseous streams may be available, the use of a liquid stream minimizes the danger of rapid fouling of the outside of the heat exchange surface due to the formation of deposits thereon. Conversely, in many cases, the product vapor stream from a high temperature thermal conversion cannot be used this way, in spite of its high heat content, because of a strong tendency to form high boiling olefin polymers which may foul the exchanger surface on partial cooling and degrade the liquid product.

The feed being preheated in exchanger **16** may remain entirely liquid, or it may be partially vaporized, leaving at a temperature of about 450° F. The preheated naphtha is then introduced into furnace 18, where it is first completely vaporized and then heated further to reforming temperature, which may be about 1100° F. In thermal reforming the vaporization section and the heat-soaking section where most of the conversion takes place will ordinarily be located within the same furnace **18**, as different tube sections. The hot product vapor stream **20** leaving the furnace **18** is ordinarily then cooled rapidly to prevent further undesirable cracking or polymerization operations, which might result in the formation of additional gas and polymer from product constituents in the naphtha boiling range.

It will be understood that this description is entirely diagrammatic, and that the usual pieces of auxiliary equipment such as valves, pumps, control devices and product recovery means will be supplied in the conventional manner known to the refining art.

The improvement with which this invention is concerned is in the operation of preheater **16**. The trouble ordinarily encountered here is not so much actual plugging of the exchanger as it is poor heat exchange. A much smaller amount of a gummy deposit may be enough to cause serious damage in this respect than that which would result in high pressure drop, or decreased mechanical through-put. The formation of a gummy deposit on these exchanger surfaces takes place largely at and just after the point where the feed passes its dry point on vaporization. This shortens the run: the preheat outlet temperature goes down,, and it is necessary to reduce the feed rate through the exchanger in order to get the outlet temperature up to the desired level. The situation finally reaches the point where the useful feed rate is too low, and it is necessary to shut down to clean out the exchanger surfaces.

It is true that this sort of trouble can be minimized by running to a lower preheat temperature so that the deposit in the preheating train is all formed in the furnace 18. This, however, means using expensive furnace heat instead of waste heat otherwise available. It also adds to the amount of coke formed in the furnace, which lim-

its the run length finally in any case. The deposit in the furnace ends up as coke, whether it starts as gum or not, and builds up toward a mechanically limiting pressure drop. At the same time there is a decrease in the useful through-put which is limited by heat transfer through the coked furnace tubes, so that it becomes impossible to get the outlet temperatures desired without decreasing the feed rate to progressively lower and lower values. Neverthless, it is much easier to remove coke from the furnace tubes than it is to clean gum from the preheater surfaces. This has resulted in the choice of lower preheat temperatures, even in thermal reforming, than might otherwise be usefully employed.

The process of the present invention is useful in thermal reforming under a variety of conditions, which may include coil outlet temperatures from 800° up to about 1,000° to 1150° F. and pressures in the range from about 250 to 1,000 p. s. i. g. The preheat for such operations is normally not over about 450° to 500° F., and the process may be useful broadly where preheat temperatures go substantially above 300° to 350° F.

The process may also be used in substantially the same way in catalytic reforming processes, where its use will be described with particular reference to catalytic hydroforming. This operation may be carried out at a reactor outlet temperature of about 900° to 1100° F., operating anywhere from about 50 to 1,000 p. s. i. g. An important difference in this case is that the reactor product is fully saturated and need not be quenched, so that the heat content of the product stream can be recovered at a high temperature level in heat exchange with the feed. At the same time a very high heat input to the conversion zone is required, to supply heat for the endothermic reaction. For this reason, the outlet temperature from preheater 16 will frequently be as high as 650° to 700° F., so that the feed stock is completely vaporized at this stage of the heating process. The preheated vapors are then superheated in furnace 18 to a temperature which is ordinarily somewhat higher than the reactor temperature range, and are fed through line 20 into the catalytic reaction chamber.

The fact that the feed stock is completely vaporized in the preheating exchanger 16 means that the present invention is particularly important in catalytic reforming processes.

A most significant feature of this invention is the fact that it requires no special processing equipment. It enjoys an important advantage in this respect over previous systems such as steam stripping, rerunning, or inert blanketing, all of which require special utilities or separate processing steps for their practice.

It will be understood that while this invention has been described with reference to thermal or catalytic reforming proceses, it may be useful in a variety of other cases where a saturated feed stock such as a virgin naphtha is to be completely vaporized as part of a process for the conversion or treatment of hydrocarbons. Such processes might be involved in a variety of distillation or solvent extraction procedures as well as in those involving thermal or catalytic conversions.

What is claimed is:

1. The process of preparing a superheated naphtha vapor feed consisting essentially of saturated hydrocarbons not susceptible to gum formation below temperatures of about 400° F. and substantially free of olefinic constituents for a hydrocarbon conversion process which comprises accumulating in storage a body of said naphtha, adding to said naphtha entering storage an amount of gasoline oxidation inhibitor equivalent to from about 0.1 to 1.0 pound per 5,000 gallons of liquid naphtha, withdrawing a naphtha stream from said storage, preheating said naphtha stream by indirect heat exchange to a temperature above about 350° F. at which at least partial vaporization takes place with minimum fouling of exchanger surfaces, subsequently heating said stream further in a separate heater to produce a superheated completely vaporized naphtha stream, and feeding said naphtha vapor to said hydrocarbon conversion process.

2. The process according to claim 1 in which said inhibitor is of the alkylated phenol type.

3. In a process for converting a virgin naphtha distillate consisting essentially of saturated hydrocarbons not susceptible to gum formation below temperatures of about 400° F. and substantially free of olefinic constituents into a thermally reformed product of improved octane rating by vaporizing the naphtha and subjecting the vapors to thermal treatment at a temperature of about 800–1100° F. and at a pressure from about 100 to 1000 p. s. i. g., the improved method of preventing fouling of heat exchanger tube surfaces in the vaporization and feed preheat portion of the system which comprises adding from about 0.1 to 5 pounds of an oxidation inhibitor per 5,000 gallons of liquid feed to the virgin naphtha in storage prior to said vaporization.

4. The process of preparing a feed stock for catalytic naphtha reforming which comprises introducing a freshly distilled virgin naphtha feed consisting essentially of saturated hydrocarbons not susceptible to gum formation below temperatures of about 400° F. and substantially free of olefinic constituents for said process into an intermediate storage tank together with from about 0.1 to 1.0 pound per 5,000 gallons of naphtha oxidation inhibitor, withdrawing a naphtha stream from said storage, preheating said naphtha stream first by indirect heat exchange to a temperature above about 450° F. at which substantially complete vaporization takes place with minimum fouling of the exchanger surfaces, passing said vaporized naphtha through a separate heating zone in indirect heat exchange with hot combustion gases and thereby superheating the naphtha vapors to a temperature above about 800° F. suitable for said catalytic reforming process, passing said superheated vapors into a catalytic reforming zone and recovering therefrom a hot product vapor stream substantially free of olefinic hydrocarbons, and passing said hot product stream in indirect heat exchange with said naphtha withdrawn from storage for said first-named heat-exchanging step.

5. The process according to claim 4 in which said inhibitor is of the polysubstituted alkylphenol type.

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