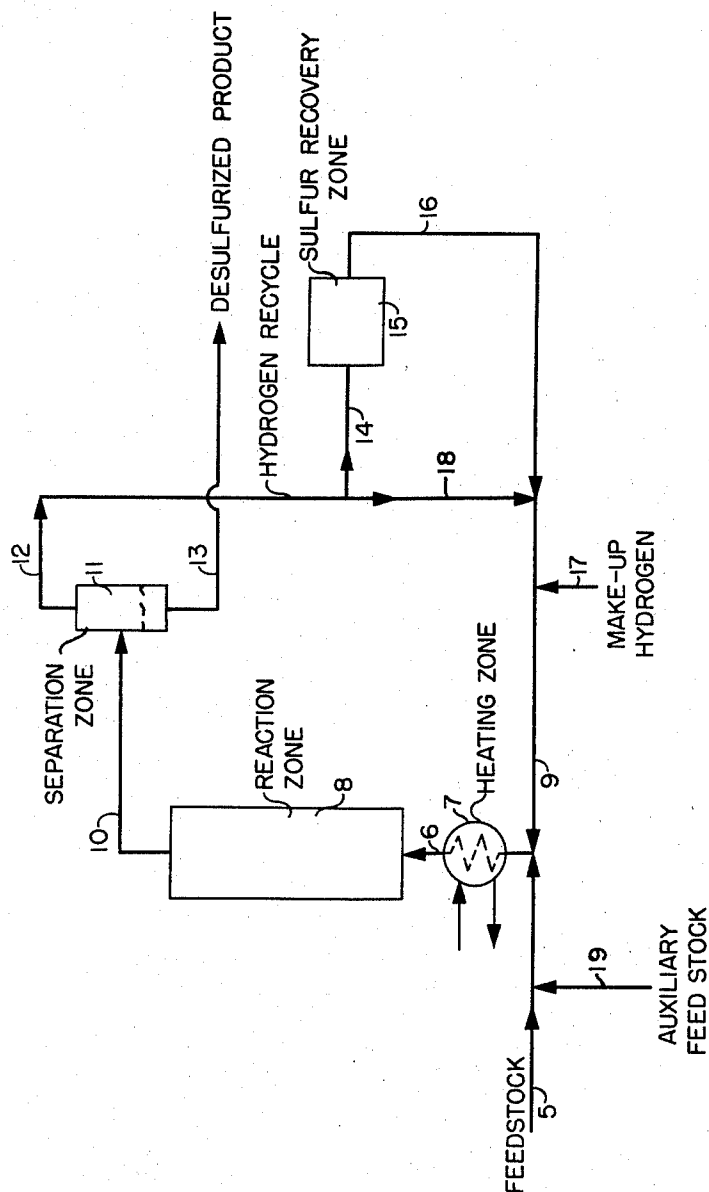


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A PRESULFIDED PLATINUM CATALYST
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HYDRODESULFURIZATION PROCESS EMPLOYING A PRESULFIDED PLATINUM CATALYST

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The present invention concerns a process for desulfurizing sulfur-containing hydrocarbons. It particularly concerns the desulfurization of hydrocarbon mixtures that contain sulfur and also aromatic and/or olefinic compounds. The invention especially relates to the desulfurization of petroleum naphtha fractions that are derived from the catalytic cracking of petroleum and petroleum fractions.

The desulfurization of hydrocarbons and hydrocarbon mixtures is a problem of growing importance in the organic chemical industry. It is a problem which particularly interests the petroleum refiner since it has been determined that the existence of sulfur in various refined products has a marked deleterious effect on the quality of the products. Petroleum refined products that have been established to be especially adversely affected by the presence of sulfur are gasoline and naphtha fractions that are incorporated within gasoline.

For many years it has been recognized in the petroleum industry that sulfur in gasoline is undesirable since its presence gives rise to serious odor, corrosion and gum formation problems. Accordingly methods have been developed and employed to counteract these problems. The methods in general have fallen into two major groups. The first group of methods has had as its objective the conversion of sulfur compounds, especially malodorous compounds, into other sulfur compounds that are less objectionable. The second group of methods including caustic washing, acid treating and the like, has had as its objective the actual removal of the sulfur compounds.

While the already existing methods of dealing with the problem of sulfur in gasoline have been at least partially successful in combating odor, gum, etc., the methods do not constitute satisfactory solutions to new problems that have arisen in the petroleum industry especially with regard to gasolines. These new problems have been occasioned by several factors. First, it has been established that sulfur, even in non-malodorous forms, causes a decrease in the lead response of a gasoline. In other words, it has been found that a gasoline that contains sulfur will experience a lesser increase in its octane rating upon the addition of tetraethyl lead than will a gasoline that possesses little or no sulfur. Second, it has been observed that a gasoline which contains both lead and sulfur, forms deposits within the combustion chambers of an internal combustion engine that markedly and adversely increase the octane requirement of the engine.

The second of the above-mentioned factors is rendered more critical by a third factor—namely, that many modern and future internal combustion engines require and will require gasoline fuels of exceptionally high octane quality. In order to manufacture fuels that will be satisfactory for use in such engines, it is necessary to (1) remove the sulfur from the fuels in order to increase the lead response of the fuels and also to avoid

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harmful sulfur-containing deposits; (2) remove the sulfur from the fuels or fuel components by methods that will not decrease the octane quality or rating of the fuels or fuel components. In connection with the latter point, it has been well recognized that certain processes, which are capable of removing sulfur from fuels such as gasolines and naphthas unfortunately remove or alter components of the fuels that possess excellent antiknock properties.

It has been recognized for some time that mild hydrogenation of a sulfur-containing gasoline or gasoline component is a very effective method for reducing the sulfur content of such hydrocarbon mixtures. In accordance with this process a sulfur-containing fraction such as petroleum naphtha is contacted with a hydrogen-containing gas in the presence of a suitable catalyst under conditions of temperature and pressure that are adapted to convert the sulfur in the naphtha to hydrogen sulfide. The hydrogen sulfide is then removed from the naphtha as by flashing, stripping, distillation or the like. It will be noted that catalysts that are suitable for such hydrogenation processes and that are well known in the art for this purpose include the so-called platinum catalysts. These catalysts essentially consist of platinum which is finely divided, dispersed or impregnated on a particulate catalyst support such as alumina, silica gel, silica-alumina, silica-magnesia, activated char, etc. In general such catalysts contain from about 0.05 to 2.0 wt. percent platinum and usually about 0.5 wt. percent platinum. The catalysts are conventionally prepared according to a variety of well-known procedures. One such procedure calls for the impregnation of alumina with chloro-platinic acid. The resulting material is calcined at about 1000° F. before use. At this point it will be observed that this material is also suitable for catalytic reforming operations and that conventional platinum reforming catalysts in general are suitable for the purposes of the present invention.

While the conventional mild hydrogenation procedures described immediately above are effective in reducing the sulfur content of a petroleum naphtha, they have the disadvantage that they are unable to achieve sulfur reduction without partially or completely altering certain valuable octane components of the naphtha. This condition has been especially true for cracked naphthas, where mild hydrogenation has succeeded in reducing the sulfur contents of such naphthas but has also converted the olefins and aromatics in such naphthas to less valuable paraffinic and naphthenic compounds. This condition has been particularly the case where platinum catalysts have been employed in the processes.

Accordingly it is an objective of the present invention to provide a process for removing sulfur primarily in the form of hydrogen sulfide from a gasoline or naphtha fraction without causing olefinic and aromatic components of the fraction to be converted to less valuable materials. It is a further object of the invention to provide a process of the type described which employs a platinum-type catalyst and which is carried out in the presence of hydrogen.

These and other objectives may be achieved in accordance with the present invention by contacting a distillate petroleum fraction with hydrogen in the presence of a platinum-type catalyst at a temperature between about 340° F. and 940° F., a pressure between 15 and 600 p.s.i.g., a feed rate between 0.1 and 20 volumes of liquid feed per hour per volume of catalyst and a hydrogen rate between 100 and 10,000 s.c.f. per barrel of liquid feed while maintaining the concentration of sulfur within the reaction zone above a critical value. In connection with the latter feature of the present process, it is neces-

sary that a mol ratio of sulfur to platinum be maintained within the catalyst bed at a value between about 1.5/1 and 3/1, and more particularly about 2/1. To this end, extraneous sulfur may be added to the feed which it is desired to desulfurize.

It is further critically necessary that the mol ratio of sulfur to hydrogen fed to the reaction zone be maintained above certain critical limits, depending upon the temperature that is maintained within the zone. In other words, for a given reactor temperature, it is necessary that a critical relationship be maintained between the mols of hydrogen and the mols of sulfur entering the zone. This relationship may be best explained by reference to the following equation:

$$\log_{10} \frac{\text{mols S}}{\text{mols H}_2} = 2.733 - \frac{5464}{T_R}$$

where "mols S" and "mols H₂" represent the mols of sulfur and hydrogen fed to the reaction zone, and T_R is the reaction temperature in degrees Rankine and lies between 800 and 1400° R.

It is apparent from the above equation that the amount of hydrogen in the expression is fixed by the amount of sulfur and by the temperature. It is also apparent that the logarithm of the S/H₂ mol ratio is fixed by the temperature alone. In this connection it is a requirement of the present invention that the logarithm of the S/H₂ mol ratio, for a given temperature, be maintained at a value at least as great as the value that is derived from the equation.

In general it is desired that the temperature of the reaction zone be maintained within the range of values presented earlier, but it is also desired that it be maintained high enough to realize the required degree of desulfurization. Likewise, the pressure should be in the range stated earlier but not so great as to cause the hydrocarbon feed to be in the liquid phase.

The figure that accompanies the present description illustrates one embodiment of the invention and the best mode contemplated for carrying out the invention. Before entering into a detailed description of the embodiment illustrated therein, however, it is considered desirable to briefly describe the feed stocks and other materials which enter into the process. Thus it will be observed that the process of the present invention is particularly adapted for the desulfurization of distillate petroleum fractions that boil within the range from about 150° to 400° F. and that contain sulfur, olefins and aromatics. Naphthas that boil within the range from about 200 to 350° F. and that are derived from cracking and/or coking processes are especially benefitted by the invention. Such naphthas generally contain about 20 to 40 volume percent aromatics, about 15 to 60 volume percent olefins and about 0.03 to 1.5 weight percent sulfur. These and other hydrocarbon feed stocks that contain from about 0.01 to 2 wt. percent sulfur, at least about 10 volume percent olefins, and at least about 10 volume percent aromatics are especially well adapted to the purposes of the invention.

As mentioned earlier, catalysts that are effective in the present process consist of conventional platinum-impregnated carriers such as alumina, silica gel, char and the like. The chemical compositions of such catalysts and their methods of preparation are well known in the art, and a detailed discussion of these features will not therefore be included in the present description.

It will be appreciated that the present process may be carried out using catalysts in the form of fixed beds, moving beds or fluidized beds. Accordingly, the particle size of the catalyst may vary depending upon the particular type of catalyst bed that it is desired to employ. In

the event that a fixed bed of a platinum-type catalyst is to be utilized, it is contemplated that the catalyst should have a range of particle sizes that falls within the range from about 1/16 to 3/8 inch and especially about 1/16 to 1/8 inch.

In this type of operation the catalyst may be present in the form of lumps, crushed particles, pills, pellets, etc. In general, it is desired that extruded pellets be employed of about 1/16 in diameter.

In the event that a fluidized bed of catalyst is used it is desired that the catalyst have a particle size range of about 20 to 150 microns and especially about 40 to 80 microns.

In the event that the catalyst is employed in a moving bed type of operation, it is contemplated that the catalyst should have a particle size range of about 1/8 to 3/16 inch and especially about 1/8 inch. In any event it is desired that the catalyst contain from about 0.05 to 2.0 wt. percent platinum and especially about 0.4 to 0.6 wt. percent.

It is particularly contemplated that the best mode of practicing the present invention lies in using the catalyst in the form of a fixed bed. It is further contemplated that the catalyst be alumina impregnated with about 0.5 wt. percent platinum, and that it possess a particle size range within the range from about 1/16 to 1/8 inch. A catalyst may be made up in accordance with any of the conventional methods of preparation. A particularly attractive method is as follows: aluminum hydrosol is prepared as described in U.S. Patent 2,656,321. The hydrosol is dried at about 250° F. The dried alumina gel is ground to pass 100 mesh and mixed with an equal weight of water to form a thick paste. The alumina paste is extruded through a 1/16" die. The extruded pellets are dried and calcined for four hours at 1100° F. The calcined pellets are covered with a solution of chloroplatinic acid containing sufficient chloroplatinic acid to introduce 0.5 wt. percent of platinum into the alumina. The alumina adsorbs the chloroplatinic acid from solution. After soaking for one hour, the water is drained from the impregnated pellets. The catalyst is then dried and heated for 3 hours at 1000° F.

As also mentioned earlier, the process of the present invention employs a hydrogen-containing gas as one of the materials that enter the desulfurization zone. The gas may be pure hydrogen or it may be a gas that contains hydrogen as one of its major components. In general, the hydrogen-containing gas should contain at least 50 volume percent hydrogen and preferably at least 65 volume percent hydrogen. It is further desired that the gas contain substantially no carbon monoxide or carbon dioxide and less than 0.5 mol percent water. The gas may contain such gaseous components as light paraffinic hydrocarbons such as methane, ethane, etc. Tail gas derived from conventional hydroforming operations with platinum or molybdena catalysts is suitable.

As will be pointed out in more detail hereinafter, it may be desirable in some instances to include a small amount of hydrogen sulfide or other sulfur compound within the hydrogen feed stream. The amount to be added is governed in accordance with the equation given earlier in this description.

Turning to the figure, it will be assumed that the feed stock in line 5 is a petroleum naphtha boiling in the range from about 200 to 380° F. that is derived from a catalytic cracking operation. It is apparent that a naphtha of this type may be produced by the cracking of petroleum fractions such as gas oils, reduced crudes, cycle stocks, residua, and even crude oils themselves. It will further be assumed that the feed stock is rich in aromatic hydrocarbons and olefinic hydrocarbons and that it contains substantial amounts of sulfur compounds.

When starting up the process which is illustrated in the figure it will be apparent that the catalyst within the reaction zone 8 will initially contain no sulfur. And in this connection it will be recalled that a critical feature of the present invention calls for the maintenance of a criti-

cal mol ratio between the amounts of sulfur and platinum that exist within the catalyst bed itself. Accordingly, a first phase of the present process is necessarily concerned with establishing the critical mol ratio of platinum to sulfur that it is desired to maintain within this zone. This step may be accomplished in several ways. A sulfur-containing gas such as hydrogen rich in hydrogen sulfide may be passed through zone 8 under conditions of temperature and pressure whereby the sulfur combines with the catalyst. Alternatively and preferably, a sulfur-containing hydrocarbon stream is passed through zone 8 for a period of time sufficient to realize the platinum/sulfur mol ratios desired. A particularly effective manner of achieving this objective lies in passing the feed stock itself through the reaction zone under conditions such that the sulfur in the feed stock will combine with the catalyst. In any case involving the use of a hydrocarbon presulfiding feed, it is desired that the feed have a boiling range of about 150 to 400° F., preferably about 200 to 350° F., and that it contain at least about 1.0 wt. percent sulfur. In general, it is desired that the presulfiding feed not contain in excess of about 2.0 wt. percent sulfur. It is further preferred that the feed stock be a virgin naphtha containing no olefins and very little aromatics, since this type of feed stock is not harmed or affected by the hydrogenating activity of the catalyst. And, as in the desulfurizing phase of the process, it is desired that hydrogen be added with the presulfiding feed to avoid carburization of the catalyst.

In starting the operation which is illustrated in the figure, it is essential that the reaction zone 8 be brought up to suitable conditions of temperature and pressure. This may be achieved by preheating the sulfiding feed stock and/or the hydrogen stream that are introduced within zone 8. This may be done by the use of a suitable heating zone 7 which may be a conventional furnace, fired coil, heat exchanger, or the like.

During the presulfiding phase of the process, reaction zone 8 must be maintained at a temperature of at least 400° F. and a pressure of at least 15 p.s.i.g., preferably about 50 p.s.i.g. The temperature and pressure should not exceed the values of 1000° F. and 600 p.s.i.g. respectively. A preferred temperature range for this step is about 500 to 600° F., and a preferred pressure range is about 50 to 200 p.s.i.g.

The presulfiding reaction should be carried out at a hydrocarbon feed rate between about 1 v./hr./v. and 10 v./hr./v. and preferably about 5 v./hr./v. The hydrogen rate should be at least about 1000 s.c.f. of hydrogen per barrel of feed, and it is particularly desired that the sulfur to hydrogen mol ratio in the feed be maintained about a certain critical value. This ratio (i.e. the minimum value) is also described by the equation given hereinafter relative to the desulfurization reaction.

The presulfiding phase of the process must be continued until the catalyst is provided with at least 1.5 mols of sulfur per mol of platinum and preferably at least 2 mols of sulfur per mol of platinum. This point may be determined by conventional chemical analyses and material balances performed on the feed and product streams. It may also be determined by running sulfur analyses on small samples of the catalyst bed itself. The presulfiding step will normally require about 30 minutes to one hour.

When the catalyst within zone 8 has arrived at the proper sulfur/platinum mol ratio, the desulfurization phase of the process should be initiated. At this point the feed stock is introduced via lines 5 and 6 and heating zone 7 into zone 8. A hydrogen-containing gas is simultaneously introduced by means of lines 9 and 6 and zone 7 into zone 8. As pointed out earlier, the relative amounts of hydrogen and hydrocarbon feed that flow into zone 8 must be determined on the basis of the temperature that is maintained within zone 8. The feed rates are further determined by the contact times that

it is desired to maintain for both of these streams within zone 8. The temperature of zone 8 will, of course, be governed by the sulfur content of the feed, the activity of the catalyst, and the degree of desulfurization desired.

Assuming that reaction zone 8 is operated at 600° F., it necessarily follows that the feed rates of hydrocarbon and hydrogen-containing gas that enter zone 8 must be regulated so as to realize a sulfur to hydrogen mol ratio within zone 8 of at least 0.004/1. A ratio much above this value, however, should be avoided since higher ratios tend to decrease the efficiency of desulfurization.

The feed rate of the hydrocarbon feed to zone 8 must additionally be maintained within the range of from about 0.1 to 20 volumes of liquid per hour per volume of catalyst and preferably about 5 v./hr./v.

The pressure within zone 8 may be maintained from atmospheric up to 600 p.s.i.g., preferably from 50 to 200 p.s.i.g. and especially about 100 p.s.i.g.

Under the conditions described above, sulfur compounds contained within the hydrocarbon feed are converted to hydrogen sulfide and without substantially hydrogenating the olefinic or aromatic components of the feed. The resulting mixture of gas, hydrocarbons and hydrogen sulfide is conveyed as by means of line 10 to a separation zone 11. Here gaseous components including hydrogen and hydrogen sulfide are separated from the desulfurized hydrocarbons as by cooling the mixture sufficiently to condense the hydrocarbons. Then the gases are conveyed by means of lines 12 and 14 to sulfur recovery zone 15. In zone 15 the gas stream may be scrubbed with alkaline materials such as aqueous sodium carbonate, caustic or lime solutions. Alternatively, the gas stream may be here treated with a reagent such as diethanolamine which recovers the sulfur as hydrogen sulfide which in turn can be converted to elemental sulfur. In any case, it is generally desired that zone 15 be operated so as to provide a hydrogen-containing gas in line 16 that contains less than 0.1 wt. percent sulfur and preferably less than 0.01%. However, when the naphtha feed does not contain enough sulfur to maintain the above-mentioned ratio of sulfur to hydrogen, to wit 0.0041, it may be advantageous to by-pass a portion of the recycle hydrogen around scrubbing zone 15 by line 18. The purified gas may then be recycled to reaction zone 8 by means of lines 16, 9 and 6.

Makeup or fresh hydrogen gas may be introduced within the system by means of line 17. Also, hydrogen gas that contains substantial amounts of sulfur may be introduced within zone 8 by merely recycling at least a portion of the stream in line 12 directly back to zone 8 by means of lines 18, 9 and 6. The use of this procedure and/or the use of auxiliary feed stocks in line 19 may be particularly followed in order to realize the sulfur/hydrogen mol ratios that are desired in zone 8. Such an eventuality may arise in those instances where the feed stock in line 5 contains such very small amounts of sulfur that the desired sulfur-hydrogen ratios within zone 8 are impossible to achieve under the feed rates that are otherwise necessary to employ. These and other operating variables will be apparent to anyone skilled in the art.

The following specific example will serve to better illustrate the nature of the present invention. In this example a hydrocarbon feed mixture consisting of about 1/3 benzene, 2/3 normal heptane and 0.5 volume percent thiophene was fed at a rate of 75 cc. per hour over 150 cc. (110 g.) of a catalyst consisting of 0.5 wt. percent Pt on an alumina base maintained at a temperature of 500° F. and 200 p.s.i.g. pressure. Hydrogen was also introduced at a rate of 2.8 c.f./hr. which is equivalent to about 6000 s.c.f. H₂/bbl. of feed. The sulphur content of the feed was equivalent in turn to 1.3 × 10⁻³ mols of sulfur per mol of hydrogen. Referring to the aforedescribed equation, it is noted that this sulfur concentration is safely above the minimum required for the operating temperature of 500° F. The following analyses

of the product collected over consecutive 30-minute periods for aromatic and sulfur content were obtained:

30-Minute Period No.	Atoms S Fed Per Atom Pt	Vol. Percent Aromatics in Product	Wt. Percent Sulfur in Product
Feed.....		33	0.275
1.....	0.9	3.5	0.009
2.....	1.8	13	0.009
3.....	2.6	25	0.032
4.....	3.5	30	0.014

After the second period when approximately 2 atoms of sulfur/atom of platinum had been fed, the aromatic content of the product was substantially that of the feed while the difficult to remove thiophene sulfur was reduced to a low level. Within the limits of experimental error in the chemical determination of sulfur, this low sulfur level was the same as that obtained with fresh catalyst. The fresh catalyst, however, had the disadvantage of hydrogenating the aromatics.

It is apparent from the example above that the invention is very effective in providing naphtha of very low sulfur content. The invention, however, is not to be limited to the scope of this particular example. Rather, it has application especially for thermally or catalytically cracked fractions that are incorporated within gasolines, since it desulfurizes such fractions without decreasing their octane ratings. Furthermore, the invention decreases the gum- and deposit-forming tendencies of the fractions without adversely affecting their lead response.

What is claimed is:

1. A method of desulfurizing a petroleum fraction boiling within the range from about 150° to 400° F. and containing olefins, aromatics and from 0.01 to 2 wt. percent sulfur which comprises initially contacting a platinum hydrogenation catalyst that contains from 0.05 to 2 wt. percent platinum with a hydrocarbon mixture boiling within the range from about 150 to 400° F.; said mixture containing no olefins, substantially no aromatics and more than 1 wt. percent sulfur; the mixture being contacted with the catalyst between 400° F. and 1000° F. and 15-600 p.s.i.g. at a feed rate of from 1-10 volumes of liquid mixture per hour per volume of catalyst until the catalyst contains at least 1.5 mols of sulfur per mol of platinum; thereafter contacting said petroleum fraction in a reaction zone with the sulfur-containing platinum catalyst at a feed rate of from 0.1 to

20 volumes of liquid fraction per hour per volume of catalyst and at a temperature and pressure adapted to maintain the fraction in vapor phase; the temperature being from about 340 to 940° F. and the pressure between atmospheric and 600 p.s.i.g.; passing hydrogen through the reaction zone with the fraction at a rate between 100 and 10,000 s.c.f. per barrel of liquid fraction and in an amount sufficient to provide a sulfur/hydrogen mol ratio within the reaction zone such that the logarithm₁₀ of the ratio is at least equal to the expression

$$2.733 - \frac{5464}{T_R}$$

where T_R is the temperature of the zone in ° Rankine ratios appreciably above the value determined by the formula being avoided since they tend to decrease the efficiency of desulfurization; withdrawing the resulting product stream including the desulfurized fraction, hydrogen, and hydrogen sulfide from the reaction zone; condensing and separating the desulfurized fraction from the product stream; and withdrawing the desulfurized fraction.

2. A method as defined in claim 1 in which the catalyst is contacted with the hydrocarbon mixture at a feed rate equivalent to 5 volumes of the liquid mixture per volume of catalyst per hour until the catalyst contains not more than 2 wt. percent sulfur; and wherein the hydrocarbon mixture is contacted with the catalyst at a temperature between 500 and 600° F. and a pressure between 50 and 300 p.s.i.g.

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