

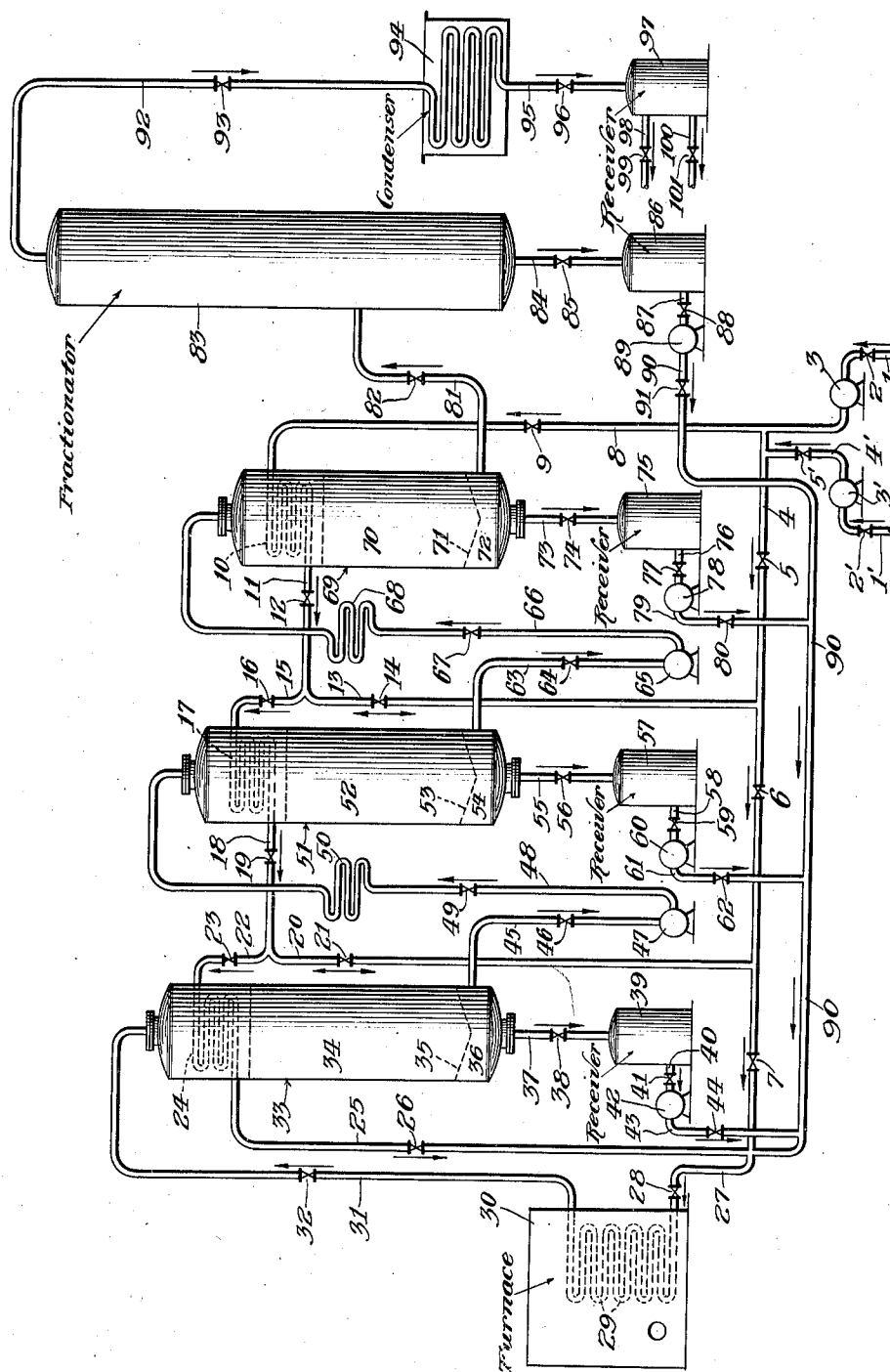
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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1 Claim. (Cl. 196—62)

This invention relates more particularly to the conversion of relatively heavy hydrocarbon mixtures into maximum yields of low boiling motor fuel fractions.

5 In a more specific sense the invention consists in a process in which temperature, pressure, time and hydrogen concentration in the reacting materials are interregulated so that a process of high efficiency results in respect to both yield and quality of product and general mechanical advantage.

10 In general the process of destructive hydrogenation for the production of large yield of low boiling liquids from heavy hydrocarbon liquid mixtures is well known at the present time and developments in this field are of the nature of improvements upon the basic process which consists essentially in cracking with a suitable excess of hydrogen in the presence of catalysts of proven character.

20 The process of the present invention is a contribution to this field and as will be shown later makes possible the efficient production of high yields of gasoline from heavy hydrocarbon liquid such as the residues and heavy distillates of petroleum in a stepwise process in which the temperature and pressure are oppositely varied in successive stages.

30 In one specific embodiment the invention comprises simultaneously subjecting hydrocarbon oils and hydrogen to elevated temperatures and pressures in a heating element, passing the heated products successively through separate beds of catalyst while progressively decreasing the temperature and increasing the pressure, fractionating the vaporous products from the final conversion stage to produce gasoline and returning liquid refluxes from the catalytic conversion stages and the final fractionator to the primary heating element for further treatment.

40 The general process thus briefly outlined can be carried out in apparatus of varying design both in respect to absolute and relative capacities of various interconnected parts. However, without unduly limiting the scope of the invention, its character may be conveniently developed by the description of an operation given in connection with a characteristic plant layout, and to assist in this description the attached drawing has been provided which shows diagrammatically in general side elevation an arrangement of cooperative elements and parts which may be employed to convert heavy hydrocarbons into gasoline by destructive hydrogenation according to the present process.

55 Referring to the drawing, heavy charging oil

may be introduced to the plant by way of line 1 containing control valve 2 while hydrogen is simultaneously introduced by way of line 1' containing control valve 2', pump or blower 3' discharging the hydrogen through line 4' containing valve 5' into line 4, the discharge line from oil feed pump 3. The mixture of oil and hydrogen then passes through valves 5, 6 and 7 and enters line 27 containing control valve 28 and leading to the heating element 29 arranged to receive heat from a suitably designed furnace 30. Line 27 may also receive preheated charging oil from line 25 by way of valve 26 and combined refluxes from line 90 respectively as will be later described.

15 In order to accomplish the stepwise temperature reduction in the series of catalytic converters, use may be made of indirect heat exchange with regulated portions of the relatively cool charging oil. Thus a portion of the direct feed from pump 3 may be diverted through line 8 containing control valve 9 and pass through indirect heat exchanger 10 positioned in the upper vapor space of final converter 59, leaving the heat exchanger through line 11 containing control valve 12. The amount of raw charging oil thus diverted will depend upon the temperature found by trial to be most suitable for the final conversion stage. The oil from line 11 may be either returned to the main feed line 4 by way of line 13 containing control valve 14 or may be passed to indirect heat exchanger 17 in intermediate converter 51 by way of line 15 containing control valve 16 as the exigencies of the case may dictate. Similarly the exit liquid from indirect heat exchanger 17 leaving through line 18 containing control valve 19 may be passed to indirect heat exchanger 24 in a primary converter 33 by way of line 22 containing control valve 23 or may return to the main oil feed line 4 by way of line 20 containing control valve 21.

45 As an alternative mode of cooling by indirect heat exchange with relatively cool raw oil, regulated portions thereof may be admitted to intermediate converter cooler 17 by way of line 13 containing control valve 14 and similarly into cooler 24 by way of line 20 containing control valve 21. Thus the temperature control in the converters may be given a sufficient degree of flexibility for practical purposes.

50 The range of temperatures and pressures to which the mixture of oil and hydrogen is brought during passage through the heating element 29 is considerable but as a rule the temperatures will be from 600 to 900° F., and the pres-

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sures from 500 to 3000 pounds, per square inch. As previously stated it is a feature of the present process that in the primary conversion stages temperatures are relatively high and pressures relatively low while the reverse conditions obtain in the final conversion stages. For example, the materials leaving the heating element may be at a temperature of 800 to 900° F., and a pressure of 750 pounds per square inch, these conditions obtaining through the succeeding primary catalytic converter except as temperature drops by accidental or regulated cooling and the pressure drops as a result of fluid friction. In the second stage the pressure may be stepped up to approximately 1500 to 2000 pounds per square inch while the temperature is reduced to some point in the neighborhood of 800° F. In a third stage the pressure may be still further increased to from 3000 to 4000 pounds per square inch while the temperature is brought down to some point in the neighborhood of 700° F. The present description of an operation is limited to three stages, but the process in general is not so limited as any number may be employed, considering of course, the proper economical balance between plant investment and improved results which may be obtained. In the drawing intermediate converter 51 may be considered as representing any number of converters of a similar character. It has been found that by this method of operation there is less tendency for the primary products of hydrogenation to undergo secondary decomposition reactions so that the overall efficiency of hydrogenation is higher and the hydrogen consumption correspondingly lower.

To trace the path of the heated materials through the plant layout shown in the drawing, they pass first to line 31 containing control valve 32 and enter the top of a primary converter 33 which contains a bed of catalytic material 34 supported upon a screen 35 above a lower vapor space 36 in which liquids and vapors separate, the vapors being further subjected to treatment for increasing the yield of light products while the liquids are returned to the heating element along with other refluxes. Thus the reflux liquids pass through line 37 containing control valve 38 to an intermediate accumulator 39 from which they are taken by a pump 42 by way of line 40 containing control valve 41 and discharged through line 43 containing control valve 44 to the combined reflux header 90.

The vapors from space 36 pass through line 45 containing control valve 46 and are taken by pump 47 for compression to a higher pressure. The compressed vapors pass through line 48 containing control valve 49 and in addition to the use of raw oil indirect heat exchangers, some of the heat of the vapors may be dissipated by the use of aerial coolers indicated by 50 in the drawing. It will be noted that the size of converter 51 is shown as somewhat smaller than primary converter 33. In the normal operation of the process the effect of high pressure and reduced temperature is to decrease the volume of the vapors and as a rule less time of contact with catalysts is necessary to further the reactions. Thus the size of the converters for the successive steps may continuously decrease to the last stage.

The path of the more highly compressed vapors through intermediate converter 51 is substantially the same as through primary converter 33, that is, they pass through a bed of catalyst 52 supported upon a screen 53 to liquid-vapor space

54. The liquids condensing at this point are drawn out by way of line 55 containing control valve 56 to an accumulator 57, from which they pass through line 58 containing control valve 59 to pump 60 and are discharged through line 61 containing control valve 62 to combined reflux line 90 for ultimate return to the heating element.

The vapors from space 54 are then passed through line 63 containing control valve 64 to a compressor 65 and the still more highly compressed vapors pass through line 66 containing control valve 67 and if desired through an aerial cooler 68 to enter the top of final stage converter 69 containing catalyst bed 70 supported on screen 71 and having a liquid vapor separating space 72. As before, the liquid condensates are withdrawn through line 73 containing a control valve 74 to a receiver 75 and are then returned to the combined reflux line 90 by way of line 76, valve 77, pump 78, line 79 and valve 80.

For convenience of operation, the foregoing system of reflux receivers having separate pumps has been shown. However, owing to the high pressures which obtain in the converters, it may be possible at times to operate and return reflux without this extra equipment. However, a pump will always be necessary to return reflux from the primary converter which will be at a somewhat lower pressure than that obtaining at the entrance to the heating element.

Also while it has been indicated that hydrogen is admitted to the raw oil feed line 4, it may also be admitted at any desired point along the feed line, such as, for example, line 27, although means for this are not shown in the drawing. Owing to consumption of hydrogen in the course of the conversion and reconversion reactions, further quantities may also be admitted between the stages into lines 48 and 66 respectively. The hydrogen may be preheated if desired.

The vaporous products from lower space 72 of final converter 69 comprises fixed gases, vapors of gasoline and heavier refluxes pass out through line 81 containing control valve 82 to enter fractionator 83 which in most instances is operated at some pressure lower than that obtaining in the final converter. The function of the final fractionator is to eliminate substantially all products heavier than the desired gasoline and enable the recovery of finished gasoline as an overhead product. The liquid refluxes from the fractionator are drawn out through line 84 containing control valve 85 to a receiver 86 and are returned to the heating element by way of line 87, valve 88, reflux pump 89, line 90 and valve 91.

The overhead vapors from fractionator 83 pass through vapor line 92 containing control valve 93 and the gasoline is condensed by condenser 94, passing along with residual fixed gases through rundown line 95 containing control valve 96 to a final receiver 97 which has a fixed gas release line 98 containing control valve 99 and a liquid draw line 100 containing a control valve 101.

Any of the effective hydrogenating catalysts may be employed in the converters at different stages. They may be employed alone or in admixture and may be further admixed with or deposited upon relatively inert and generally siliceous spacing materials and sized to effect a compromise between contact surface and loss of head due to flow of the vapors through the mass. As examples of catalysts which may be employed may be mentioned such metals as those of the iron group, to-wit: iron, nickel, cobalt, their oxides and sulphides and more particularly the oxides

and sulphides of metals of the sixth group including chromium, molybdenum and tungsten. The preparation and manipulation of such composite solid catalysts is fairly well established in the art at this time and no claim is made to the use of such compounds or combinations thereof as a feature of the present process.

It may be of advantage, however, to vary the type of catalyst or catalyst mixture employed in the successive stages. For example, some of the less energetic but at the same time more resistant types of catalyst such as molybdenum and cobalt sulphides may be employed in the primary converters while more active catalysts may be employed at the lower temperatures in the later stages. The exact choice of a catalyst more suitable for a given stage is best determined by trial, however, since the present knowledge of mechanism of catalyst action rarely if ever permits a prediction as to the more effective substance for accelerating a given reaction.

As an example of improved results obtainable by the use of the present process the following may be cited although numerous other data could be given.

A heavy petroleum distillate fraction from Mid-Continent crude oil may be cracked and hydrogenated. In the first stage of the reactions obtaining through the primary reaction zone the temperature may be maintained at approximately 850° F., and the pressure at 50 atmospheres. In the second stage the temperature may be reduced

to 800° F., and the pressure increased to 100 atmospheres. Following this, the third stage may be conducted at a temperature of 750° F., and a pressure of 150 atmospheres. By this procedure it may be possible to produce a yield of 95% of good octane number 400° F., end point gasoline, an increase of 10 to 15% over the possible yield when operating at mean temperature and pressure conditions in a single stage.

The nature of the present invention, its bearing upon the hydrogenation art and the type of improved results obtainable by its use are evident from a consideration of the preceding specification and example respectively, neither of which, however, is to be construed in a limiting sense as imposing corresponding limitation upon the generally broad scope of the invention.

I claim as my invention:

A process which comprises subjecting heavy hydrocarbon material to destructive hydrogenating conditions in a first stage and converting a substantial portion thereof into gasoline boiling hydrocarbons by the destructive hydrogenation, separating the resultant reaction products into vapors and liquids, returning at least a portion of the latter to the first stage, and subjecting the vapors to further gasoline-producing destructive hydrogenating conditions in a second destructive hydrogenating stage maintained under higher pressure and lower temperature than the first stage.

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