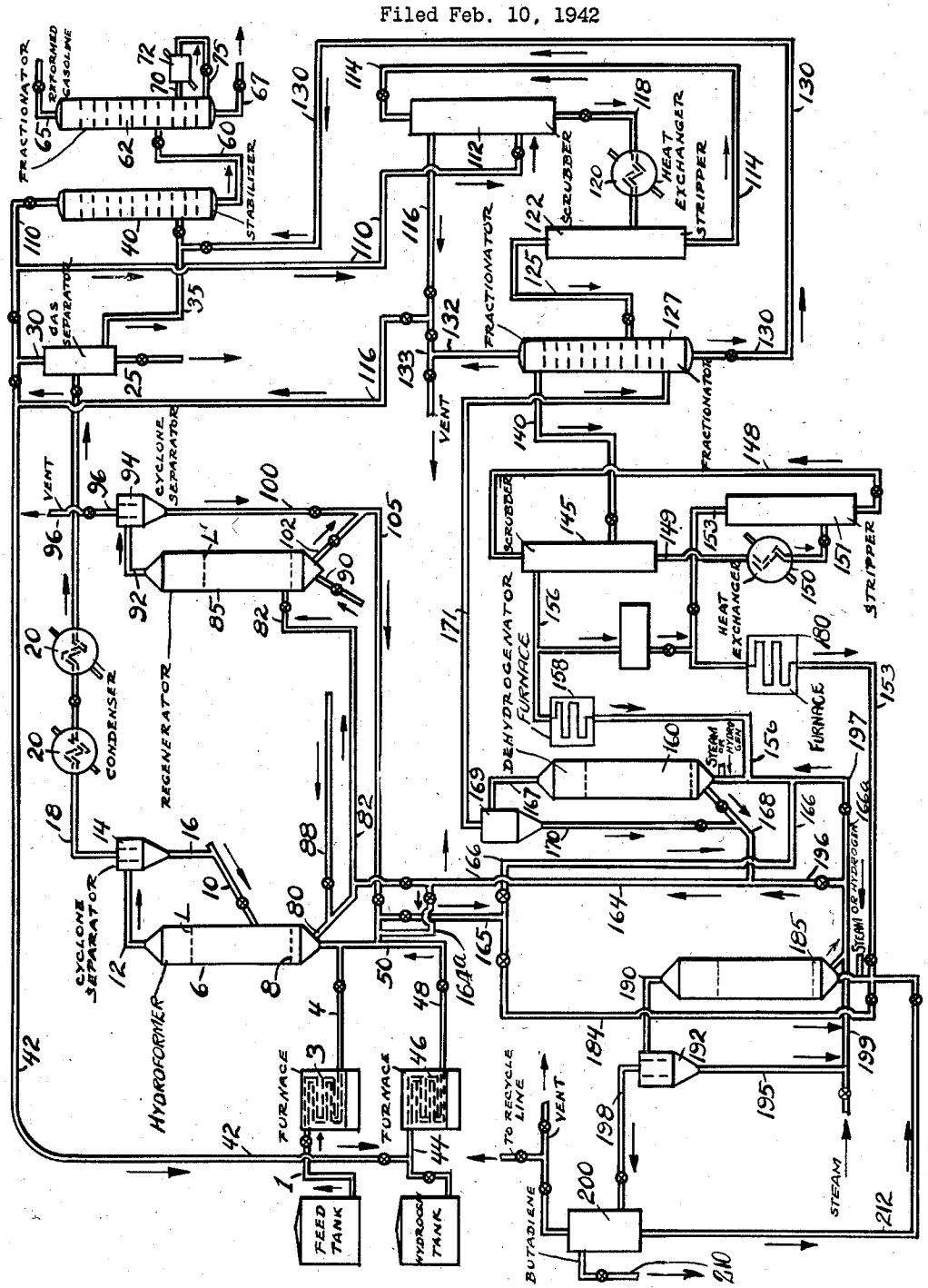
May 29, 1945. N. F. LINN 2,377,087

REFINING PROCESS

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Norman F. Linn Inventor

By P. L. Young Attorney

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REFINING PROCESS

Norman F. Linn, Roselle Park, N. J., assignor, by mesne assignments, to Standard Catalytic Company, a corporation of Delaware

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The present invention relates to improvements in the art of producing motor fuels and in particular, it relates to a combined and continuous process which utilizes the advantages of fluidized powdered catalyst for the hydroforming of naphthas and for the dehydrogenation of light hydrocarbon gases evolved in the hydroforming process.

It is generally known that hydrocarbons boiling substantially within the gasoline range may be improved as to quality, particularly as regards octane number, by subjecting them to what is known as a "hydroforming" operation, that is to say, to a treatment carried out at elevated temperatures in the presence of hydrogen and a suitable catalyst at elevated temperatures.

It is further known that in the hydroforming process certain gases are formed and in stabilizing the hydroformed product these gases may be recovered separately from the hydroformed naphtha or the like. If, for example, butadiene is desired, the overhead product from the stabilizer may be further fractionated to obtain a C_4 fraction which fraction may be subjected to dehydrogenating conditions.

Both the reforming and the dehydrogenation may be carried out in the presence of added hydrogen from a common feed line.

One object of my invention is to carry out a combined process in which I hydroform a naphtha or gasoline and in which I also dehydrogenate the C_4 hydrocarbons which are formed in the hydroforming operation to recover olefins or diolefins such as butadiene.

A further object of my invention is to hydroform a naphtha and to dehydrogenate selected fractions of the lighter hydrocarbon gases produced in the hydroforming process by a common fluidized catalyst which when deactivated is regenerated in a common regeneration vessel and then recycled.

A more specific object of my invention is to reform naphtha or gasoline in a continuous operation in the presence of a powdered hydroforming catalyst, such as molybdena or chromia on a support comprising aluminum oxide or magnesium oxide, or a mixture of aluminum oxide and magnesium oxide.

My invention will be best understood by the recitation of a preferred modification thereof in the form of a specific example, and I shall now set forth such an example with the understanding that the precise details I am about to specify are purely illustrative and are not limitative.

A better understanding of my invention may be had by reference to the accompanying drawing which indicates a flow plan in which my improved process may be carried out, and I shall refer to the drawing in setting forth the said specific example.

Referring therefore in detail to the drawing, a heavy naphtha comprising a virgin cut from an East Texas crude and boiling within the range of from about 150° F. to 400° F. or higher is introduced into the system through line 1 and thence discharged into a furnace coil 3 where it is heated to a temperature of from about 900° F. to 1100° F. whereupon the oil is withdrawn through line 4 and thence discharged into an upflow reactor 6. This reactor carries a grid 8 located in the bottom portion thereof but spaced apart from the actual base a relatively short distance. Hydrogen is discharged through line 44 into a furnace coil 46 and then through lines 48 and 50 into the bottom of the said reactor. The amount of hydrogen fed into the reactor may vary from 10 to 90 mol per cent of the naphtha feed. The catalyst may be fed into the reactor at a point above the grid by any convenient means as by, for example, a screw conveyor indicated simply by line 10. The hydrocarbon vapors pass upwardly through the reactor at such a linear velocity that the catalyst which may, for example, be chromia admixed with alumina in such proportion that the mixture contains 20 to 30% by weight of chromia, the balance being alumina, and which catalyst has a particle size of from 200 to 400 mesh that a dense suspension of catalyst is maintained within the reactor up to a point indicated by L in the drawing. The density of this suspension from the grid to the level L may be from 5 to 40 lbs./cu. ft. This condition may be maintained by controlling the linear velocity of the gas through the reaction zone at a volume within the limits of from 0.5 to 3.0 ft./second. Furthermore, conditions are so maintained that the hydrocarbon oil remains resident in the reactor for a period of time which may vary from a few seconds to 20 minutes. Above L in the reactor 6, the hydrocarbon vapors contain only a relatively small amount of catalyst of the order of 0.025 lb./cu. ft. or less, indicating of course that there is only a small amount of catalyst in this region.

These vapors are withdrawn from the reactor through line 12 and discharged into a cyclone separator 14 where the catalyst contained in the vapors is separated from said vapors and then is withdrawn through line 16 and returned

through line 10 to the reactor. Following the vapor product, the same is withdrawn from cyclone separator 14 through line 18 and may be sent to other solid gas separating devices, such as other cyclone separators or an electrical precipator, to remove the last traces of catalyst contained therein. These other separating devices are not shown in the drawing. In any event, the vapors are then passed through condensers 20 and thence into a separation chamber 25. The chamber operates at a temperature of about 110° F., and from this chamber water may be withdrawn from the bottom while gaseous constituents are withdrawn overhead through line 30. The reformed naphtha is taken off the separation chamber 25 as a side stream through line 35 and thence discharged into a stabilizer 40 which may be in the form of a fractionating column. The gases withdrawn through line 30 comprise hydrogen or gases rich in hydrogen, and these gases are recycled through line 42 into line 44 leading into furnace coil 46 where they are mixed with hydrogen which may be withdrawn through any outside zones, or these gases may be passed through a scrubbing tower 112 and then recycled. Once the operation has begun, it is no longer necessary to use any extraneous hydrogen-containing gas since sufficient hydrogen is produced by dehydrogenation of the feed.

Referring back to stabilizer 40, the bottoms are withdrawn therefrom through line 60 and discharged into a fractionator 62 from which the reformed gasoline may be withdrawn through line 65 while the heavy bottoms are withdrawn through line 67. In order to carry out the distillation taking place in fractionator 62, the material may be withdrawn through line 75, passed through a reboiler 72 and returned to the fractionator through line 70.

Referring back to the reactor 6, the same may be of the bottoms draw-off type, that is to say, catalyst may be withdrawn through outlet pipe 80 and thence discharged into line 82 and thereafter into a regenerator 85. Regenerator 85 may be of the same construction and operated in the same manner as reactor 6; that is to say, it may have a grid located at near the bottom thereof, and the catalyst which is regenerated may be withdrawn from the bottom. The catalyst may be conveyed in line 80 by means of a carrier gas, such as flue gas or by any other convenient means adapted to convey the material into the regenerator. Preferably the catalyst leaving the reaction zone 6 through the pipe 80 may be stripped by means of steam discharged into pipe 80 through line 88. In the regenerator 85 the carbonaceous components present in the catalyst as a result of its contact with the oil in reactor 6 may be consumed by combustion by discharging air or other free oxygen-containing gas into the bottom of the regenerator through line 90. The conditions for regenerating catalyst are well known in the art and need not be repeated herein; suffice it to say that conditions are controlled in the regenerator to prevent overheating or fusing of catalyst. As previously indicated, the catalyst is maintained in a dense suspension in the regenerator up to some convenient level such as L', as was the case in reactor 6. Above the level L' the flue gas contains only a very small amount of catalyst, less than about 0.025 lb./cu.ft. This flue gas from regeneration is withdrawn through line 92 and preferably discharged into a cyclone separator 94 where the catalyst is separated from the flue gas and the latter is vented from the system through line 96, or it may be used to strip the catalyst withdrawn from reactor 6 through line 80. Instead of using one cyclone, two or more may be used to insure complete removal of catalyst, or other separating devices, such as electrical precipitators, may be used for the purpose indicated.

The catalyst separated in the cyclone separator 94 and the other cyclones, if they are used, is returned to the system. As indicated, the regenerated catalyst is withdrawn through line 102 from regenerator 85, and this catalyst may be conveyed by line 105 into line 50 where it mixes with the hydrogen previously referred to and returns to the hydroforming reactor. Alternatively, however, the catalyst or at least a portion thereof is used in a dehydrogenation step subsequently to be described.

With respect to the dehydrogenation step, one source of the gases to be dehydrogenated may be those withdrawn overhead from stabilizer 40 through line 110. These gases by the modification shown in the drawing are discharged into a scrubber 112 into the top of which through line 114 a heavy naphtha or some other solvent may be discharged. The naphtha serves to remove from the gas in line 110 at least a portion of the hydrocarbon gases and the undissolved hydrogen may be recovered overhead through line 116 and returned to line 42 for reuse in the process, as previously described. The fat oil containing the dissolved hydrocarbons is withdrawn from the scrubber 112 through line 118, thence passed through a heat exchanger 120 and thence discharged into a stripper 122 where the fat oil at a temperature of about 150° F., more or less, is stripped of its hydrocarbon material dissolved therein in scrubber 112 and the thus stripped oil, commonly called lean oil, is recycled through line 114 to scrubber 112. The hydrocarbon material stripped from the fat oil is withdrawn through line 125 and discharged into a fractionator 127. From fractionator 127, as shown in the drawing, the product charged thereto is divided into three fractions as follows: a heavy cut boiling within the gasoline range is withdrawn from the fractionator through line 130 and discharged into line 35 leading into stabilizer 40; a light fraction containing hydrogen and hydrocarbons lighter than a C_4 cut are withdrawn from the fractionator through line 132, thence discharged through line 133 into line 116 for recycling through line 42 to furnace coil 46 for reuse in the process taking place in reactor 6.

The main product, that is to say, the C_4 cut is taken off fractionator 127 through line 140, and this cut contains a mixture of saturated and unsaturated C_4 hydrocarbons primarily. This cut is discharged into a scrubber 145 where it is treated with an adsorbent such as aqueous ammonia introduced into the top of the scrubber through line 148. This aqueous ammonia dissolves out of the C_4 cut preferentially the unsaturated hydrocarbons such as the butenes and the butadienes, and the fat liquor containing these unsaturates is withdrawn through line 149 and discharged into a stripper 151 after passage through a heater 150 disposed in line 149. In the stripper the unsaturates are volatilized off from the adsorbent liquid and withdrawn overhead through line 153. The lean adsorbent is withdrawn from the bottom of the stripper through liine 148 and returned to the scrubber 145 for reuse in the process. The saturated C_4

hydrocarbons are withdrawn from the absorber through pipe 156 and thence discharged into a heater 158 and thence discharged into the bottom of a dehydrogenation reactor 160. Catalyst is withdrawn from line 105 through lines 165, 166 and discharged into the dehydrogenation reactor 160. The reactor 160 is of the same construction as hydroformer 6 and regenerator 85, that is to say, it is an elongated vertical vessel having a grid located in the lower portion thereof through which the C_4 hydrocarbons are discharged into the dehydrogenator and where they form with the catalyst a dense fluidized mass and further wherein the catalyst is drawn off from the bottom of the dehydrogenator.

The temperature conditions maintained within the dehydrogenator vary from 950 to 1150° F.; the dense phase suspension of catalyst in the gases has a density of from 5 to 30 lbs./cu. ft.; the gas velocity varies from 0.5 to 3 ft./sec.; a pressure of from —10 to 5 lbs./sq. in. gauge is maintained in the dehydrogenator; and a contact time of from 1 to 50 seconds represents the range of residence time of the C_4 hydrocarbons in the dehydrogenator to effect satisfactory results.

As indicated, the catalyst is continuously withdrawn from the dehydrogenator through draw-off pipe 168, and this catalyst may be mixed with a carrier gas such as steam and discharged into spent catalyst line 82 for recycling to regenerator 85. The dehydrogenated products are withdrawn from dehydrogenator 160 through line 167 and discharged into a cyclone separator 169 where entrained catalyst may be separated and returned through line 170 to the regenerator. The concentration of catalyst in separator 169 is very low, namely, of the order of 0.025 lb./cu. ft. Usually one cyclone separator or the equivalent thereof is sufficient to completely separate the catalyst from the reaction products. However, additional separating equipment may be used.

The gases containing saturated and unsaturated hydrocarbons are withdrawn overhead from cyclone separator 169 through line 171 and discharged into fractionator 127.

Referring again to stripper 151, the unsaturated hydrocarbons are withdrawn, as indicated, through line 153, passed through a furnace 180 and thence discharged into a second dehydrogenation vessel 185, of the same construction as dehydrogenator 160. The butene stream is diluted with from 1 to 10 volumes of an inert gas such as flue gas, CO_2, N_2, H_2O, etc., per volume of butene. Catalyst is supplied to this dehydrogenator through lines 165 and 184. The overhead product from dehydrogenator 185 is withdrawn through line 190 and thence discharged into a cyclone separator 192 where entrained catalyst may be separated, withdrawn through lines 195, 199, 166—*a* and 197 and passed to the dehydrogenator 160. Or, the catalyst in line 195 may be passed through lines 199, 196, 164 and 82 to regenerator 85. A carrier gas such as steam is used to fluidize the catalyst.

The bulk of the catalyst in dehydrogenator 185 is withdrawn through line 166—*a*, thence discharged into line 197 and thereafter discharged into dehydrogenator 160. Alternately, the catalyst in line 166—*a* may be passed to regenerator 85 via lines 196 and 82. Also, the catalyst in line 164 from both dehydrogenators 160 and 185 may be discharged directly through line 164*a* into 105 and thereafter into reformer 6.

The advantage of this modification of my invention is that I use the hot catalyst from the dehydrogenators to supply heat to reformer 6, which latter operates at a much lower temperature than the said reactors 160 and 185, the catalyst issuing from the last-named reactors being at temperatures several hundred degrees higher than the average temperature prevailing in reactor 6. The overhead product is withdrawn from the separator 192 through line 198 and, if desired, may be passed through other separating devices to recover the last traces of catalyst. Eventually the product which contains mono-olefins, diolefins and hydrogen is discharged into a separator 200 and from this separator a desired product, namely, butadiene is recovered through line 210. The bottoms containing mono-olefins are withdrawn through line 212 and recycled to dehydrogenator 185. It should be pointed out that the separation in vessel 200 may be effected by extraction, distillation or any other convenient method. In the dehydrogenation operations taking place in reactors 185 and 160 hydrogen is preferably present, although other diluents, such as flue gas, nitrogen, steam, carbon dioxide, or mixtures thereof may be used instead.

Having described one method of operating my process, I wish to point out that the essential features of the invention reside in carrying out a hydroforming operation in connection with a dehydrogenation operation employing the same catalyst in both operations and employing also a common regenerator where the catalyst fouled in the dehydrogenation or the reforming operation may be revivified. The modification which I have shown in the drawing employs the so-called fluid catalyst technique, that is to say, a continuous operation in which the catalyst is in the form of a fluent stream of powder. In the below tabulation, I have set forth operating conditions which give good results:

		Temp. range, °F.[1]	Cat. density, lbs./cu. ft.	Operating pressure, lbs./sq. in.	Gas vel., ft./sec.	Hydrocarbon contact time, sec.	Recycle gas rate, cu. ft./bbl.	Mol per cent H_2 in recycel gas stream	Ratio wt. oil to wt. cat. per hour
A	Hydroforming	(*a*) 850–1200	1–50	0–700 gauge	0.1–15	May vary from few secs. to about 20 min.	500–4000 preferably 1000–3000.	20–90	2–25
		(*b*) 900–1100	5–40	40–625 gauge	0.5–3.0			30–70	
B	Butane dehydrogenation.	(*a*) 850–1300	1–50	—10–10 gauge	0.1–15	0.1 sec.–2 min			
		(*b*) 950–1150	5–30	—10–5 gauge	0.5–3.0	1.0–50 sec			
C	Butene dehydrogenation.	(*a*) 900–1400	1–50	—10–10 gauge	0.1–15.0	0.01 sec.–2 min			
		(*b*) 1000–1200	5–40	—10–0 gauge	0.5–3.0	0.1 sec.–30 sec			

Steam or inert gas as a diluent in B or C—5–10 mols of steam per mol hydrocarbon aids in removing coke from catalyst during dehydrogenation by causing water gas reaction.

[1] (*a*) Broad range, (*b*) preferred range.

Catalysts include the oxides or sulfides of metals of the IV, V, VI, and VIII groups used alone, in combination or supported on carriers such as alumina, alumina gels, magnesia, or natural or activated clays. These carriers may be treated with hydrofluoric acid or fluosilicic acid.

What I claim is:

1. In the combined process of reforming naphtha and dehydrogenating C_4 hydrocarbons formed during the reforming step, the improvement which comprises heating the naphtha to reforming temperatures, suspending a powdered catalyst therein, adding hydrogen to form a dense fluidized mass of catalyst in hydrogen gas and naphtha vapors, subjecting the naphtha to reforming in the presence of the hydrogen and fluidized catalyst, separating catalyst from the reformed products, recovering C_4 hydrocarbons from said reformed products, heating the said C_4 hydrocarbons to dehydrogenation temperatures, suspending the same kind of catalyst in the said heated C_4 hydrocarbons, subjecting the C_4 hydrocarbons to dehydrogenation in the presence of a fluidized mass of catalyst, separating the catalyst from the products of dehydrogenation, combining a portion of the catalyst thus removed from the dehydrogenation products with the catalyst separated from the reformed products, regenerating the mixture in the same regenerator and passing the remaining portion of the dehydrogenation catalyst while still hot directly to the reforming reaction.

2. In a combined continuous catalytic naphtha reforming and normally gaseous paraffin dehydrogenation process wherein the said normally gaseous paraffins are produced during the said reforming, the improvement which comprises carrying out the reforming and the dehydrogenation reactions in the presence of a powdered catalyst present as a dense fluidized mass in the reactant vapors and gases, respectively, separating the catalyst from the products of each reaction, regenerating the catalyst recovered from the naphtha reforming operation, employing the catalyst thus regenerated as the catalyst for the dehydrogenation reaction and introducing the hot catalyst recovered from the dehydrogenation directly into the reforming operation.

3. In the combined process of catalytically reforming naphtha in the vapor phase in the presence of a powdered catalyst and hydrogen and catalytically dehydrogenating C_4 hydrocarbons in two separate stages and in the presence of the same kind of catalyst employed in the reforming operation, the catalyst being present as a dense fluidized mass in the said C_4 hydrocarbons during the dehydrogenation reaction, the improvement comprising employing regenerated catalyst in the dehydrogenation operations and employing catalyst recovered substantially uncooled and unregenerated from the dehydrogenation operations in the reforming reaction.

4. The method set forth in claim 3 in which extraneous hydrogen is added during the dehydrogenation reactions.

5. The method set forth in claim 3 in which catalyst is recovered from a second stage of the dehydrogenation and passed directly to a first dehydrogenation stage.

NORMAN F. LINN.