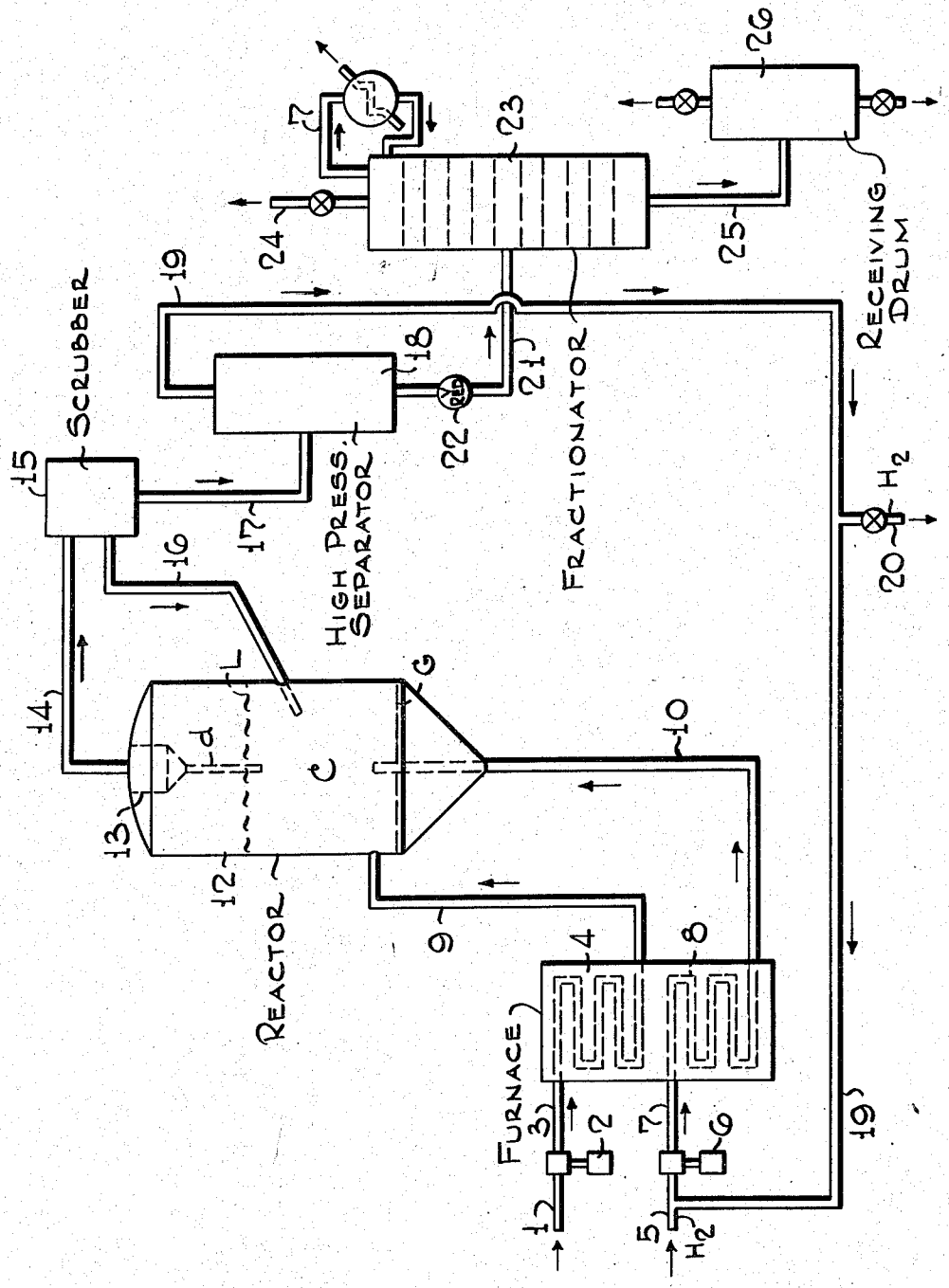
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CONTINUOUS FLUID HYDROFORMING

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CONTINUOUS FLUID HYDROFORMING

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The novelty of the present invention is fully disclosed in the following specification and claims, considered in connection with the accompanying drawing.

Heretofore and prior to the present invention, it was a matter of record and commercial practice to hydroform hydrocarbons, particularly those containing appreciable amounts of naphthenic hydrocarbons in the presence of solid catalysts and added hydrogen to form a product of increased aromaticity. It is generally considered that the main reaction involved is one of dehydrogenation of the naphthenes to the corresponding aromatics, and at the same time the hydrogenation of olefinic hydrocarbons that may be present in order to convert them to the corresponding paraffinic hydrocarbons. Furthermore, it is generally considered that a certain amount of isomerization of olefinic and paraffinic hydrocarbons occurs during this hydroforming operation. It is also generally considered that isomerization of naphthenic compounds takes place during the hydroforming reaction, as where ethyl-cyclopentane is converted to methyl-cyclohexane.

This hydroforming operation, according to prior practice, was carried out at elevated temperatures and pressures. The operation results in the deposition of carbonaceous materials on the solid catalyst, and periodic regeneration of the catalyst to restore its activity is necessary. Furthermore, the commercial operation was carried out in the presence of fixed beds of catalyst disposed in a plurality of reactors operating in series. Due to the high endothermic nature of the reaction, a severe temperature drop was encountered particularly in the lead reactor. This is a very unsatisfactory condition because the feed to the lead reactor generally had to be heated to a temperature far above that desired in order that the reactants would be at sufficiently high temperature to cause the reaction to proceed at a reasonable rate downstream from the inlet point. This excessive heating of the feed to the lead reactor resulted in the formation of inordinately large quantities of normally gaseous material and carbon.

The present invention constitutes an improvement over prior practice in many respects. In the first place, the catalyst is disposed in the form of a dense fluidized bed in the reactor. This technique, due to the intimate and thorough mixing of all portions of the catalyst, tends to maintain the catalyst bed at a substantially uniform temperature.

Another advantage of the present improvements resides in the fact that the operation of hydroforming may be carried out continuously without interruption of the productive phase to regenerate the catalyst, using the same catalyst,

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previously requiring regeneration with air or some other gas in prior practice.

Another advantage of the present invention resides in the possibility of obtaining very high octane rating motor fuel or aviation gasoline.

The main object of the present invention is to carry out hydroforming operation under conditions which afford greater flexibility of operation, more efficient operation, and at the same time, important savings in the cost of operation are secured.

A more specific object of the present invention is to subject hydrocarbons to hydroforming under conditions such as to produce a product having an octane number up to about 95 CFRR.

Other and further objects are of the present invention will appear from the following more detailed description.

In the accompanying drawing there is shown diagrammatically in Fig. 1, a suitable apparatus for carrying the present invention into effect.

Referring in detail to Fig. 1, feed stock enters the present system through line 1, is pumped by pump 2, through line 3, into suitable heating means 4, which may be an ordinary fired coil. Simultaneously hydrogen from some source enters the present system through line 5, is thereafter forced through compressor 6, then passed via line 7 into a fired coil 8 where it is also preheated. The heated oil is withdrawn from the furnace into line 9 and the heated hydrogen is withdrawn through line 10 and the two are separately introduced into hydroforming reactor 12 as shown in the drawing. Generally it is preferable to heat the hydrogen-containing gas to a higher temperature than the oil in order to prevent thermal cracking of the latter, and in this connection therefore, the heated oil and the heated hydrogen-containing gas are preferably separately introduced into reactor 12, the former below a gas distributor G and the latter above. The catalyst C in 12 is maintained in the form of a dense fluidized bed extending from the distributing grid G to an upper dense phase level L. The catalyst itself will be described more fully hereinafter as to composition. For the present it will simply be stated that the catalyst may be a group VI metal oxide on a suitable carrier and is ground to a powder of fluidizable size, say having a particle size of from about 200–400 mesh or finer. The superficial velocity of the oil vapors and the hydrogen-containing gas in the reactor 12 is maintained at a value of from about $\frac{2}{10}$ to 1 foot per second. The reactants are maintained in contact with the catalyst under conditions of temperature, pressure, contact time, etc., more fully described hereinafter, to effect the desired conversion and eventually issue from the dense fluidized bed toward the top of the reactor 12. As usual in this type of operation, a light dispersed phase of cata-

lyst in gasiform material exists in the reactor above the level L. The reaction vapors, before issuing from the reactor 12, are forced through one or more gas-solids separating devices 13, for the purpose of separating entrained catalysts, this entrained catalyst being withdrawn through one or more dip pipes *d* from the separating device and returned to the bed of catalyst C. The reactant products are withdrawn from the reactor 12 through line 14 and preferably are passed through conventional oil scrubbing means 15 in which catalyst still contained in the vapors is removed and returned via line 16 to the bed of catalyst C. An alternative method of removing these last traces of catalyst is to effect a partial condensation of the vapors in S whereby the entrained catalyst is washed out of the said vapors to form an oil and catalyst slurry, which is then returned to the reactor 12 as previously noted. The product substantially free of catalyst, passes from S via line 17 in a high pressure separator 18. A gas rich in hydrogen is recovered overhead via line 19 from separator 18 and recycled to hydrogen supply line 5 for further use in the process. A portion of the recycled gas may be continuously or intermittently bled from the system through line 20. Referring again to high pressure separator 18, the crude liquid product is withdrawn from 18 via line 21 and forced through pressure reducing valve 22 and thereafter introduced into fractionating tower 23 where it is subjected to fractionation and distillation to recover the desired product. Light material, that is to say, low boiling material is withdrawn from the fractionator 23 through line 24 and rejected from the system. The hydroformed product is recovered from fractionator 23 through line 25 and collected in receiving drum 26.

It will be understood that a petroleum engineer would understand that in a commercial plant a great deal of accessory apparatus not shown in the drawing would be required for efficient operation. Thus, the drawing does not include such devices as would ordinarily be used, such as flow meters, temperature recording devices, filtering devices, etc.

In order further to illustrate the present invention the following specific examples are set forth.

There is set forth below, an inspection of the naphtha which was used in these runs.

Feed inspection	West Texas heavy naphtha, approximately 200°–430° F. Boiling range
A. P. I. gravity	53.3
Octane No., CFRR	43
Reid vapor pressure	0.7 lbs.
Aromatics	8.2 vol. per cent
Naphthenes	47.6 vol. per cent
Paraffins	49.2 vol. per cent
Sulfur	0.113 wt. per cent
Aniline point	128° F.

EXAMPLE I

Run No	60–3
Catalyst 8.5 wt. per cent MoO_3 on alumina.[1]	
Temperature, °F	950
Pressure, p. s. i. g	750
Feed rate, w/hr./w	0.5
Recycle rate, SCF/bbl	6500–7000

Hydrogen concentration in recycle gas, vol. percent	70–75
Hydrogen partial pressure in reactor, p. s. i. g	460
Hydrogen consumption SCF/bbl	(250–380)
Length of run, hours	210
Deactivation rate, Δ O. N./hr	0.0

[1] Prepared by co-precipitation of $(NH_4)_2$ MoO_4 in aqueous solution with $AlCl_3$.

An inspection of the product revealed the following:

Product

A. P. I. gravity	62.2
Yield in vol. per cent C_4^+	85.8
Octane No., CFRR	92.0
Reid vapor pressure	16.00
Aromatics, vol. per cent	28.00
Olefins, vol. per cent	2
Sulfur	Trace
Naphthenes	2.5%
Paraffins	65–70%

In the below Examples II and III, the same feed was employed, as noted above, as in Example I, but it will be noted that in these examples the catalyst became deactivated since the octane number decreased 0.061 in Run No. 60–4 (Example II) and 0.065 octane number per hour in Run No. 61–3 (Example III).

EXAMPLE II

Run No	60–4
Catalyst 8.5 wt. per cent MoO_3 on alumina.[1]	
Temperature, °F	950
Pressure, p. s. i. g	750
Feed rate, w/hr./w	0.5
Recycle rate, SCF/bbl	4000–4500
Hydrogen concentration in recycle gas, vol per cent	68–72
Hydrogen partial pressure in reactor, p. s. i. g	410
Hydrogen consumption, SCF/bbl	(230–280)
Length of run, hours	200
Deactivation rate, Δ O. N./hr	0.061

[1] Prepared by co-precipitation of $(NH_4)_2$ MoO_4 in aqueous solution with $AlCl_3$.

EXAMPLE III

Run No	61–3
Catalyst 8.5 wt. per cent MoO_3 on alumina.[1]	
Temperature, °F	930
Pressure, p. s. i. g	500
Feed rate, w/hr./w	0.25
Recycle rate, SCF/bbl	6000–7000
Hydrogen concentration in recycle gas, vol. per cent	60–65
Hydrogen partial pressure in reactor, p. s. i. g	270
Hydrogen consumption, SCF/bbl	[2] 10–(60)
Length of run, hours	210
Deactivation rate, Δ O. N./hr	0.065

[1] Prepared by co-precipitation of $(NH_4)_2$ MoO_4 in aqueous solution with $AlCl_3$.
[2] Some hydrogen was produced in this run.

It will be noted that in Run 60–3 (Example I), the hydrogen partial pressure was 460 p. s. i. g. and under these conditions the activity of the catalyst was maintained or, in other words, the process of hydroforming was continuous, not requiring interruption to regenerate the catalyst. However, in Run 60–4 (Example II) where the hydrogen partial pressure was 410 p. s. i. g., the octane number of the product decreased at a rate of 0.061 number per hour which, of course, means that the catalyst continuously deactivated.

In Run 61–3 (Example III) where the hydrogen partial pressure was 270 p. s. i. g., the octane rating fell off 0.065 number per hour showing that the process was not continuous and would require intermittent regeneration of catalyst to maintain its activity.

The data also showed that it is not possible to operate effectively at hydrogen partial pressures above 460 for the yield in desired products decreased. Thus, the data show that hydrogen partial pressures of 450–460 p. s. i. g. are critical in that the activity of the catalyst is maintained and the yields are high. In other words, hydrogen partial pressures within the restricted range indicated, result in a process in which the yield-octane number relationship is good, and this result is attainable in continuous on-stream operation.

The conclusion to be drawn from these runs, therefore, is clearly that there is a critical hydrogen partial pressure which will enable operation of the process continuously while maintaining the process so as to produce a good yield of a high octane product.

It will be understood that the foregoing examples are merely illustrative of the present invention and do not impose any limitation thereon. For example, the temperatures set forth in the above examples referred to catalyst bed temperature. This temperature range may vary within the limitations of from about 875°–950° F.; a total pressure in the reaction zone may vary within the limitation of from about 600–1000. The amount of hydrogen per barrel of oil feed to the reaction zone varies according to the total pressure, and is so adjusted that the hydrogen partial pressure maintained in the reactor is of the order of about 450–460 p. s. i. g. It has been noted that this range is critical to secure best results. Continuous operation without catalyst regeneration has been shown to be possible at hydrogen partial pressure levels within the approximate range of from about 450–460 p. s. i. g. However, at hydrogen partial pressures above this critical pressure range of 450–460 p. s. i. g., the octane value of the product is lowered and this value decreases as the hydrogen partial pressure increases. The hydrogen production likewise decreases with increasing hydrogen partial pressures above said critical range, thus making it necessary to supply additional extraneous hydrogen to the processes, and thereby increasing the cost of producing the product. At hydrogen partial pressures below the said critical range the catalyst tends to become deactivated and this condition worsens as the hydrogen partial pressure decreases and the production phase of the process must be interrupted periodically to regenerate the catalyst. Thus, the operation should be carried out at the lowest hydrogen partial pressure commensurate with obtaining continuous operation, this hydrogen partial pressure being substantially within the said critical 450–460 p. s. i. g. range, herein disclosed.

With respect to the catalyst, although molybdenum oxide on alumina gel is preferred, many difficulty reducible oxides, such as the oxides of the IV, VI and VIII groups of the Periodic System may be used in lieu of molybdenum oxide. Instead of using a gel alumina carrier, any active and/or high surface form of alumina may be used, such as calcined and low soda alumina, various clays, active carbon, etc., which carriers also possess good mechanical strength. The carrier may also contain up to 10 weight percent of silica, preferably in the form of a gel, where alumina constitutes the remainder of the carrier. The inclusion of 0.1 to 5% by weight of the total catalyst of boron oxide may be included in the catalyst composition for the purpose of imparting to the catalyst composition, the faculty of isomerizing the olefins and paraffins in the original feed.

It is to be noted that although the continuous hydroforming operation given as Example I was carried out at 6500–7000 SCF/bbl. recycle rate and 70–75 vol. percent hydrogen concentration in the recycle gas, these variables are not limited to these precise ranges. Recycle rates of 5500–7500 SCF/bbl. and hydrogen concentrations from 55–75 vol. percent may be used provided the operation is carried out at an appropriate pressure level between 750 and 1000 p. s. i. g. which will result in a hydrogen partial pressure in the reaction zone of 450–460 p. s. i. g. It is also possible to operate at total pressures as low as 600 p. s. i. g., provided steps are taken to increase the hydrogen concentration in the recycle gas to 85–90% and thus produce the critical 450–460 p. s. i. g. hydrogen partial pressure.

Numerous modifications of the invention may be made without departing from the spirit thereof.

What is claimed is:

1. The method of hydroforming naphtha containing a substantial amount of naphthenic hydrocarbons which comprises feeding the said naphtha to a reaction zone simultaneously feeding to said reaction zone a hydrogen-containing gas, the amount of hydrogen-containing gas being from about 5500–7500 cu. ft. per barrel of oil, the said hydrogen-containing gas having a concentration of from 55–75% hydrogen, maintaining in said reaction zone a fluidized bed of hydroforming catalyst comprising essentially a difficulty reducible heavy metal oxide of a metal of the IV and VI groups of the Periodic System, maintaining a temperature in the said reaction zone of from about 875–950° F., maintaining a hydrogen partial pressure within the said reaction zone of from about 450–460 p. s. i. g., permitting the reactants to remain resident in the reaction zone for a sufficient period of time to effect the desired conversion and recovering from said reaction zone a product of increased aromaticity.

2. The method set forth in claim 1 in which the catalyst is molybdenum oxide on active alumina.

3. The method set forth in claim 1, characterized in that the hydroformed product of high octane value is obtained with a minimum amount of hydrogen consumption during the process by correlating the hydrogen partial pressure responsive to the amount of hydrogen fed to the reaction zone per barrel of liquid oil feed.

4. The method set forth in claim 1 in which the total pressure in the hydroforming zone is from 600 to 1000 p. s. i. g.

5. The method set forth in claim 1 in which the hydrogen-containing gas fed to the reaction zone contains up to 85–90% hydrogen.

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