

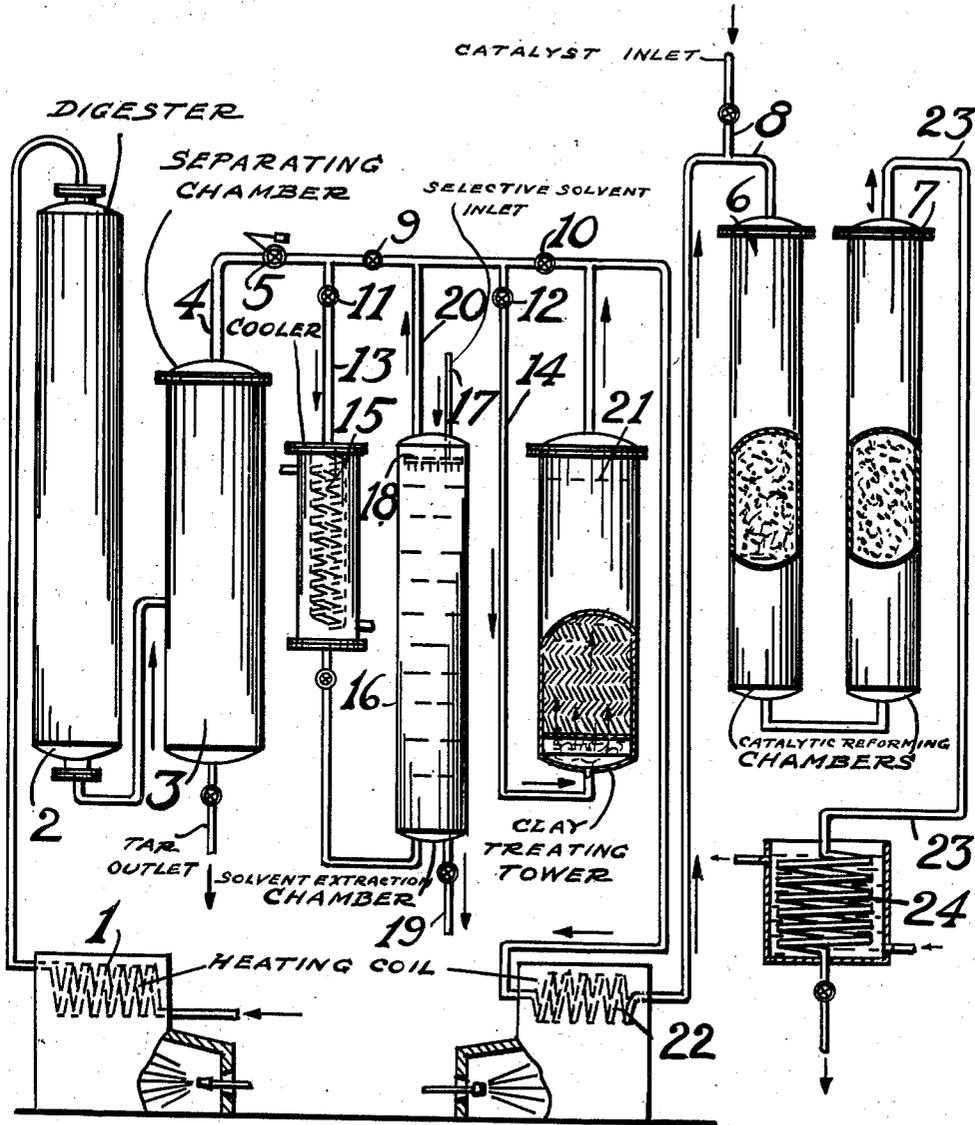
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NAPHTHA REFORMING

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## NAPHTHA REFORMING

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The present invention relates to a process for the improvement of the octane number of straight run naphthas and those obtained by the cracking of heavier stocks. It has for its particular object the provision of a process by which straight run naphthas can be reformed so as to have the proper volatility and a satisfactory octane number without an accompanying prohibitive gas loss.

As is known, straight run naphthas are ordinarily possessed of an unusually large percentage of constituents boiling within the range of heavy naphtha and are poor in those low boiling constituents which are so essential to the proper volatility of motor fuels. In addition, these straight run naphthas, probably by reason of their poor volatility as well as by reason of their saturated nature, have an octane number much below the standard set for commercial fuels. It has commonly been the practice to subject such straight run naphtha to a treatment, referred to as reforming, for the purpose of reducing its initial boiling point and increasing its content of unsaturates and aromatics, thereby improving its octane number.

Hitherto, the reforming of straight run naphthas has been accomplished by one of three general methods, namely, vapor-phase cracking conducted under atmospheric pressure and at a temperature above 1000° F., pressure cracking or, as it is called, pressure reforming conducted at a temperature between 800° F. and 1000° F. and under a pressure ranging from 250 to 1000#, and catalytic reforming conducted at a temperature between 850° F. and 1100° F. in the presence of a dehydrogenating catalyst. In the order listed these methods will give a larger increase in octane number for a given gas loss up to a certain point after which they converge to a point where, for a maximum increase in octane number, the gas loss in each instance is about the same and is prohibitively large. In the case of vapor-phase cracking the gas loss becomes excessive for an octane number increase which is smaller than that at which gas loss becomes excessive in pressure reforming. In like manner catalytic reforming is superior to pressure reforming.

In the reformation of straight run naphthas, vapor phase cracking has been largely superseded by pressure reforming and catalytic reforming. Pressure reforming offers the advantage over catalytic reforming that it sufficiently increases the light ends of the naphtha. It is attended by the disadvantage, however, that in addition to the gas loss involved it is accompanied by the forma-

tion of polymers which represent a loss of initial material. Thus, as between pressure reforming and catalytic reforming the advantages of either could not be derived without incurring the disadvantages attending each.

By any one of the methods above referred to, octane number can be increased rapidly at its lower levels. Thus, an increase of octane number from 40 to 65 can be readily accomplished by any one of the methods. When the octane number reaches 70, any further increase becomes more and more difficult of attainment. It may be said without exaggeration that to increase an octane number from 75 to 76 presents a greater problem than an increase in octane number from 40 to 60. Increases in octane number in the upper range indicated above can be achieved with any one of the methods referred to, only with gas losses which are for practical purposes prohibitive.

It has now been ascertained that increases in octane number in the upper range can be achieved by catalytic reforming with a smaller gas loss than with either of the other types of reforming. To accomplish the full increase in octane number by catalytic reforming, however, would mean that the resulting naphtha would be deficient in light ends. According to the present invention, therefore, the desired increase in octane number is obtained with a minimum gas loss and with a satisfactory adjustment of the distillation curve of the resulting naphtha by effecting a partial increase in the octane number by pressure reforming, conducted to a point where the content of the naphtha in light ends is nearly sufficient to satisfy market specifications, and completing the increase by catalytic reforming. By this combination of steps the excessive gas loss and polymer loss incurred in effecting the total improvement in octane number by pressure reforming are avoided, and the deficiency in light ends incurred in effecting the total improvement in octane number by catalytic reforming is avoided. This combination is based on the realization that the greatest benefit derivable from pressure reforming is obtained when a substantial portion of the heavier constituents are converted into light constituents and before these light constituents are cracked to a considerable extent to gases or to substances of a more unsaturated nature which readily polymerize to gums. Up to the point where these undesirable by-reactions occur, pressure reforming offers a distinct advantage over catalytic reforming.

Conditions best suited for pressure reforming are commonly known. In general, naphtha to

be reformed is passed through a heating coil and through a soaking drum maintained under a pressure between 250 and 1000# and at a temperature between 800 and 1000° F. Likewise the conditions best suited for catalytic reforming are common knowledge. The temperature employed may be between 850° F. and 1100° F., preferably between 950° F. and 1050° F. In practice the process is conducted under atmospheric pressure, although, if desired, elevated pressures can be employed. The catalyst employed is usually one of the known dehydrogenation catalysts. In general, refractory metal oxides, such as alumina, thorium, oxides of metals of groups 5 and 6, and mixtures of such refractory oxides are suitable. Phosphates and meta-phosphates exercise particular utility in this process. Vaporous catalysts, such as readily vaporizable metal halides, particularly the halides of boron, such as boron fluoride, may also be employed. A particularly effective catalyst is one mainly composed of a reduced mixture of zinc oxide and chromium oxide, preferably on a support such as pumice, refractory oxides, etc. Other catalysts of a specific nature which are suitable for this purpose are disclosed in Patent Nos. 1,844,998, 1,851,726, 1,881,692, 1,900,739, 1,910,910, 1,913,940, 1,913,941, 1,937,619, 1,938,086, 1,955,829, 1,975,476.

According to the present invention the initial straight run naphtha is subjected to pressure reforming until a substantial part, at least about one-third, of the desired octane number increase is effected, and the remainder of the increase in octane number is attained by catalytic reforming. For example, a stock having an initial octane number of about 47 may be pressure reformed to an octane number between 60 and 75 and then subjected to catalytic reforming to bring the octane number up to a value between 75 and 80. While pressure reforming may be employed to effect from  $\frac{1}{3}$  to  $\frac{2}{3}$  of the total desired increase in octane number, it is preferred to effect only such an increase in octane number by pressure reforming as can be obtained without any appreciable loss due to polymerization.

In the event that pressure reforming is employed to attain the major portion of the desired increase in octane number whereby loss through polymerization is incurred, it is advantageous to subject the vapors leaving the pressure reforming unit to a treatment suitable for removing polymerizates and highly unsaturated components which would polymerize under the conditions in the catalytic reforming unit prior to the introduction of the vapors into the catalytic reforming unit. The purpose of this step is to prevent deposition of the polymers on the catalyst and the consequent reduction in activity of the catalyst. Among the treatments suitable for removing polymers and readily polymerized unsaturates are scrubbing with sulfuric acid and a contact treatment of the vapors with absorbent substances, such as clays, active carbon, etc.

Where heat loss is not of practical significance, such as where heating gases which are normally wasted are available, the process can be improved by interposing between the two reforming steps a solvent extraction step. This can be performed by reducing the temperature of the vapors to a point where a solvent having selectivity for aromatics and unsaturates, such as tricresyl phosphate, phenol, aniline, nitro-

benzene, chlorex, etc., can be employed as a liquid medium for scrubbing the vapors, or by condensing the vapors and subjecting them to liquid phase extraction with any of the above enumerated solvents or with liquid sulfur dioxide. Such an extraction would remove those constituents which are not substantially affected by catalytic reforming, leaving the constituents, such as naphthenes, which are extremely sensitive to catalytic reforming, in a concentrated form. By this expedient the gas loss in the catalytic reforming step can be reduced since it is undoubtedly true that this gas loss is enhanced by the extent of exposure of the unsaturates to the high temperatures employed. In addition, the octane number of the naphtha resulting from the catalytic reforming step will be increased because the effect of the step on the substances which are sensitive to it will be greater due to the avoidance of the diluent effect of the aromatics and unsaturates.

Where such an extraction step is included in the process the vaporous mixture not absorbed by the solvent, in the case of vapor phase extraction, or the raffinate, in the case of liquid phase extraction, is subjected to the catalytic reforming step. The product of the catalytic reforming step is then combined with the extract of the extraction step.

A front elevation of one form of apparatus for carrying out the process according to the present invention is illustrated diagrammatically in the accompanying drawing in which 1 represents a heating coil in which the naphtha is vaporized and the vapors are brought to a temperature between 800 and 1000° F. and from which they are passed to a digester 2, which may be termed a soaker and which is maintained at a temperature between 800 and 1000° F. and under a pressure between 250 and 1000 lbs./sq. in. The products leaving the bottom of the soaker are introduced into a separating chamber 3 in which such tar as may be formed falls out and the vapors leave through line 4 which is provided with a pressure release valve 5 so that the catalytic reforming may be conducted under atmospheric pressure. The line 4 conducts the vapors to chambers 6 and 7 which are packed with a dehydrogenation catalyst, in case the latter is a solid, or which may be packed with a solid refractory material, such as clay sherds, porcelain balls, Raschig rings or other suitable material in the event that the catalyst employed is liquid or gaseous. In the latter event the catalyst is added to the vaporous material through line 8. Line 4 is provided with valves 9 and 10 which may be manipulated in conjunction with valves 11 and 12 respectively, to permit the vapors leaving separator 3 to be shunted through either lines 13 or 14 respectively, or both, to other treating units. Line 13 is provided with a cooler 15 and leads to chamber 16 which is packed with any suitable filling material or provided with discs and doughnuts, and which at its upper end is provided with an inlet tube 17 having at its inner end a nozzle 18 through which a selective solvent may be sprayed. Condenser 15 is operated so as to either reduce the temperature of the vapors to such a level that the vapors can be extracted by a liquid introduced through tube 17 or may be operated so as to condense the vapors, in which event the condensed vapors pass through chamber 16 in countercurrent to the selective solvent. In either event, the solvent containing the extracted components is drawn off through outlet 19 and the vapors or

the raffinate, as the case may be, is led off through line 20 back to line 4.

Line 14 is connected to a clay treating tower 21 which is ordinarily operated at a temperature of about 500° F. and which contains Attapulugus clay or a similar absorbent clay or other absorbent material.

Since either of the above mentioned intermediate treatments would require a reduction in temperature of the vapors, a heating coil 22 is provided in line 4 for bringing the vapors to the proper temperature for the catalytic reforming. The catalytically reformed vapors leave tower 7 through line 23 and are condensed in condenser 24.

In a practical embodiment of the process according to the present invention a west Texas heavy naphtha was reformed in soaker 2 at a temperature of 950° F. and under a pressure of 800 lbs./sq. in., the feed rate being about 18 gallons per hour per cubic foot of soaker space. In this step there was incurred a 13.3% gas loss and a 5% polymer loss. The vapors leaving separator 3 were conducted to towers 6 and 7 which were packed with a catalyst composed of a reduced mixture of zinc oxide and chromium oxide supported on alumina. At this stage the naphtha was fed through the catalyst at a rate of .8 volume of liquid naphtha by volume of catalyst per hour. The towers were maintained under atmospheric pressure and at a temperature of 1000° F. In this step a 4.6% gas loss was incurred. The inspections of the initial naphtha, the pressure reformed naphtha, and the catalytically reformed pressure reformed naphtha are as follows:

Original West Texas heavy naphtha	Pressure reformed West Texas heavy naphtha	Catalytic re-forming of pressure reformed West Texas heavy naphtha
Init. 248	99	90
86		
104	0.5	2.5
122	4.0	6.5
140	7.5	11.0
158	11.5	15.0
176	15.5	19.5
194	20.0	24.5
212	25.5	30.0
221	29.0	33.5
230	32.0	37.0
245	39.0	45.0
257	43.5	49.0
265	48.0	53.5
284	57.0	62.0
302	66.5	70.0
320	73.0	77.5
338	72.5	79.5
356	84.0	84.5
374	91.0	89.0
392	95.0	91.5
410	97.0	94.5
F. B. P. 414	437	403
90% at 370	383	371
Rec. 98	95	93
Loss 1.0	3.7	6.0
Res. 48.9	1.3	1.0
Grav. 127.0	52.3	52.9
An. Pt. 47.0	79	70
Octane # (C. F. R.-M. M.) 72.5		77

It may be noted from the above table that whereas the pressure reforming affected only that increase in octane number which is most easily obtained, it reduced the initial point of the naphtha from 248 to 99 and increased the amount going over at 266° F. from 3.5 to 48%. Catalytic reforming, on the other hand, while it raised the octane number through that range in which the attainment of an increase is most difficult, decreased the initial point only to 90 and increased the amount going over at 266 only from 48% to 53.5%. The figures given under "loss" must not

be confused with gas loss or polymerization loss. The loss listed in the table is the loss incurred in distillation.

Where the vapors resulting from the pressure reforming are subjected to extraction with tricresyl phosphate an extract is obtained having an octane number of 76. The vapors not absorbed are subjected to the catalytic reforming step and yield a product having an octane number of 80. This product, upon being blended with the constituents extracted by the tricresyl phosphate, gives a naphtha having an octane number of 78.5.

From the above table it is to be noted that the octane number of the initial naphtha was raised from 47 to 77 with a gas loss of 17.9 and a polymer loss of 5%. To effect a similar improvement by pressure reforming alone would entail a gas loss of 21% and a polymer loss of 8.5%. A similar improvement in octane number could be effected by catalytic reforming alone with a gas loss of about 19%, but the product obtained would have a distillation curve such that light ends would have to be blended with it to meet market specification.

The present invention is also applicable to the improvement of the octane number of a cracked naphtha from any source providing the naphtha has approximately the final desired content of light ends, and particularly if it has a relatively high octane number with respect to straight run naphtha. It has been demonstrated that the octane number of a cracked naphtha obtained by the cracking of a heavier feed stock and having an octane number above 70 can be improved without a prohibitive gas loss by catalytic reforming without any substantial change in its distillation curve. A naphtha obtained from a Quire-Quire crude by cracking was passed at a temperature of 1000° F. over a catalyst composed of magnesite combined with zinc sulphate and lead chromate. The inspections of the feed stock and the final product are given in the following table:

Reforming of Quire-Quire cracked distillate

	Feed stock	Reformed product run RU-74
Gas loss		6.2%
Thru-put		0.82
Block temp.		1000° F.
Percent off at °F.:		
104	1.0	2.0
122	4.5	6.0
140	9.0	10.0
158	14.0	14.0
176	19.0	18.0
194	24.0	22.5
212	28.5	27.0
221	31.0	29.5
230	34.0	32.5
248	40.0	38.5
257	43.5	41.5
266	46.5	45.0
284	54.0	52.5
302	62.0	61.5
320	70.5	67.5
338	78.0	75.0
356	86.0	82.0
374	92.0	87.5
392	95.0	91.0
410	96.5	93.0
428		
I. B. P. °F.	99	93
F. B. P. °F.	412	455
90%	369	388
Recov. percent	97	97
Aniline Pt. °F.	77	53
Gravity °A. P. I.	52.4	48
C. F. R.-M. M. octane No.	77.0	79
Kauri butanol No.	47.7	55.8

While the improvement in octane number of a

naphtha from any source is contemplated by the present invention, it is to be understood that in its preferred embodiment the present invention resides in the combination of pressure reforming with catalytic reforming of straight run naphthas in such a manner as to utilize the most advantageous features of both while minimizing the objectionable features of both, the pressure reforming being used only to the extent that gas loss and polymer loss do not become objectionable and that the content of light ends in the naphtha approaches that desired in the final product. Various types of apparatus, other than that illustrated, can be employed for carrying out the process. No novelty is alleged in the specific conditions employed in each step of the process or in the specific catalyst employed in the catalytic reforming step, except insofar as these conditions and catalyst represent the preferred mode of operation.

The term "reforming" as employed in the specification and claims is here defined to mean a treatment wherein the chemical composition of the naphtha is changed without being combined with any other reagents.

The nature and objects of the present invention having been thus described and a specific embodiment of the same having been given without any intention, however, of limiting the invention to that specific embodiment, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for improving the octane number and distillation curve of a heavy straight run naphtha which comprises subjecting said naphtha to a non-catalytic pressure reforming for a length of time sufficient to substantially increase the octane number thereof and to increase its content in light ends to a quantity approximating that desired in the final product, and completing the increase in octane number by subjecting the pressure reformed naphtha to a dehydro-

genating catalytic reforming and for a time limited so that no substantial increase in light ends is obtained.

2. A process according to claim 1 in which the pressure reformed naphtha is subjected to extraction with a solvent having a selective solvent action for cyclic hydrocarbons and only the portion not dissolved in the selective solvent is subjected to the catalytic reforming.

3. A process for improving the octane number and distillation curve of a heavy straight run naphtha which comprises subjecting said naphtha to non-catalytic pressure reforming for a length of time sufficient to effect at least  $\frac{1}{2}$  of the desired increase in octane number and to increase its content in light ends to a quantity of that approximating that desired in the final product and completing the increase in octane number by subjecting naphtha so reformed to a dehydrogenating catalytic reforming maintained under conditions such that the ratio of the amount of octane improvement to the amount of lower boiling hydrocarbons formed is substantially higher than in the pressure reforming treatment and for a time limited so that no substantial increase in light ends is obtained.

4. A method of producing a motor fuel having improved volatility and octane number which comprises subjecting a low octane heavy naphtha fraction of low volatility to a non-catalytic pressure reforming to produce a relatively low ratio of octane improvement to lower boiling hydrocarbon formation to thereby materially improve the volatility of said fraction, thereafter subjecting naphtha so reformed to a dehydrogenating catalytic reforming treatment controlled to produce a relatively higher ratio of octane number improvement to the amount of lower boiling hydrocarbons formed than in said first mentioned reforming treatment.

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