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REFORMING-HYDROFORMING SYSTEM

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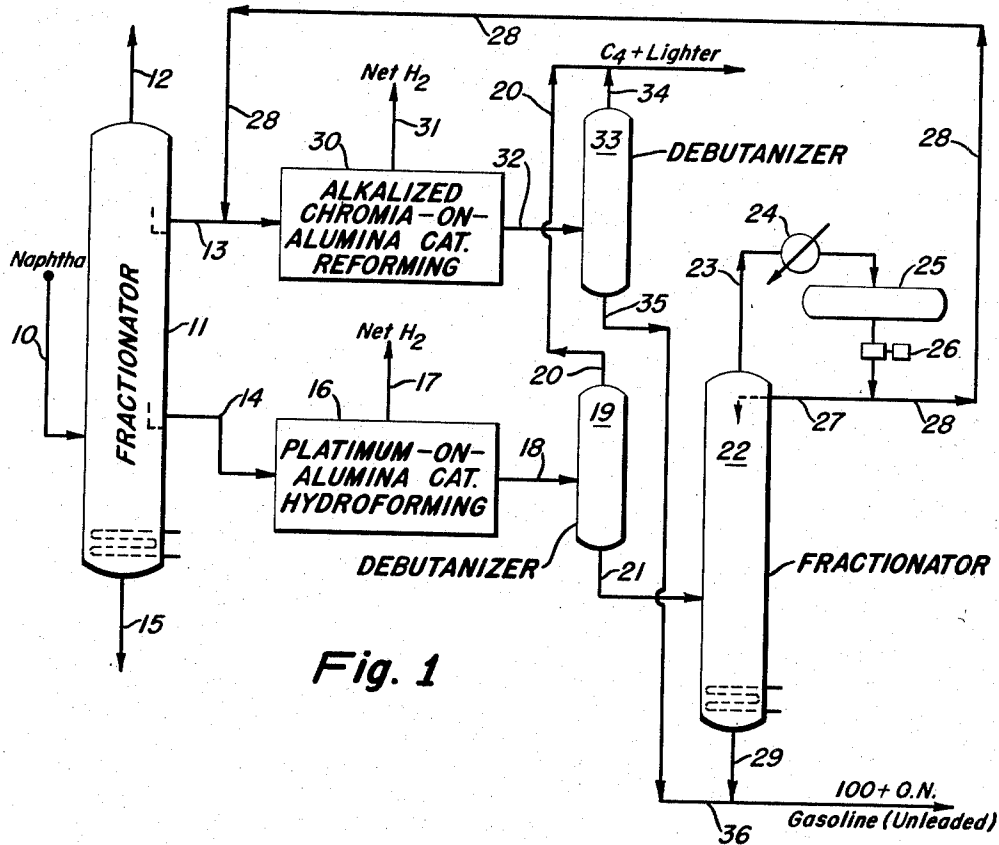


Fig. 1

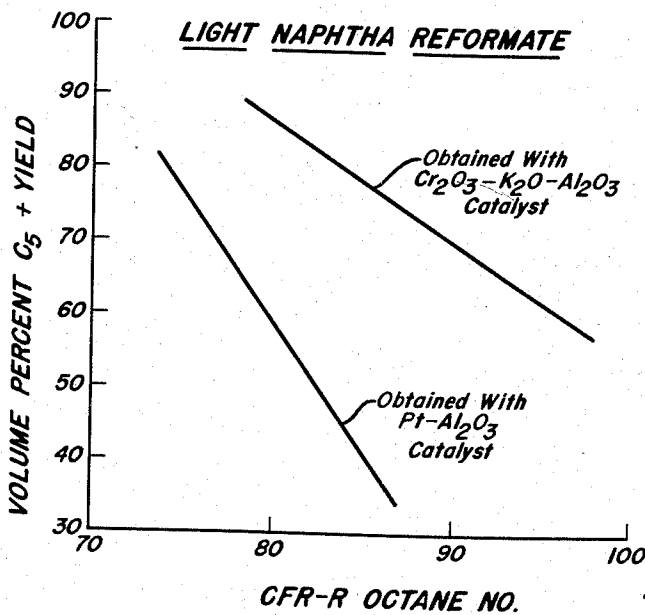


Fig. 2

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REFORMING-HYDROFORMING SYSTEM

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2 Claims. (Cl. 208—79)

This invention relates to an improved reforming-hydroforming system and it pertains more particularly to an improved method and means for converting a naphtha of relatively low octane number in high yields to a gasoline having a clear octane number of about 100 or higher.

The demand for higher and higher octane number gasolines has presented refiners with problems which cannot be met by techniques heretofore employed. An object of this invention is to provide a combination reforming-hydroforming process which will produce from ordinary low octane number naphthas gasolines of 100 octane number or more in higher yields and/or at lower costs than has heretofore been possible. A further object is to avoid the necessity of using expensive extraction and isomerization techniques in conjunction with reforming and/or hydroforming in order to achieve yield octane goals. A further object is to obtain by-products of increased value, i.e. larger yields of net hydrogen and normally gaseous olefins. Other objects will be apparent as the detailed description of the invention proceeds.

In practicing our invention we fractionate a naphtha to form a C₅-C₇ fraction having an end point of about 200° F. (plus or minus 10 to 15° F.) and a heavy fraction boiling substantially in the range of about 200 to 400° F. The light fraction is reformed by contact with an alkalized chromia alumina catalyst at about 975 to 1125° F., preferably about 1050° F., under a pressure in the range of about atmospheric to 200 p.s.i., preferably about 10 to 100, e.g. about 25 p.s.i.g., with a weight space velocity in the range of about .1 to 10 and preferably about 1 to 4 volumes of light naphtha per hour per volume of catalyst. The reforming of the light naphtha may be in the presence of recycled hydrogen in a fixed bed, moving bed or fluid system but since the recycle of hydrogen is not as essential in this step as it is in the case of platinum-on-alumina catalysts (particularly in a fluid system), the conversion of the light fraction under the defined conditions is herein termed reforming; it is chiefly dehydrogenation and aromatization with some isomerization. The heavy naphtha fraction is hydroformed by contact in the presence of recycled hydrogen with a platinum-on-alumina catalyst, preferably by the Ultraforming technique ("Ultraforming—A New Catalytic Reforming Process" by Forrester, Conn and Malloy, Petroleum Refiner, vol. 33, No. 4 (April 1954), pp. 153-156), i.e. at a temperature in the range

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of about 850 to 1000° F. under a pressure of about 100 to 400 p.s.i. with a space velocity in the range of about .1 to 10 volumes of heavy naphtha per hour per volume of catalyst, the hydroforming being effected in a regenerative system employing at least 3 stages of heating and reaction. The light naphtha reformate may be debutanized to render it suitable as a blending stock. The hydroformed heavy naphtha is first debutanized and then fractionated to separate components boiling below about 200° F. which components are introduced as a part of the charge to the light naphtha reforming step. The remaining hydroformed heavy naphtha when blended with the debutanized reformed light naphtha results in a full bodied gasoline of balanced volatility having a clear (unleaded) octane number of the order of 100 or higher.

Many multistage hydroforming techniques have heretofore been proposed (note U.S. 2,659,692, 2,698,829, 2,758,062, etc.) but none of them attain the unique advantages of our system. By hydroforming the heavy naphtha fraction under the defined conditions, a hydroformed product is obtainable which may itself be of 100 octane number or higher but which is usually deficient in light ends. The higher boiling fractions of such hydroformed product have octane numbers far above 100 but the lower boiling components thereof have undesirably low octane numbers, such components having been formed perhaps by undesired hydrocracking and/or ring splitting. The recycle of the low boiling fractions of hydroformed heavy naphtha to the hydroforming step or its treatment with platinum-on-alumina catalyst in a separate hydroforming step will, of course, lead to some improvement but will not give the remarkably enhanced yield octane number improvement attainable with alkalized chromia-on-alumina under the conditions defined for the reforming of the light naphtha fraction. The alkalized chromia alumina catalyst, however, is more susceptible to carbon formation and it should be employed only for low boiling charging stocks, i.e. heavy naphtha fractions should be excluded from charge thereto. The reforming step produces about as much, if not more, net hydrogen than is produced from a like amount of charge in the hydroforming step, which is an important consideration since by-product hydrogen is valuable for up-grading other hydrocarbons and/or for the manufacture of ammonia or other chemicals.

The invention will be more clearly understood from the following test data and description of a specific example thereof read in conjunction with the accompanying drawings which form a part of this specification and in which:

Figure 1 is a schematic flow diagram of our improved reforming-hydroforming system and

Figure 2 is a graph showing the remarkable improvement in yield-octane number relationship obtainable by employing alkalized chromia catalyst instead of platinum for the reforming of light naphtha.

To show the remarkable effectiveness of alkalized chromia-on-alumina catalyst for the reforming of pentane, hexane and light naphthas with hydrogen, the following

results were obtained in tests made under the indicated conditions:

the aromatic-olefinic products produced in our chromia reforming of light naphtha but our process can be

	n-Pentane	n-Hexane	MCP	n-Heptane	Light Naphtha
Charge O.N. CFR-R.....	61.7	24.8	91.3	0	66.2
Alkylized Chromia Cat. at 25 p.s.i. and 1,050° F. + H ₂			(?)	(?)	(No H ₂)
Vol. percent C ₅ +.....	76.5	62.8	76.6	66.9	68.5
O.N. CFR-R of C ₅ +.....	82.7	99.2	(93)	95.8	90.9
Percent Olefins.....	30	10.5	5	7.5	23.5
Percent Aromatics.....	3	68	22	64.5	23.5
Wt. percent Gas.....	16	16	5	11.9	22.5
Wt. percent C on feed.....	2	.9	9.0	0.4	5.4
Net H ₂ produced cu. ft./bbl.....	280	2,590	926	2,640	970
Platinum Cat. at 200 p.s.i., 930° F. + H ₂	(?)				937° F. 990° F.
Vol. percent yield of C ₅ +.....	39	64.4	81.9	59.4	71.0
O.N. CFR-R of C ₅ +.....	84	(63)	(93)	(86)	76.5
Percent Olefins.....					0.5
Percent Aromatics.....		9.5	47.0	35.0	8.5
Wt. percent Gas.....	60.5	32.3	15.6	35.1	33.7
Wt. Percent C on feed.....	Trace	Trace			1.5
Net H ₂ Produced.....		1,147	622	453	21.0
					54.1
					840
					1224

(?) Calculated octane number.

¹ H₂ consumed.

² 1,000° F.

³ 275 p.s.i.

The n-pentane, n-hexane, etc. were technical grades, i.e. about 95 mol percent pure; the light naphtha was a so-called "plant-hexane" having a sulfur content of about 41 p.p.m. and an ASTM boiling range of 117 to 167° F. and comprising about 15 percent pentanes and 75 percent hexanes. With n-pentane it will be noted that the alkylized chromia catalyst (as compared to platinum catalyst) produced approximately double the yield of C₅+ gasoline of over 82 octane number, produced 30 percent olefins and 3 percent aromatics where substantially none was produced by platinum and produced only 16 weight percent of gas where platinum produced 60 weight percent. In the case of normal hexane with approximately equal C₅+ volume percent yields the alkylized chromia catalyst gave a product octane number of 99.2 as compared to only 63 when employing platinum catalyst; here again the product produced by the alkylized chromia catalyst is characterized by a large olefin content and a remarkably large aromatics content with much less weight percent gas than was produced with platinum catalyst. For methylcyclopentane the platinum catalyst provides a somewhat better yield-octane number relationship than alkylized chromia but since most light naphthas contain such a small amount of methylcyclopentane, its effect is usually negligible. With normal heptane the alkylized chromia catalyst not only achieved remarkably superior results with respect to yield and octane number but also with respect to percent olefins, percent aromatics, the smaller percent gas and the remarkably large amount of net hydrogen produced.

Both the data in the table and the graph shown as Figure 2 in the drawing illustrate the benefits of using alkylized chromia catalyst for reforming a light naphtha of about 190° F. end point. Since the amount of such light naphtha in a 360° F. end point virgin naphtha may be about 20 to 40 percent, the overall yield advantage for our combination process may be as much as 10 to 12 percent higher than for a two-stage platinum hydroforming process. It should be pointed out that it is only necessary for the CFR-R octane number of the light naphtha to be increased to a level of about 85 in order for the total gasoline to have a clear octane number upwards of 100.

The isomate or aluminum chloride isomerization process is, of course, advantageous from the standpoint of yield but it produces no olefins or aromatics and consumes a considerable amount of hydrogen instead of effecting net hydrogen production. Furthermore, the isomate process is not effective for C₇ hydrocarbons and its investment and operating costs are relatively high in the case of pentane and hexane. Isomerized pentanes and hexanes have a better lead tetraethyl response than

employed for producing naphthas having lead octane numbers substantially above 95 CFR-R while such products cannot be produced by the use of platinum-on-alumina catalysts or by aluminum chloride isomerization without extensive and expensive recycle operations. A feature of our reformed light naphtha is its high olefin content.

Referring to Figure 1, a naphtha charge from line 10 is introduced to fractionation system diagrammatically represented by tower 11 from which C₄ and lighter hydrocarbons are removed through line 12, a C₅-C₇ fraction (having an end point of about 200° F. plus or minus about 15° F.) is withdrawn through line 13 for charging to the alkylized chromia reforming system, a 200° F.-360° F. naphtha fraction is withdrawn through line 14 as a charging stock for a platinum catalyst hydroforming (Ultraforming) system and higher boiling materials are withdrawn through line 15. The platinum catalyst hydroforming charge withdrawn through line 14 may require a desulfurization step (not shown) since it preferably should contain only about 5 to 30 p.p.m. of sulfur. It may also contain about 1 to 6 p.p.m. (but not more than 10 p.p.m.) of chloride, about 2 to 20 p.p.m. of water and less than 5 p.p.m. of nitrogen. The hydroforming of the 200-360° F. naphtha fraction may be effected with platinum-on-alumina catalyst as described in pending U.S. applications Serial Nos. 347,635, now U.S. 2,773,014, and 425,461, now U.S. 2,773,008; i.e. a regenerative, fixed-bed, swing reactor system is preferably employed with at least three heater-reactor stages each operating in the pressure range of about 100 to 400 p.s.i. and in the temperature range of about 850 to 1000° F. with a hydrogen recycle rate of the order of 1000 to 8000 standard cubic feet per barrel. The catalyst in the various reaction stages may be regenerated in any desired time sequence, the catalyst in each reactor preferably being on stream at least about 50 to 100 hours between periods of regeneration. In such a hydroforming system 16 there is a production of net hydrogen which is removed through line 17. The hydroformed product is introduced by line 18 to debutanizer 19, the C₄ and lighter hydrocarbons being taken overhead through line 20 and the C₄₊ hydrocarbons being introduced by line 21 to fractionator 22. Portions of the charge boiling below about 200° F. are taken overhead through line 23 and condenser 24 to receiver 25 from which condensate is withdrawn by pump 26, a part of it being returned by line 27 as reflux for the fractionator and the remainder being introduced by line 28 to the reforming step along with virgin naphtha from line 13. The naphtha product withdrawn from the base of fractionator 22 through line

29 may have a CFR-R octane number substantially higher than 100.

The light naphtha streams from lines 13 and 28 are charged to an alkalized chromia-on-alumina catalyst reforming system under conditions hereinabove set forth. Such a catalyst may, for example, contain about 18 percent Cr_2O_3 , 4 percent K_2O , 4 percent SiO_2 and 74 percent Al_2O_3 . No novelty is claimed in the alkalized chromia-on-alumina catalyst per se since such catalysts are well known to those skilled in the art (note U.S. 2,249,337, U.S. 2,378,209, etc.). Any type of contacting system may be employed for the alkalized chromia-on-alumina reforming which takes place in system 30 but we prefer to employ a fluid catalyst system as conventionally used for effecting catalytic cracking of gas oil with silica alumina catalyst. It is not even essential that hydrogen be recycled in such a system because large amounts of coke can be conveniently burned from such catalysts in a fluidized solids system and the heat thereby produced can be utilized for effecting the reforming operation. While a fluidized chromia reforming system is preferred, it should be understood that a fixed bed chromia system may be employed with hydrogen recycle in the same manner as molybdena-on-alumina fixed bed hydroforming operations have heretofore been carried out. A net amount of hydrogen is produced in the reforming system and removed therefrom through line 31. Reformate from the chromia-on-alumina system is withdrawn through line 32 to debutanizer 33 from which C_4 and lighter hydrocarbons are removed through line 34 and withdrawn to a condensables recovery system through line 20. The debutanized light naphtha product is withdrawn through line 35 to line 36 wherein it is blended with high octane number Ultraformate from line 29 to give a total product gasoline having a clear (unleaded) octane number of at least about 100. It will thus be seen that the objects of our invention are accomplished and that we obtain a product gasoline in which the low boiling components are characterized by CFR-R octane numbers substantially higher than could be obtained by isomerization. The yield of the high octane number light naphtha is enormously greater than could be obtained by use of platinum catalyst for light naphtha conversion. At the same time, we obtain an increased yield of by-product hydrogen and a considerable amount of olefinic gas which may be employed as polymerization or alkylation charging stock for even further increasing ultimate gasoline yields.

We claim:

1. The method of converting a naphtha in high yields to motor fuel of about 100 octane number (CFR-R), which method comprises fractionating said naphtha to form a light fraction having an end point of approximately 200° F. and a heavy fraction boiling in the range of about 200 to 400° F., reforming the light fraction by

dehydrogenation and aromatizing of the light fraction by contact with alkalized chromia-on-alumina catalyst at about 975 to 1125° F. under a pressure in the range of atmospheric to 200 p.s.i.g. with a space velocity in the range of .1 to 10 volumes of light naphtha per hour per volume of catalyst, removing normally gaseous hydrocarbons from the reformed light fraction to obtain debutanized reformate, hydroforming the heavy fraction by contact in at least 3 heating-reaction stages with platinum-on-alumina catalyst at about 850 to 1000° F. and 100 to 400 p.s.i. in the presence of recycled hydrogen to produce hydroformed heavy naphtha, removing normally gaseous hydrocarbons from the hydroformed heavy naphtha, fractionating the remaining hydroformed heavy naphtha to remove from heavy hydroformate components boiling below about 200° F., introducing said last named components together with said light fraction to the light fraction contacting step for reforming with said alkalized chromia-on-alumina catalyst and combining said debutanized reformate with said heavy hydroformate to obtain a full boiling range gasoline of at least about 100 CFR-R octane number on an unleaded basis.

2. The method of converting a naphtha charge into a superior motor fuel which comprises hydroforming with a platinum-alumina catalyst that portion of the naphtha boiling above about 200° F., splitting the hydroformed product to obtain a hydroformed heavy naphtha fraction boiling above about 200° F. and a debutanized light hydroformed naphtha fraction boiling below about 200° F., reforming the light debutanized hydroformed naphtha fraction in admixture with that portion of the original naphtha boiling below about 200° F. by dehydrogenating and aromatizing said light, debutanized naphtha mixture with an alkalized chromia-on-alumina catalyst at a pressure in the range of atmospheric to 200 p.s.i.g. and at a temperature in the range of about 975 to 1125° F. with a weight space velocity in the range of .1 to 10 for upgrading the mixture of hydrocarbons boiling below 200° F. to a high anti-knock rating and blending the upgraded high anti-knock product with the hydroformed heavy naphtha to obtain a full boiling range motor fuel having a CFR-R octane number of at least about 100 on an unleaded basis.

References Cited in the file of this patent

UNITED STATES PATENTS

2,409,695	Laughlin	Oct 22, 1946
2,653,175	Davis	Sept. 22, 1953
2,758,062	Arundale et al.	Aug. 7, 1956
2,767,124	Myers	Oct. 16, 1956

OTHER REFERENCES

"Progress in Petroleum Technology," Amer. Chem. Soc., Wash., D.C., Pub. August 7, 1951, pages 365 and 368.