

## UNITED STATES PATENT OFFICE

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## RE-FORMING NAPHTHA STOCKS

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Our invention relates to improvements in reforming of hydrocarbon naphtha fractions to obtain a high recovery of liquid products of improved octane number by reaction at a temperature within the cracking range and in the presence of a promoted high area-activated carbon catalyst. Carbon catalysts have been proposed for use in cracking operations, but so far as we know they have not been used successfully because the high area materials are too non-selective in promoting the various cracking reactions so that even where the conversion level is satisfactory, the product distribution is very poor. The yield of liquid products is low and the percentage of coke make is excessive. In addition, the carbon catalysts, unlike the clays or clay-like gels, are not good heat carriers so that there is a definite problem of maintaining the reaction temperature in view of the endothermic nature of cracking reactions without employing a series of reactors with intermediate reheating or using special and costly reaction tubes which are indirectly heated during the reaction period. The consideration of process heat is particularly important with respect to reforming operations which are conducted at the higher temperature ranges, e. g., 950° to 1200° F., although the considerations of non-selectivity, low liquid products yield and excessive coke make have led proponents of carbon catalysts for cracking heavier stocks away from proposing their use for naphtha reforming operations. Also it has been found very difficult to maintain the activity of carbon catalysts under process conditions. Due to the high rate of coke make, it has proved difficult to effect in situ regeneration by high ratios of steam or hydrogen dilution.

We consider three criteria of performance particularly significant in devising a commercially acceptable reforming process. First, there is the relation between yield of useful liquid products and the octane value of those products. Neither alone is determinative of value, for the refiner must evaluate gasoline stocks on an over-all or average basis of quantity and quality. Obviously both the quantity and the quality of the reformate produced determine the value of a reforming operation for directly upgrading stocks or for upgrading stocks by providing high value blending stocks. The spread or "jump" between neat octane numbers determined by the Motor Method and by the Research Method is important. The greater the spread, the better in general is the road performance. A third criterion of value is the amount of coke make per unit of octane increase which should be small if the process is to operate economically. We have found that certain seemingly small changes in operating conditions develop unpre-

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dictably large gains in terms of the criteria of yield-octane relation, "jump," and coke make per octane increase.

According to the present invention, the naphtha reforming operation is conducted in the presence of a carbon catalyst which has been specially modified by incorporation of an alkaline compound or salt of an alkali metal as a promoter and under particular reaction conditions which effect significant improvement in the selectivity of reaction and in product distribution, particularly with respect to the liquid product yield-octane relationship. The alkaline salt promoters are particularly effective in enhancing the reforming activity of the carbon catalysts while suppressing their inherent cracking activity. Also the low coke make with our promoted catalysts combined with their activity in promoting coke removal by steam permit operation according to a continuous regenerative reforming process. The naphtha stock to be reformed is subjected to a temperature of about 950° to 1150° F. in the presence of a high area-activated carbon catalyst promoted with about 1 to 10 percent of a stable alkaline compound or salt of an alkali metal, at a liquid hydrocarbon space velocity of about 0.5 to 3.0 under a pressure of about 0.1 to about 1 atmosphere, preferably in the presence of steam. The hydrocarbons boiling in the gasoline range are recovered from the reaction mixture, and the catalyst is periodically regenerated with high temperature steam or in regenerated in situ by operation at high steam to hydrocarbon ratios; e. g., upwards of 8-10 moles to 1.

We have found that the specified process conditions are necessary to obtain satisfactory selectivity and a desirable yield-octane relationship. Particularly, we have found that the product distribution and yield-octane relationship are improved by operation at low total pressure even when relatively high proportions of process steam are employed. Advantageously the process is operated at sub-atmospheric pressures, pressures at low as 0.1 atmosphere being desirable. We have found that the promoted high area-activated carbon catalysts under these conditions are relatively insensitive to steam so that steam in mole ratios to hydrocarbon as high as 5 to 1 or more may be employed for purposes of providing process heat and reducing the hydrocarbon partial pressure. Under these conditions of high steam to hydrocarbon ratio, the activity of the catalyst is maintained due to the water gas activity of the alkaline salt promoters. Thus the small amount of coke produced in the reforming reaction is continuously removed as formed and/or activated so that continuous hydrocarbon processing for long periods of time results. We also have found that contrary to

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most catalytic reforming processes, the use of process steam as a diluent is more desirable in terms of product distribution and in terms of yield-octane relation than hydrogen which represents a substantial advantage in terms of the cost of hydrogen and the cost of compression equipment for providing tail gas recycle.

In the practice of our invention, conventional refinery equipment is employed. Thus, the naphtha stock is preheated in a conventional fired heater to a temperature above about 950° F. The preheated stock is passed through a reaction vessel containing a bed of the promoted high area-activated carbon catalyst advantageously in granular pelleted form. The process steam employed is separately superheated and injected into the hydrocarbon feed stream before it is introduced to the reactor. At the lower steam to hydrocarbon ratios, i. e., less than about 8 or 10, continuous processing is obtained by providing a second reaction vessel connected in parallel, in which intermittent regeneration of the catalyst is performed while the carbon charge stock is processed in the on-stream reaction vessel. The regeneration is readily effected by exposing the catalyst to steam at high temperature, e. g., about 1300° F. The reaction mixture is passed from the reaction vessel to the usual condensing, fractionating and stabilizing equipment for recovery of liquid products and fixed gases.

The catalysts of our invention are high area-activated charcoal or carbon catalysts having surface areas by the nitrogen adsorption method of 100 square meters per gram or more, preferably above 500, which are promoted by the addition of a stable alkaline compound or salt of an alkali metal as by impregnation. Although a number of alkaline salts are useful, we have found that the sodium compounds, such as sodium silicate, sodium phosphate, sodium hydroxide and sodium carbonate are particularly valuable. Catalysts promoted with these materials are particularly active and are surprisingly useful in producing a reformat of high octane level, e. g., 85 to 86 neat by the Research Method. The sodium salts and the lithium salts, e. g., lithium carbonate and lithium hydroxide, also are advantageous in producing a reformat characterized by a significant spread or "jump" between the neat octane number determined by the Motor Method and the neat octane number by the Research Method. We also have found that salts of potassium have value as promoters for carbon catalysts in the reforming reaction. However, there is a surprising difference between the capacity of potassium phosphate and potassium carbonate in activating and improving the selectivity of the carbon catalysts. Thus potassium phosphate gives a comparable performance to the salts of sodium in terms of reformat octane level. For example, with a feed stock having an initial octane number by the Research Method of 42, reforming with a carbon catalyst promoted by 5 per cent potassium phosphate resulted in about 81 per cent yield of a reformat of 10 pounds Reid vapor pressure and 86 octane (R. M.) whereas processing of the same stock under similar conditions with a carbon catalyst promoted by 6.5 per cent potassium carbonate resulted in about 93 per cent reformat of 10 pounds Reid vapor pressure and only 74 octane number (R. M.). Also on the basis of coke make per octane increase, potassium carbonate is in-

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ferior to potassium phosphate which, however, in turn is inferior to the salts of the sodium series. Possibly the lower activity of the potassium carbonate may be a characteristic of potassium oxide, formed on the carbon surface by dissociation of the carbonate. With potassium phosphate, the formation of potassium oxide would be more difficult, depending upon the hydrolysis of the phosphate with dry steam which does not appear to occur to any substantial extent under the reaction conditions employed. For this reason, in the case of potassium salts we favor the use of compounds which are stable against hydrolysis or decomposition to the free oxide or the free metal under the reaction conditions.

The concentration of alkaline salt employed advantageously is about 5 per cent, but may be varied over the range of about 1 to 10 per cent. The promoters are added to the catalysts conventionally by impregnating the materials with aqueous solutions of about 1 to 5 normal, preferably 1 to 2 normal, concentration before drying and activating with steam at high temperature. The catalysts may be handled conventionally and in conventional forms, but in our continuous processing system with high steam dilution, it is desirable to handle the catalyst in the form of granules or pellets arranged in a fixed bed. It will be noted that in some cases the alkali promoter is somewhat volatile and tends to migrate from the catalyst bed. This can be compensated for by replenishing with additional promoter, as by spraying the bed with aqueous alkali, introducing the alkali during processing, or by placing solid particles of alkali in the reactor above the bed of catalyst or dispersed throughout the bed.

In the process of our invention, it is particularly desirable to operate at low total pressures. The operating pressure should not exceed atmospheric to any substantial extent, and most favorable product distribution is obtained by operation at sub-atmospheric pressures. In terms of yield and product distribution, we have found that it is desirable to maintain a substantial steam to hydrocarbon ratio. Advantageously, the mole ratio exceeds 2 to 1 and preferably is as high as 10 or 15 to 1. Further selectivity of reaction is had with steam dilution rather than hydrogen dilution which appears to favor hydrocracking and production of considerably more fixed gases than in the case of steam dilution. With the promoted catalysts, operation at the higher steam to hydrocarbon ratios permits continuous processing without the necessity of interrupting the reaction for intermittent catalyst regeneration. As noted above, the temperature of the reaction advantageously is maintained between about 1000° and 1100° F. The space velocity for best results should be maintained within the range of about 0.5 to 2.0 liquid hydrocarbon space velocity, preferably 0.5 to 1.0.

The principles of our invention will be further illustrated by reference to a number of exemplary runs, the process and yield data of which are tabulated below. In the runs, various fractions of Midcontinent naphtha were passed at the temperature, pressure and space velocity conditions indicated over activated carbon catalysts.

The type BP activated carbon used in these experiments was purchased from the Pittsburgh

Coke and Chemical Company, and had the following properties:

Surface area.....	1623 sq. meters/gram
Apparent density.....	48 gm./100 ml.
Na.....	0.08 weight per cent
K.....	0.10 weight per cent
Ca.....	0.29 weight per cent
Ash.....	9.52 weight per cent

Example I.—Alkaline promoters

Runs 1 to 5 of Table I illustrate the effect of employing different promoters at 1100° F., atmospheric pressure, 2.0 hourly liquid space velocity and a steam to hydrocarbon mole ratio of 10.

pending upon the hydrolysis of the phosphate with dry steam, and this did not appear to be substantial under the test conditions employed. This difference in ease of K<sub>2</sub>O formation would still be a limiting factor if the relative inactivity of K<sub>2</sub>CO<sub>3</sub> was traceable to the solid state reaction of potassium metal (formed by the reduction of K<sub>2</sub>O) and carbon.

On the basis of coke deposition per octane increase, K<sub>2</sub>CO<sub>3</sub> is also inferior to K<sub>3</sub>PO<sub>4</sub>, which in turn is quite inferior to the sodium series.

Example II.—Effect of total pressure

Although two different feed stocks were employed in the following comparison, the catalyst composition was essentially equivalent in the

TABLE I

Run No.....	1		2		3		4		5	
	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent
Product Distribution.....										
10# RVP Gasoline.....	80.3	80.2	84.9	84.8	82.2	81.8	81.5	81.4	94.7	92.7
Excess C <sub>4</sub> .....	0.1	0.1	-2.2	-2.9	1.0	1.3	1.1	1.4	-2.0	-2.6
Dry Gas C <sub>3</sub> .....	19.4	-----	16.5	-----	16.5	-----	15.9	-----	5.8	-----
Coke Deposit.....	0.2	-----	0.8	-----	0.3	-----	1.5	-----	1.5	-----
	100.0	-----	100.0	-----	100.0	-----	100.0	-----	100.0	-----
Products:										
Dry Gas, Weight Percent on Feed—										
H <sub>2</sub> .....	0.55	-----	0.92	-----	0.75	-----	0.91	-----	0.36	-----
CH <sub>4</sub> .....	3.26	-----	2.81	-----	2.77	-----	3.25	-----	0.45	-----
CO <sub>2</sub> .....	0.31	-----	0.16	-----	0.51	-----	1.2	-----	0.51	-----
10# RVP Gasoline: Feed <sup>2</sup> .....	Reformate	10# RVP	Reformate	10# RVP	Reformate	10# RVP	Reformate	10# RVP	Reformate	10# RVP
O. No., R. M.....	42.0	84.5	85.2	86.1	83.9	84.9	84.6	85.8	71.7	74.0
M. M.....	43.3	72.8	74.6	76.3	74.0	74.7	74.4	76.5	66.6	69.1
Initial B. P.....	228	123	116	113	113	-----	122	-----	116	-----
Percent over @228° F.....	40	-----	37	-----	39	-----	34	-----	24	-----
Catalyst Type.....	Carbon+ 5% Na <sub>2</sub> SiO <sub>3</sub>	-----	Carbon+ 5% Na <sub>2</sub> OP <sub>4</sub>	-----	Carbon+ 3.5% Na <sub>2</sub> CO <sub>3</sub>	-----	Carbon+ 5% K <sub>3</sub> PO <sub>4</sub>	-----	Carbon+ 6.5% K <sub>2</sub> CO <sub>3</sub>	-----

<sup>1</sup> Questionable, large amount of air in sample.

<sup>2</sup> 228°-335° F.

It is seen from the data in Table I that Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> give comparable performances as measured by a reformate octane level (R. M.) of 85 to 86 in tests under equivalent conditions. When K<sub>2</sub>CO<sub>3</sub> was tested under these same conditions the reformate

four tests with promoted catalysts. In tests 7 and 8, a straight-run naphtha, (311°-413° F.) was charged, while in tests 9 and 10, a lower boiling naphtha (228°-335° F.) was used. Variation in product distribution with varying total pressures can be seen in the following table.

TABLE II

Run No.....	6	7	8	9	10
Catalyst Type.....	Unpromoted B. P. Carbon	B. P. Carbon +3.64% Na <sub>2</sub> CO <sub>3</sub>	B. P. Carbon +3.64% Na <sub>2</sub> CO <sub>3</sub>	B. P. Carbon +3.46% Na <sub>2</sub> CO <sub>3</sub>	B. P. Carbon +3.46% Na <sub>2</sub> CO <sub>3</sub>
Conditions Temp., °F.....	1,100	1,000	1,045	1,100	1,010
Press., Atm.....	1.0	35.0	1.0	1.0	0.2
L. H. S. V.....	1.0	1.3	1.35	2.0	2.0
Mole Ratio Steam/HC.....	14.0	2.4	2.45	9.8	-----
P. P. of HC over Catalyst, Atm.....	0.065	10.3	-----	0.092	0.2
Product Distribution, Weight Percent on Feed:					
Stab. Reformate.....	84.3	61.6	81.5	74.4	90.1
Stab. Overhead.....	8.1	18.6	8.0	12.7	3.1
Dry Gas.....	7.6	13.3	8.3	12.6	5.4
Coke.....	0.02	6.5	2.2	0.3	1.4
	100.0	100.0	100.0	100.0	100.0
Products, Dry Gas, Weight Percent on Feed:					
H <sub>2</sub> .....	0.38	-----	-----	-----	-----
CH <sub>4</sub> .....	1.75	-----	-----	-----	-----
CO <sub>2</sub> .....	0.04	-----	-----	-----	-----
10# RVP Gasoline: Feed Stocks	A B	B	B	A	A
O. No., R. M.....	42.0 30	76.5	80.2	84.9	80.2
M. M.....	43.3 33	69.7	77.0	74.7	68.7
Yields, Vol. Percent Gasoline.....	93.0	77.1	84.5	81.8	89.3
Outside B B Required.....	4.0	-----	-----	-----	5.9
Excess B B Produced.....	-----	-----	-----	1.3	-----

octane level was only 74. The low activity observed with K<sub>2</sub>CO<sub>3</sub> may be a characteristic of K<sub>2</sub>O, formed directly by the dissociation of the carbonate on the carbon surface. With K<sub>3</sub>PO<sub>4</sub>, the formation of K<sub>2</sub>O would be more difficult, de-

75 It will be noted in Table II that a better product distribution is obtainable if sub-atmospheric pressures are employed in reforming with carbon catalysts. The use of a lower total pressure to reduce the partial pressure of the naphtha over

the catalyst seems to give a more favorable product distribution than that observed when the partial pressure is lowered through steam dilution of the naphtha feed. The yield-octane variations observed in tests 9 and 10 may be due to a preferential adsorption of steam on the catalyst surface during processing with a steam diluent. This would account for the lower selectivity observed when the steam diluent is employed, since a higher processing temperature or a lower space velocity would be required to obtain an equivalent conversion.

*Example III.—Sodium and lithium promoters*

Mid-Continent naphtha was subjected to reforming in the presence of activated coconut charcoal catalysts. One batch of charcoal was boiled 30 minutes with dilute HCl (10H<sub>2</sub>O:1 concd. HCl) and washed with hot water until the wash water was neutral. This catalyst was used in run #207-52. Another batch was impregnated with 2 N NaOH and still another with 2 N LiOH at room temperature. The latter catalysts were used in runs #248-6 and 207-64. Before use, each catalyst was dried in an oven at 250° F., and calcined at 900° F., under nitrogen atmosphere.

The reforming operation was effected at 1040° F., atmospheric pressure, 1.33 hourly liquid space velocity, and a steam to hydrocarbon mole ratio of 2.5 to 2.9. The results of these runs are shown in the following table.

TABLE III

Run No.	207-52		248-6		207-64	
Charcoal Catalyst	Neutral (HCl-washed)		0.2% NaOH plus 3.64% Na <sub>2</sub> CO <sub>3</sub>		0.2% LiOH plus 2.77% Li <sub>2</sub> CO <sub>3</sub>	
	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent	Wt. Percent	Vol. Percent
Product Distribution:						
10# RVP Gasoline	74.4	76.0	87.4	89.1	74.0	78.6
Excess C <sub>4</sub>	3.4	4.4	-2.1	-2.7	-1.4	-1.9
Dry Gas, C <sub>2</sub>	20.1		12.4		25.1	
Coke Deposit	2.1		2.3		2.3	
	100.0		100.0		100.0	
Products Dry Gas, Moles/Mole Naphtha Feed:						
H <sub>2</sub>	0.17		0.56		0.33	
CH <sub>4</sub>	0.36		0.20		0.35	
CO <sub>2</sub>	0.0088		0.0052		0.0072	
	Reformate	10# RVP	Reformate	10# RVP	Reformate	10# RVP
Gasoline:						
O. No. R. M.	30	86.8	79.2	80.6	86.6	87.1
M. M.	33	74.7	70.1	72.0	76.7	77.7
Spread	-3	12.1	9.1	8.6	9.9	9.4
Initial B. P., °F.	311	103	114		98	
Percent over at 311° F.		70.0	51.6		64	
Regeneration with Steam (1 liter H <sub>2</sub> O/l of catalyst/hr.) Rate of Gas Make, liters/hr.:						
at 1300° F.		2.6	15.0		13.6	
at 1400° F.		7.2	48.5		38.0	
Gas Composition, mol. percent:						
H <sub>2</sub>		62.2	62.0		64.1	
CO		26.8	2.5		2.5	
CO <sub>2</sub>		6.2	28.5		28.5	

It will be noted that although the octane number of the reformat was 74.7 (M. M.) in

the case of the neutral charcoal compared to 70.1 for the sodium carbonate impregnated charcoal, the liquid yield was considerably lower and the dry gas make more pronounced. It is also apparent from the relative amounts of hydrogen and methane produced, that the alkali impregnant has decreased the cracking activity and increased the reforming activity of the charcoal catalyst. Lithium carbonate does not appear to be as effective as sodium carbonate in controlling the selectivity of the catalyst.

The data in Table III show also that impregnation with alkali is particularly desirable in connection with the regeneration of the catalysts with steam, since the impregnated catalysts can be regenerated approximately five times more rapidly than the neutral catalyst.

*Example IV.—Sodium vs. potassium*

In Table IV are listed results obtained in reforming naphtha over carbon catalysts impregnated with various amounts of sodium and/or potassium bases. The runs were conducted at atmospheric pressure, using a steam to hydrocarbon mole ratio of 2.75.

The catalyst was prepared as follows. Untreated BP carbon was dried at 212° F. under 20 mm. pressure and impregnated at room temperature under vacuum with an aqueous solution of the alkaline promoter. The catalyst was dried

for 8 hours in an oven at 230° F. and calcined, before use, at 900° F. in the presence of nitrogen.

TABLE IV

Run #207-	63	81	82	71	74
Impregnating Solution	2 N KOH	2 N KOH	0.5 N KOH, 1.5 Na OH	1 N NaOH	2 N NaOH
L. H. S. V. (Naphtha)	1.35	1.97	1.96	2.0	2.0
Temperature, °F.	1,075	925	950	980	945
Coke on Feed, Weight percent	1.8	0.94	0.74	0.80	0.43
Dry Gas, Mol percent:					
H <sub>2</sub>	61.2	70.9	62.3	49.2	60.1
CO <sub>2</sub>	4.3	1.5	3.1	0.3	0.6
10#R. V. P. Reformat: Yield (100% Recovery), Vol. percent	93.3	102.2	100.4	88.2	97.0
Feed:					
O. Nos., R. M., 30	64.5	53.0	61.2	81.6	72.3
M. M., 33	63.0	53.9	59.3	74.6	66.9
Spread	1.5	-0.9	1.9	7.0	5.4

It will be noted from the data in Table IV that impregnation with sodium hydroxide produces a catalyst which has greater activity, forms much less coke, and produces a reformat with a much higher spread between M. M. and R. M. octane numbers than does impregnation with potassium hydroxide. Impregnation with a 1:3 mixture of potassium and sodium hydroxides gives a catalyst which produces more coke and yields a gasoline with a lower spread than would be expected on the basis of proportions of each alkali used. It is therefore apparent that the potassium hydroxide should be removed—for example, by preliminary leaching of the carbon, before impregnation with sodium and/or lithium alkali.

#### Example V.—Promoter concentration

Table V gives data relating to the effect of promoter concentration. Steam dilution was employed in these tests.

Table V

Run #	207-71	207-74	248-6	207-49
Carbon Base	(1)	(1)	(2)	(2)
Concentration of impregnating Solution	1 N.	2 N.	1 N.	5 N.
Temperature, °F.	980	945	1,045	1,085
L. H. S. V. (Naphtha)	2.0	2.0	1.37	1.37
Per cent Coke on Feed	0.80	0.43	2.28	2.10
10# R. V. P. Reformate Feed:				
Yield, Vol. Per cent	88.2	97.0	89.0	88.0
O. N. R. M., 30	81.6	72.3	80.6	73.6
M. M., 33	74.6	66.9	72.0	67.4
Vol. Per cent Yield + O. N. (R. M.)	169.8	169.3	169.6	161.6

<sup>1</sup>Type B. P.  
<sup>2</sup>Coconut Char.

It is seen that impregnation with 1 N. or 2 N. sodium hydroxide gives satisfactory catalysts, but there is a definite disadvantage in employing the 5 N. solution.

#### Example VI.—Product characteristics

It will be noted from data in Table VI that the reformat contains considerable concentrations of aromatics as well as olefins. Furthermore the reformat contains much material boiling lower than the feed stock. There is also a large reduction in sulfur content.

Table VI

	Feed	Reformat (Test 207-71)
API	49.5	50.2
IBP	311	115
10 Per cent	323	170
30	333	246
50	340	295
70	347	324
90	363	353
BP	413	434
Per cent over at 311° F.		60
Per cent Sulfur	0.029	0.0065
Per cent Olefins	0.0	32.1
Per cent Aromatics	15.9	41.2

#### We claim:

1. In the reforming of hydrocarbon naphtha stocks, the method of subjecting the naphtha stock to a temperature of about 950° to 1150° F. in the presence of a high area-activated carbon catalyst which contains about 1 to 10 per cent of an alkaline compound of an alkali metal at a liquid hydrocarbon space velocity of about 0.5 to 3.0 and under a pressure of about 0.1 to 1 atmosphere,

and recovering hydrocarbons in the gasoline range from the reaction mixture.

2. In the reforming of hydrocarbon naphtha stocks, the method of subjecting the naphtha stock to a temperature of about 950° to 1150° F. in the presence of steam and a high area-activated carbon catalyst which contains about 1 to 10 per cent of an alkaline compound of an alkali metal at a liquid hydrocarbon space velocity of about 0.5 to 3.0 and under a pressure of about 0.1 to 1 atmosphere, and recovering hydrocarbons in the gasoline range from the reaction mixture.

3. In the reforming of hydrocarbon naphtha stocks, the method of subjecting the naphtha stock to a temperature of about 1000° to 1100° F. in the presence of steam and a high area-activated carbon catalyst which contains about 1 to 10 per cent of an alkaline salt of an alkali metal at a liquid hydrocarbon space velocity of about 0.5 to 2.0 and under a pressure of about 0.1 to 1 atmosphere.

4. In the reforming of hydrocarbon naphtha stocks, the method of continuously charging the naphtha stock and steam in a mole ratio of steam to hydrocarbon of at least about 10 to 1 and at a liquid hydrocarbon space velocity of about 0.5 to 3.0 to a reaction zone containing a high area-activated carbon catalyst which contains about 1 to 10 per cent of an alkaline salt of an alkali metal and which is maintained at a temperature of about 950° to 1150° F. and under a pressure of about 0.1 to 1 atmosphere and recovering hydrocarbons in the gasoline range from the reaction mixture.

5. In the reforming of hydrocarbon naphtha stocks, the method of continuously charging the naphtha stock and steam in a mole ratio of steam to hydrocarbon of at least about 10 to 1 and at a liquid hydrocarbon space velocity of 0.5 to 2.0 to a reaction zone containing a high area-activated carbon catalyst which contains about 1 to 10 per cent of an alkaline salt of an alkali metal and which is maintained at a temperature of about 1000° to 1200° F. and under a pressure of about 0.1 to 1 atmosphere, and recovering hydrocarbons in the gasoline range from the reaction mixture.

6. The method of claim 5 in which the alkaline salt is a sodium compound.

7. The method of claim 6 in which the alkaline compound is sodium silicate.

8. The method of claim 6 in which the alkaline compound is sodium carbonate.

9. The method of claim 6 in which the alkaline compound is sodium phosphate.

10. The method of claim 4 in which the alkaline compound is a lithium compound.

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#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

Number	Name	Date
1,913,940	Mittasch et al.	June 13, 1933
1,967,636	Towne	July 24, 1934
2,231,803	Drennan	Feb. 11, 1941
2,249,461	Diwoy	July 15, 1941
2,353,119	Workman	July 4, 1944
2,481,300	Engel	Sept. 6, 1949
2,490,975	Mathy	Dec. 13, 1949