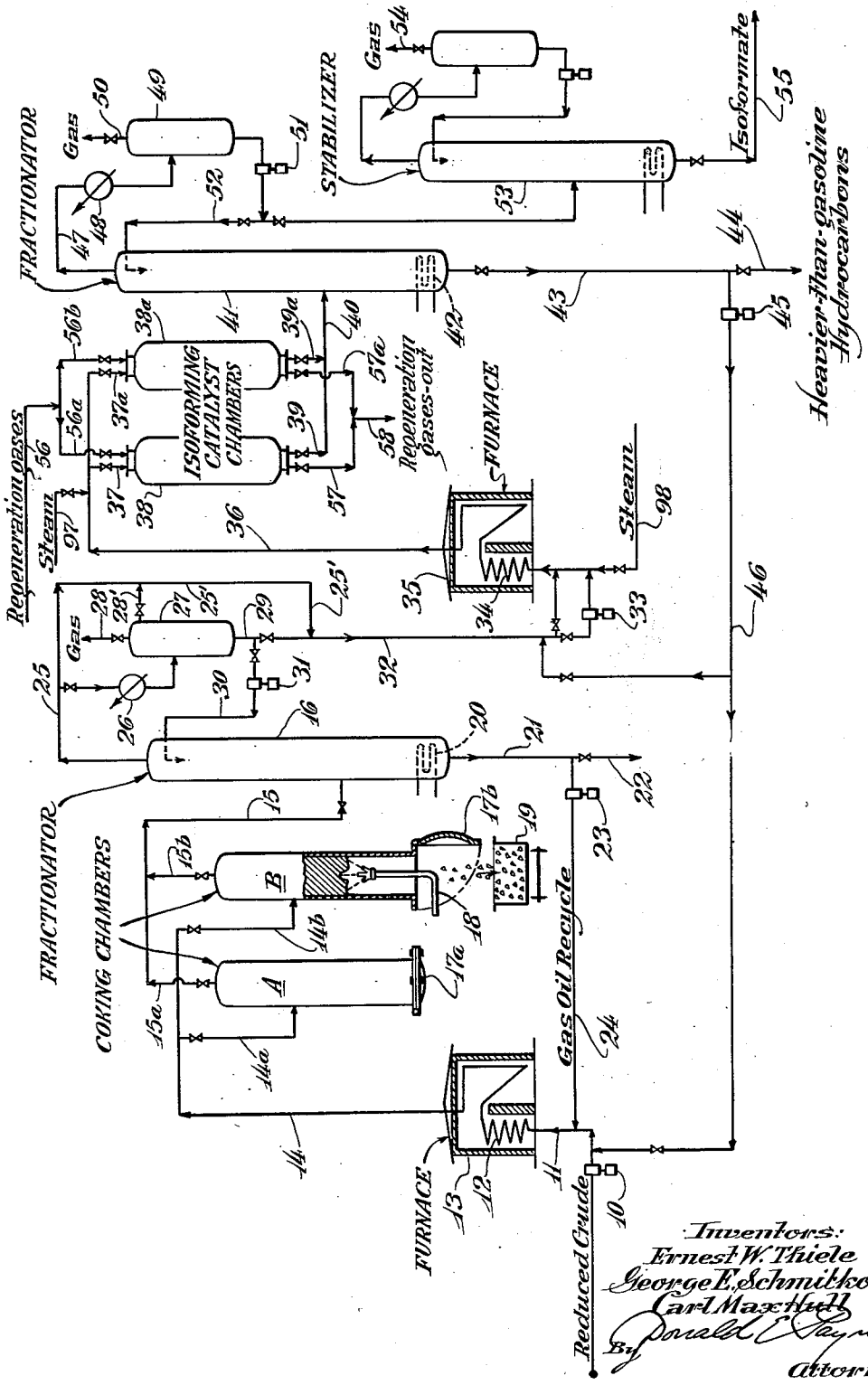
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COKER-ISOFORMING SYSTEM

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COKER-ISOFORMING SYSTEM

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This invention relates to an improved coker-isoforming system and it pertains more particularly to an improved method of converting heavy or residual hydrocarbon oils into marketable coke and high quality motor fuel the latter characterized by a clear A. S. T. M. octane number of at least 65 to 70. This is a continuation-in-part of our co-pending application Serial No. 350,270 filed August 3, 1940.

An object of our invention is to provide an improved system for refining petroleum residuums and other carbonaceous materials having a marked tendency to deposit coke when heated to cracking temperatures and which, therefore, cannot be economically processed by the usual thermal or catalytic cracking processes. Our object is to provide a system wherein the coke produced from such charging stocks may be recovered in marketable form.

Coker gasoline is characterized by a relatively low knock rating, usually in the region of 55 to 60 octane number, and it is characterized by a high degree of unsaturation (50 to 70% olefin content) which in turn leads to numerous refining difficulties. Acid treating to improve stability, particularly gum stability, has resulted in large losses. Thermal reforming likewise results in large losses and produces insignificant increases in knock rating. Catalytic reforming, even in the presence of hydrogen, has likewise given a disappointingly low increase or even a decrease in knock rating. An object of this invention is to provide a unitary system whereby the gasoline or naphtha fraction from the coking operation may be isoformed to produce maximum yields of a stable high quality motor fuel characterized by a clear A. S. T. M. octane number which is about ten units higher than could heretofore be obtained on coker naphtha by any other known process.

Isoforming is distinctly different from all prior art processes in that it employs thermally cracked naphtha as its charging stock and in that it produces 95% to 99% yields based on this charging stock with surprisingly low losses to gas, coke and heavier-than-gasoline hydrocarbons.

In catalytic reforming and cracking processes the yield-octane curve tends to flatten out, but it does not bend backwards; in isoforming we have found that yield-octane curve actually does bend backwards, showing a definite optimum octane number with a yield of 94 to 99%, the maximum in most cases being with a yield of about 96% or 97%. Also in catalytic reforming and cracking the octane number is gradually lower with increasing space velocities (shorter times of contact) while in the isoforming reaction there is a definite peak in the curve. At atmospheric pressures and with active catalysts this peak usually is within the range of 4 to 40, usually at about 12 volumes of liquid thermally cracked naphtha per volume of catalyst space per hour.

Thermally cracked naphtha has been contacted with clay for improving its stability against gum formation, for lowering its sulphur content, etc. but the conditions of these clay contacting processes have been such that very little if any improvement in octane numbers was accomplished. Both thermal and catalytic reforming or isomerization have been applied to virgin naphtha, but always with yields considerably below 100% and with considerable losses to gas, coke and heavier-than-gasoline hydrocarbons. Hydrogenation, aromatization and hydroforming have been proposed for increasing the octane number of naphtha but experience has shown that coker naphtha is not particularly responsive to such processes, that only a very small improvement is obtained in octane number and that losses are much higher than those obtainable by isoforming. Our isoforming process makes it possible to utilize existing coking equipment and to meet octane requirements with minimum losses to gas and carbon and with a catalyst holding time, i. e., time between regenerations, which far exceeds the catalyst holding time possible in catalytic cracking processes. An important feature of the isoforming process is the fact that it markedly increases the susceptibility of the finished gasoline, which we call isoformate, to tetraethyl lead. In addition to obtaining increases of 5 to 15 octane numbers at a relatively high octane number level, we obtain the advantage of increased responsiveness to lead tetraethyl.

In practicing our invention the reduced crude petroleum or other charging stock is heated in a pipe still to a temperature of about 800 to 950° F., preferably about 875 to 925° F., and introduced into a large reaction chamber which is empty except for the possible provision of cables or other suitable means for obtaining a discharge of coke therefrom. The temperature of this reaction chamber is maintained by the continuously introduced hot charging stock and in this reaction chamber a thermal conversion takes place in which about 10 to 20% of the stock is converted into solid coke and the remainder of the stock is converted into lower boiling hydrocarbons, namely, gas oil, gasoline and gases. The coker gas oil is preferably recycled in a coking system although it may be utilized per se or subjected

to other refining or conversion processes. The coke still naphtha fraction together with some or all of the gases is heated in other pipe still coils to a temperature of about 625 to 1100° F., preferably to about 900 to 975° F., and contacted with an isoforming catalyst which is preferably of the silica-alumina type, preferably at a pressure of from atmospheric to 15 pounds per square inch gauge, at a temperature of about 925° F. and with a space velocity of about 4 to 40, preferably about 12 v/v/hr. This catalytic treatment of the coker naphtha is called isoforming and is characterized by gasoline yields of about 96 to 97%, coke yields of about .05 to .1%, gas yields of about 1% and heavier-than-gasoline yields of about 1% all based on the coker naphtha charge. The conversion may be carried out for periods of 4 to 24 hours, preferably about 12 hours, between catalyst regeneration steps, the catalyst being regenerated in the same way that regeneration is effected in other catalytic processes. The invention will be more fully understood from the following detailed description of a preferred embodiment thereof.

The accompanying drawing which forms a part of this specification diagrammatically illustrates a flow sheet of our improved coker-isoforming system.

Our process is particularly applicable to heavy residuums, for example 15 to 25% bottoms from crude oil distillation. It should be understood, however, that this invention is also applicable to heavy distillate oils and to any bituminous, tarry or carbonaceous material which can be subjected to destructive distillation or cracking for producing coke and naphtha vapors.

In a preferred operation a 20% reduced Mid-Continent crude is charged by pump **10** through line **11** to coils **12** of pipe still furnace **13** wherein the charging stock is heated to a temperature of about 800 to 950 or 1000° F. at a pressure of from a few pounds to about 100 pounds gauge, preferably about 50 pounds per square inch. The charge is forced through the heater coils at sufficient velocity to avoid any substantial thermal decomposition or coke deposition in said coils. The hot reaction products are passed by transfer line **14** either through line **14***a* or line **14***b* to one of the coking chambers A or B. In this chamber the pressure may range from about atmospheric to 100 pounds per square inch, preferably about 50 pounds per square inch, and the temperature is maintained preferably at about 850 to 900° F. by the heat of the incoming vapors. The chambers are preferably hollow cylindrical vessels except that suitable cables or other means may be provided for later discharging the coke as will hereinafter be described. Since one of the objects of the invention is to produce a marketable coke it is essential to avoid the use of contact material in these chambers which would increase the ash content of the coke. The contained heat of the vapors in these vessels effects a thermal decomposition of a charging stock to form solid coke, coker gas oil, coker naphtha and gases. The gas oil, naphtha and gases are continuously withdrawn as vapors through lines **15***a* or **15***b* and line **15** to fractionating column **16**. The hot charging stock is introduced into chamber A until that chamber becomes substantially filled with coke at which time the charging stock is transferred to chamber B and the coke is removed from chamber A. Usually about 10 to 20% or more of the charging stock is converted into coke and the remainder is converted into gas oil, naphtha and gases.

While coking chamber A is on stream, coke is removed from chamber B by removing bottom plate **17***b*. If cables have previously been wound in the chamber the coke may be removed by simply pulling out such coils. We prefer, however, to remove the coke by hydraulic cutting means **18** which are well known in the art and require no detailed description. The coke may be discharged into suitable containers or conveying means **19** for storage or marketing. Cover **17***b* is then secured to the base of chamber B and this chamber is ready to go on stream while coke is discharged from chamber A.

We prefer to employ six coke drums in a unit, the coking cycle of each drum being 96 hours. Using a two-stream system through the coking furnace this system is operated so that one drum will be full at the end of every 16 hours. The coke after being allowed to stand for about a day is quenched with steam and water and then discharged as hereinabove described.

Fractionator **16** may be provided with suitable reboiler means **20** at the base in order to insure the removal of all coker naphtha from the gas oil which is withdrawn from the base of the tower through line **21** and which may be withdrawn from the system through line **22** or recycled by pump **23** and line **24** to line **11** for further coking.

The coker naphtha and lighter hydrocarbons are taken overhead through line **25** and cooler **26** and are then introduced into gas separator or receiver tank **27** from which gases are vented through line **28** and liquid coker naphtha is withdrawn through line **29**. A portion of this naphtha may be recycled through line **30** by pump **31** for reflux in the top of bubble tower **16**. The remainder of the coker naphtha is introduced through line **32** to the isoforming step of our process. The coker naphtha does not have to be stabilized before it is introduced to the isoforming system. We may either introduce the total overhead products from tower **16** directly to line **32** through line **25'** (when no part of it is required for reflux in tower **16**) or we may condense only the liquid required for reflux and all of the remaining naphtha and vapors may pass through lines **28'** and **25'** to line **32** as a charge for the isoforming step of our process.

The coker naphtha for isoforming should have an end point of about 400 to 450° F. It should be substantially free from gas oil since such material tends to foul the catalyst and to interfere with the proper operation of the isoforming process. A 410° F. end point coker naphtha thus produced may have an octane number of about 50 to 60, an olefin content of about 50 to 70% and Reid vapor pressure of about 3.2 pounds. This coker naphtha is introduced by pump **33** through coils **34** of pipe still furnace **35** and thence through transfer line **36** and valved line **37** or valved line **37***a* into isoforming catalyst chamber **38** or **38***a*. The reaction products are withdrawn through line **39** or **39***a* and line **40** to fractionator tower **41** which is provided with suitable reboiler means **42** at the base thereof. The amount of heavier-than-gasoline hydrocarbons removed from the base of fractionator **41** through line **43** is extremely small if cracked naphtha of 400° F. end point or lower is fed to reactors **38** and **38***a* and such heavier-than-gasoline hydrocarbons may, therefore, be removed either continuously or intermittently and withdrawn from the system through line **44** or recycled by pump **45** through

line 46 to line 11 for thermal cracking or to line 32 for further treatment in the isoforming process.

End point isoformate together with hydrocarbon gases is taken overhead from tower 41 through line 47 and cooler 48 to receiver 49. Uncondensed gases are withdrawn from receiver 49 through line 50 and they may be compressed or absorbed in oil to recover gasoline components by procedures familiar to the petroleum industry. A part of the liquid from receiver 49 is introduced by pump 51 and line 52 into the top of tower 41 to serve as reflux. The rest of this liquid is introduced into stabilizer system 53 from which propane and lighter gases are withdrawn through line 54 and finished isoformate is withdrawn through line 55.

The calalysts employed for isoforming are preferably the type generally employed for cracking virgin gas oils and heavier hydrocarbons to obtain high octane numbers. Activated hydrosilicate of alumina has been found to give excellent results. Such catalysts may be prepared from acid treated bentonite by making a dough of such bentonite and water, forming pellets, and thoroughly drying said pellets by heating to a temperature of about 850 to 1000° F. The catalyst may also be prepared by depositing alumina or other metal oxides on silica gel by impregnation with appropriate salts of the metals. Examples of such other metal oxides are copper, magnesium, beryllium, and thorium. Cadmium, titanium, manganese, zirconium, vanadium and cerium have shown slight activity in particular catalysts tested. A ball-milled 50–50 mixture of magnesium oxide and silica gave less coke and less gas than the preferred alumina-on-silica-gel catalyst, but it likewise gave less octane number improvement. Catalysts of the natural or synthetic zeolite type may be employed, preferably after sodium is displaced or leached out of the catalyst. An example of a typical synthetic zeolite is described in United States Patent 2,197,861. Catalyst may be obtained by the treatment of blast furnace slag with hydrochloric acid followed by coagulation of the acid solution, washing and drying. Acid treated clay commonly marketed as Super Filtrol can be formed into catalyst pellets of high activity and long life. Applicants are not herein claiming any novelty in the catalyst per se but they do not employ catalysts of the dehydrogenation, hydroforming or aromatization type. Generally speaking, catalysts of the dehydrogenation or aromatizing type, such as bauxite, activated alumina, or oxides of certain metals (such as those of chromium, tungsten, nickel, or molybdenum) on alumina, are inferior and may be detrimental. Likewise, ordinary untreated clays are inferior in the isoforming process.

While ordinary cracking catalysts of the type that produce high octane numbers are also good isoforming catalysts it does not follow that all cracking catalysts are suitable for isoforming or vice versa. Silica gel is a cracking catalyst, but is not effective for isoforming. Boron phosphate is a good isoforming catalyst but it is not effective for catalytic cracking.

Any type of catalyst contacting system may be employed in the isoforming process, i. e., we may use a fixed bed process, a moving bed process, or a powdered catalyst process. In the fixed bed process, illustrated in the drawing the catalyst may simply be mounted in one or more beds over foraminous supports and conventional heat exchange means may be supplied throughout the bed either for supplying heat during the isoforming reaction or for abstracting heat during catalyst regeneration. The regeneration of the catalyst is effected in the same way as it is effected in catalytic cracking processes. When catalyst becomes spent (usually after about 8 to 24 hours on stream, i. e. 8 to 24 hours "holding time") it may be purged by an inert gas such as fuel gas, or the tail gas from line 28 of the cracking system, followed by a hydrocarbon-free gas such as flue gas, and after the purging step, the catalyst may be regenerated preferably under pressure by means of an oxygen-containing gas preferably at a temperature of about 900 to 1100° F. After regeneration the catalyst may be purged with flue gas. The purge and regeneration gases may be introduced through line 56 and one of the lines 56*a* or 56*b*. Enriched purge gases or hot regeneration gases may be removed through lines 57 or 57*a* and thence through line 58.

The pressure employed for isoforming is preferably about atmospheric to 15 pounds per square inch gauge. Pressures of 125 to 200 pounds may be employed but high pressures cause a pronounced increase in coke deposition as will be hereinafter pointed out.

The space velocity through the catalyst chamber will vary with different catalysts but for a relatively good silica-alumina catalyst or for activated clay of the type commonly known as Super Filtrol the space velocity is preferably about 12 v/v/hr. The range of space velocities is considerably above the permissible range of other catalytic processes such as catalytic cracking or catalytic reforming and may generally vary between about 4 and 40 volumes of liquid charging stock per volume of catalyst space per hour. Another way of expressing the same thing is to define the reaction by the tons of catalyst employed per 100 barrels of charging stock per hour; on this basis we prefer to operate at about one ton of catalyst per 100 barrels per hour and the optimum range is from about .3 to 3 tons of catalyst per hundred barrels of charging stock per hour.

The temperatures employed for isoforming coker naphtha may range from about 625 to 1100° F. but the optimum temperatures are about 900 to 1000° F., preferably about 925° to 950° F. The transfer line temperature should be about 25° higher than the temperature desired in the isoforming reaction chamber.

The on-stream period between regenerations may vary from about 4 to 24 hours. We have found that during the first few hours on-stream the gas production may be about double the gas production near the end of the on-stream period and that octane number improvement falls off slightly during the progress of a run. The amount of coke deposited on the catalyst likewise becomes less and less during the course of a run. For minimum coke and gas losses and maximum yields and octane numbers we have found that the optimum on-stream, holding or "catalyst residence time" between regenerations will run from about 4 to 24 hours, preferably from about 8 to 12 hours. The following examples will illustrate the effect of operating conditions on the isoforming of coke still naphtha.

EXAMPLE I

A coker naphtha having an A. S. T. M. octane number of 59.8 was isoformed with a synthetic aluminum zeolite catalyst having a silica-alumina

ratio of about 3½ (such catalysts may be prepared in accordance with the teachings of U. S. Patent 2,197,862). The isoforming was at 850° F. and a space velocity of 3.94 v/v/hr. (30.2 barrels per ton per hour). The effect of run length on octane number and gas production is shown by the following table:

Knock rating—C. F. R.—M				Per cent gas produced—C_3 and lower	
Bbls./T.	Hours	Grab sample	Cumulative	Grab sample	Cumulative
50	1.7	67.9	68.3	0.8	1.1
100	3.3	67.5	68.0	0.6	0.9
150	5.0	67.1	67.8	0.5	0.8
200	6.6	66.8	67.7	0.4	0.7
226	7.5	66.6	67.6	0.3	0.6

Coke 0.10 wt. per cent of total feed.

It will be seen from the foregoing example that our process effects an outstanding improvement in the knock rating of gasoline produced from the coking of petroleum residues substantially without loss. Yields based on coker naphtha treated are generally above 99% and always above 95%. The cause of the increase in knock rating of coker naphtha obtained by our isomerizing process is not clearly understood but it is believed that certain hydrocarbons are produced in the coking operation which are peculiar to this type of naphtha and that these hydrocarbons are rearranged in structure by contact with the isomerizing catalyst. In addition to the improvement in knock rating, the gasoline also has an increased gum stability as indicated by the fact that the induction period on oxidation in the glass bomb test (Industrial and Engineering Chemistry, 397 (1933)) was increased in one example from 5.8 hours for the coker naphtha to 12.3 hours for the gasoline after isomerization.

Example II

A coke still naphtha having an A. S. T. M. octane number of 59 and a research octane number of 63.1 was isoformed over a silica-alumina catalyst similar to that employed in Example I, having a silica-alumina ratio of about 3.5. In this case the isoforming was effected at 950° F., at 15 pounds per square inch gauge, and with a space velocity of about 4 v/v/hr. (3 tons of catalyst per 100 barrels per hour.) The results of analyses on products produced throughout the 24 hour run are as follows:

Results of isoforming coke still naphtha in H 89

Period	Hours		Results by periods			Results cum. to end of period		
	In period	At end of period	Percent gas	CFR—M	CFR—R	Percent gas	CFR—M	CFR—R
1	3	3	6.4	69.0	75.4	6.4	69.0	75.4
2	6	9	4.8	68.1	76.7	5.3	68.4	76.3
3	6	15	4.4	67.9	74.9	4.9	68.2	75.7
4	6	21	3.9	67.3	74.9	4.6	68.0	75.5
5	3	24	3.0	66.9	73.0	4.4	67.8	75.2

From this table it will be noted that gas production falls off markedly with increased run lengths without substantial losses in octane improvement. By the end of 24 hours, however, considerable coke has been deposited on the catalyst and regeneration at this point is usually desirable. In some instances we find the optimum catalyst holding time to be about 12 hours.

A comparison of runs employing different space velocities with this same catalyst at 950° F. and 15 pounds per square inch gauge pressure for a 24 hour reaction period on the 59 A. S. T. M. octane number coker naphthas is as follows:

Tons of catalyst/100 bbls./hr.	Vol. feed/vol. catalyst space per hour	Per cent coke based on feed	Per cent gas based on feed	Reid vapor pressure	A. S. T. M. octane number	Research octane number
Feed				3.2	59.0	63.1
.67	18	.05	1.2	4.7	65.9	71.3
1.0	12	.08	2.2	4.3	66.8	72.4
1.5	8	.12	2.3	6.2	66.5	72.5
3.0	4	.26	4.4	8.0	67.8	75.2

Considering losses to coke and gas, and formation of low boiling hydrocarbons as shown by the Reid vapor pressure, and octane number improvement, it will be seen that a space velocity of about 12 v/v/hr. is optimum.

If the reaction is effected at 125 pounds pressure the coke deposit is about seven times that which is produced at atmospheric pressure, the gas production is about doubled and the octane improvement is not so great. We, therefore, prefer to operate the isoforming step at a pressure of about atmospheric to about 15 pounds per square inch.

Example III

When the same catalyst as was employed in Example II was employed to isoform the same coker naphtha at atmospheric pressure, 925° F., 12 v/v/hr. space velocity (one ton of catalyst per 100 barrels of feed per hour) with a reaction period of 4 hours, we obtained about 97% yield of isoformate. The coker naphtha charge had a Reid vapor pressure of 3.2, an A. S. T. M. octane number of 59 and a research octane number of 63.1. The resulting isoformate had a Reid vapor pressure of 6.3, an A. S. T. M. octane number of 68.6 and a research octane number of 75.3. The cumulative octane numbers at the end of the first, second, third and fourth hours in this test were 68.7, 69.1, 69.0 and 68.6. Extensive test results have shown that octane number improvement is actually greater after the initial period on-stream than it is when the system first goes on-stream.

While steam is not essential in the isoforming of coke still naphtha it should be understood that steam may be employed in amounts from 1 to 15% or more by weight. Substantially superheated steam may be introduced directly in transfer line **36** through line **97**. Alternatively it may be introduced through line **98** into the charge entering the pipe still. In some instances the steam apparently promotes high catalyst activity and since it has the effect of decreasing the partial pressure of the hydrocarbon vapors it may also

serve the function of minimizing carbon deposition.

While we have described in detail a preferred embodiment of our invention and preferred examples of the isoforming step in our process it should be understood that the invention is not limited to the particular conditions hereinabove stated.

We claim:

1. The method of refining high boiling carbonaceous materials for the production of marketable coke and high quality motor fuel having a clear A. S. T. M. octane number of at least 65 which method comprises rapidly heating said high boiling carbonaceous material to a temperature of about 850 to 1000° F., introducing said heated material into an enlarged coking drum at a pressure of about atmospheric to 100 pounds per square inch, withdrawing vapors from said coking drum until said drum becomes substantially filled with coke, then transferring the heated materials to another enlarged coking drum, removing marketable coke from said first named drum, fractionating the vapors leaving said coking drums to remove therefrom materials boiling above about 450° F. from a coker naphtha, heating said coker naphtha to a temperature of about 625 to 1100° F. under a pressure of about atmospheric to 50 pounds per square inch gauge, contacting said heated coker naphtha vapors with an isoforming catalyst at a rate within the approximate range of 4 to 40 volumes of liquid coker naphtha per hour per volume of catalyst space for obtaining a volume percent liquid yield within the approximate range of 94 to 99 and an octane number improvement of at least about 5 to 15 A. S. T. M. octane units and recovering a motor fuel of the gasoline boiling range from the products of said contacting step.

2. The process of claim 1 wherein the on-stream period in the contacting step is about 4 to 24 hours and wherein the catalyst is regenerated between on-stream periods.

3. The method of claim 1 wherein the temperature of the contacting step is about 900 to 950° F.

4. The method of producing marketable coke and high octane number motor fuel from charging stock of the class consisting essentially of residual hydrocarbon oils, heavy distillate oils, and other carbonaceous materials which method comprises coking said charging stock to produce marketable coke, coker gas oil, coker naphtha and gases, heating said coker naphtha to a temperature of about 850 to 1025° F. at a pressure of about atmospheric to 50 pounds per square inch gauge and contacting it with an isoforming catalyst at a rate of about 4 to 40 volumes of liquid coker naphtha per hour per volume of catalyst to obtain a volume percent liquid yield based on coker naphtha within the approximate range of 94 to 99 and an octane number improvement of about 5 to 15 A. S. T. M. octane units and separating a motor fuel of the gasoline boiling range from the products leaving said contacting step.

5. The method of claim 4 wherein the on-stream period of contacting step is about 4 to 24 hours and wherein the catalyst is regenerated between on-stream periods.

6. The method of converting a coke still naphtha having a clear A. S. T. M. octane number below 60 into a high quality motor fuel having a clear A. S. T. M. octane number of about 68 to 70 which method comprises vaporizing and superheating said coker naphtha to a temperature of about 850 to 1025° F., at about atmospheric to 50 pounds per square inch gauge pressure, contacting said vapors with a silica-alumina catalyst at a rate of about 4 to 40 volumes of charging stock per volume of catalyst space per hour in on-stream periods of about 4 to 24 hours, regenerating said catalyst between on-stream periods, and fractionating the products of said contacting step to obtain a motor fuel of the gasoline boiling range which motor fuel constitutes about 94 to 99 volume percent of the coker naphtha charged to the contacting step and which motor fuel has a clear A. S. T. M. octane number of about 68 to 70.

7. The method of converting coke still naphtha into a high octane number motor fuel without suffering as much as 5% loss due to the formation of gas, coke and heavier than gasoline components which method comprises fractionating coke still vapors to obtain a coke still naphtha fraction having an end point below about 450° F., heating said coke still naphtha to a temperature of about 850 to 1025° F. and contacting said heated naphtha with an isoforming catalyst at a rate of about 4 to 40 volumes of liquid coker naphtha per hour per volume of catalyst in the contacting step for producing a motor fuel yield of at least 95 volume percent based on coke still naphtha and to obtain an octane number improvement of at least 5 A. S. T. M. octane units.

8. The method of claim 7 wherein the pressure in the contacting step is about atmospheric to 15 pounds per square inch gauge.

9. The method of claim 7 wherein the on-stream period of the contacting step is about 4 to 24 hours.

10. The method of claim 7 wherein from about 1 to 15% by weight of steam is admixed with the coker naphtha vapors in the catalyst contacting step.

11. The process of making a gasoline of improved knock rating from petroleum residuum which comprises subjecting the residuum to coking at an elevated temperature of the order of 800 to 950° F., thereby producing naphtha and heavier hydrocarbon distillate fractions, separating from the products naphtha fractions boiling below about 450° F., heating the said naphtha fractions and subjecting the vapors thereof to the action of an isomerizing catalyst at a conversion temperature above 800° F. and a space velocity above about 4 volumes of naphtha per hour per volume of catalyst in the absence of hydrocarbons boiling above 450° F., and controlling the temperature and time of contact between said naphtha vapors and said catalyst to produce an increase in knock rating of at least 5 CFR—M and a yield of at least 95% gasoline boiling below the maximum boiling point of the naphtha fraction treated with said catalyst.

12. The process of claim 11 wherein the said isomerizing catalyst consists essentially of activated silica.

13. The process of increasing the knock rating of gasoline obtained from the coking of petroleum residuums wherein are produced naphtha and heavier oils, which comprises separating from the products of said coking operation a naphtha boiling substantially within the gasoline boiling range, vaporizing said naphtha and subjecting the vapors thereof at a temperature of about 900° F. and a pressure of about atmospheric to 50 pounds per square inch to the action of an activated silica catalyst, with a contact time indicated by the rate of above 4 volumes of naph-

tha per volume of catalyst per hour, controlling the reaction conditions to produce an increase in knock rating of at least 5 CFR—M with a yield of at least 95% by weight of liquid products based on the naphtha treated, and thereafter recovering the isomerized naphtha vapors and fractionating them to produce the desired gasoline.

14. The process of making a gasoline of improved knock rating from petroleum residuum which comprises subjecting the residuum to coking at an elevated temperature of the order of 800 to 950° F., thereby producing naphtha and heavier hydrocarbon distillate fractions, separating from the products a naphtha fraction boiling below about 450° F., heating and vaporizing said naphtha fraction and subjecting the vapors thereof to the action of a solid, siliceous isomerizing catalyst at a high conversion temperature and at a rate above about 4 volumes of naphtha per volume of catalyst per hour and controlling the temperature and time of contact between said naphtha vapors and said catalyst to produce an increase in knock rating of at least 5 CFR—M and at least 95% gasoline boiling below the maximum boiling point of the naphtha fraction treated with said catalyst.

15. The process of claim 14 wherein said siliceous isomerizing catalyst is a synthetic zeolite.

16. The process of making gasoline of improved knock rating from petroleum residuums which comprises subjecting the residuum to coking at elevated temperature thereby producing naphtha and gas oil and heavier distillate fractions, separating the naphtha from the gas oil and heavier fractions, vaporizing the naphtha and subjecting the vapors at a high conversion temperature and a space velocity of at least 4 volumes of naphtha per hour per volume of catalyst to the action of an isomerizing catalyst under conditions effecting an increase in the knock rating of said naphtha of at least about 5 CFR—M with a yield, once-through, of at least 95% of liquid products based on the weight of naphtha treated and thereafter condensing the isomerized naphtha vapors to produce the desired gasoline.

17. The process of claim 16 wherein the catalyst contains activated silica as an essential ingredient.

18. The process of increasing the knock rating of gasoline obtained from the coking of petroleum residuums wherein are produced naphtha and heavier oils, which comprises separating from the products of said coking operation a naphtha boiling substantially within the gasoline boiling range, vaporizing said naphtha and subjecting the vapors thereof at a temperature of about 800 to 900° F. and a pressure of about atmospheric to 50 pounds per square inch to the action of an activated silica catalyst, with a contact time corresponding to the rate of about 4 to 10 volumes of naphtha per volume of catalyst per hour, controlling the conditions to produce an increase in the knock rating of naphtha treated of at least about 5 CFR—M with a yield of at least 95%, the loss of naphtha by conversion to gas, tar and coke being less than 5%, and thereafter recovering the isomerized naphtha vapors and fractionating them to produce the desired gasoline.

19. The process of claim 16 wherein the catalyst contains active alumina as an essential ingredient.

20. The process of claim 18 wherein the catalyst is an acid activated bentonite clay.

21. The method of improving the octane number of a coke still naphtha which method comprises vaporizing and superheating said coke still naphtha to a temperature within the approximate range of 900 to 950° F. at a pressure within the approximate range of about atmospheric to about 15 pounds per square inch gauge, contacting said vapors at approximately said temperature and pressure with an isoforming catalyst at a rate in the general vicinity of 12 volumes of liquid coke still naphtha charge per hour per volume of catalyst space in the contacting zone and fractionating the products from the contacting step to obtain a fraction of the gasoline boiling range.

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