Nov. 12, 1946. E. W. THIELE ET AL 2,410,908

ISOFORMING

Filed Aug. 3, 1940 3 Sheets-Sheet 1

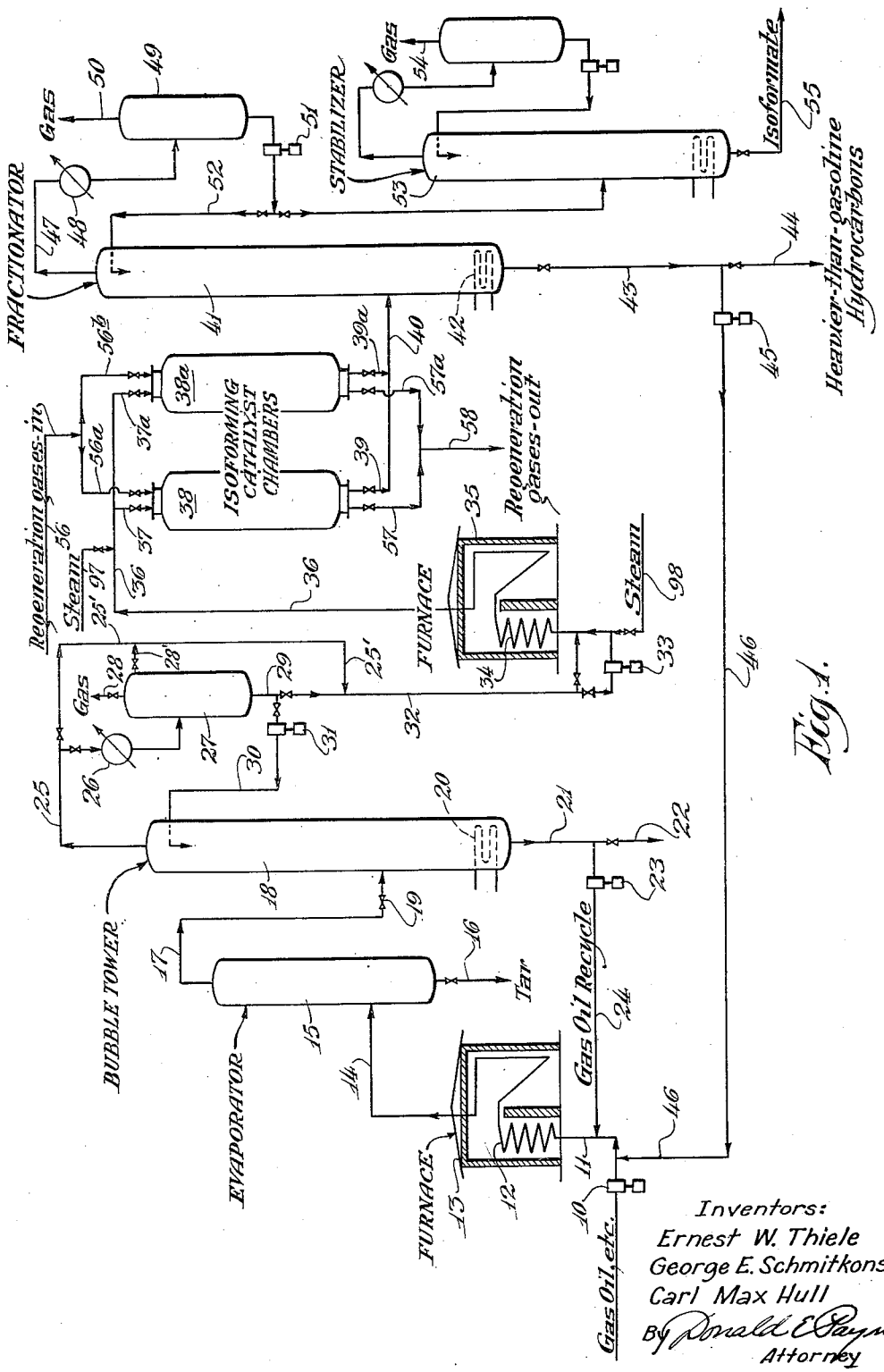


Fig. 1.

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ISOFORMING

Filed Aug. 3, 1940 3 Sheets-Sheet 2

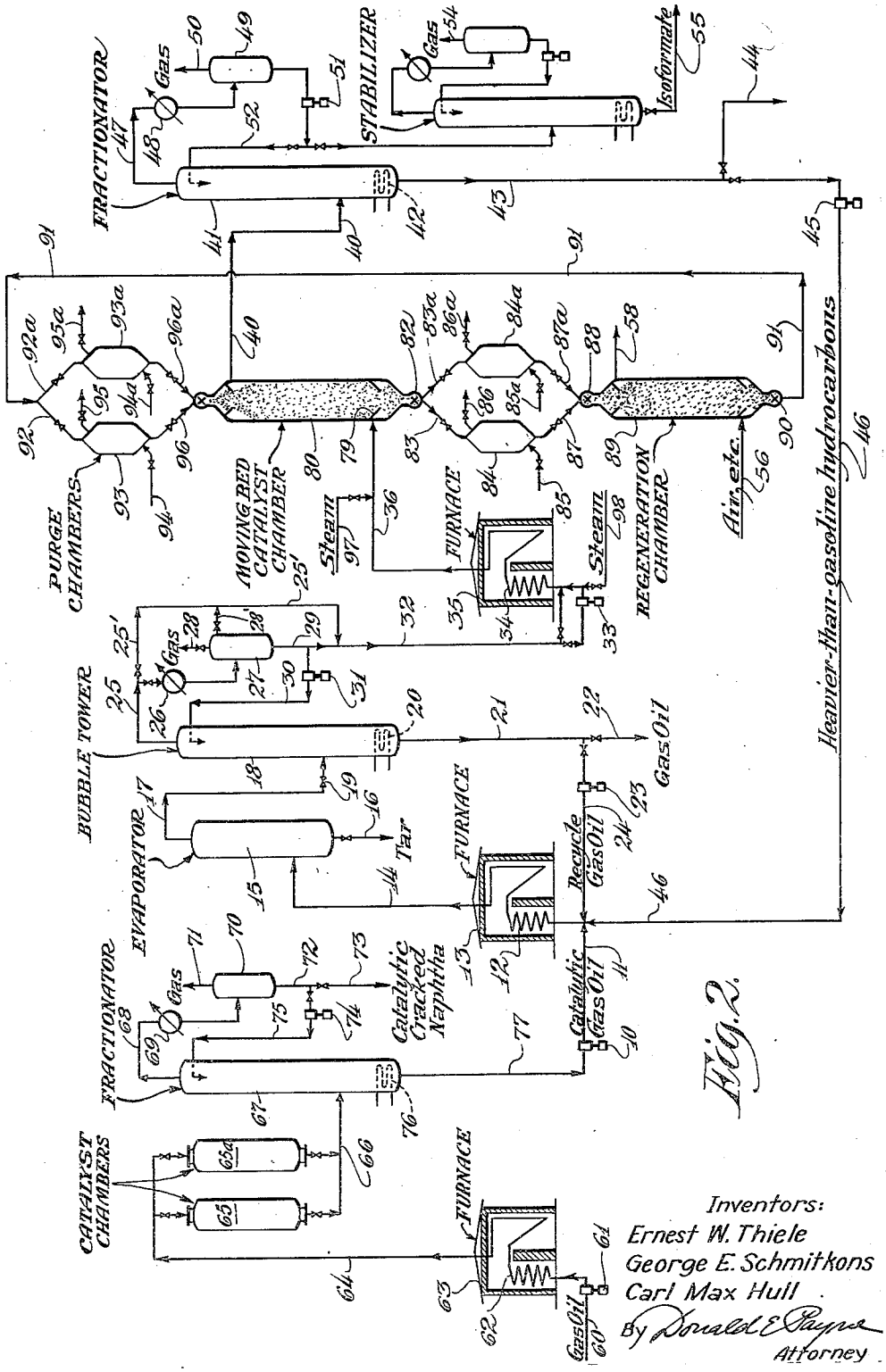


FIG. 2.

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Filed Aug. 3, 1940 3 Sheets-Sheet 3

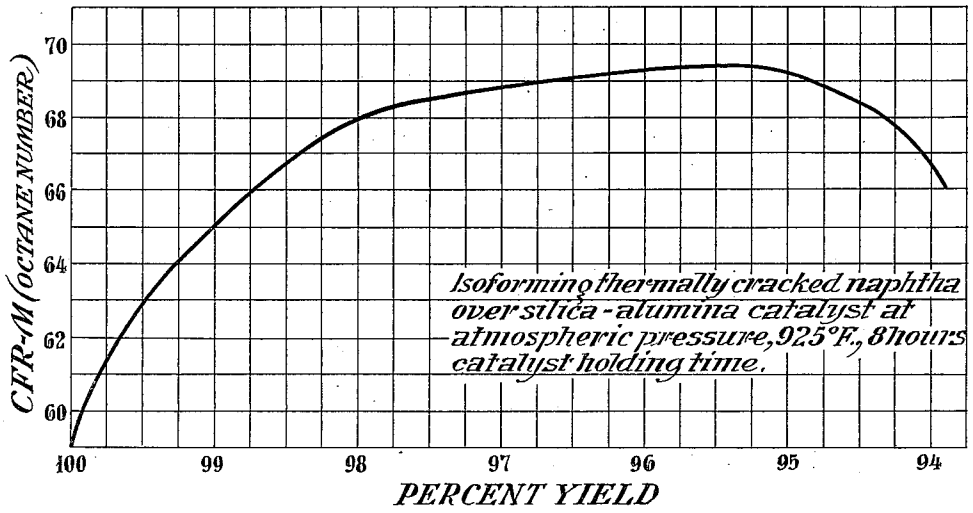


Fig. 3.

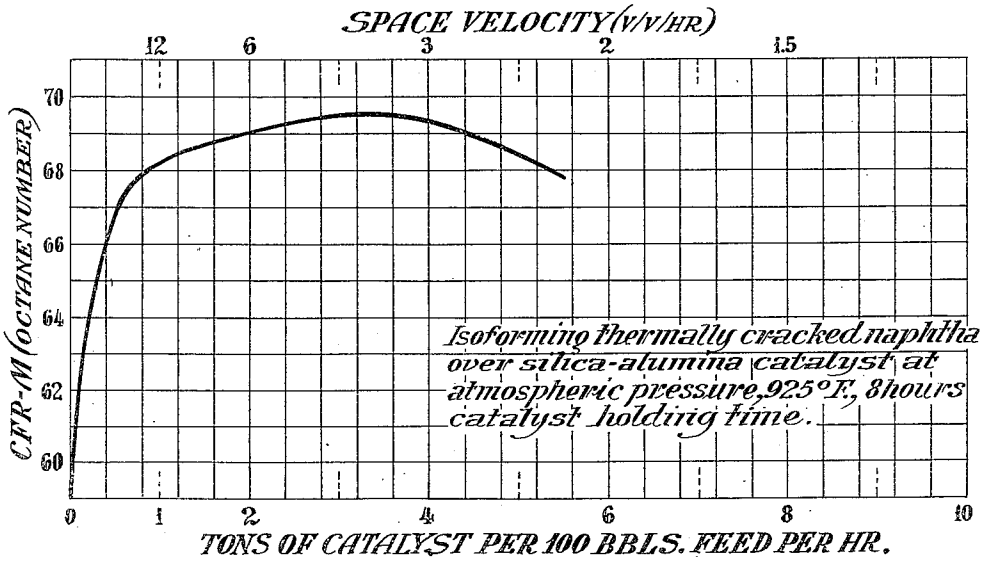


Fig. 4.

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UNITED STATES PATENT OFFICE

2,410,908

ISOFORMING

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Application August 3, 1940, Serial No. 350,270

17 Claims. (Cl. 196—50)

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This invention relates to an improved method of making high antiknock motor fuels from charging stocks consisting essentially of gas oils and heavier hydrocarbons.

Heretofore, most motor fuel has been produced by thermal cracking and most refineries are, therefore, equipped with thermal cracking systems. Demands for higher octane number gasoline have given rise to a new problem because the maximum octane number obtainable by commercial thermal cracking is about 65 to 74 CFR–M. Furthermore, thermally cracked naphtha is not sufficiently responsive to tetraethyl lead to make it commercially feasible to obtain the desired higher octane numbers by this route. Hence refiners have turned to expensive and complicated processes of catalytic cracking, destructive hydrogenation, hydroforming, aromatization, alkylation, isomerization, polymerization, etc. We have discovered that the problem can be solved most advantageously and economically by subjecting thermally cracked naphtha to a simple high temperature contacting with a catalyst to effect what we term "isoforming."

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, 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 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

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heavier-than-gasoline hydrocarbons. Hydrogenation, aromatization and hydroforming have been proposed for increasing the octane number of naphtha but experience has shown that thermally cracked 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. Innumerable complicated and expensive processes have been proposed in an effort to solve this problem and since it appeared to be practically unsolvable, many refiners are electing to change their refining processes, to substitute catalytic cracking, destructive hydrogenation, etc., in order to meet the demands for higher octane number gasoline. Our isoforming process makes it possible to utilize existing thermal cracking 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.

Isoforming has practically no effect on catalytically cracked naphtha. We have discovered, however, that the gas oil from a catalytic cracking process may be thermally cracked to give a thermally cracked naphtha which does respond to the isoforming treatment. Thermal cracking, evidently ruptures the molecules to form a different type of naphtha than is formed by catalytic processes. The initial thermal cracking step is thus an essential element of our combined process. The thermal cracking should preferably be effected at relatively low pressures and high temperatures although pressures of 300 to 750 pounds or even higher pressures may be advantageously used. The thermal cracking may be carried out on a once through or on a recycle basis. Our invention is applicable to all types of thermally cracked naphtha. The expression "thermally cracked naphtha" as used in this specification refers only to naphtha in the gasoline boiling range produced by the thermal cracking of gas oil and other hydrocarbon charging stocks which boil above the gasoline boiling range. The species of the invention hereinafter described will be the isoforming of naphthas from conven-

tional thermal processes, referred to as continuous pressure stills and as "combination" cracking which latter includes a mixture of thermally cracked naphthas from various parts of the combination unit.

The invention will be more clearly understood from the following detailed description and from the accompanying drawings which form a part of this specification and in which

Figure 1 is a diagrammatic flow sheet of our process employing fixed bed isoforming.

Figure 2 is a diagrammatic flow sheet of our process employing moving bed isoforming.

Figure 3 is a chart showing the unusual yield-octane relationships that are characteristic of the isoforming process, and

Figure 4 is a chart showing the unusual relationship between octane number and space velocity in the catalyst chamber.

The charging stock to our system may be a Mid-Continent gas oil although it may comprise a gas oil from any other source and it may include any hydrocarbons heavier than gasoline, i. e., reduced crudes, residual stock, etc. Any conventional thermal cracking process may be employed for preparing the feed stock for isoforming.

In Figure 1, we have diagrammatically illustrated thermal cracking of the continuous pressure still type wherein Mid-Continent gas oil is forced by pump 10 through line 11 to coils 12 of pipe still furnace 13 under a pressure of about 300 pounds per square inch and a temperature of about 925° F. The thermally cracked products are then introduced by transfer line 14 either directly or through a conventional soaking drum (not shown) to evaporator 15 which is provided with a tar-drawn-off line 16 at the bottom. Cracked naphtha and gases are taken overhead through line 17 leading to a bubble tower 18. A pressure reducing valve 19 may be employed in line 17 if it is desired to obtain the fractionation in the bubble tower at lower than reaction pressures. A reboiler 20 at the base of the bubble tower insures the removal of all of the 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 cracking.

The naphthas and lighter hydrocarbons are taken overhead through line 25 through cooler 26 and then introduced into a gas separator or receiver tank 27 from which gases are vented through line 28 and liquid naphtha is withdrawn through line 29. A portion of the naphtha is recycled through line 30 by pump 31 for reflux in top of bubble tower 18. The remainder of the naphtha is introduced through line 32 to the isoforming step of our process. A feature of our invention is the fact that the thermally cracked naphtha does not have to be stabilized before it is introduced to the isoforming system. In fact the total overhead products from tower 18 may be introduced directly to line 32 through line 25' when no part of it is required for reflux in tower 18. Alternatively, cooler 26 may condense only the liquid required for reflux and all of the naphtha and vapors may pass through lines 28' and 25' to line 32 for charging to the isoforming process.

The thermally cracked naphtha for our isoforming process should have an end point of 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. The boiling range of the thermally cracked naphtha may be relatively wide but the greatest improvement is effected on the high boiling portions. The lower limit of this boiling range may be lower than 100° F. and in fact normally gaseous hydrocarbons may be beneficial in reducing the partial pressure of the thermally cracked naphtha undergoing the isoforming treatment. In other words, when normally gaseous hydrocarbons are employed with the naphtha the overall pressures may be superatmospheric while the effective pressure is only atmospheric or even sub-atmospheric.

The thermally cracked naphtha produced as hereinabove described may have an olefin content of about 25–70%, an octane number of about 60 to 70 CFR–M and an A. P. I. gravity of about 50–60. A feature of our process is the octane improvement obtained at this relatively high octane level. In the specific example herein described, this thermally cracked naphtha had the following inspection:

Per cent olefins	44
Initial boiling point	169° F.
10% off	204° F.
50% off	252° F.
90% off	319° F.
End point	381° F.
Octane number	65.3 CFR–M
Reid vapor pressure	1.8 lbs.
A. P. I. gravity	55.2°

This thermally cracked naphtha feed stock 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.

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.

When isoforming is effected at 925° F. and atmospheric pressure with a feed rate of 32 barrels per hour per ton of catalyst (about four volumes per hour per gross volume catalyst) and a cycle time of twelve hours on stream for naphtha conversion between regenerations of the catalyst, said catalyst being a synthetic alumina-silica catalyst, we obtain as an average for the entire twelve hours an isoformate yield of 98.3% (by volume), a coke yield of only .1% and a dry gas yield of 1.9%, the remainder of about 1%

being heavier-than-gasoline materials. The knock rating of the isoformate is 70.5 CFR–M thus showing an octane number increase of 5.2. One cc. of tetraethyl lead will increase this octane number by about 6.5 and 3 cc. of tetraethyl lead will increase its octane number to about 81 or 82. The Reid vapor pressure of our isoformate in this example was 4.1 pounds and the boiling range of the isoformate was:

	° F.
Initial boiling point	90
10% off	176
50% off	245
90% off	334
End point	400

A similar thermally cracked naphtha of 0.5 unit lower octane number (64.8 CFR–M) was treated with a somewhat more active catalyst of the same type at 950° F. and 2 atmospheres pressure with a feed rate of 100 barrels per hour per ton of catalyst (about 12 volumes per hour per gross volume of catalyst) and cycle times of 24 and 66 hours on stream for naphtha conversion with the following results (average for the entire period of time on stream):

	Cycle time	
	24	66
Octane No. of isoformate, CFR–M	69.8	68.8
Octane No. improvement	5.0	4.0
Coke, wt. percent of naphtha feed	0.06	0.04
Gas, wt. percent of naphtha feed	2.2	1.3
Heavier-than-gasoline, naphtha feed, percent	About 2	About 1
Isoformate, vol. percent of naphtha feed, percent.	About 97	About 99

Isoforming is not primarily a cracking reaction as evidenced by the 97 to 99% volume percent of liquid gasoline yield. The remarkably high yield for the octane number improvement obtained and the increased susceptibility to tetraethyl lead place this process in a class by itself as far as isomerization is concerned since such results can only be obtained by the isomerization of a thermally cracked naphtha as hereinabove described and under operating conditions and with catalysts which will now be described in further detail.

The catalysts 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. 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 Figure 1 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 isoforming reaction may be effected at pressures ranging from atmospheric to 200 pounds or more per square inch but in our preferred embodiment it is effected at relatively low pressures, i. e., about atmospheric to about 50 pounds per square inch.

The space velocity through the catalyst chamber is a function of pressure. In this respect, isoforming appears to be radically different from catalytic processes such as catalytic isomerization of straight run naphtha, catalytic cracking, catalytic aromatization, catalytic hydroforming, etc.

The space velocity to be used in our isoforming process when operating with a fixed bed of catalyst depends on the following factors:

1. Naphtha to be treated.
2. Activity of catalyst (lower space velocity with lower activity).
3. Temperature (higher space velocity at higher temperatures).
4. Cycle time (higher space velocity at shorter cycle time).
5. Pressure (higher space velocity at higher pressures).

We have found that the octane number improvement of naphthas goes through a maximum at a definite space velocity when space velocity is varied with all other conditions remaining constant although the yield of gasoline isoformate steadily decreases with decreased space velocity. Under atmospheric pressure with ordinary catalysts, 8 hour holding times and temperatures of about 925° F. the space velocity may range from about 4 to 40, preferably about 8 to 20 volumes of liquid feed per volume of catalyst space per hour. With more active catalysts the optimum space velocity may be as high as 20 to 40. An important feature of our invention is the use of space velocities much higher than have been successfully used for other catalytic processes such as catalytic isomerization of straight run naphthas, catalytic cracking, aromatization, hydroforming, etc.

The optimum space velocity is markedly increased with increased pressure and at 125 pounds may be four or five times the values above stated. Higher temperature also permits the use of higher space velocities. The space velocity-octane number relationship is radically different from that obtained in thermal reforming or dehydro-aromatization processes in that there is an actual decrease in octane number improvement when space velocities are lower than the optimum as well as when they are higher than the optimum, as is shown in Figure 4.

The temperatures employed in the isoforming steps may range from about 850 to 1100° F. and beneficial results may be obtained at even lower temperatures. In the preferred example hereinabove set forth, the temperature was 925° F. and we have found that temperatures of about this order of magnitude, i. e., about 900 to 1025° F. or even higher offer extremely important and wholly unexpected advantages in the amount of charging stock which can be treated by a given amount of catalyst between regenerations. In previous catalytic processes, catalyst life was prolonged by the use of relatively low temperatures but in the isoforming process using a synthetic zeolite catalyst and a treating rate of 33 barrels per ton per hour the catalyst treated about ten to fifteen times as much feed stock between regeneration of the catalyst without loss of yield or octane number in the finished product when operating at 925° F. as could be treated at 850° F. The distribution of by-products is not the same for 50 barrels per ton at 850° F. as for 720 barrels per ton at 925° F. but since the amount of by-products is so extremely small in the isoforming process this matter is not of great importance. The important fact is that about ten to fifteen times as many regenerations would have to be performed for a process at 850° F. as for a process at 925° F. when operated at the same space velocity. Only about one-sixth as much coke would have to be burned off per regeneration at the lower temperature but about 2.6 times the total coke would have to be burned per barrel of feed. Our invention contemplates the use of a relatively wide temperature range but the extremely important and unexpected advantages of the high temperature isoforming, i. e. temperatures of about 925 to 1025° F., makes this feature one of particular importance.

The yield-octane relationship in the isoforming process as shown in Figure 3 is another striking feature of the process. The maximum octane number is obtained when the yield is about 94 to 99%, usually about 96 to 97%.

Another feature of the isoforming process is the high road octane number as distinguished from the motor octane number of the finished isoformate particularly when a small amount of lead tetraethyl has been added thereto. The product produced as hereinabove described had a higher road octane number than CFR–M octane number. With 3 cc. of lead added to the isoformate the road octane number was 4.3 units higher than the CFR–M octane number. Since it is the road octane number which is of practical importance to motorists, and since tetraethyl lead is now added to most motor gasoline, the advantages of the isoforming process are even greater than would be indicated by the improvement in the CFR–M octane number. Other features of the isoforming process are that the isoformate is relatively stable against gum formation and requires little or no further refining to produce finished motor fuel. The surprisingly small amount of gases and heavier-than-gasoline components which have to be removed from the isoformate makes the final stabilization process relatively simple.

In Figure 2 we have illustrated the application of our invention to a "catalytic gas oil," i. e., a gas oil resulting from catalytic cracking, and we have illustrated the use of moving bed catalytic isoforming instead of fixed bed isoforming. Virgin gas oil is introduced into the system through line **60** and forced through pump **61**, coil **62** of pipe still furnace **63**, thence through transfer line **64** to one of the catalytic cracking chambers **65**. The catalytic cracking may be effected in any one type of process and the regeneration may be accomplished in any conventional manner. Fixed bed cracking chamber **65** is shown for illustrative purposes and may be replaced by moving bed catalyst chambers or powdered catalyst systems, etc.

Catalytically cracked products are withdrawn from chamber **65** or **65***a* through line **66** to fractionator **67**. Catalytically cracked naphtha and lighter hydrocarbons are taken overhead through line **68**, cooled in cooler **69** and introduced into separator or reflux drum **70** from which uncondensed gases are vented through line **71**. Catalytically cracked naphtha is withdrawn from receiver **70** through line **72** and may be passed by line **73** to a stabilizer such as stabilizer **53**. A part of the liquid product is returned by pump **74** through line **75** to serve as reflux in fractionator **67**.

A reboiler **76** at the base of fractionator **67** insures the removal of cracked gasoline from the catalytic gas oil which is withdrawn through line **77** and introduced by pump **10** and line **11** into coils **12** of the thermal furnace. The thermal cracking of this catalytic gas oil may be accomplished in the same manner as the thermal cracking described in connection with Figure 1.

Passing on to the isoforming step, the superheated thermally cracked naphtha is introduced through transfer line **36** under baffle plate **79** at the lower part of chamber **80** which contains a moving catalyst bed of granular or pelleted catalyst material. The temperatures and pressures in the moving bed catalyst chamber **80** are substantially the same as those for the fixed bed catalyst process and, therefore, will not be described in further detail. In moving bed operation a higher octane number product can be produced than can be obtained in fixed bed operation by any combination of space velocities and time between regenerations and less catalyst need

be regenerated for a given amount of naphtha treated in moving bed operation than in fixed bed operation. The isoformed products leave the top of chamber 80 through line 40 and are stabilized as hereinabove described in connection with Figure 1.

Spent catalyst from the base of chamber 80 is discharged through a vapor sealed discharge mechanism 82 either through line 83 to purging chamber 84 or through line 83a to purging chamber 84a, one of these chambers being filled while the other is being emptied. Purge gases may be introduced through line 85 and withdrawn through line 86. The catalyst which has been freed from oil by purging is then introduced through line 87 and vapor tight transfer means 88 into regeneration chamber 89. It should be understood, however, that any conventional regeneration means may be employed in place of the continuous regeneration system illustrated by Figure 2, wherein oxygen-containing gas is introduced through line 56 and hot regeneration gases are withdrawn through line 58.

Regenerated catalyst is withdrawn through vapor tight discharge mechanism 90 through line 91 and introduced either through line 92 to purge tank 93 or through line 92a to purge tank 93a. Oxygen-containing gases are purged by means of steam or flue gas introduced through line 94 and withdrawn through line 95. Purged catalyst may then be re-introduced through line 96 to chamber 80 for reuse.

While countercurrent flow between vapors and catalysts is illustrated in Figure 2, it should be understood that we may use concurrent flow and, in fact, concurrent flow is desirable with the large space velocities which are permissible in our process.

Maximum octane improvement in the isoforming step is obtained when the thermal cracking is on a once through basis. We prefer, therefore, to thermally crack the gas oil or heavier charging stock under such conditions as to obtain high once through yields and to withdraw the heavier-than-gasoline components of the thermally cracked products through line 22 to some other conversion system or to storage rather than to recycle through line 24.

Steam may be employed in amounts of from 1 to 15% or more by weight. If sufficiently superheated, this steam may be introduced directly into the transfer line 36 through line 97. Alternatively it may be introduced through line 98 into the charge entering the pipe still. The steam apparently promotes high catalyst activity.

While we have described in detail a preferred embodiment of our invention, it should be understood that the invention is equally applicable to other thermally cracked naphthas or mixtures thereof and that the invention is applicable to a fairly wide range of operating conditions and procedural steps. The isoforming step of our invention is applicable only, however, to thermally cracked naphthas, preferably having an end point of 400 to 450° F. and it is not applicable to catalytically cracked naphtha nor to virgin naphtha. The thermal cracking step is preferably at high temperature and low pressure because thermally cracked naphtha so formed gives a much greater octane number improvement on isoforming than does a naphtha produced by thermal cracking at high pressure and high temperature or at low pressure and low temperature.

We claim:

1. A method of producing high octane number motor fuel from charging stock of the class consisting essentially of gas oil and heavier hydrocarbons which comprises thermally and non-catalytically cracking said charging stock to produce a thermally cracked naphtha having an end point below about 450° F. together with lighter and heavier products, removing the heavier products from the thermally cracked naphtha, heating the thermally cracked naphtha to a temperature of about 850° F. to 1100° F., contacting the heated thermally cracked naphtha with an isoforming catalyst at such space velocity within the approximate range of 4 to 40 volumes of naphtha (liquid basis) per volume of catalyst space per hour that a volume percent liquid yield within the approximate range of 94 to 99 and an octane number improvement of at least about 5 A. S. T. M. octane number units are obtained.

2. The process of claim 1 wherein the thermal cracking step is effected at a pressure of 50 to 750 pounds per square inch and wherein the catalyst contacting step is effected at a pressure of about atmospheric to about 50 pounds per square inch.

3. The method of claim 1 wherein the catalyst contacting temperature is at least about 925° F.

4. The method of producing high octane number motor fuel from charging stocks consisting substantially of gas oil and heavier hydrocarbons which comprises thermally and non-catalytically cracking said charging stocks to produce a thermally cracked naphtha having an end point below about 450° F. together with lighter and heavier products, separating the thermally cracked naphtha from the heavier products, superheating said separated naphtha to a temperature of about 925° F., contacting said superheated naphtha with an isoforming catalyst and employing such space velocity in said contacting step within the approximate range of 4 to 40 volumes of liquid feed per volume of catalyst space per hour at a pressure of about atmospheric to 50 pounds per square inch that a volume percent liquid yield within the approximate range of 94 to 99 and an octane number improvement of about 5 to 15 A. S. T. M. octane number units are obtained.

5. The method of claim 4 wherein the catalyst consists essentially of silica and alumina with the alumina forming the minor component.

6. The method of obtaining high octane number motor fuels from charging stocks consisting essentially of gas oils and heavier hydrocarbons which comprises catalytically cracking feed gas oils to form catalytically cracked gas oil, catalytically cracked gasoline and lighter hydrocarbons, separating said catalytically cracked gas oil from said catalytically cracked gasoline, thermally and non-catalytically cracking said catalytically cracked gas oil to produce thermally cracked naphtha having an end point below about 450° F., together with lighter and heavier products, separating the thermally cracked naphtha from said heavier products, heating said separated thermally cracked naphtha to a temperature of about 850° F. to 1025° F., and contacting said heated naphtha with a catalyst comprising silica and an oxide of aluminum, under a pressure of from about atmospheric to about 50 pounds per square inch and at such space velocity within the approximate range of 4 to 40 volumes of liquid thermally cracked naphtha feed per hour per volume of catalyst space that a volume percent liquid yield within the approx-

imate range of 94 to 99 and an octane number improvement of about 5 to 15 A. S. T. M. octane number units are obtained.

7. The method of claim 6 wherein the thermally cracked naphtha is heated to a temperature of at least 925° F. prior to contacting it with catalyst.

8. The method of converting thermally and non-catalytically cracked naphtha into a motor fuel of higher octane number without suffering as much as 5% losses due to the formation of gas, coke and heavier-than-gasoline components which method comprises fractionating thermally cracked products to obtain a thermally cracked naphtha fraction having an end point below about 450° F., heating said thermally cracked naphtha to a temperature of about 850° F. to 1025° F. and contacting said heated naphtha with a synthetic catalyst of the silica-alumina type at such space velocity within the approximate range of 4 to 40 volumes of liquid feed per volume of catalyst space per hour that a volume percent liquid yield within the approximate range of 94 to 99 and an octane number improvement of at least about 5 A. S. T. M. octane number units are obtained.

9. The method of claim 1 wherein the thermal cracking is on a once through basis at high temperature and low pressure.

10. The method of claim 4 wherein the thermal cracking is on a once through basis at high temperature and low pressure.

11. The method of claim 1 wherein from 1 to 15% by weight of steam is admixed with the thermally cracked naphtha vapors in the catalyst contacting step.

12. The method of claim 4 wherein about 1 to 15% by weight of steam is admixed with the thermally cracked naphtha in the catalyst contacting step.

13. The method of producing high octane number motor fuel from charging stocks consisting substantially of gas oil and heavier hydrocarbons which method comprises thermally and non-catalytically cracking said charging stocks to produce a thermally cracked naphtha, heating said thermally cracked naphtha to a temperature of about 925° F. for effecting vaporization and superheating of said naphtha, contacting said superheated naphtha with a catalyst of which the major constituent is silica and the minor constituent is alumina, effecting the contacting step under a pressure of from atmospheric to 50 pounds per square inch with a space velocity of about 8 to 20 volumes of liquid feed per volume of catalyst space per hour and with a catalyst holding time between regenerations of about 8 to 24 hours, removing heavier-than-gasoline components from the products leaving the contacting step and stabilizing the products leaving said last-named separation step.

14. The method of increasing the octane number of a thermally and non-catalytically cracked naphtha having an end point of about 400 to about 450° F. which method comprises vaporizing and heating said thermally cracked naphtha to a temperature within the general vicinity of 925° F. and contacting said naphtha vapors with an isoforming catalyst at a pressure of about atmospheric to about 50 pounds per square inch

with a space velocity within the approximate range of 8 to 20 volumes of liquid feed per volume of catalyst space per hour and with a catalyst holding time between regenerations of about 8 to 24 hours, and fractionating the resulting products to obtain a high octane number motor fuel and a small amount of gases and heavier-than-gasoline components.

15. A process for the production of high octane number motor fuel from hydrocarbon charging stocks which boil above the gasoline boiling range which process comprises thermally and non-catalytically cracking said charging stocks to produce a thermally cracked naphtha of the gasoline boiling range together with lower boiling and higher boiling products, separating the cracked naphtha from the higher boiling products, heating said cracked naphtha to a temperature within the approximate range of 850° F. to 1100° F., contacting said heated cracked naphtha at a temperature within said range of 850 to 1100° F. with a catalyst comprising silica and alumina at a pressure within the approximate range of atmospheric to 50 pounds per square inch and at such space velocity within the approximate range of 5 to 40 volumes of liquid cracked naphtha per hour per volume of catalyst space that a volume percent liquid yield of at least 95% is obtained.

16. The method of converting a thermally and non-catalytically cracked naphtha of the gasoline boiling range into a motor fuel of high octane number without suffering as much as 5% losses due to the formation of gas, coke and heavier-than-gasoline components which method comprises fractionating thermally cracked products to obtain a thermally cracked naphtha, of the gasoline boiling range, heating said thermally cracked naphtha to a temperature within the approximate range of 850 to 1100° F. and contacting said heated naphtha at a temperature within said range of 850 to 1100° F. with a catalyst comprising silica and alumina at a pressure within the approximate range of atmospheric to 50 pounds per square inch and at a space velocity within the approximate range of 5 to 40 volumes of liquid thermally cracked naphtha feed per hour per volume of catalyst space.

17. The method of converting a thermally and non-catalytically cracked naphtha of the gasoline boiling range into a motor fuel of high octane number without suffering as much as 5% losses due to the formation of gas, coke and heavier-than-gasoline components which method comprises fractionating thermally cracked products to obtain a thermally cracked naphtha of the gasoline boiling range, heating said thermally cracked naphtha to a temperature in the approximate range of 900 to 950° F. and contacting said heated naphtha at a temperature in the approximate range of 900 to 950° F. with a catalyst comprising silica and alumina at a pressure within the approximate range of atmospheric to 50 pounds per square inch and at a space velocity within the approximate range of 5 to 40 volumes of liquid thermally cracked naphtha feed per hour per volume of catalyst space.

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