

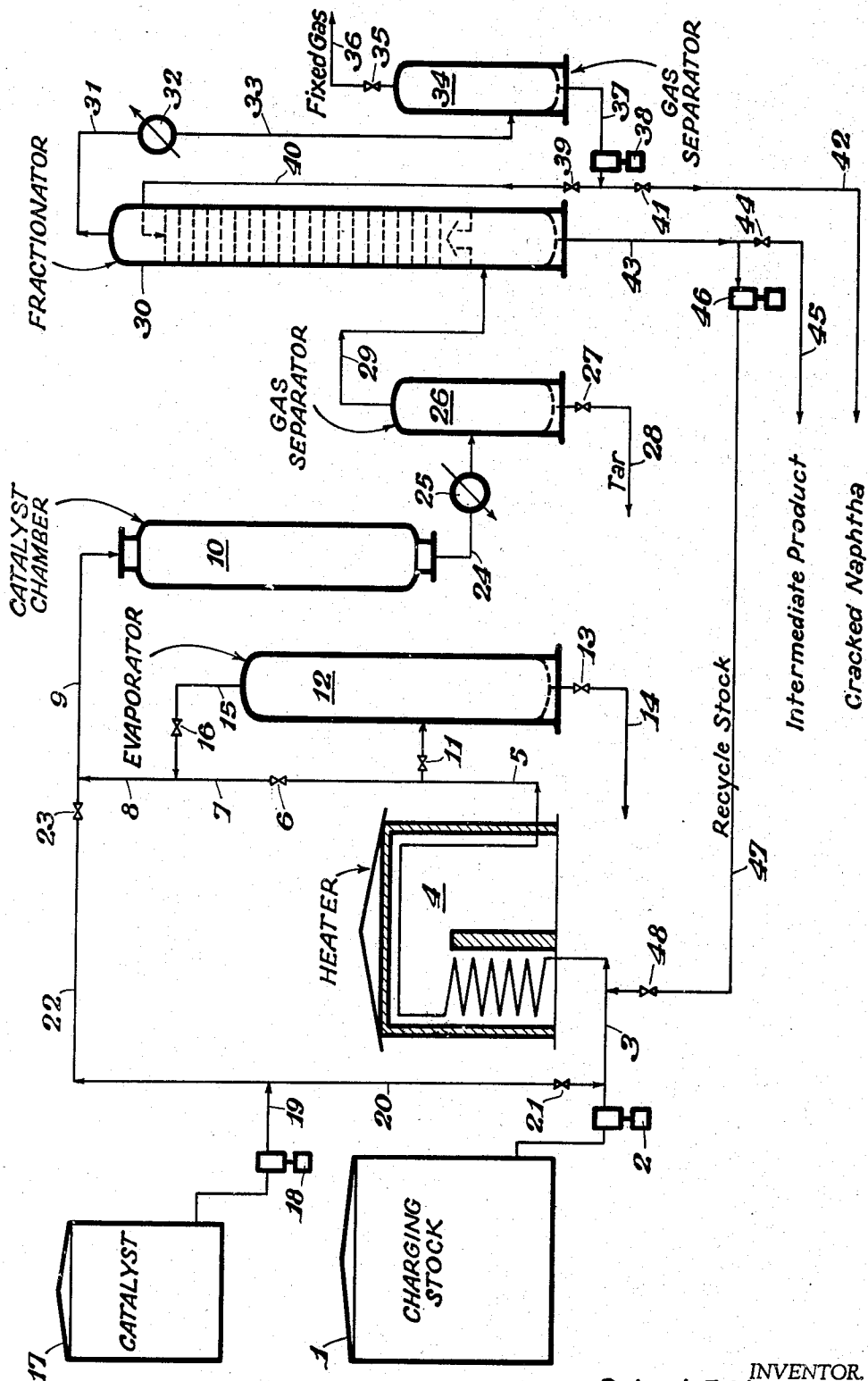
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PROCESS OF PRODUCING HIGH ANTIKNOCK MOTOR FUELS

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PROCESS OF PRODUCING HIGH ANTI-KNOCK MOTOR FUELS

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This invention relates to the production of high antiknock motor fuels from heavier hydrocarbons. More particularly it relates to a catalytic vapor-phase cracking process for the manufacture of high antiknock motor fuels in which a heterogeneous and a homogeneous catalyst are used in combination.

Many catalysts have heretofore been proposed for the cracking of heavy hydrocarbon oils into light hydrocarbon fractions suitable for use as motor fuels. These catalysts may be divided into two classes: heterogeneous catalysts, i. e. those which are not in the same phase as the hydrocarbons being treated, usually the solid phase, and homogeneous catalysts, i. e. those which are in the same phase as the hydrocarbons being treated.

In the patent literature, and particularly in certain foreign patents, it has been suggested that hydrocarbons might be cracked in the liquid phase in the presence of both heterogeneous and homogeneous catalysts, but it does not appear that any of these suggestions have led to the development of successful processes. In the characteristic manner of certain foreign disclosures it has been suggested that oil may be cracked at high pressures and at any temperature throughout a wide range in the presence of elements of Group II to Group VII of the periodic system or their compounds. Coupled with such vague and all-inclusive definitions of suitable heterogeneous catalysts, are equally vague definitions of homogeneous catalysts. These foreign patents suggest indiscriminately the use of any and all halogens or halogen compounds, both organic and inorganic acids such as sulfuric, nitric or organic acids, etc., and as specific examples they suggest the use of hydrochloric acid and organic chlorides.

I have found that by passing heavy hydrocarbons to be cracked, together with a small amount of certain homogeneous cracking catalysts, under controlled conditions in contact with a heterogeneous cracking catalyst contained in a reaction chamber, I obtain a product in an amount only slightly less than would be obtained if the catalytic effect of each catalyst were additive, which product has a higher antiknock value than may be obtained by using either catalyst alone. The homogeneous catalysts which I have found to be effective in my process are bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides. Chlorine and its compounds, which are stated to be equivalent or even superior to bromine, iodine and their com-

pounds in the processes described in the above-mentioned foreign patents, are quite ineffective in my process.

The outstanding problem which now confronts gasoline manufacturers is that of obtaining high antiknock motor fuels without the necessity of adding tetraethyl lead, which is both expensive and toxic, thus requiring extremely careful handling. In order to raise the octane number of a gasoline by 5 or 10 points, large amounts of tetraethyl lead are required, and it is impossible to obtain motor fuels having a sufficiently high octane number by ordinary cracking processes.

It is an object of my invention to provide a process for the production of high antiknock motor fuels in good yields from heavy hydrocarbons, thereby eliminating or greatly reducing the amount of tetraethyl lead required in the finished motor fuel. Another object is to provide an efficient process for cracking heavy hydrocarbon oils to light hydrocarbon oils suitable for use as motor fuels in the presence of heterogeneous and homogeneous catalysts simultaneously. Still another object is to provide a process for maintaining a substantially constant yield of light hydrocarbon products from a catalytic cracking system as the activity of the catalyst decreases. Further objects will become apparent from the following detailed description and the drawing, which represents diagrammatically one form of apparatus suitable for practicing my invention.

In accordance with my invention, a heavy hydrocarbon fraction together with a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides is passed in the vapor phase through a catalyst chamber containing a heterogeneous cracking catalyst under such conditions that the yield of products boiling in the gasoline range in the absence of any catalysts would be approximately in the range 1-10%, and preferably 2-5%.

Although any vaporizable hydrocarbon oil less volatile than gasoline may be used as charging stock for my process, I prefer to use a clean distilled petroleum fraction such as gas oil or kerosene. As homogeneous cracking catalysts I may use bromine, hydrogen bromide, and organic bromides such as methyl, ethyl, propyl, isopropyl, normal, secondary and tertiary butyl and higher alkyl bromides, ethylene, propylene and homologous dibromides, bromoform, phenyl bromide, etc., and the corresponding iodine compounds. The bromine compounds are preferred, however, because they are relatively inexpensive. It is also

preferable to add the homogeneous catalyst to the stream of charging stock in the form of an oil solution containing 10-25% by weight of the catalyst, so that a relatively non-corrosive bromide, such as butyl bromide, is preferred to bromine, which is difficult to handle and reacts with the solvent oil.

The amount of my homogeneous cracking catalysts which may be used depends upon the particular catalyst involved. I have found that approximately equivalent effects are obtained with different homogeneous catalysts when about the same concentrations of halogen atoms are present, and believe that this is due to the formation of the corresponding hydrogen halides from these catalysts under the reaction conditions. If an organic halide is employed, it is desirable to use not more than will substantially completely decompose during the process to the hydrogen halides. Generally the homogeneous catalyst supplied to my process may contain from about 0.02 to about 0.3 gram-atoms of halogen per kilogram of oil treated, but preferably about 0.05 to 0.2 gram-atoms of halogen per kilogram are used, and usually about 0.1 gram-atoms per kilogram represents the optimum concentration.

As heterogeneous cracking catalysts, I may use any material which markedly increases the gasoline yield under mild cracking conditions without excessive deposition of carbonaceous matter thereon. Materials of the clay type, including natural clays such as Attapulgius clay or Death Valley clay, and artificial clays such as aluminum silicates and hydrosilicates are suitable for use in my process. Other heterogeneous cracking catalysts which may be used include activated alumina, and oxides of metals such as chromium and titanium and especially oxides of aluminum and boron mounted on silica. These catalysts have, of course, various degrees of activity, and for use in connection with my invention the more active catalysts are preferred.

One type of synthetic clay which I have found to be very active is an aluminum silicate prepared by precipitating a soluble silicate with a soluble aluminum salt, the mol ratio of silicon compound used to the aluminum compound used ranging from 2:1 to 4:1 and preferably ranging from 2.5:1 to 3.5:1. These catalysts may be made by warming a solution of sodium silicate to 125° F., adding a water solution containing the proper quantity of aluminum nitrate, filtering the resulting precipitate, washing it thoroughly, and drying the washed material at about 210° F. Of the various oxides mounted on silica which may be used, I have found that aluminum oxide hydrolytically adsorbed on silica is extremely active. This catalyst may be prepared by adding hydrochloric acid in slight excess to sodium silicate solution, washing the resulting precipitate free from chlorides, digesting the precipitate with a solution of aluminum sulfate for about two hours at about 210° F., washing the precipitate free from sulfates and drying at 210° F. By using water-soluble compounds of other elements in a similar way, catalysts of the same type containing the oxides of those elements may be obtained.

The reaction conditions chosen are such that only a small amount of purely thermal cracking occurs, and consequently they may be varied considerably depending upon the character of the charging stock. In general the temperature may range from about 800° F. to about 1100° F., but when the charge is virgin gas oil or a sim-

ilar stock, the temperature should not exceed about 1000° F., and preferably lies in the range 850° F. to 950° F. The space velocity, which is defined as the number of volumes of feed measured as liquid charged per total volume occupied by the catalyst per hour, may range from about 0.5 to about 3.0, and preferably ranges from 1.0 to 2.0. The pressure is preferably substantially atmospheric, although subatmospheric and somewhat raised pressures may also be used, but the pressure must always be sufficiently low to allow the substantially complete vaporization of the material being treated at the reaction temperature.

I have found that the activity of the heterogeneous catalyst gradually diminishes during use with a resulting diminution in gasoline yield, and that this yield may be maintained for a longer period of time than would otherwise be possible by gradually increasing the proportion of homogeneous catalyst added. Eventually of course, the heterogeneous catalyst becomes so inactive that it must be regenerated or replaced. I am also able to compensate for variations in the ease with which the materials passing through my process decompose by increasing the proportion of homogeneous catalyst added when the proportion of more refractory stock, e. g. recycle stock, increases.

Referring now to the drawing, fresh charging stock, preferably gas oil, is withdrawn from tank 1 by means of pump 2 and passed through line 3 to heater 4, in which it is raised to the desired reaction temperature. The heated oil is then passed through line 5, valve 6, and lines 7, 8 and 9, directly into the top of catalyst chamber 10. If the charging stock is not one which would be substantially completely vaporized under the chosen reaction conditions, valve 6 is closed and valve 11 is opened so that the heated charge is introduced into evaporator 12, in which the vapors are separated from the heavy residual material. This residual material is withdrawn from the system through valve 13 and line 14. The vapors are sent to the top of catalyst chamber 10 through line 15, valve 16 and lines 8 and 9. The homogeneous catalyst, which is a member of the class hereinabove defined and which is preferably dissolved in oil, is simultaneously withdrawn from tank 17 by means of pump 18 and introduced in the proper proportion into the stream of oil being treated. The homogeneous catalyst may be added either before heating by means of lines 19 and 20 through valve 21, or to the vaporized material just prior to its introduction into catalyst chamber 10 by means of lines 19 and 22 through valve 23. I prefer to use the latter method, especially when the nature of the charging stock makes it necessary to use evaporator 12.

The vaporized mixture of oil and homogeneous catalyst passes down catalyst chamber 10 in intimate contact with the heterogeneous catalyst contained therein under conditions which have been fully described above, and the oil is thereby cracked to produce a high yield of a gasoline fraction having a high antiknock value. The entire stream including the products is withdrawn from the bottom of catalyst chamber 10 through line 24, and passed through cooler 25 into separator 26, in which the small amount of heavy tarry material formed during the reaction is allowed to collect. This heavy material is removed from the bottom of separator 26 by means of valve 27 and line 28. The vapors

are then introduced by means of line 29 into fractionating tower 30, which is operated under conditions well-known in the art to give an overhead fraction containing substantially no material heavier than gasoline and a bottom product consisting of material boiling above the gasoline range. The vapors from fractionating tower 30 are withdrawn through line 31 and passed through condenser 32 and line 33 to gas separator 34, from which the uncondensed gases are withdrawn through valve 35 and line 36. The

the results which may be obtained by my process. In all of these runs a Mid-Continent gas oil having an A. P. I. gravity of 35° was cracked once-through in the vapor phase at atmospheric pressure.

The pertinent data on runs made under similar conditions in the absence of a catalyst, and using alumina hydrolytically adsorbed on silica, n-butyl bromide alone, and alumina on silica plus n-butyl bromide, respectively, are summarized in the following table:

	1	2	3	4
Heterogeneous catalyst.....	None	Al ₂ O ₃ on SiO ₂	None	Al ₂ O ₃ on SiO ₂
Homogeneous catalyst.....	do	None	C ₄ H ₉ Br	C ₄ H ₉ Br
Percent by weight.....			1.50	1.50
Gram-atoms of halogen/kilogram.....			0.11	0.11
Temperature, °F.....	925	925	925	925
Space velocity.....	1.15	1.15	1.10	1.11
Gasoline yield, percent by volume.....	4.0	18.7	16.6	28.0
Octane number.....	89.2	80.0	70.0	89.5

condensed gasoline fraction in the bottom of separator 34 is withdrawn through line 37 by means of pump 38 and divided into two streams, one of which passes through valve 39 and line 40 into the top of fractionating tower 30 to act as reflux therein, and the other of which is withdrawn from the system through valve 41 and line 42 for the usual finishing treatment or to storage.

The liquid fraction in tower 30 is withdrawn through line 43 and may be removed from the system through valve 44 and line 45 to storage or for further treatment, e. g., in another unit embodying my invention, or a thermal cracking unit of the conventional type. I prefer, however, to recycle this material by means of pump 46 through line 47 and valve 48 into line 3 in which it is mixed with fresh charging stock. In this way the ultimate gasoline yield is substantially increased.

Since the recycle stock passing through line 47 has been subjected to the catalytic treatment, and therefore contains a greater proportion of the more refractory hydrocarbons, it gives somewhat lower yields than fresh charging stock. In order to avoid fluctuations in the operation of my process, I prefer to vary the amount of homogeneous catalyst introduced into the system to compensate for variations in the amount and the refractoriness of the cycle stock, more of the homogeneous catalysts being used as the amount and refractoriness increase. This method may be used simultaneously with the method hereinabove described for compensating for the diminution in activity of the heterogeneous cracking catalyst by gradually increasing the amount of homogeneous cracking catalyst used, thereby avoiding fluctuations in gasoline yield.

It will be quite apparent to one skilled in the art that other types of apparatus may be used in practicing my invention, and that many features not shown or described herein would normally be included in a refinery unit, such as heat exchangers, control equipment, catalyst regenerating equipment, etc. Also a plurality of catalyst chambers would be provided so that the process could continue uninterruptedly when the heterogeneous catalyst in a particular chamber had become inactive.

The following examples show the nature of

From these data it is apparent that the addition of the butyl bromide gave an increased gasoline yield of 9.3%, and that the octane number of the product obtained by the process of my invention is much higher than that of products made using either catalyst alone. By adding the yields obtained in runs 2 and 3 and subtracting 4.0 to avoid duplication of the thermal cracking effect, it is seen that the yield in run 4 lacks only about 3.3% of being additive. In the case of simpler gas oils such as those of Pennsylvania and Michigan which contain a smaller proportion of refractory hydrocarbons, the combined effects would be more nearly additive.

Runs 5 to 8 inclusive, summarized below, were made using an activated alumina known as "Alorco activated alumina" alone and together with n-butyl bromide and with ethylene dichloride:

	5	6	7	8
Heterogeneous catalyst.....	Activated Al ₂ O ₃	Activated Al ₂ O ₃	None	Activated Al ₂ O ₃
Homogeneous catalyst.....	None	C ₄ H ₉ Br	C ₂ H ₄ Cl ₂	C ₂ H ₄ Cl ₂
Percent by weight.....		1.50	0.542	0.542
Gram-atoms of halogen/kilogram.....		0.11	0.11	0.11
Temperature, °F.....	925	925	925	925
Space velocity.....	1.21	1.19	1.29	1.21
Gasoline yield, percent by volume.....	14.9	23.9	3.3	15.6
Octane number.....	78.6	83.1	71.0	71.6

It will be noted from these data that although activated alumina alone is not as good a heterogeneous cracking catalyst as alumina on silica, since it gives a somewhat lower yield of a product having a lower octane number, nevertheless, by using butyl bromide the yield and octane number are both much improved. By adding the yields in runs 3 and 5 and subtracting 4.0 as before, it is seen that the yield in run 6 lacks only about 3.6% of being additive. The data on runs 7 and 8 are given to show that ethylene dichloride is ineffective as a cracking catalyst alone and that it does not cause any substantial improvement when used together with activated alumina.

Runs 9 to 13 inclusive were made on boron

oxide and chromic oxide adsorbed on silica, with and without n-butyl bromide:

maintained under such conditions that the quantity of gasoline formed due to thermal cracking

	9	10	11	12	13
Heterogeneous catalyst.....	B ₂ O ₃ on SiO ₂	B ₂ O ₃ on SiO ₂	B ₂ O ₃ on SiO ₂	Cr ₂ O ₃ on SiO ₂	Cr ₂ O ₃ on SiO ₂
Homogeneous catalyst.....	None.....	C ₄ H ₉ Br.....	C ₄ H ₉ Cl.....	None.....	C ₄ H ₉ Br.....
Percent by weight.....		1.50.....	1.04.....		1.50.....
Gram-atoms of halogen/kilogram.....		0.11.....	0.112.....		0.11.....
Temperature, °F.....	925.....	925.....	925.....	925.....	925.....
Space velocity.....	1.13.....	1.2.....	1.15.....	1.20.....	1.15.....
Gasoline yield, percent by volume.....	9.7.....	20.2.....	10.7.....	9.0.....	18.7.....
Octane number.....	75.3.....	79.5.....	75.0.....	72.1.....	86.0.....

These data show that the addition of butyl bromide increases the gasoline yield markedly and simultaneously raises the antiknock value. Run 11 is included to show that n-butyl chloride has practically no effect on the yields or octane number of the gasoline obtained using boron oxide on silica.

Runs 14 to 21 inclusive were made primarily to determine the effect of the amount of homogeneous catalyst used on the gasoline yield obtained, and although run 17 using ethylene dichloride is not pertinent to this point, the data thereon are given as further evidence of the inactivity of chlorine compounds in my process. The same sample of heterogeneous catalyst was used in all of these runs without regeneration and each run was about six hours long.

is in the range from about 1% to about 10%.

2. The process of producing a high antiknock motor fuel from a heavier hydrocarbon oil which comprises passing said hydrocarbon oil and a small amount of a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides in the vapor phase at a space velocity in the range from 0.5 to 3.0 through a reaction zone containing a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting of aluminum and silicon, said reaction zone being maintained at a temperature in the range from about 800° F. to about 1100° F. and under substantially atmospheric pressure.

	14	15	16	17
Heterogeneous catalyst.....	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂
Homogeneous catalyst.....	None.....	None.....	C ₂ H ₄ Br.....	C ₂ H ₄ Cl.....
Percent by weight.....			0.75.....	0.543.....
Gram-atoms of halogen/kilogram.....			0.055.....	0.11.....
Temperature, °F.....	950.....	950.....	950.....	955.....
Space velocity.....	1.19.....	1.25.....	1.26.....	1.22.....
Gasoline yield, percent by volume.....	19.0.....	20.5.....	25.7.....	21.5.....

	18	19	20	21
Heterogeneous catalyst.....	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂	Al ₂ O ₃ on SiO ₂
Homogeneous catalyst.....	None.....	C ₄ H ₉ Br.....	C ₄ H ₉ Br.....	None.....
Percent by weight.....		1.50.....	3.00.....	
Gram-atoms of halogen/kilogram.....		0.11.....	0.22.....	
Temperature, °F.....	950.....	951.....	952.....	950.....
Space velocity.....	1.20.....	1.18.....	1.24.....	1.24.....
Gasoline yield, percent by volume.....	17.9.....	25.7.....	30.1.....	13.9.....

It is apparent from runs 16, 19, and 20 that increasing the quantity of butyl bromide used increased the gasoline yield, even though the activity of the heterogeneous catalyst has diminished as shown by comparison of runs 15, 18 and 21. By gradually increasing the amount of homogeneous catalyst used the gasoline yield may be maintained substantially constant for a long period of time.

While I have described my invention in connection with certain specific embodiments thereof, I do not desire to be limited thereto, but only by the following claims, which should be construed as broadly as the prior art will permit.

I claim:

1. The process of producing a high antiknock motor fuel from a heavier hydrocarbon oil which comprises passing said hydrocarbon oil and a small amount of a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides in the vapor phase through a reaction zone containing a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting of aluminum and silicon, said reaction zone being

3. The process of producing a high antiknock motor fuel from a heavier hydrocarbon oil which comprises admixing a small amount of a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides with said hydrocarbon oil, and passing the resulting mixture in the vapor phase through a reaction zone containing a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting of aluminum and silicon, said reaction zone being maintained at a temperature in the range 800° F. to 1000° F. under substantially atmospheric pressure.

4. The process of producing a high antiknock motor fuel from a petroleum gas oil which comprises passing said gas oil in the vapor phase in contact with a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting of aluminum and silicon in a reaction zone in the presence of a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides at a temperature of 850° F. to 950° F. with a space velocity of said

gas oil through said heterogeneous catalyst of from about 1.0 to about 2.0, removing the products from said reaction zone and fractionating said products to form a motor fuel fraction.

5 5. The process of producing high antiknock motor fuel from a heavier hydrocarbon oil which comprises heating said oil to a temperature of 800° F. to 1100° F., forming a vapor fraction from said heated oil, admixing a small amount of a
10 homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides with said vapor fraction, and passing the
15 resulting mixture at substantially atmospheric pressure without substantial cooling through a reaction zone containing a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting of aluminum and silicon.

20 6. The process of producing a high antiknock motor fuel from a heavier hydrocarbon oil which comprises admixing a homogeneous cracking catalyst adapted to form a hydrogen halide selected from the group consisting of hydrogen bromide
25 and hydrogen iodide under the reaction conditions with said hydrocarbon oil in such amount that the resulting mixture contains from about 0.02 to about 0.3 gram-atoms of halogen per kilogram and passing the resulting mixture in the
30 vapor phase at a space velocity of about 0.5 to 3.0 through a reaction zone containing a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from

the group consisting of aluminum and silicon, said reaction zone being maintained under substantially atmospheric pressure at a temperature in the range 800° F. to 1100° F.

7. The process of producing a high antiknock
5 motor fuel from a petroleum gas oil which comprises passing said gas oil in the vapor phase in contact with a solid heterogeneous cracking catalyst comprising an oxygen-containing compound of an element selected from the group consisting
10 of aluminum and silicon in a reaction zone in the presence of a homogeneous cracking catalyst selected from the group consisting of bromine, iodine, hydrogen bromide, hydrogen iodide, and organic bromides and iodides in such amount
15 that from 0.05 to 0.2 gram-atoms of halogen are present per kilogram of said gas oil at a temperature of 850° F. to 950° F. with a space velocity of said gas oil through said heterogeneous
20 catalyst in the range from about 1.0 to about 2.0, removing the products from said reaction zone, and fractionating said products to form a motor fuel fraction.

8. The process of producing a high antiknock
25 motor fuel from a petroleum gas oil which comprises passing said gas oil in the vapor phase in contact with a heterogeneous cracking catalyst comprising alumina adsorbed on silica in a reaction zone in the presence of about 1.5% by
30 weight of butyl bromide at a temperature of about 925° F. with a space velocity of said gas oil through said heterogeneous catalyst of about 1.0.

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