

Dec. 9, 1969

R. P. SIEG ET AL

3,482,952

PROCESS FOR PRODUCTION OF GASOLINE

Filed April 29, 1968

COMPARISON OF THE ATMOSPHERIC
REACTIVITY OF AN OLEFINIC FCC C₅-C₆
FRACTION BEFORE AND AFTER ETHERATION

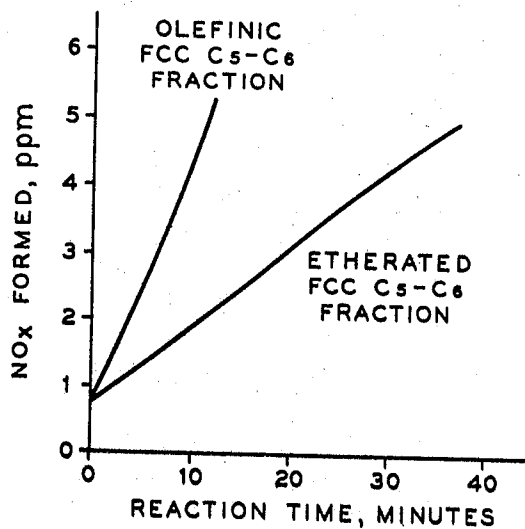


FIG. 1

COMPARISON OF THE ATMOSPHERIC
REACTIVITIES OF ISOBUTENE AND
t-BUTYL METHYL ETHER

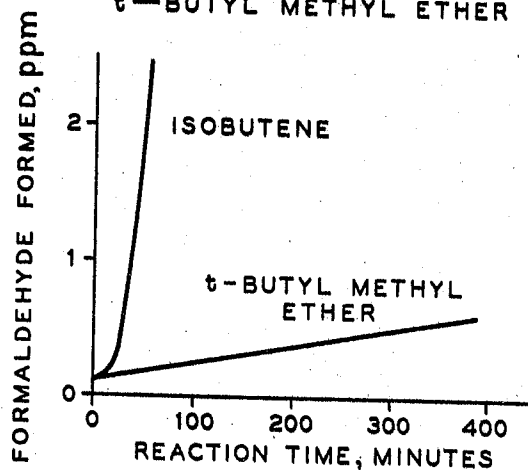


FIG. 2

INVENTORS
ROBERT P. SIEG
JACOB D. KEMP

BY E. E. Johnston
James W. McClain
ATTORNEYS

1

3,482,952

PROCESS FOR PRODUCTION OF GASOLINE

Robert P. Sieg, Piedmont, and Jacob D. Kemp, El Cerrito, Calif., assignors to Chevron Research Company, San Francisco, Calif., a corporation of Delaware
Filed Apr. 29, 1968, Ser. No. 724,831
Int. Cl. C10I 1/30, 1/24

U.S. Cl. 44—56

8 Claims

ABSTRACT OF THE DISCLOSURE

A process for the production of high octane gasoline having reduced volatility and atmospheric reactivity by fractionation of cracking reactor effluent to obtain a 15°–170° F. cut, containing C₄–C₆ tertiary olefins, etheration of those olefins by reaction with a lower alcohol over an etheration catalyst, preferably a —SO₃H group containing carbonaceous catalyst, followed by blending of the etherated cut with at least one other hydrocarbon stream, preferably a hydroprocessed fraction from the cracking reactor. Portions of the etherated material may be alkylated with an alkylatable hydrocarbon to further reduce atmospheric reactivity and volatility of the final gasoline product. Catalysts and alkylatable hydrocarbons are specified. Solvent extraction is not required.

Background of the invention

This invention is related to processes to make gasoline. More specifically, it is related to processes to make ether-containing gasolines with decreased tendencies to produce smog and other forms of air pollution.

Air pollution in its various forms is one of the most serious problems presently facing the nation. Vast sums of money are being spent or allocated by industry, governmental agencies, and research organizations to develop methods of reducing the amount of air pollution. One of the principal forms of air pollution, particularly in those urban areas which have a high density of automobile traffic, such as Los Angeles and San Francisco, is photochemical smog. Gasoline-powered motor vehicles are among the principal sources of photochemical smog. It is believed that the gasoline fuel contributes to smog because of the nature of its components. Gasoline contains numerous light components which are highly volatile and evaporate easily into the atmosphere from the fuel systems of vehicles. These components are highly reactive in the presence of air and sunlight, and are catalyzed in the atmosphere to produce materials which contribute to the atmospheric opacity common to smog. A number of these reaction products are also irritants to the eyes, throats, and respiratory systems of the residents of the urban areas.

Progressive refiners are presently engaged in research programs and developmental work to overcome the problems of volatility and reactivity. These programs have centered around the search for new gasoline compositions and methods of gasoline production by which gasolines which have reduced volatility and atmospheric reactivity can be produced. A number of processes have been proposed in the prior art for the production of gasolines which meet these criteria. Some processes have used expensive catalysts which require rare elements as components or precise and complex combinations of several elements, and which have relatively short useful lives, particularly under severe operating conditions. Others have required expensive and complex processing steps, such as solvent extraction, to separate certain types of compounds to be subjected to further processing.

Prior researchers into this general subject matter have

2

described their work in U.S. Patents 2,046,243, 2,384,866, 2,391,084, 2,399,126, 2,480,940, 2,891,999, 2,952,612, and 3,224,848.

Summary of the invention

We have now discovered a process for the production of high octane gasoline having reduced volatility and atmospheric reactivity, without the necessity of employing solvent extraction, which comprises fractionating the effluent from a cracking zone into a plurality of streams including at least a first stream and a second stream, the first stream boiling in the range of about 15°–170° F. and containing the major portion of C₄–C₆ tertiary olefins present in the effluent, contacting the first stream with a lower alcohol in the presence of an etheration catalyst to convert a substantial portion of the tertiary olefins in the first stream to ethers, then combining the ether-containing first stream with at least one hydrocarbon stream boiling in the range of about 15°–425° F. to form a gasoline having reduced volatility and atmospheric reactivity. The preferred etheration catalyst is a carbonaceous catalyst containing at least one —SO₃H group as the functional group. More preferred is a sulfonated resinous catalyst.

In a preferred embodiment, the process of this invention is further characterized by the presence in the ether-containing first stream of at least one nontertiary olefin selected from the group consisting of primary and secondary C₄–C₆ olefins, and wherein the ether-containing first stream is separated into a plurality of fractions, including at least a first fraction and a second fraction, the first fraction containing relatively less of the ethers and relatively more of the nontertiary olefins than the second fraction, the first fraction is contacted with at least one alkylatable hydrocarbon in the presence of an acidic alkylation catalyst to alkylate at least a portion of the nontertiary olefins in the first fraction, and the alkylated first fraction is combined with the second fraction and the hydrocarbon stream boiling in the range of about 15°–425° F. to form a gasoline having reduced volatility and atmospheric reactivity.

Brief description of the drawings

Both figures illustrate the reduced atmospheric reactivity of ethers and etherated hydrocarbon fractions. FIGURE 1 illustrates the results of a standard NO_x formation test, while the data of FIGURE 2 are derived from a standard formaldehyde formation test.

Detailed description of the invention

In its broadest form, the process of this invention is a process for the production of high octane gasoline having reduced volatility and atmospheric reactivity, which comprises fractionating the effluent from a cracking zone into a plurality of streams including at least a first stream and a second stream, the first stream boiling in the range of about 15°–170° F. and containing the major portion of C₄–C₆ tertiary olefins present in the effluent, contacting the first stream with a lower alcohol in the presence of an etheration catalyst to convert a substantial portion of the tertiary olefins in the first stream to ethers, then combining the ether-containing first stream with at least one hydrocarbon stream boiling in the range of about 15°–425° F. to form a gasoline having reduced volatility and atmospheric reactivity.

Several factors, heretofore unrecognized by the art, contribute to the ability of the process of this invention to produce high octane gasoline while simultaneously reducing the volatility and atmospheric reactivity of that gasoline. For instance, it has now been found that the high degree of improvement in the present gasoline product over those etherated gasolines described in the prior art is obtained only when the fraction of effluent of the

cracking process subjected to etheration is limited to those hydrocarbon materials boiling in the range of about 15°–170° F. This fraction will be found to contain the major portion of those tertiary C₄–C₆ olefins which were in the cracking reactor feed or may have been produced by the cracking operation. In a typical premium gasoline, a sizeable portion of the tertiary C₄–C₆ olefin content would consist of isobutene, methyl- and dimethyl-butenes, and methyl-pentenenes. If wider boiling ranges of materials are used, the improvement in octane rating is substantially decreased, rapidly approaching that of the whole untreated gasoline blend. This restriction may be accomplished by control of the fractionation zone in which the effluent of a cracking zone is divided into various hydrocarbon fractions based on boiling ranges. This procedure eliminates the costly and less efficient solvent extraction step upon which the processes of the prior art relied. By eliminating the necessity of separating certain components of the effluent by solvent extraction, this process also eliminates the need for extensive solvent recovery, purification, and make-up apparatus.

The cracking zone employed in the process of this invention may be any type of thermal or catalytic reactor from which the required tertiary olefins can be obtained. Thermal cracking units operate at temperatures of about 800°–1,100° F. and pressures of about 1–50 atmospheres. Their operation is conventional and will not be described further here.

It is preferred to employ a catalytic cracker in the cracking zone of the process of this invention. This may be any type of catalytic cracker and may employ fluidized beds or moving compact beds of solid catalysts. In common practice, the catalyst circulates back and forth between a reaction zone in which it contacts the oil to be cracked and a regeneration zone in which the coke, which accumulates on the catalyst in the reaction zone, is burned off in the presence of air and the catalyst is heated for return to the reaction zone. Conventional operating conditions for these types of catalytic crackers are reaction zone temperatures of 850°–1,100° F., regeneration zone temperatures of 1,000°–1,400° F., pressure of about 10 to 50 p.s.i.g., and 30 to 80 percent per pass conversion. Any conventional cracking catalyst may be used; typical examples are silica-alumina, silica-zirconia, silica-magnesia, synthetic crystalline aluminosilicates, such as the zeolites, and natural and treated clays and combinations thereof.

The feed to the cracking zone may be any conventional type of hydrocarbon feed, such as, for example, a straight-run gas oil obtained from a crude distillation column. In general, the boiling range of the feedstock is about 400°–1,100° F. In the cracking step of the process of this invention, the cracking reactor is associated with a distillation column in which the effluent is separated into a plurality of fractions including in the process of this invention a fraction boiling between 15° and 170° F.

The 15°–170° F. cut, which contains the major fraction of the tertiary C₄–C₆ olefins, is then contacted with a lower alcohol in the presence of an etheration catalyst in order to convert as large a portion as possible of the tertiary C₄–C₆ olefins to ethers. A number of etheration catalysts are known in the art. These include "strong" acids, such as H₂SO₄ and HF, as well as other materials, such as aluminum chloride and boron fluoride. Combinations of these materials, such as HF-BF₃, may also be used.

The preferred etheration catalysts of the present invention are relatively high molecular weight, water-insoluble, carbonaceous materials containing at least one —SO₃H group as the functional group. These catalysts are exemplified by the sulfonated coals (Zeo-Karb H, Nalcite X, and Nalcite AX) produced by the treatment of bituminous coals with sulfuric acid and commercially marketed as zeolitic water softeners or base exchangers. These materials are usually available in a neutralized form and, in this case, must be activated to the hydrogen form by treatment with a mineral acid, such as hydrochloric acid,

and water washed to remove sodium and chloride ions prior to use. Also suitable are the sulfonated resin type catalysts which include the reaction products of phenol-formaldehyde resins with sulfuric acid (Amberlite IR-1, Amberlite IR-100, and Nalcite MX). Also useful are the sulfonated resinous polymers of coumarone-indene with cyclopentadiene, sulfonated polymers of coumarone indene with furfural, sulfonated polymers of coumarone-indene with cyclopentadiene and furfural and sulfonated polymers of cyclopentadiene with furfural. The most preferred cationic exchange resins are strongly acidic exchange resins consisting essentially of sulfonated polystyrene resin, for instance, a divinylbenzene cross-linked polystyrene matrix having about 0.5 to 20 percent, preferably about 4 to 16 percent, of copolymerized divinylbenzene therein to which are attached ionizable or functional nuclear sulfonic acid groups. These resins are manufactured and sold commercially under various trade names; e.g., Dowex 50, Nalcite HCR, and Amberlyst 15. As commercially obtained, they have solvent contents of about 50 percent and can be used in the instant process in this form or can be dried and then used with little or no differences in results ascertainable.

The resin particle size is chosen with a view to the manipulative advantages associated with any particular range of sizes. Although a small size (200–400 mesh) is frequently employed in autoclave runs, a mesh size of 10–50 or coarser seems more favorable for use in fixed bed or slurry reactors. The catalyst concentration range in a batch process should be sufficient to provide the desired catalytic effect—e.g., between about 0.5 and 50 percent (dry basis) by weight of the reactants—with the preferred range being between about 1 to 25 percent (dry basis), for example, 5 percent.

In a continuous reactor, the catalyst concentration may be defined by volumetric hourly space velocity; that is, the volume of feed processed per volume of catalyst per hour. The volumetric hourly space velocity can be about 0.1 to 100 based on hydrocarbon feed, with the preferred range being about 0.5 to 25, with the most preferred range being about 0.5–10.

The ether is formed by reacting the tertiary olefin in the hydrocarbon mixture with a primary alcohol, whether mono- or polyfunctional. A ratio of about 0.1 to 100 mols of primary alcohol per mole of tertiary olefin may be used in the etheration with the usual amount being between about 0.25 to 10 mols, preferably about 1 to 10 mols, of primary alcohol per mol of tertiary olefin. A high ratio of alcohol to tertiary olefin increases the amount of olefin removed from the mixed hydrocarbon feed stream.

Primary alcohols, whether mono- or polyfunctional, are preferred in the etheration step of this process. Secondary alcohols will react with the tertiary olefins, although it is to be expected that a primary alcohol will be considerably more reactive than a secondary alcohol of the same carbon number. However, secondary alcohols of low carbon number may be more reactive than primary alcohols of higher carbon number. Economy and ease of volatilization generally dictate the use of lower alcohols; i.e., those of 1 to 6 carbon atoms per molecule. Another factor which influences the choice of alcohol is the boiling point difference between the alcohol and the azeotrope of the alcohol with its ether, if it is preferred to separate excess alcohol from the etheration reaction mass. In general, ethanol and methanol are preferred because of economy and, usually, they afford higher conversion rates.

Etheration of the tertiary olefins eliminates the highly reactive olefins from the gasoline products and replaces them with less reactive ethers.

This is illustrated in FIGURES 1 and 2. Both figures show the data derived from standard experiments in which a measured sample of the reactant material in filtered air is irradiated with ultraviolet light and the

amount of photochemically catalyzed product formed is measured. Essentially ambient conditions are maintained. In FIGURE 1, the data show the reactivity of an olefinic fluid catalytic cracker C₅-C₆ fraction as measured by its ability to convert NO to NO_x (where x>1). The NO_x compounds are indices of smog formation. It is apparent that, when the fraction is etherated to eliminate many of the olefins, its reactivity is substantially decreased. Similarly, in FIGURE 2, data showing the reactivity of isobutene illustrate that it is much more reactive than the ether derived from the reaction of isobutene with methanol. In this experiment, the reaction product formed upon ultraviolet irradiation of the reactants is formaldehyde. These standard tests are used in air pollution research to compare reactivities of various compounds and types of compounds. Etheration also serves to reduce the vapor pressure of the product by replacing the more volatile olefins with the less volatile ethers. The degree of reduction of volatility will depend on the degree of etheration and the original olefinic content of the feed.

The following table will illustrate the advantages of the process of this invention. The data in this table were derived from a series of experiments in which methanol and several designated fractions of the effluent from a fluidized bed catalytic cracker were passed, in a 3:2 weight ratio, over a 60 cc. bed of the Dowex 50X-8 catalyst (described above) maintained at a temperature of 125° F.

TABLE

FCC effluent fraction:				
Predominant olefin carbon number.....	C ₅	C ₆	C ₇	C ₈
Boiling range, ° F.....	80-110	110-165	165-210	210-250
Bromine number.....	171	144	136	123
Octane numbers:				
F-1 clear.....	97.3	93.0	91.2	92.8
F-2 clear.....	81.5	78.4	77.6	78.6
Hourly vol. of feed/vol. of catalyst.....	0.40	0.59	0.45	0.38
Product:				
Ether content, wt. percent.....	48.5	37.6	30.8	20.7
Bromine number.....	79	56	48	43
Octane numbers:				
F-1 clear.....	100.8	96.2	92.5	93.0
F-2 clear.....	86.8	81.7	78.3	78.5
Change on etheration:				
Δ F-1 clear.....	+3.5	+3.2	+1.3	+0.2
Δ F-2 clear.....	+5.3	+3.3	+0.7	-0.1

It will be immediately seen from these data that reaction of the C₅ and C₆ effluent fractions with methanol gives a considerably higher ether yield and improvement in F-1 and F-2 clear octane numbers than does similar reaction of the C₇ and C₈ fractions. A decrease of over one-half in the bromine number is also obtained.

Other experiments have provided data on the etheration of fractions containing C₄ olefins, which extend the applicable range of the process of this invention down to 15° F. These data show that a gasoline base containing an etherated C₄ portion has even higher octane numbers than those exhibited by the etherated C₅ and C₆ cuts shown in the above table.

It is thus apparent that the process of this invention, wherein the 15°-170° F. portion of the cracking reactor effluent is separated and etherated prior to blending into gasoline, provides a significant and unexpected benefit not heretofore found in etheration of whole catalytic cracker effluent.

Of the olefinic portion of the original 15°-170° F. fraction of the cracking reactor effluent, the tertiary olefins generally comprise the major portion. However, a certain portion is made up of other types of olefins which, being considerably less reactive than the tertiary olefins, pass virtually unchanged through the reaction chamber in which the tertiary olefins are reacted with alcohol over a carbonaceous catalyst. These unreacted olefins appear in the etherated reaction product and, although the total olefin content is considerably reduced as compared to the original 15°-170° F. fraction by reaction of the ter-

tiary olefins, the remaining olefins still pose a potential, though reduced, threat of smog formation. Consequently, it is desirable to reduce to a minimum the final olefinic content of the product passed to gasoline blending.

Therefore, in one embodiment of the process of this invention, the etherated material, including all unreacted hydrocarbons and ethers formed and from which there may or may not have been separated any unreacted alcohol, is passed into an alkylation zone wherein it is contacted in the presence of an alkylation catalyst with a suitable alkylatable hydrocarbon. Examples of such alkylatable hydrocarbons are aromatics or side chain aromatics boiling in the gasoline range, such as benzene, or tertiary paraffins having no more than six carbon atoms per molecule, preferably isobutane. The alkylation step results in formation of a material rich in branched chain aliphatic or aromatic hydrocarbons boiling principally in the gasoline range. The alkylation unit may be of any of the conventional types well known in the art, for example, sulfuric acid, aluminum chloride or hydrofluoric acid alkylation units. In the sulfuric acid type process, the reaction temperature is preferably of the order of 40° to 70° F.; and the pressure is of the order of 5 to 50 pounds per square inch gauge. In the reaction mixture, about 50 to 70 percent by volume of sulfuric acid catalyst is used. This acid may range from 98 to 100 percent concentration at the start of the operation to about 90 percent concentration when it is discarded. In the case of hydrofluoric acid alkylation, the reaction temperature is maintained in the range of about 75° to 100° F.

Where all the etherated material is passed to alkylation, consumption of the acidic alkylation catalyst tends to be high. Consequently, in a preferred embodiment of this process, the etherated material is first separated into a plurality of fractions, usually two, including a first fraction and a second fraction. This separation may be, e.g., by distillation. The first fraction is relatively leaner in ethers and richer in nontertiary olefins than the second fraction. Preferably the olefin content of the first fraction and the ether content of the second fraction are maximized. The first fraction is then alkylated in the manner stated above. After alkylation, the alkylated material is recombined with the ether-rich second fraction; and the combined materials are passed on to further processing as described.

The light (C₄-C₆) isoparaffins usually appear as components in gasoline blends, and may comprise as much as 20 percent of the total blend. These compounds are highly volatile and, when present as a significant portion of a gasoline blend, contribute disproportionately to the total volatility of the blend. As noted earlier, it is desirable to reduce the volatility of gasoline to aid in reducing air pollution. Consequently, it is a preferred embodiment of the process of this invention to employ, as the alkylatable hydrocarbon, at least one light isoparaffin. Particularly preferred are isobutane and isopentane which are quite likely to be present in some quantity in the 15°-170° F. cut from the catalytic cracker. In this case, the etherated material, which would contain both the C₄-C₆ nontertiary olefins and the light isoparaffins, could be contacted with the alkylation catalyst (with or without the separation mentioned above) and converted to alkylate without the requirement of any additional source of either component. The light isoparaffin may also be supplied in part or in whole from external sources, if desired.

Following etheration and, if desired, alkylation, the etherated (and alkylated) materials are blended into gasoline stocks. This involves combination with at least one hydrocarbon stream which boils in the range of 15°-425° F. In actual practice, a number of such streams would be combined with the etherated stream. In one preferred embodiment, a fraction of the cracking reactor effluent, which boils above the 15°-170° F. range of the fraction discussed above, is passed to a hydroprocessing unit and hydroprocessed. Typical hydroprocessing units which may

be employed are catalytic reforming, hydrocracking, and hydrofining. Which of these or other typical hydroprocessing units is used will depend on the nature of fraction to be processed. The hydroprocessed stream is thereafter combined with the etherated material.

The above data are to be considered to be merely illustrative of the process of this invention. Numerous other embodiments of the process of this invention will be apparent to those skilled in the art. Consequently, the process of this invention is intended to be limited only in the manner indicated in the appended claims.

We claim:

1. A process for the production of high octane gasoline having reduced volatility and atmospheric reactivity, which comprises fractionating the effluent from a cracking zone into a plurality of streams including at least a first stream and a second stream, said first stream boiling in the range of about 15°–170° F. and containing the major portion of C₄–C₆ tertiary olefins present in said effluent, contacting said first stream with a lower alcohol in the presence of an etheration catalyst comprising a carbonaceous catalyst containing at least one —SO₃H group as the functional group to convert a substantial portion of the tertiary olefins in said first stream to ethers, then combining the ether-containing first stream with at least one hydrocarbon stream boiling in the range of about 15°–425° F. to form a gasoline having reduced volatility and atmospheric reactivity.

2. The process of claim 1 wherein said second stream is subjected to hydroprocessing, and then said hydroprocessed second stream comprises said hydrocarbon stream which is blended with said ether-containing first stream.

3. The process of claim 1 wherein said carbonaceous catalyst is a sulfonated resinous catalyst.

4. The process of claim 3 wherein said resinous catalyst comprises a sulfonated cross-linked polystyrene matrix having 0.5–20 percent divinylbenzene incorporated therein.

5. The process of claim 1 further characterized by the presence in said ether-containing first stream of at least

one nontertiary olefin selected from the group consisting of primary and secondary C₄–C₆ olefins, and wherein said ether-containing first stream is separated into a plurality of fractions, including at least a first fraction and a second fraction, said first fraction containing relatively less of said ethers and relatively more of said nontertiary olefins than said second fraction, said first fraction is contacted with at least one alkylatable hydrocarbon in the presence of an acidic alkylation catalyst to alkylate at least a portion of said nontertiary olefins in said first fraction, and said alkylated first fraction is combined with said second fraction and said hydrocarbon stream boiling in the range of about 15°–425° F. to form a gasoline having reduced volatility and atmospheric reactivity.

6. The process of claim 5 wherein said alkylatable hydrocarbon is an isoparaffin selected from the group consisting of isobutane, isopentane, and isohexane.

7. The process of claim 6 wherein said isoparaffin is isobutane.

8. The process of claim 1 further characterized by the presence in said ether-containing first stream of at least one nontertiary olefin selected from the group consisting of primary and secondary C₄–C₆ olefins, and contacting said ether-containing first stream with at least one alkylatable hydrocarbon in the presence of an acidic alkylation catalyst prior to said combining with said hydrocarbon stream.

References Cited

UNITED STATES PATENTS

2,384,866	9/1945	Wiczer	44—56
2,391,084	12/1945	Carmody	44—53
2,480,940	9/1949	Leum et al.	260—614
2,891,999	6/1959	Langer	260—641
2,952,612	9/1960	Trainer	44—56 XR

DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44—77