Sept. 13, 1960 R. P. TRAINER 2,952,612

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AN ALKYL ETHER ADDITIVE
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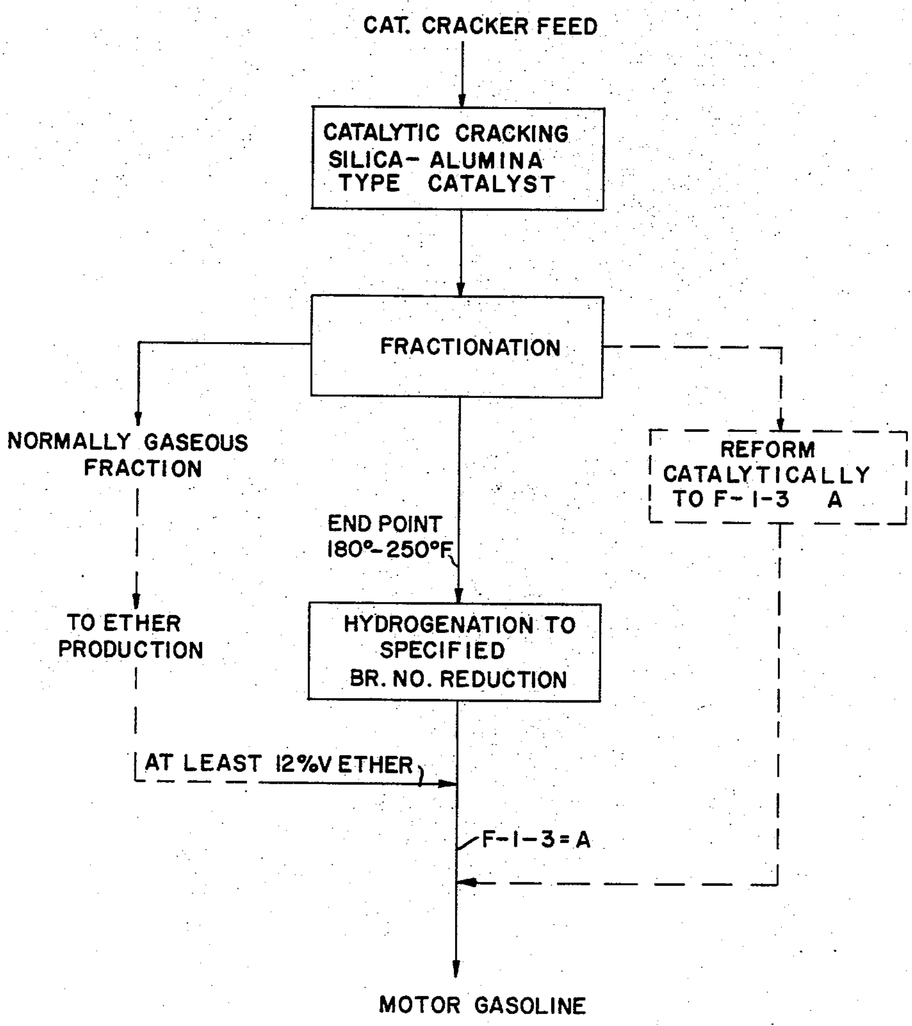

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PRODUCTION OF HIGH OCTANE MOTOR FUEL WITH AN ALKYL ETHER ADDITIVE

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9 Claims. (Cl. 208—67)

This invention relates to the production of quality automotive motor fuel through catalytic cracking, hydrotreating, and blending.

The backbone, so to speak, of gasoline for automotive use is catalytically cracked gasoline. It is the practice to charge the maximum amount of suitable oils boiling above gasoline to catalytic cracking to thereby maximize the yield of this material. Due to the excellent quality of catalytically cracked gasoline it is possible to blend with it minor amounts of lower quality materials such as straight run gasoline. In order to maximize the utilization of such low cost materials it is the practice in many instances to add to the blend other high octane materials such, for example, as alkylate, aromatic extracts and catalytically reformed gasoline. Of course, small amounts of butane are incorporated to obtain the desired vapor pressure of the final blend and the gasoline is usually leaded.

Among such high octane materials which have been suggested for use in gasolines are the saturated alkyl ethers, and particularly those having a branched chain and boiling within the range of about 89° F. to about 180° F. Di-isopropyl ether was used to a limited extent during World War II in aviation gasoline. These ethers would be effective in automotive motor fuel. They are, however, so costly that they have not been used in automotive fuel, or, for that matter, even in aviation gasoline, since the war.

It has now been found that the effectiveness of these ethers may be materially improved in combination with catalytically cracked gasoline in automotive fuel, provided the catalytically cracked gasoline is first partially hydrogenated to reduce its bromine number and certain minimum concentrations of ether are used. This finding is considered quite unexpected since blends of the ethers with hydrogenated catalytically cracked gasoline normally have considerably lower octane numbers than the corresponding blends with the non-hydrogenated catalytically cracked gasoline. Another way of putting it is to say that the more the catalytically cracked gasoline is hydrogenated to reduce its bromine number the more of the costly ether is normally required to achieve a given octane number.

This is best illustrated by the data in Table I which show the amounts of methyl tertiary butyl ether that must be added to a 100.9 F–1–3 octane number catalytically cracked gasoline unhydrogenated and hydrogenated (to reduce the bromine number to various extents) to produce blends having octane numbers of 100.0, 100.5, 101.0 and 101.5, respectively. The percentages of ether are the concentrations by volume in the blend.

Table I

Bromine No. Reduction, percent (by hydrogenation)	F-1-3 Octane Number			
	100	100.5	101	101.5
	Percent Ether Required in Blend			
0	--------	--------	1	6
25	--------	--------	3	7
50	1	4	7	10
70	8	10	13	15
80	11	13	16	18
90	14	16	18	20
100	16	18	19	21

It is clearly evident that the more the bromine number is reduced by hydrogenation the greater is the concentration of ether required to achieve a given octane number. A similar effect is found if the methyl tertiary butyl ether is substituted by other low boiling ether such as methyl isopropyl ether, di-isopropyl ether, ethyl isopropyl ether and isopropyl tertiary butyl ether. It is also found with some of the higher boiling cyclic ethers wherein ether-oxygen is in a ring with carbon atoms, such as 4,4-dimethyl-1,3-dioxane.

It is found, however, that at high concentrations of these ethers in the blend with the catalytically cracked gasoline a point is reached where partial reduction of the bromine number of the catalytically cracked gasoline by hydrogenation does not show this advantage but is distinctly advantageous. In this region of high ether concentration partial (25–95%) reduction of the bromine number allows the production of super blends to which larger amounts of other lower octane materials may be added while still producing premium quality automotive fuel.

The transition point where reduction of the bromine number by hydrogenation passes from bad to good is at about 11% ether based on the catalytically cracked gasoline or about 10% in the blend. At this point a small reduction of the bromine number by a very light hydrogenation has no effect; a more drastic reduction in the bromine number is still harmful. At still higher ether concentrations the partial reduction of the bromine number by hydrogenation is advantageous and the advantage increases as the concentration of ether in the blend is increased. This trend persists at least up to about 44% concentration of the ether beyond which tests were considered to be unwarranted due to the high cost of blends with such high concentrations of ether. At this point (44%) the saving in ether effected through the partial reduction of the bromine number is around 40%, i.e. the amount of ether required to produce a given volume of a blend having a given octane number is 40% less than would be required without the hydrogenation.

For concentrations of the ether up to the above-mentioned break point the concentration has only one meaning. As already pointed out, however, the present invention allows a desired octane level to be reached with reduced amounts of ether. At concentrations above this break point there are therefore two ether concentrations to be considered, namely, (1) the concentration of ether required to achieve a given octane level without partial reduction of the bromine number of the catalytically cracked gasoline and (2) the concentration of ether required to achieve the same octane level with partial reduction of the bromine number. For all concentrations beyond the break point it will be understood that the latter concentration is meant. This is the concentration that will be meaningful in the practice of the invention since it is directed to the concentrations that will be used rather than to the concentrations that would otherwise have to be used. For example, in the above-mentioned case of 44% concentration of ether with a saving in ether of about 40%, this means that about 78% of the ether, based on the partially hydrogenated catalytically cracked gasoline, is added to produce a blend containing about 44% ether by volume, whereas about 285% would otherwise have to be added to produce a blend containing about 74% by volume of ether.

The beneficial effect of partial bromine number reduction at high ether concentrations is shown in the following Table II.

Table II

Hydrogenation-Bromine No. Reduction	Percent Ether by Volume Required for Equivalent F-1-3 Octane Numbers		Approximate Reduction in Ether Requirement, percent
	Without Hydrogenation	With Hydrogenation	
25	12	11	8
35	17	15	12
40	22+	18+	18
45	28	22	21
50	33	25	24
50	38	28	26
50	43	31	28
60	48	33	31
60–95	53	37	30
60–95	56	38+	31
60–95	61	40+	34
60–95	68	42+	38
60–95	74	44+	40

The above data are for blends of methyl tertiary butyl ether in the same catalytically cracked gasoline mentioned above in connection with Table I. The partial reduction of the bromine number was effected by partially hydrogenating the catalytically cracked gasoline with a commercial alumina-supported cobalt, molybdenum catalyst at temperatures in the range of 536 to 698° F. and pressures of 200 and 400 p.s.i.g. using 2900 s.c.f. hydrogen per barrel of gasoline. The catalytically cracked gasoline was obtained from a commercial operation using a synthetic silica-alumina cracking catalyst and before partial hydrogenation had the following properties:

Gravity, ° API	79.1
I.B.P., ASTM, ° F	102
F.B.P., ASTM, ° F	187
Percent S	0.014
Br No	141
F-1-3 Octane No	100.9

The figures in the first column of Table II labelled "Hydrogenation Bromine No. Reduction" give the approximate optimum extent of bromine number reduction affording the savings listed. These figures are only approximate since the optimum bromine number reduction is not sharply defined. In all cases hydrogenation to any extent up to the indicated approximate optimum bromine number reduction is advantageous. Hydrogenation to reduce the bromine number beyond the indicated approximate optimum, although less desirable, still affords a substantial saving in ether except at the lowest concentrations listed (11–22%) where some loss occurs if the percent bromine number reduction is more than about three times the percent ether in the blend. For example in the case of the blend containing 31% ether where a saving of about 28% is indicated at a bromine number reduction of 50%, the saving is still 23% if the bromine number reduction is increased to 90%.

The effects noted are obtained with catalytyically cracked gasoline produced by the catalytic cracking of any hydrocarbon oil boiling above gasoline with a solid silica-alumina type cracking catalyst. It is known that the silica-alumina cracking catalysts whether of high or low alumina content or of natural or synthetic origin give practically identical gasolines from various oils. Other cracking catalysts such as silica-magnesia and HF treated alumina give different product distributions and the gasolines produced with them may not behave in the manner shown when blended with the ethers.

The catalytically cracked gasoline is produced by the catalytic cracking of a higher boiling hydrocarbon oil at temperatures in the range of 900 to about 1100° F., pressures in the range of 5 to about 75 p.s.i.g. The cracking may be effected in a fluid bed reactor, moving bed reactor or a riser reactor such as described in U.S. application Serial Number 586,105, filed May 21, 1956. The products from the cracking reactor are preferably separated into a normally gaseous fraction including substantial amounts of olefins, a catalytically cracked gasoline boiling up to about 185–250° F., and a heavy naphtha. This naphtha fraction is advantageously catalytically reformed and then combined with the blend of the hydrogenated catalytically cracked gasoline and the ether. The reforming may be affected by any of the known catalytic reforming processes. In a typical case the naptha is "Platformed" by a platinum-alumina-halogen catalyst at a temperature of 900–960° F. and pressure of 150–450 p.s.i.g. in the presence of recycled hydrogen.

Since the effect of a given amount of ether in the blend with the catalytically cracked gasoline is considerably improved by the partial reduction in the bromine number, the amount of reformed naphtha or other blending materials that may be incorporated to produce the finished gasoline of desired octane number may be increased; such components can in fact become the chief component in the gasoline. On the other hand, the advantage can be exploited in a different way. Thus, in view of the greater effectiveness of the amount of ether used the naphtha may be used in the same amount but may be reformed to a lesser degree as by the use of less severe reforming conditions, thereby lowering the reforming cost and improving the yield of reformed product.

The catalytically cracked gasoline is catalytically hydrogenated to reduce the bromine number at least to some degree and preferably to about the extents indicated. The bromine number is initially at least around 100. The hydrogenation may be effected with any of the various hydrogenation catalysts hitherto used for hydrogenation of petroleum products. Preferred catalysts are prepared by incorporating oxides or sulfides of one or more fo the metals Cu, Co, Ni, Cr, Mo, W with an aluminous carrier material such as activated alumina or microporous silica-alumina composites. The hydrogenation is effectd at temperatures in the range of about 300 to 800° F., preferably about 500 to 700° F. The process may be carried out under pressures from slightly above atmospheric up to about 100 atmospheres. Under any given set of these conditions the rate of gasoline and hydrogen feed to the hydrogenation zone may be adjusted such that the desired degree of bromine number reduction is obtained. When effecting the hydrogenation under conditions to obtain a bromine number reduction of from about 50 to about 95% there is a substantial exothermic heat effect which makes control of the temperature difficult. This difficulty can be minimized by using two small reactors in series with intermediate cooling of the reactant stream, or by adding to the feed a sizable amount of a substantially inert hydrocarbon diluent material having a sufficiently different boiling range that it may be separated from the partially hydrogenated catalytically cracked gasoline product by a subsequent fractional distillation.

The ether is advantageously made from the olefinic gaseous fraction mentioned above. This is advantageous in two respects. In the first place this materially upgrades this gaseous product. In the second place the conversion of propylene and/or butylene to ethers reduces the amount of polymers which would otherwise be made from them. This is advantageous since the polymers tend to degrade the quality of the gasoline in which they are blended.

The conversion of the gaseous olefins to ethers may be effected by reacting them with a suitable alcohol such as methanol, or isopropanol by known methods e.g., as described in U.S. Patent No. 2,480,940 to Leum. A very desirable arrangement which produces large volumes of the ether is to hydrate the propylene to isopropyl alcohol (a known process) and then react this alcohol with the butylene-butane fraction or additional propylene whereby isopropyl tertiary butyl ether or di-isopropyl ether is formed. Still larger volumes of the ether may be produced but at increased cost, by reacting both the propylene and the isobutylene with methanol to produce methyl isopropyl and methyl tertiary butyl ethers.

The etherification reaction normally does not consume all of the alcohol in the reaction mixture. Unreacted alcohol may be removed by water washing the ether product or in some cases by distillation. The ethers in question are normally liquid and are easily separated from the unreacted hydrocarbons (e.g., butane-butylene fractions) by a simple distillation.

Example

A reduced petroleum was vacuum flashed to produce a flashed distillate and the residue was then propane deasphalted to produce a deasphalted oil. The flashed distillate and deasphalted oil were catalytically cracked together in a commercial fluidized catalyst cracking unit using a synthetic silica-alumina cracking catalyst. The product was fractionated in the plant in the normal manner to separate a propane-propylene fraction, a butane-butylene fraction, a catalytically cracked gasoline having the properties given above, and various heavier materials.

Separate propane-propylene and butane-butylene fractions from a different source were reacted with methanol and isopropanol to produce methyl isopropyl ether, methyl tertiary butyl ether, diisopropyl ether, and isopropyl tertiary butyl ether.

The catalytically cracked gasoline was partially hydrogenated with a commercial Co-Mo/alumina catalyst at 536–608° F. and 200 p.s.i.g. at a hydrogen to oil mole ratio of 2.8 and a liquid hourly space velocity of 4 to reduce the bromine number by 63%.

To the thus partially hydrogenated catalytically cracked gasoline there was added 44% by volume of methyl tertiary butyl ether giving a blend containing about 31% of the ether. To this blend there was then added 104% by volume of a reformed naphtha having an F–1–3 octane number of 96.8 which it will be noted is considerably below that of the catalytically cracked gasoline (100.9). The resulting blend had an F–1–3 octane number of 100.4. When di-isopropyl ether was substituted the octane number of the blend was 100.0. Isopropyl tertiary butyl ether was found equally effective as the methyl tertiary butyl ether and methyl tertiary amyl ether and ethyl tertiary butyl ether were intermediate the isopropyl tertiary butyl and di-isopropyl ether.

The F–1–3 octane number is the CFR designation for the ASTM Research Octane Number D908–47T for the material containing 3 cc. of ethyl fluid per U.S. gallon.

The bromine numbers were determined by the method described by A. Polgar et al. in "Organic Analysis," vol. III, p. 237, Interscience Publishers, N.Y.

I claim as my invention:

1. In the production of high octane automotive motor gasoline the improvement which comprises catalytically cracking a hydrocarbon oil boiling above gasoline with a silica-alumina type cracking catalyst, separating from the products of said cracking a fraction of normally gaseous hydrocarbons containing olefins, an unsaturated catalytically cracked gasoline having an end point between about 180 and 250° F., and a catalytically cracked naphtha, catalytically hydrogenating said catalytically cracked gasoline until its bromine number is reduced between about 25 and 95%, and combining with the partially hydrogenated catalytically cracked gasoline at least over 12% by volume thereof of a saturated alkyl ether boiling in the range of about 89° F. to 180° F.

2. Process according to claim 1 further characterized in that the said catalytically cracked naphtha is catalytically reformed to an F–1–3 octane number less than that of the catalytically cracked gasoline ether mixture and is then combined with said mixture.

3. Process according to claim 1 in which the ether is methyl tertiary butyl ether.

4. Process according to claim 1 in which the ether is methyl isopropyl ether.

5. Process according to claim 1 in which the ether is di-isopropyl ether.

6. Process according to claim 1 in which the ether is isopropyl tertiary butyl ether.

7. Process according to claim 1 in which the ether is methyl tertiary amyl ether.

8. In the production of high octane automotive motor gasoline the improvement which comprises catalytically cracking a hydrocarbon oil boiling above gasoline with a silica-alumina type cracking catalyst, separating from the products of said cracking a fraction of normally gaseous hydrocarbons containing olefins, an unsaturated catalytically cracked gasoline having an end point between about 180 and 250° F., and a catalytically cracked naphtha, catalytically hydrogenating said catalytically cracked gasoline until its bromine number is reduced between about 25 and 95%, and combining with the partially hydrogenated catalytically cracked gasoline at least over 12% by volume thereof of a saturated alkyl ether boiling in the range of about 89° F. to 180° F., the extent of bromine number reduction being correlated with the percent by volume of ether in the blend approximately as follows:

Percent ether in blend:	Percent bromine No. reduction
11	25
15	35
18	40
22	45
25–31	50
33	60
37–44	60–95

9. In the production of automotive motor gasoline having a given desired F–1–3 octane number above that of a catalytically cracked gasoline having an end point between about 180 and 250° F. by blending with said catalytically cracked gasoline a saturated alkyl ether boiling in the range of 89 to 180° F., to increase the F–1–3 octane number to the desired value of the blend, the improvement which comprises partially hydrogenating said catalytically cracked gasoline to a bromine number reduction depending upon the amount of said ether required to achieve said desired F–1–3 octane number with

the unhydrogenated catalytically cracked gasoline about as follows:

%v. ether required to be added to the unhydrogenated catalytically cracked gasoline	partial hydrogenation to bromine number reduction, percent
12	25
17	35
22	40
28	45
33–43	50
48	60
53–74	60–95

whereby the amount of ether actually required is reduced.

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