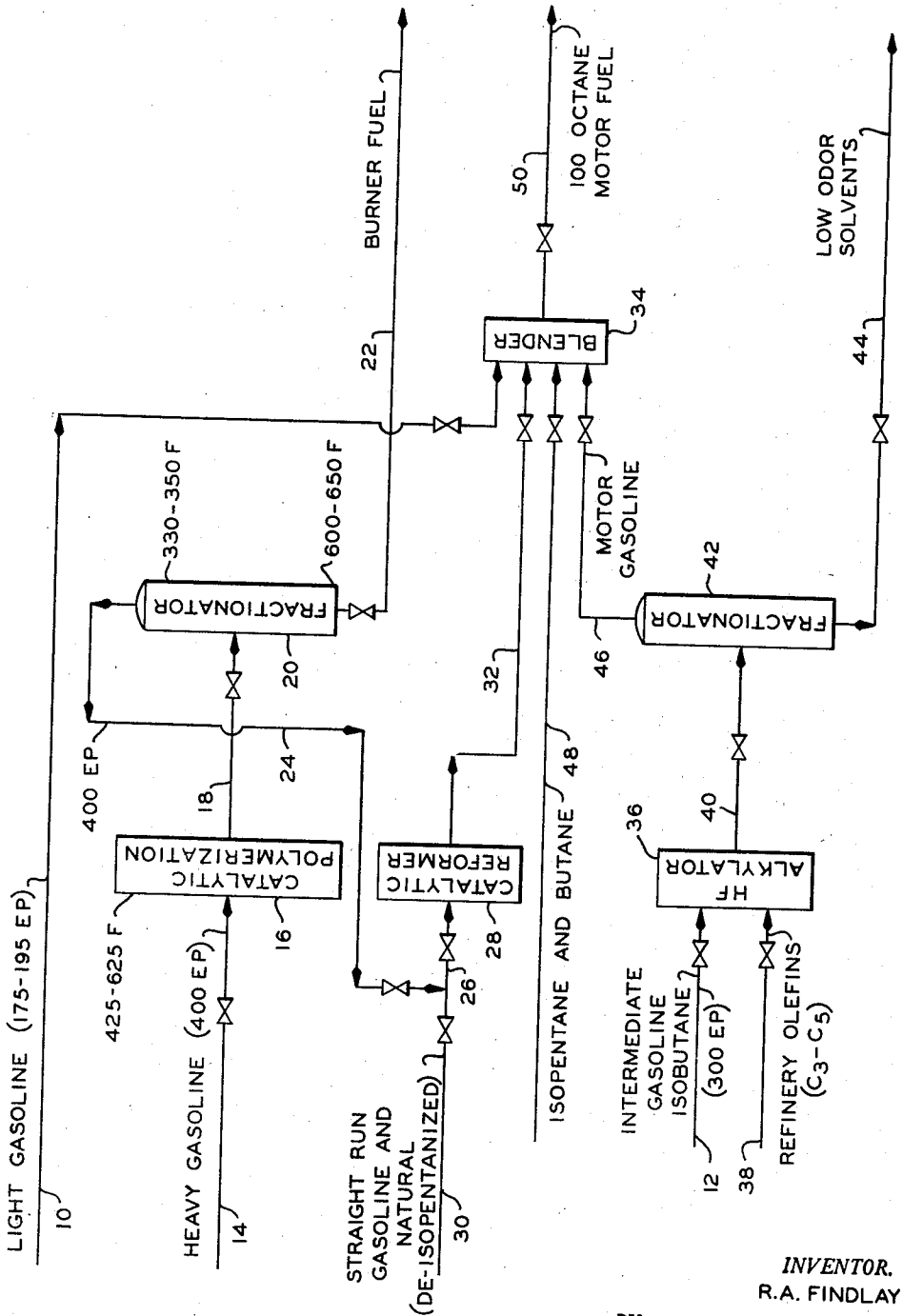
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PROCESS FOR PRODUCING HIGH OCTANE MOTOR FUELS

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PROCESS FOR PRODUCING HIGH OCTANE MOTOR FUELS

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The invention relates to a process for upgrading cracked gasoline to produce high-octane, clean-burning motor fuel.

One of the major sources of motor fuels is from cracked gasoline stocks. Recently developed high compression engines are placing increasingly greater demands on motor fuels in the way of octane number rating (anti-knock characteristics) and clean-burning qualities. It is frequently found necessary to undercut the end point of cracked gasoline in order to promote engine cleanliness and decrease "octane requirement increase" (ORI) of the engine during use. This method of handling the problem by distillation is non-selective, i.e., it removes hydrocarbons according to molecular weight rather than according to type. It is preferable to remove from the fuel (cracked gasoline) only those hydrocarbons which tend to cause trouble. While not all of the factors of this phenomenon are fully understood, there is some evidence that high reactive materials including olefins and certain impurities such as sulfur compounds can be the source of trouble. The process of the invention is concerned with the removal of reactive materials from cracked gasoline and purifying and upgrading the same.

The principal object of the invention is to provide a process for converting a maximum amount of cracked gasoline into clean-burning, high-octane motor fuel. Another object is to provide a process for upgrading heavy cracked gasoline. A further object is to provide a process for converting cracked gasoline into high octane motor fuel which is exceptionally clean burning. It is also an object of the invention to provide a flexible process for converting cracked gasoline into high quality motor fuel and burner fuel which permits variation in the proportions of these products. Other objects of the invention will become apparent upon consideration of the accompanying disclosure.

A broad aspect of the invention comprises subjecting a heavy cracked gasoline fraction to catalytic polymerization under conditions which polymerize the more reactive components and substantially reduce the olefin content of the fraction; fractionating the polymerizate to recover an overhead gasoline fraction having an end point not substantially in excess of about 400° F. and a bottoms fraction including the polymerized material from the polymerization step; and catalytically reforming the overhead gasoline fraction so as to improve its octane rating, thereby upgrading the same. The reformate may then be blended with other high octane gasoline components such as isopentane and butane, light cracked gasoline, and/or a gasoline fraction obtained by alkylating an intermediate cracked gasoline fraction together with a light isoparaffin, with or without the addition of C_3 to C_5 refinery olefins to the feed to the alkylation step. It is generally preferred

to admix the gasoline fraction from the fractionator following the polymerization step with straight run gasoline and/or natural gasoline which has been deisopentanized.

In one embodiment of the invention a cracked gasoline stock is fractionated to recover a light overhead fraction having an end point in the range of about 275 to about 310° F. and a bottoms fraction comprising the balance of the cracked gasoline which has an end point of approximately 400° F. This heavy gasoline fraction is subjected to catalytic polymerization, fractionated to exclude the polymerized material which is suitable for burner fuel, and to catalytic reformation, preferably admixed with straight run gasoline and/or natural gasoline as described above. In accordance with one procedure the light gasoline fraction may be blended with the reformate along with other blending ingredients. In accordance with another procedure the light gasoline fraction is again fractionated into an overhead fraction having an end point in the range of 175 to 195° F. and preferably about 190° F. and a bottoms fraction comprising an intermediate gasoline having an end point of about 300° F. The bottoms fraction comprising intermediate gasoline is admixed with a C_4 to C_5 isoparaffin, such as isobutane or isopentane with or without the addition of C_3 to C_5 olefins, and the admixture is subjected to alkylation to produce high quality alkylate boiling in the gasoline range. The resulting alkylate is fractionated to recover as an overhead fraction the gasoline boiling range material and the higher boiling range materials as a bottoms fraction which is suitable for use as low-odor solvents.

To more fully illustrate the invention, reference is made to the drawing which shows a schematic arrangement of apparatus for effecting the process of the invention in some of its various aspects. A cracked gasoline is fractionated into three cuts including a light gasoline in line **10**, an intermediate gasoline in line **12**, and a heavy gasoline in line **14**. The heavy gasoline fraction having an end point of about 400° F. is introduced to catalytic polymerization vessel **16** where it is subjected to polymerization under conventional polymerization conditions including a temperature in the range of 425 to 625° F., a pressure in the range of 400 to 600 p.s.i.g., a space velocity in the range of 2.5 to 3.0 volumes of feed per volume of catalyst per hour (v./v./hr.), and in contact with a suitable polymerization catalyst, such as synthetic silica-alumina. Any conventional polymerization catalyst may be used in this step. The effluent from the polymerization step is passed via line **18** to fractionator **20** in which a separation is made into an overhead fraction having an end point of about 400° F. and a bottoms fraction of higher boiling materials which are suitable for burner fuel. The temperature in the top of fractionator **20** is preferably maintained in the range of about 330 to 350° F., while the bottom temperature is maintained in the range of about 600 to 650° F. The burner fuel is recovered via line **22** and the 400 end point gasoline fraction is passed via lines **24** and **26** to catalytic reforming vessel **28**. Straight run gasoline and/or natural gasoline, which is preferably deisopentanized, may be introduced via line **30** to reformer **28**. In instances where light components make up a sizable proportion of the overhead gasoline from fractionator **20**, it is desirable to separate the light ends therefrom, taking overhead a cut boiling up to a temperature in the range of about 175 to 195° F., such as 190° F.

The reforming step in vessel **28** is conducted under

conditions well known in the art including contacting the feed with a platinum-containing reforming catalyst in admixture with hydrogen at a temperature in the range of 850 to 950° F. and at a pressure in the range of 200 to 900 p.s.i.g. The preferred catalyst is a platinum-containing catalyst comprising platinum deposited on a cracking catalyst such as silica-alumina or alumina and containing combined halogen, particularly, fluorine. Other catalysts which may be utilized in this reaction include platinum deposited on at least one metal oxide of the group alumina, silica, thoria, and zirconia containing chemically combined alkali metal (sodium); metal oxides or sulfides of groups IV, V, VI and VIII, such as molybdena on a support of silica, alumina, and magnesia, alone, or in admixture; and platinum or palladium on a silica-alumina cracking catalyst. It has been found that removal of olefins from the feed to the reforming zone has materially increased catalyst life. The reformate is passed via line **32** to blending zone **34** for blending with other gasoline components hereinafter described.

The intermediate gasoline fraction, together with a light isoparaffin, such as isobutane, is introduced via line **12** into alkylator **36**. It is feasible and highly desirable where an abundance of light isoparaffins and olefins are available to introduce C_3 to C_5 olefins to alkylator **36** such as via line **38**. The alkylation step is effected in the presence of and in contact with a suitable alkylation catalyst, preferably HF, of 85 to 95 percent concentration. Other alkylation catalysts, such as sulfuric acid, metal halides, etc., may also be used. The temperature in the alkylator is maintained in the range of 50 to 120° F. with sufficient pressure to maintain liquid phase, such as approximately 140 p.s.i.g. Reaction time is controlled in the range of 2 to 20 minutes, preferably, about 10 minutes. The isoparaffin to olefin ratio is preferably at least 6:1 but may be maintained in the range of 3:1 to 10:1 on a volume basis.

Reactions taking place in alkylator **36** are complex. By hydrogen exchange a portion of the olefins is saturated to the corresponding paraffins or naphthenes. This reaction produces isobutylene as a byproduct from supplying hydrogen which promptly alkylates more isobutane resulting in highly branched octanes of high octane number. Another portion of the olefins alkylates isobutane to produce highly branched nonanes, decanes, undecanes, and dodecanes which are also of high octane number. In this manner high octane blending stock is made indirectly from isobutane without having to separately crack or dehydrogenate it, the isobutane dehydrogenation taking place in the alkylator.

The alkylate from alkylator **36**, after removal of isoparaffins, HF (or other catalyst) and fluorides in conventional manner, is passed via line **40** to fractionator **42** for separation of the alkylate into a deolefinized gasoline fraction taken overhead and having an end point not substantially above 400° F. The bottoms fraction comprising higher boiling hydrocarbons suitable as low-odor solvents is recovered via line **44**. The gasoline fraction from fractionator **42** taken overhead is passed via line **46** to blender **34**.

Isopentane and n-butane are introduced to blender **34** as desired via line **48** and in the same manner light gasoline is introduced to this blending zone via line **10**. The resulting motor fuel is recovered from blender **34** via line **50**.

To illustrate the invention, data are presented in Table I below which are obtained from fractionating a cracked gasoline stock and polymerizing the heavy gasoline fraction (about 400° F. end point) to cause the more reactive materials, principally olefins, to be polymerized to a good quality burner fuel. Operating conditions include a synthetic 90% silica-10% alumina (by weight) catalyst, a space velocity of 2.5 to 3.0 v./v./hr., a pressure in the range of 400 to 600 p.s.i.g., and a temperature in the range of 425 to 625° F.

TABLE I

Original distillation of cracked gasoline and catalytic polymerization treatment

	Distillation			Poly-treating heavy cracked gasoline		
	Feed to dist.	Light cracked gasoline	Heavy cracked gasoline	Light ends	Treated heavy cracked	Burner oil
Yield, volume percent	--------	48.5	51.5	6.3	78.7	12.5
ASTM dist. (° F.):						
IBP	120	132	272	106	306	465
10%	177	202	323	164	319	504
50%	267	238	341	267	344	597
90%	357	265	373	301	374	675
EP	395	300	403	332	407	--------
Reid vapor press	3.6	2.7	0.7	6.6	0.2	--------
Grav., ° API, at 60 °F	53.3	56.9	40.9	56.8	41.5	17.6
Bromine number	48	43	26	2	1	22
Oxygen stability, minutes	720	--------	690	--------	>840	--------
Sulfur, weight percent	0.150	--------	0.218	--------	0.054	--------
ASTM octane numbers:						
Clear	66.9	70.6	60.9	--------	53.6	--------
+1 ml. TEL	72.0	78.4	67.4	--------	61.2	--------
+3 ml. TEL	75.9	84.7	71.2	--------	68.8	--------
Research octane numbers:						
Clear	71.9	--------	66.0	--------	57.1	--------
+1 ml. TEL	80.2	--------	72.3	--------	65.5	--------
+3 ml. TEL	83.8	--------	78.8	--------	73.4	--------

The treatment removes olefins and sulfur compounds. Extent of removal can be controlled by varying severity of treating conditions. Some loss of octane number results but this is rectified by catalytic reforming of the product which is now low in olefin content. Also a small amount of catalytic cracking takes place during the polymerization treatment, producing the light ends shown. Octane numbers of the light ends were not determined but they should be high.

This method of operation can also be used to some extent to fly-wheel seasonal demand. In winter when gasoline demand is low (storage may be for a longer period) and extra burner fuel is needed, a wider-boiling range (i.e., more gasoline) can be charged to the polymerization process, increasing gasoline stability to allow for slower movement, decreasing amount of gasoline, and increasing burner fuel production.

The heavy, deolefinized, cracked gasoline is catalytically reformed along with straight run and natural, using conventional platinum-type catalyst and hydrogen at 200 to 900 p.s.i.g., and 850 to 950° F., to produce a high octane product.

The light cracked gasoline formed in the fractionation step can be further fractionated where necessary to produce a material which will lead to 100 octane number with 3 ml. TEL. This was not done in the example because the gasoline was somewhat deficient in light ends. Choice of end point depends on composition of the cracked gasoline available. Normally, hydrocarbons boiling up to 175 to 195° F. may be included. In many cases 190° F. is a good cut point. Amount depends largely on the normal-hexane content of the gasoline. The more n-hexane, the lower the cut point must be.

Intermediate cracked gasoline contains olefins mainly in the heptene and octene range with some nonenes. These may be fed to the alkylation unit with regular refinery olefins, such as propylene and butylenes, giving good yields of gasoline boiling-range materials. Materials boiling above 400° F. produced from this alkylation step may be used in manufacture of low-odor solvents or may go to high quality jet fuel.

Processing may be balanced to make the total refinery gasoline high octane number. For example, if 100 octane number is desired, the cut point for light cracked gasoline is chosen to make 97 to 100 octane (Research) with 3 ml. TEL. A wide-range (say 250 to 400° F.) heavy cracked

gasoline may be polymerization treated and catalytically reformed (along with straight run) to give 97 to 98 octane number (Res.) with 3 ml. TEL. The alkylation unit is operated at high isobutane to olefin ratio to produce material having 102 to 105 octane (Res.) with 3 ml. TEL. The gasoline produced in this manner is also very clean burning, consisting mainly of light olefins, heavier aromatics, and isoparaffins.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

1. A process for producing high octane motor fuel which comprises fractionating a cracked gasoline into a light, an intermediate, and a heavy gasoline fraction; subjecting said heavy fraction to catalytic polymerization at a temperature in the range of 425 to 625° F., a pressure in the range of 400 to 600 p.s.i.g., and a space velocity in the range of 2.5 to 3.0 v./v./hr., so as to polymerize the major portion of the olefins present; fractionating the effluent from said polymerization to recover an overhead gasoline fraction having an end point of about 400° F. and a bottoms fraction comprising heavy polymerized materials; catalytically reforming said overhead gasoline fraction in contact with a platinum-containing reforming catalyst and in admixture with hydrogen at a temperature in the range of 850 to 950° F. and a pressure in the range of 200 to 900 p.s.i.g. so as to produce a high octane reformate; subjecting said intermediate gasoline fraction in admixture with C_3–C_4 isoparaffins and added C_3–C_5 olefins to HF alkylation at a temperature in the range of 50 to 120° F., a pressure sufficient to maintain liquid phase, and a reaction time in the range of 2 to 20 minutes; fractionating the resulting alkylate to recover an overhead gasoline fraction having an end point not substantially above 400° F.; and blending the alkylate overhead fraction with said reformate to produce a high octane blend motor fuel.

2. The process of claim 1 including the step of blending said light gasoline fraction with said alkylate overhead and said reformate.

3. The process of claim 1 wherein straight run and deisopentanized natural gasoline are incorporated in the feed in the reforming step.

4. The process of claim 1 wherein said light gasoline fraction has an end point of about 190° F., said intermediate fraction has a boiling range of about 190 to about 300° F., and said heavy fraction has a boiling range of about 300 to about 400° F.

5. A process for producing high octane motor fuel which comprises subjecting a heavy cracked gasoline fraction to catalytic polymerization at a temperature in the range of 425 to 625° F., a pressure in the range of 400 to 600 p.s.i.g., and a space velocity in the range of 2.5 to 3.0 v./v./hr., so as to polymerize the more reactive components of said fraction to fuel suitable for burner fuel; fractionating the effluent from said polymerization to recover an overhead gasoline fraction having an end point of about 400° F. and a bottoms fraction comprising polymerized material from the polymerization step; catalytically reforming said overhead gasoline fraction in admixture with at least one gasoline of the group consisting of straight run and natural so as to improve the octane rating thereof; catalytically alkylating an alkylatable mixture comprising C_4–C_5 isoparaffins and C_3–C_5 olefins; fractionating the resulting alkylate to recover a gasoline fraction of high octane number; and blending last said fraction with at least a portion of the reformed gasoline to produce a high octane motor fuel.

6. A process for producing high octane motor fuel which comprises fractionating a cracked gasoline and recovering a light overhead fraction having an end point in the range of about 275 to about 310° F. and a bottoms fraction; catalytically polymerizing said bottoms fraction to substantially free same of olefins; catalytically reforming the effluent from said polymerizing together with at least one gasoline of the group straight run and natural; fractionating said light overhead fraction into an overhead light gasoline fraction having an end point in the range of 175 to 195° F. and an intermediate gasoline bottoms fraction; catalytically alkylating said intermediate gasoline fraction with a C_4–C_5 isoparaffin; fractionating the resulting alkylate to recover an overhead gasoline fraction having an end point not substantially above 400° F.; and blending at least a portion of said light gasoline fraction and at least a portion of said overhead gasoline fraction with at least a portion of said reformate.

7. The process of claim 5 wherein n-butane and isopentane are blended with the reformate.

8. The process of claim 6 including the step of blending isopentane and n-butane with said fuel.

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