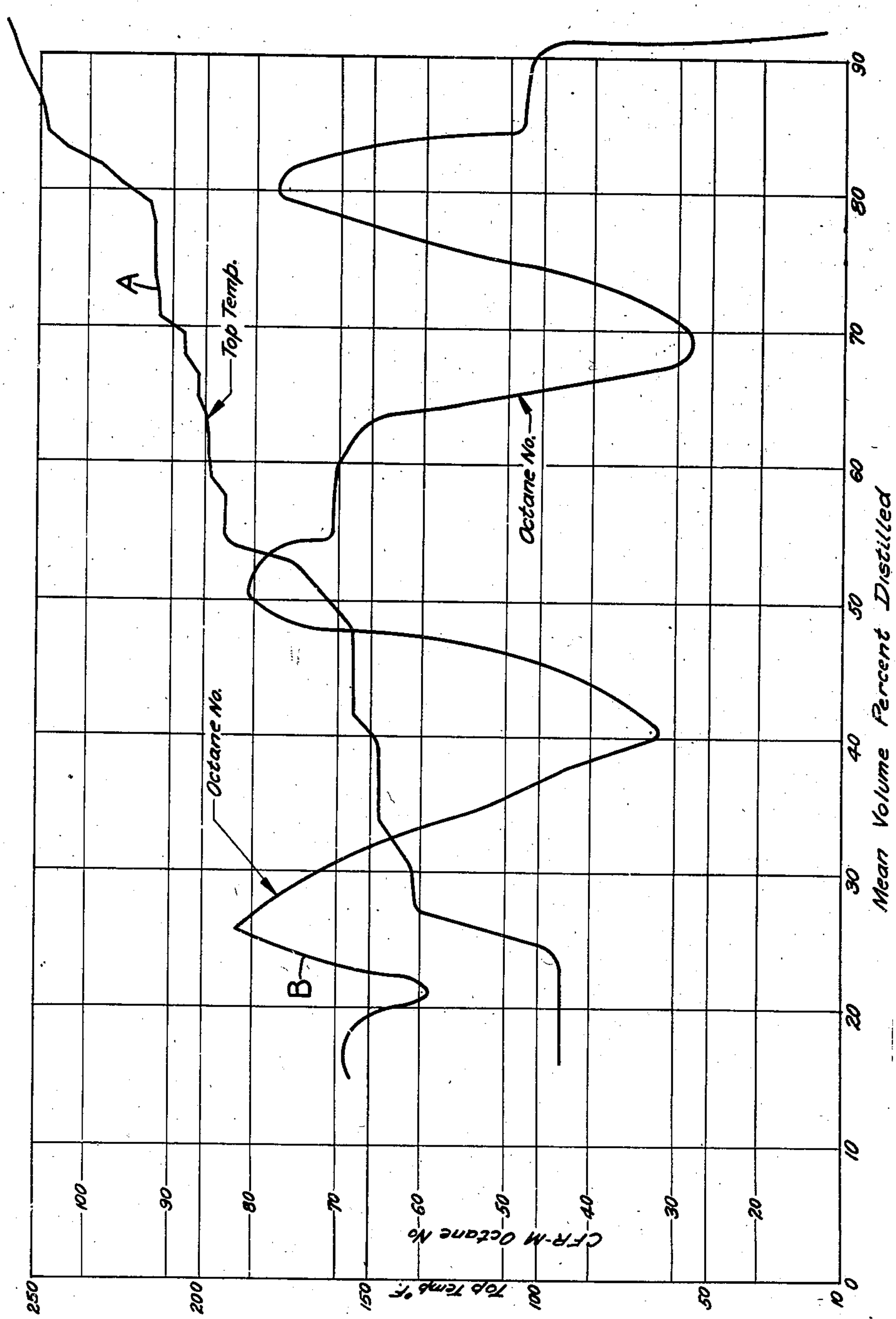
July 15, 1941. F. F. DIWOKY 2,249,461

MANUFACTURE OF ANTIKNOCK GASOLINE

Filed Aug. 17, 1937 3 Sheets-Sheet 1

FIG. 1.



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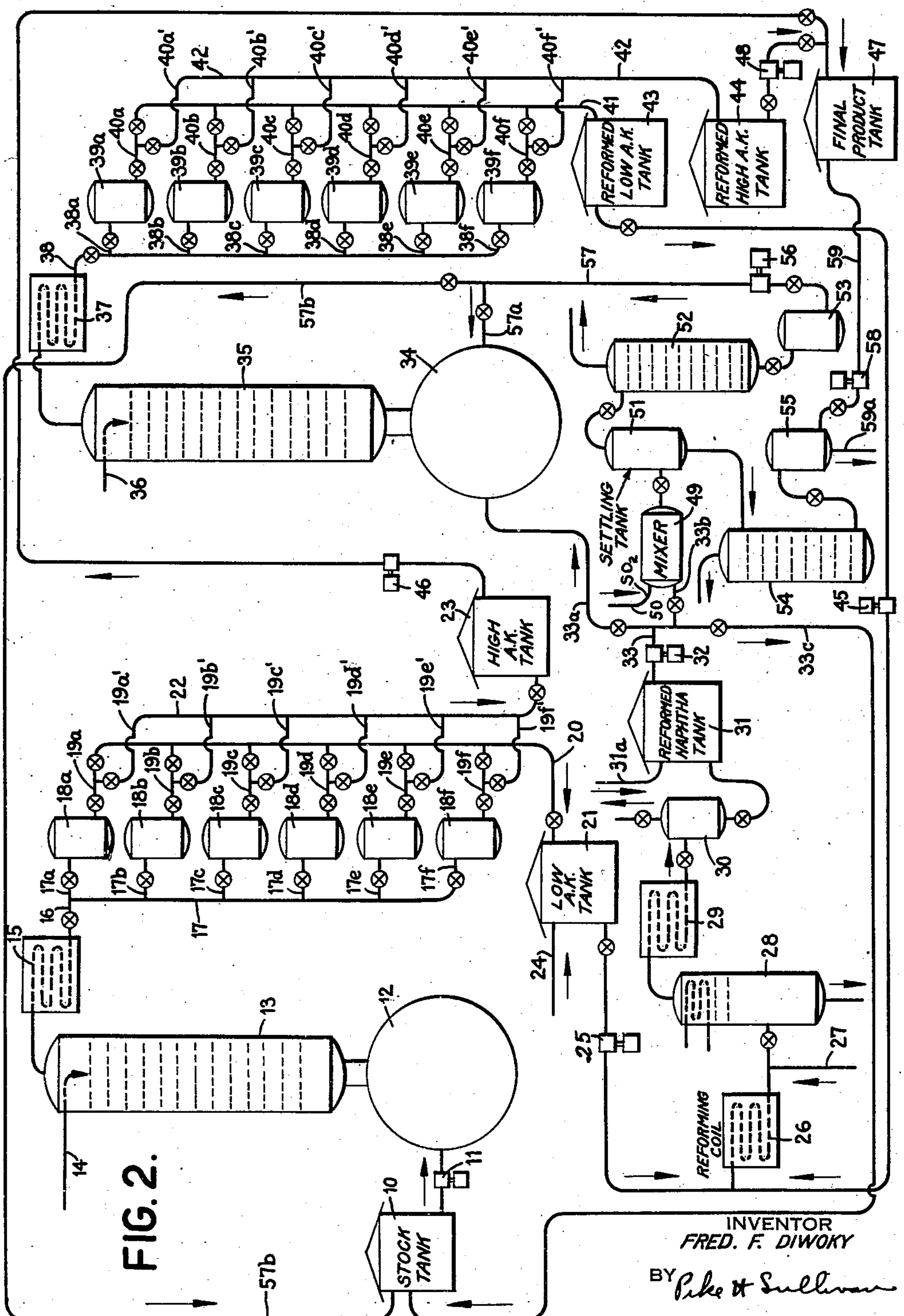

FIG. 2.

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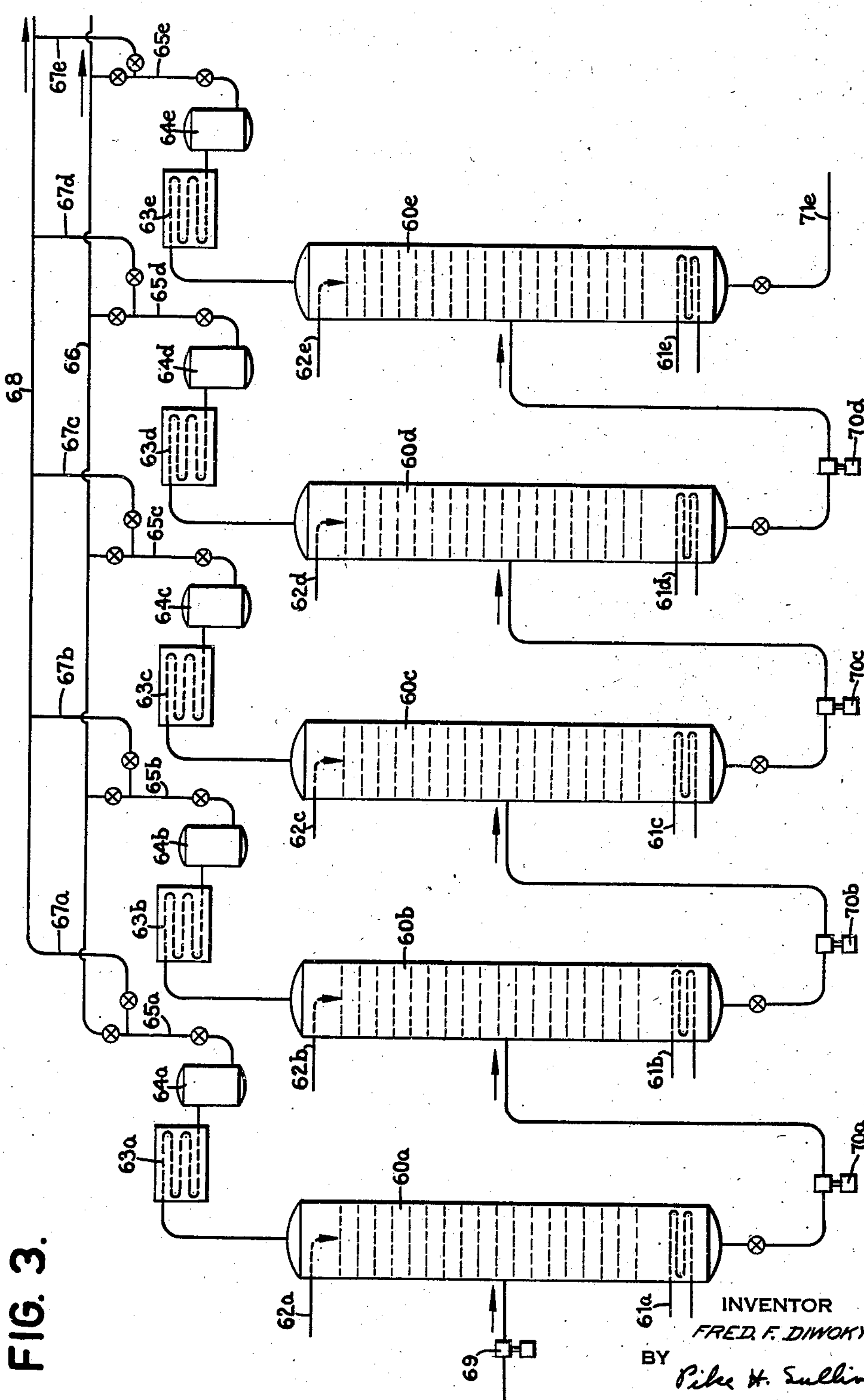
FIG. 3.



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UNITED STATES PATENT OFFICE

2,249,461

MANUFACTURE OF ANTIKNOCK GASOLINE

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Application August 17, 1937, Serial No. 159,473

4 Claims. (Cl. 196—50)

This invention relates to the manufacture of motor fuel of superior quality, particularly as regards anti-knock characteristics.

The invention contemplates a process in which a gasoline or naphtha stock is closely fractionated to form a plurality of relatively narrow boiling range cuts and the cuts of relatively lower anti-knock values collected and subjected to reforming to increase the anti-knock value of such cuts. In accordance with the invention a gasoline-containing stock is subjected to a sufficiently close fractionation as to at least approximate an analytical fractionation of the stock with reference to its hydrocarbon content. In other words, the stock is fractionated to such a degree as to concentrate individual hydrocarbons whose anti-knock value is an irregular function of boiling point. Thus when the fractionation is carried out to a sufficient degree the anti-knock value curve will exhibit marked irregularities and the cuts or fractions representing the valleys of the curve may be collected for reforming while the cuts or fractions representing the peaks of the curve may be collected to constitute a high anti-knock product, or used for blending with the gasoline product or fractions thereof produced in the reforming operation.

The invention also contemplates that the products produced in the reforming operation may be subjected to a high degree of fractionation to segregate constituents which have not been sufficiently reformed from constituents of sufficiently high anti-knock quality and subjecting the insufficiently reformed products to further reforming.

In fractionating a stock to separate low anti-knock fractions from high anti-knock fractions by means of the difference in boiling points of the fractions, a difficulty is presented due to the fact that many of the high anti-knock hydrocarbons have boiling points approximating those of the straight-chain paraffin hydrocarbons. In accordance with the invention the gasoline stock is treated, prior to fractionation, with an agent or solvent capable of selectively removing olefinic constituents. By treating the stock with a polymerizing agent to polymerize the olefins or by treating the stock with a solvent, such as liquid sulphur dioxide, the olefins may be removed so that a sharper separation between relatively high and low anti-knock constituents may be accomplished by subsequent fractionation. Highly cracked stock will ordinarily contain, in addition to olefins, proportions of aromatics and naphthenes. Many of these high anti-knock hydrocarbons will have boiling points approximating the boiling points of certain of the straight-chain paraffin hydrocarbons. In the practice of the invention the stock containing olefins, aromatics and naphthenes as well as paraffins is treated with a solvent, such as sulphur dioxide, capable of removing the bulk of the olefins and to a greater or less extent aromatics and naphthenes, thus concentrating the branched chain or iso-paraffins in the raffinate with the straight-chain paraffins and facilitating the separation, by subsequent fractionation of the raffinate, of the low anti-knock constituents from the high anti-knock constituents. The branched chain or iso-paraffins possess maximum anti-knock qualities and by removing from the gasoline stock olefins as well as aromatics and naphthenes and concentrating the iso-paraffins in the raffinate, the subsequent fractionation operates to separate the iso-paraffins from the straight-chain paraffins. It is advantageous to use solvents such as liquid sulphur dioxide from which the absorbed high anti-knock constituents may be recovered, thus accomplishing a maximum yield of high anti-knock constituents.

The invention may well be described as applied to the treatment of a gasoline stock for the production of a high grade gasoline suitable for aviation service. Thus in an example of the invention, a light naphtha obtained by the distillation of a Mid-Continent crude petroleum is subjected to fractionation with a reflux ratio of 30:1 into some seventy closely cut fractions. The following table gives the temperatures at which the several cuts are made, the octane number of the cuts (by the Cooperative Fuel Research Motor method) and the volumes of the several cuts. The first eleven cuts, being of very light character, are not used and hence the data in reference to these cuts are omitted from the table. The cuts are shown assembled in two groups, the one group including the cuts having an octane number above 68 and the other group containing the cuts having an octane number below 68.

Cuts above 68 O. N. C. F. R-M.				Cuts below 68 O. N. C. F. R-M.			
Cut No.	Temp., °F.	O. N.	Volumes c. c. at 60° F.	Cut No.	Temp., °F.	O. N.	Volumes c. c. at 60° F.
12	94	68.5	1,017				
13	88?	*69.0	857				
14	--------	69.0	881				
				15	94	*64.0	732
				16	94	61.0	549
				17	94	*59.5	515
				18	94	62.5	846
19	96	*70.0	857				
20	106	*76.0	486				
21	--------	82.0	914				
22	137	79.0	869				
23	138	77.0	789				
24	139	74.0	857				
25	--------	*68.5	857				
				26	146	*(63.0)	823
				27	148	*56.0	811
				28	147	51.0	903
				29	148	*44.0	880
				30	147	43.0	846
				31	150	*30.0	915
				32	155	32.5	915
				33	156	*37.5	915
				34	156	39.0	926
				35	155	*45.0	892
				36	157	51.5	886
37	518	*68.0	920				
38	--------	78.5	875				
39	--------	*80.0	880				
40	176	79.5	915				
41	--------	78.0	846				
42	195	*75.0	868				
43	194	71.5	824				
44	--------	*71.0	890				
45	194	70.5	901				
46	198	*70.0	841				
47	199	70.0	828				
48	199	*69.0	838				
49	200	68.0	940				
				50	202	*58.0	901
				51	202	*43.0	917
				52	206	32.5	950
				53	206	*26.0	961
				54	214	*30.0	802
				55	214	32.0	1,010
				56	215	*37.5	852
				57	215	*47.0	736
				58	216	52.0	827
				59	215	62.5	890
60	217	*70.0	947				
61	224	76.5	824				
62	230	*75.0	769				
63	240	74.5	813				
				64	247	*54.0	890
				65	248	48.5	945
				66	250	*48.0	775
				67	253	*48.0	852
				68	256	47.5	857
				69	257	*40.0	835
				70	259	14.0	865
			Total 23,103				Total 27,219

*Octane number estimated.

Résumé of fractionation

	c. c.
Light end discard	9,478
Above 68 octane number	23,103
Below 68 octane number	27,219
Bottoms	4,700
Total	64,500
Charged	64,070

The cuts having octane numbers below 68 made up a composite charge for the reforming unit having an A. P. I. gravity of 70.5, an octane number of 45.5, and an Engler distillation test as follows:

	°F.
Initial	140
10%	166
20%	174
30%	180
40%	184
50%	192
60%	200
70%	208
80%	218
90%	228
Max	266

A portion of this charging stock is subjected to reforming in one run at a temperature of 1005° F. under 300 lbs. pressure and another portion is subjected to reforming in a second run, at a temperature of 1007° F. under 300 lbs. pressure, to produce reformed gasoline products testing as follows:

	Product of 1st run	Product of 2nd run
Grav. A. P. I.	71.4	70.5
Octane No.	59.0	62.0
Engler distillation	°F.	°F.
Initial	94	92
10%	154	157
20%	171	172
30%	180	181
40%	187	188
50%	195	196
60%	201	204
70%	213	214
80%	224	225
90%	240	240
Max	358	334

Referring to the accompanying drawings:

Fig. 1 is a curve showing the octane values of a typical gasoline stock which has been highly fractionated in accordance with the invention.

Fig. 2 is a flow diagram illustrating apparatus adapted for practicing the invention.

Fig. 3 is a flow diagram of a modified type of fractionating apparatus adapted for practicing the invention.

Fig. 1 illustrates results obtained by close fractionation under batch distillation with a reflux ratio of 37:1 of a 72 A. P. I. gravity Mid-Continent light naphtha, which it was desired to use for the production of an aviation gasoline. The temperatures taken at the top of the fractionating tower are plotted as ordinates and the mean volumes in proportions distilled off are plotted as abscissa. An additional scale as ordinates is indicated for the octane values (Cooperative Fuel Research Motor method) of the several cuts or fractions. Curve A represents the top temperature of the fractionator and shows the temperatures at which the several fractions are distilled. Curve B presents marked irregularities and is in the nature of an irregular or discontinuous function with respect to the boiling points of the fractions.

In practicing the invention with the apparatus illustrated in Fig. 2, the gasoline or naphtha stock to be treated is contained in charging stock tank **10**. The stock is a highly paraffinic stock or gasoline stock of low anti-knock quality. The charging stock is drawn from the tank **10** by pump **11** and directed to a still **12** equipped with a fractionating tower **13**. The still is heated by suitable means (not shown) and reflux is supplied from a suitable source as by means of the pipe **14**. The fractionating tower is designed to effect a highly efficient fractionation and accordingly is equipped with a large number of plates or the equivalent thereof such, for example, as 30 to 50 plates and the tower and still are adapted for sustaining high reflux rates such as 20–50:1. The vapors from the tower **13** are condensed in condenser coil **15** having an outlet **16** extending to a manifold **17** provided with branch lines, as ***17a, 17b, 17c, 17d, 17e*** and ***17f***, extending to a desired number of receiving drums, as ***18a, 18b, 18c, 18d, 18e*** and ***18f***, respectively. During the distillation as the temperature in the vapor line from the fractionating tower rises, the distillate passing through the condenser outlet **16** is diverted to the several tanks ***18a, 18b***, etc., in order to collect the particular fractions desired. The distillate receivers are provided with drawoff lines ***19a, 19b, 19c, 19d, 19e*** and ***19f***, respectively, leading to a manifold line **20** and with branch lines ***19a', 19b', 19c', 19d', 19e'*** and ***19f'*** leading to another manifold line **22**. The distillates of insufficiently high anti-knock value and which it is desired to reform, are directed through manifold line **20** to the low anti-knock tank **21**. The distillates of sufficiently high anti-knock value which it is not desired to subject to reforming are drawn through manifold line **22** into the high anti-knock tank **23**.

Low anti-knock gasoline thus collected in tank **21**, to which may be added low anti-knock gasoline from an extraneous source charged into tank **21** through line **24**, is drawn by pump **25** and passed to a reforming coil **26** which is provided with suitable heating means (not shown) for raising the gasoline constituents to temperatures upwards of 850° F. to effect reformation into constituents of increased anti-knock value. The reforming operation is preferably carried on in a continuous manner. The hot products from the reforming coil **26** may be quenched with a cooling stock introduced through line **27** and the products subjected to distillation in the still **28**, the separated vapors being passed through condenser **29** and the resultant distillate collected in receiving tank **30**. The distillation is preferably so conducted as to collect a gasoline or naphtha distillate in **30** which is passed to the reformed naphtha tank **31**. A line ***31a*** is provided for introducing additional stock, such as cracked gasoline into the tank **31**.

The reformed gasoline or naphtha stock which collects in tank **31**, or the mixture of reformed stock and cracked gasoline, is withdrawn by a pump **32** having a discharge line **33** manifolded with branches ***33a, 33b*** and ***33c***. Branch line ***33a*** extends to fractionating apparatus consisting of a still **34** having a fractionating tower **35**. Branch line ***33b*** extends to treating apparatus for removing olefins which is described hereinafter and branch line ***33c*** extends to the stock tank **10**.

The still **34** is provided with suitable heating means (not shown) and with means **36** for introducing reflux and is, like still **12** and fractionating tower **13**, adapted for accomplishing a very high degree of fractionation of the gasoline or naphtha stock introduced thereto. The overhead vapors from the tower **35** pass through condenser coil **37** from which the distillate is withdrawn through the outlet **38**. The outlet **38** is manifolded with branch lines as ***38a, 38b, 38c, 38d, 38e*** and ***38f***, which lead to a desired number of receivers, as ***39a, 39b, 39c, 39d, 39e*** and ***39f***, respectively.

During the distillation as the temperature in the vapor line from the fractionating tower **35** rises, the distillate passing through the condenser outlet **38** is diverted to the several tanks ***39a, 39b***, etc. in order to collect the particular fractions desired. The distillate receiving drums are provided with drawoff lines ***40a, 40b, 40c, 40d, 40e*** and ***40f***, respectively, leading to manifold line **41** and with branch lines, ***40a', 40b', 40c', 40d', 40e'***, and ***40f'***, respectively, leading to another manifold line **42**. The distillates of insufficiently high anti-knock value and which it may be desirable to subject to additional reforming are directed through a manifold line **41** to a tank **43**, and the distillates of sufficiently high anti-knock value which may not require additional reforming, are drawn through manifold line **42** into a tank **44**. The distillate collecting in tank **43**, which is of relatively low anti-knock value as compared with the distillate in tank **44**, is subjected to further reforming and in accordance with the invention, distillate may be withdrawn from tank **43** by pump **45** and directed to the reforming coil **26**. Thus in accordance with the invention the fractionating operations carried on in still **12** with its tower **13**, and in still **34** with its tower **35**, may be run as batch operations but by accumulating distillate in tanks **21** and **43**, a continuous feed of gasoline stock may be drawn from those tanks and subjected to reforming in the reforming coil **26**.

Distillate collected in tank **23** may be withdrawn by pump **46** and directed to a final product tank **47** and distillate collected in tank **44** may be withdrawn by pump **48** and also directed into the product tank **47**. Thus the high anti-knock constituents segregated by the initial fractionating operation in still **12** and tower **13**, may, in accordance with the invention, be blended with the high anti-knock constituents of the reformed products which are segregated by means of the fractionation in the still **34** and tower **35** in the proportions desired to produce a final gasoline product of desired boiling range and high anti-knock quality.

In some cases it is not necessary to subject the products of the reforming operation to the high degree of fractionation as is accomplished in tower 35 and a single gasoline distillate of desired boiling range may be recovered from the reformed products and may be blended with the high anti-knock constituents withdrawn from the tank 23 to form a gasoline product of desired boiling range and anti-knock quality.

In a modification of the invention, reformed gasoline or naphtha stock collecting in the tank 31 may be withdrawn by means of a pump 32 and directed through the branch line 33c into the stock tank 10 or passed directly to the fractionating still 12. In this method of operation the reformed gasoline or naphtha constituents are fractionated in the still 12 and tower 13 together with the naphtha charging stock, the fractions separated out from the composite stock which are of insufficiently high anti-knock value being collected in tank 21 and directed to the reforming coil 26 while the fractions of sufficiently high anti-knock quality are directed into the tank 23 to constitute the desired gasoline product of high anti-knock quality.

When it is desired to treat the reformed gasoline or naphtha stock which collects in tank 31, or the mixed reformed stock and cracked gasoline in tank 31, for the removal of olefins, the stock is directed by pump 32 through branch line 33b into a mixer 49 for treatment with an agent adapted for selectively removing olefinic constituents. A line 50 is shown for admitting liquid sulphur dioxide into the mixer. The commingled liquid sulphur dioxide and hydrocarbons pass into a settling tank 51 in which the raffinate is separated from the extract. The raffinate, comprising largely straight-chain paraffins as well as branched-chain paraffins, is drawn off to a still 52 and subjected to distillation to distill off any sulphur dioxide contained in the raffinate and the hydrocarbon material thus freed of sulphur dioxide is directed into a tank 53. The extract in tank 51 is drawn off to a still 54 and subjected to distillation to remove the sulphur dioxide and the hydrocarbon material thus freed of sulphur dioxide and having a high concentration of olefinic constituents as well as aromatic and naphthenic constituents, is drawn off to a tank 55.

The highly paraffinic hydrocarbon material collecting in tank 53 is withdrawn by a pump 56, having a discharge line 57 with a branch line 57a leading to the still 34 and a branch line 57b leading to the still 12, and the material is subjected to fractionation in the still 34 and tower 35, or in the still 12 and tower 13, in the manner that has been previously described herein. The removal of olefinic constituents prior to this fractionation facilitates a better separation as between high and low anti-knock constituents.

The highly olefinic product collecting in tank 55 is withdrawn by a pump 58 and conducted through line 59 to the final product tank 47 for blending with the distillate from either or both of the tanks 23 and 44, or the highly olefinic product may be removed as a separate product through a line 59a.

Referring now to Fig. 3, this drawing illustrates fractionating equipment adapted for continuous operation, which may be employed in accordance with the invention in lieu of either or both of the batch operations conducted in stills 12 and 34 of Fig. 2. The continuous fractionating equipment thus illustrated includes a battery of continuous column stills, as 60a, 60b, 60c, 60d and 60e. The stills are provided with heating means 61a, 61b, 61c, 61d and 61e, respectively, and with refluxing means 62a, 62b, 62c, 62d and 62e, respectively. Each of the towers 60a, 60b, etc. is designed to effect a highly efficient fractionation and each is accordingly equipped with a large number of plates or the equivalent thereof, such for example as 30–50 plates and each is adapted for sustaining high reflux rates such as 20–50:1. Condenser coils 63a, 63b, 63c, 63d and 63e and receiving drums 64a, 64b, 64c, 64d and 64e are provided for the respective towers. Drawoff lines 65a, 65b, 65c, 65d and 65e extend, respectively, from the several receiving drums 64a, 64b, etc. to a manifold line 66. Branch lines 67a, 67b, 67c, 67d and 67e extend respectively, from the several lines 65a, 65b, etc. to a manifold line 68.

In practicing the invention with the fractionating apparatus illustrated in Fig. 3, the stock to be fractionated, such as that withdrawn from the stock tank 10, or the reformed naphtha tank 31 or the raffinate tank 53 (shown in Fig. 2) is introduced by pump 69 to the fractionating tower 60a, being preferably introduced at an intermediate point of the tower. Liquid is withdrawn from tower 60a and directed by pump 70a to tower 60b; liquid is withdrawn from tower 60b and directed by pump 70b to tower 60c; liquid is withdrawn from tower 60c and directed by pump 70c to tower 60d; and liquid is withdrawn from tower 60d by pump 70d and directed to tower 60e. Liquid from tower 60e is withdrawn through line 71e.

The fractionating operation in the towers 60a, 60b, etc. is carried on in a continuous manner with continuous charging to tower 60a by means of pump 69 and continuous passage of liquid to the other towers in succession. Constant temperature conditions are maintained in the several towers so as to take off from each tower the particular fraction desired and collect in the several receivers 64a, 64b, etc. distillates of desired boiling range. When using the continuous fractionating apparatus for the treatment of stock withdrawn from tank 10 the distillates collected in receivers 64a, 64b, etc., which are of insufficiently high anti-knock value, are directed through manifold line 66 to the low anti-knock tank 21 and to the reforming coil 26, and distillates of sufficiently high anti-knock value are directed through manifold line 68 to the high anti-knock tank 23. When using the continuous operation for fractionating the products from the reformed naptha tank 31 or from the raffinate tank 53, the distillates that are of insufficiently high anti-knock value are directed through manifold line 66 to the reformed low anti-knock tank 43 for cycling to the reforming coil and the distillates of sufficiently high anti-knock value are directed through manifold line 68 to the reformed high anti-knock tank 44.

In a specific example of the invention a stock such, for example, as the 72 A. P. I. gravity Mid-Continent light naphtha hereinbefore mentioned, is analyzed by close fractionation and shows the distillation and octane curves of Fig. 1 of the drawings. The peak and valleys in the octane curve indicate the several points at which the cuts should be made in the stock in order to segregate the high anti-knock fractions from the low anti-knock fractions. In this particular stock it may be seen that the naphtha may in a practical operation be fractionated into six cuts which will serve to divide the stock into desired high anti-knock and low anti-knock fractions. In employing the apparatus illustrated in Fig. 2, the naphtha may be charged to still 12 and five of the fractions taken off as overhead cuts being collected in receivers 18a, 18b, etc. while the still bottoms at the end of the run may constitute the sixth cut. An advantgeous operation is to include in the charging stock some heavier material which will serve as still bottoms in the still 12 in which case all of the six cuts may be collected as overhead cuts.

Describing in detail the latter method of operation, the mixed stock is charged to the still 12 and heat is applied while supplying the necessary reflux. The temperature at the top of the tower is progressively raised during the run and the several cuts taken off at the temperatures determined upon. The following tabulation shows the temperatures at which the several cuts are taken off the tower, with the tower under approximately atmospheric pressure, and gives the approximate volumes recovered, expressed as percentages of the naphtha charge (excluding the added heavier stock) and indicates the receiving drums in which the different fractions are collected:

Cut	Top temperature	Volume	Collected in
	°F.	Percent	
1	94-145	* 32½	18a
2	145-155	15	18b
3	155-200	15	18c
4	200-215	15	18d
5	215-245	6	18e
6	245-260	7½	18f

* About 16% liquid recovery due to gas loss.

Cuts 1, 3 and 5, which represent the peaks of the octane curve, are directed into the high anti-knock tank 23 and cuts 2, 4 and 6, which represent the valleys of the octane curve, are directed into the low octane tank 21. The naphtha collected in tank 21 is directed to the reforming coil 26 and subjected to reforming temperature and the reformed naphtha fractionated in still 34 or cycled back to the stock tank 10, as has been described hereinbefore.

In case it is desired to fractionate this naphtha stock in a continuous operation as by means of the apparatus in Fig. 3, the stock, preferably after being preheated, is introduced into the tower still 60a and the operation carried on as has been explained for this continuous apparatus. In making cuts similar to those made in the batch operation, with the tower stills under approximately atmospheric pressure, the top temperatures of the towers may be held as follows:

Tower	Temperature
	°F.
60a	145
60b	155
60c	200
60d	215
60e	245

In this way cuts 1, 2, 3, 4 and 5 are collected in receivers 64a, 64b, 64c, 64d and 64e respectively, and cut 6 is drawn off through line 71e. Cuts 1, 3 and 5 are directed into the high anti-knock tank 23 and cuts 2, 4 and 6 are directed into the low octane tank 21 for reforming.

In carrying on the reforming step of my invention the thermal treatment may be aided with catalysts, such as oxides of the metals of the sixth group of the periodic system, activated carbon or mixtures of activated carbon and alloys of chromium and nickel or oxides of the metals of the sixth group of the periodic system, bauxite impregnated with oxides of zinc or nickel, silica gel impregnated with activated carbon, selenium, alloys of chromium, nickel and aluminum, or the improvement in anti-knock quality may be accomplished with an isomerization agent, such as aluminum chlorid.

While I have described a particular embodiment of my invention for the purposes of illustration, it should be understood that various modifications and adaptations thereof which will be obvious to one skilled in the art, may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. In the manufacture of high anti-knock gasoline, the process that comprises primarily subjecting a gasoline stock to fractionation to separate it into a plurality of fractions of different boiling points, collecting from said fractions those fractions having relatively lower anti-knock values, subjecting the fractions thus collected to reforming conditions to effect transformation into products of increased anti-knock value including olefinic constituents, treating resultant liquid products of the reforming to separate out liquid olefinic constituents, subjecting the remaining products to fractionation to form a plurality of fractions of such narrow boiling ranges that each fraction possesses substantially only relatively high or low anti-knock values which, when plotted in relation to boiling points, exhibit an irregular or discontinuous curvilinear function, and collecting resultant fractions of higher anti-knock values and blending the same with higher anti-knock value fractions separated out in the primary fractionation to form a composite gasoline of high anti-knock value.

2. In the manufacture of high anti-knock gasoline, the process that comprises primarily subjecting a gasoline stock to fractionation to separate it into a plurality of fractions of different boiling points, collecting from said fractions those fractions having relatively lower anti-knock values, subjecting the fractions thus collected to reforming conditions to effect transformation into products of increased anti-knock value including olefinic constituents, treating resultant liquid products of the reforming to separate out liquid olefinic constituents, subjecting the remaining products to fractionation to form a plurality of fractions of such narrow boiling ranges that each fraction possesses substantially only relatively high or low anti-knock values which, when plotted in relation to boiling points, exhibit an irregular or discontinuous curvilinear function and blending one or more of the resultant fractions with one or more of the fractions of high anti-knock value produced in the primary fractionation to form a composite gasoline of high anti-knock value.

3. In the manufacture of high anti-knock gasoline, the process that comprises subjecting a gasoline stock to reforming in a reforming zone under conditions to effect transformation into products of increased anti-knock value including liquid olefinic constituents, treating resultant products of the reforming to remove liquid olefinic constituents therefrom, subjecting products remaining, after said removal of liquid olefinic

constituents, to fractionation to form a plurality of gasoline fractions of such narrow boiling ranges that each fraction possesses substantially only relatively high or low anti-knock values which, when plotted in relation to boiling points, exhibit an irregular or discontinuous curvilinear function, separately collecting resultant fractions of relatively higher and lower anti-knock values and directing lower anti-knock fractions thus collected to the reforming zone.

4. In the manufacture of high anti-knock gasoline, the process that comprises subjecting a gasoline stock to reforming in a reforming zone under conditions to effect transformation into products of increased anti-knock value including liquid olefinic constituents, treating resultant products of the reforming to remove liquid olefinic constituents therefrom, subjecting products remaining, after said removal of liquid olefinic constituents, to fractionation to form a plurality of gasoline fractions of such narrow boiling ranges that each fraction possesses substantially only relatively high or low anti-knock values which, when plotted in relation to boiling points, exhibit an irregular or discontinuous curvilinear function, separately collecting resultant fractions of relatively higher and lower anti-knock values and subjecting lower anti-knock fractions thus collected to reforming conditions to effect transformation into products of increased anti-knock value.

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