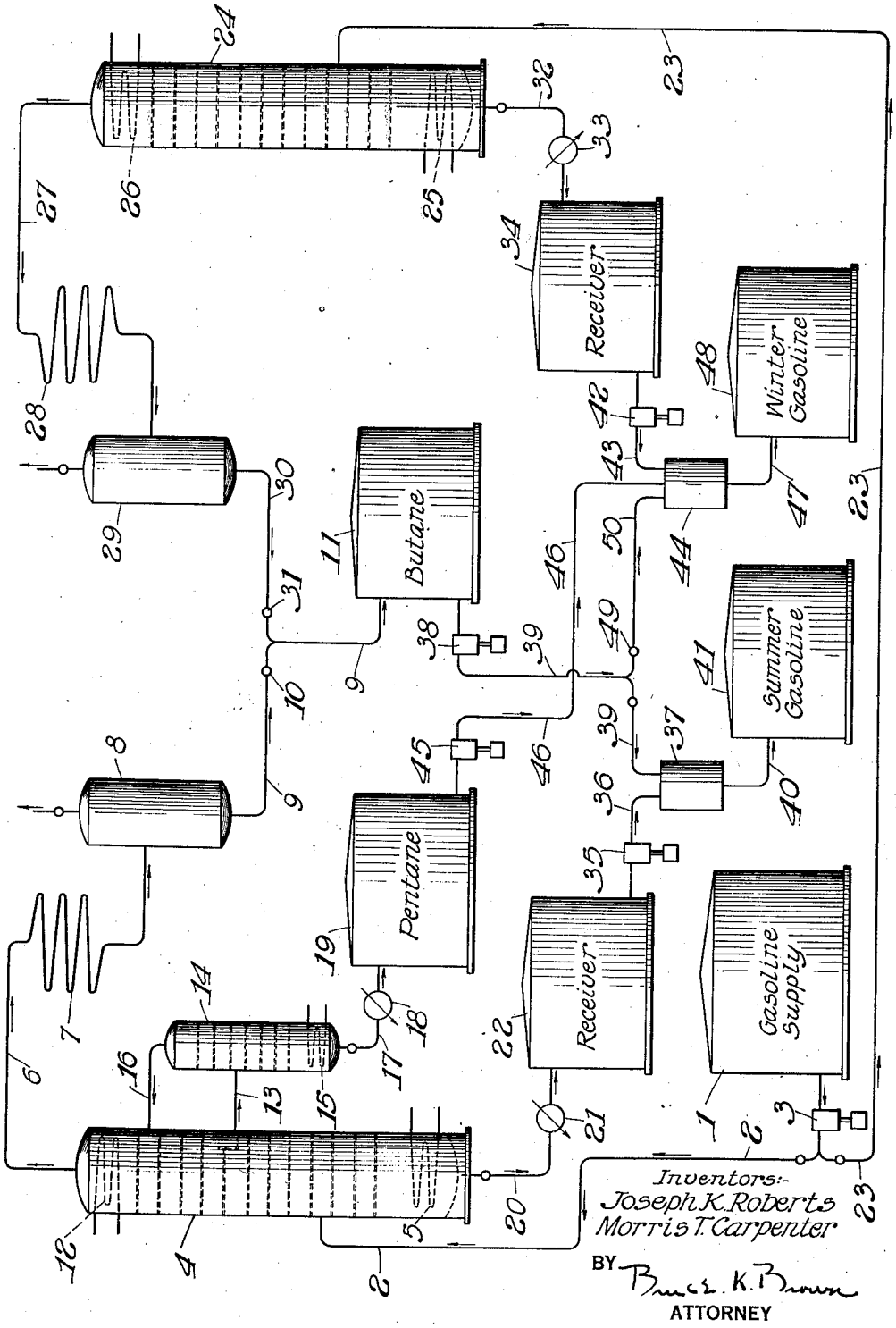
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GASOLINE MANUFACTURING PROCESS

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GASOLINE MANUFACTURING PROCESS

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This invention relates to a process of manufacturing gasoline and more particularly gasoline derived, to a large extent, from the so-called cracking process. One of the objects of the invention is to produce two grades of gasoline for use in different seasons, specifically, a summer grade for use in warm weather and a winter grade for use in cold weather. Formerly it was the practice to use the same grade of gasoline for all seasons but it has more recently been found desirable to market a more volatile grade of gasoline during the winter season than during the summer season. Higher volatility is required in cold weather in order to obtain better starting and warming up characteristics in gasoline engines resulting from more nearly complete vaporization of the gasoline in the colder induction system. The volatility of summer gasoline, on the other hand, is limited by the consideration of vapor lock which occurs when the vapor pressure of the motor fuel is sufficiently high to interfere with proper carburetion. A most convenient indication of the suitability of the gasoline in use in winter is the percent distilled off at 158° F. in an Engler distillation. The suitability of a summer gasoline for use without vapor locking trouble is best expressed by the Reid vapor pressure described as A. S. T. M. Tentative Standard—D 323—32T.

A specific object of this invention is to produce from a given source of supply of gasoline a winter gasoline having a maximum volatility as measured by percent off at 158° F. and a summer gasoline having a minimum tendency to vapor locking as measured by the Reid vapor pressure. A still further object of the invention is to produce such winter and summer gasolines from a gasoline stock of substantially unvarying composition without adding or discarding any valuable component thereof.

The invention will be readily understood by reference to the accompanying drawing which shows diagrammatically a plant suitable for carrying out the necessary operations. Referring to the drawing, a gasoline supply is indicated by tank 1 which may contain stabilized end point gasoline produced by a cracking process or a blend of cracked gasoline and virgin gasoline from crude distillation. Gasoline is withdrawn from supply tank 1 by line 2 and pump 3 to fractionator 4 where it is subjected to rectification by heat which is supplied to reboiling coil 5. The purpose of this rectification is to remove from the gasoline a substantial part of the butane and pentane fractions. The butane fraction is withdrawn from the fractionating column in the form of vapor and passed by vapor line 6 to condenser 7. The liquefied butane is collected in receiver 8 from whence it is discharged by line 9 through valve 10 and into butane storage tank 11. The fractionator 4 is preferably operated under sufficient pressure to obtain condensation of the butane vapors in the condenser 7 at ordinary cooling water temperatures. A pressure of 50–75 lbs. gage is sufficient for this purpose. A reflux coil 12, disposed in the top of the fractionator, supplies the necessary reflux liquid for obtaining separation of the butane from the heavier constituents in the gasoline, or an outside reflux condensation system may be provided. From an intermediate point in the fractionator 4 there is withdrawn by line 13 a second fraction consisting largely of pentanes. This stream is introduced into side stripper supplied by heat from reboiler coil 15 where butanes are separated from this fraction and returned, in the form of vapors, to the main rectifier by line 16. The substantially butane-free pentanes are discharged by line 17 through cooler 18 and into pentane storage tank 19.

From the base of the main fractionator 4 there is withdrawn by line 20 the remainder of the gasoline free from butanes and substantially free from pentanes. After passing through cooler 21 this stock is introduced into storage tank 22 where it is retained until further required for blending, as will hereinafter be described.

Simultaneously with the operation of fractionator 4, another stream of gasoline from supply tank 1 or other source may be passed by line 23 to fractionator 24 which is similar to fractionator 4 and operated under substantially the same conditions of temperature and pressure. Heat is supplied by reboiler coil 25 to effect satisfactory rectification in this column and refluxing is obtained by supplying a cooling fluid to reflux coil 26 or a portion of the distillate may be returned for this purpose. Butane vapors withdrawn by line 27 pass to condenser 28 and thence to receiver 29, whence condensed butane is discharged by line 30, valve 31, and line 9 into butane storage tank 11. The pressure in storage tank 11 may be maintained substantially atmospheric by means of suitable heat insulation surrounding the tank and refrigerating means to maintain the contents of the tank at a sufficiently low temperature to prevent excessive loss by evaporation in any season, or if desired, the contents of tank 11 may be held under slight pressure.

Gasoline which may be substantially butane-

free is withdrawn from tower 24 by line 32 to cooler 33 and thence to storage tank 34. This stock is later used for blending purposes, as hereinafter described.

For the manufacture of summer gasoline, stock from tank 22 is withdrawn by pump 35 and line 36 to mixer 37 where it is mixed with the proper amount of butane withdrawn from tank 11 by pump 38 and line 39. The blended gasoline thus obtained is passed by line 40 into gasoline storage tank 41.

For the manufacture of winter gasoline, stock is withdrawn from tank 34 by pump 42 and line 43 to mixer 44 where it is blended with pentane removed from tank 19 by pump 45 and line 46; after mixing in mixer 44, the resulting stock is transferred by line 47 to gasoline storage tank 48. Ordinarily the desired amount of butane will be obtained in the winter gasoline by allowing some butane to remain in the gasoline from supply tank 1. In order to obtain increased flexibility, however, butanes may be withdrawn from tank 11 by pump 38, line 39, valve 49 and line 50 to mixer 44 where they are blended with the winter gasoline stock in the desired amount.

It should be understood that in the foregoing discussion the terms butane and pentane are used to describe stocks comprised chiefly of these hydrocarbons and that for practical operation these stocks will contain a certain percentage of other hydrocarbons closely related in boiling point; for example, the butane fraction may contain from 25 to 30% of pentanes, whereas the pentane fraction may conveniently contain from 15 to 20% of butanes on the one hand and 15 to 20% of hexanes on the other. It is obviously not essential to separate from the gasoline pure butanes and pentanes for blending purposes. The composition of the fractions which are produced will naturally be considered when calculating the proportions to use in subsequent blends.

In a typical operation, cracked gasoline which has been stabilized to remove substantially all of the undesired "wild" hydrocarbons presents the following analysis:

Propane	Butanes	Pentanes	Heavier constituents	Reid vapor pressure	Percent off at 158° F.
0.1%	10.35%	11.5%	78.0%	10.3 lbs.	22

One part of this stock gasoline is fractionated in tower 4, removing therefrom substantially all the butanes or 10.35% of the gasoline, and a large part of the pentanes as required, in this case 10.9% of the gasoline. Another portion of the stock, in this case an equal volume, is fractionated in tower 24 where a substantial amount of its butane content is removed, for example 5% of the stock.

In preparing the desired summer and winter gasoline, sufficient butane from tank 11 is blended with gasoline from tank 22 to produce a summer gasoline of approximately the following composition:

Propane	Butanes	Pentanes	Heavier constituents	Reid vapor pressure	Percent off at 158° F.
0.1%	8.0%	6.1%	85.9%	8.5 lbs.	17.0

It will be noted that the amount of butanes in this gasoline exceeds the amount of pentanes by 1.9% and that the ratio of pentane to butane is 0.76.

In making the winter gasoline sufficient pentane is withdrawn from tank 19 and blended with gasoline from tank 34 to produce a winter gasoline having approximately the following composition:

Propane	Butanes	Pentanes	Heavier constituents	Reid vapor pressure	Percent off at 158° F.
0.1%	12.8%	17%	70.1%	12.6 lbs.	40

In the above analyses the term propane is intended to include both propane and propylene, the term butane includes all the four carbon atom hydrocarbons present in the gasoline and the term pentane includes all the five carbon atom hydrocarbons present.

Another example of our invention is illustrated in the following table:

Example 2

	Gasoline stock	Summer gasoline	Winter gasoline
Propane	0.1	0.1	0.1
Butane	8.6	9.0	8.0
Pentane	12.1	1.0	29.0
Balance	79.2	89.9	62.9
Percent at 158° F.	22	15	40
Reid vapor pressure	8.5	7.5 lb.	10.0

Still another example of our invention is shown in the following table:

Example 3

	Gasoline stock	Summer gasoline	Winter gasoline
Propane	0.1	0.1	0.1
Butane	10.3	10.5	10.0
Pentane	12.4	1.5	29.0
Balance	77.2	87.9	60.9
Percent at 158° F.	24	17	42
Reid vapor pressure	10.2	9.0	11.5

It will be noted that the ratio of pentane to butane in the summer and winter gasolines differs very greatly. In the Examples 2 and 3 this ratio in summer gasoline is only 0.11 and 0.14 respectively, whereas in winter gasolines the ratio is 3.6 and 2.9. This ratio is characteristic of our winter and summer gasolines and is always lower for the summer gasoline than for the winter gasoline. It will be noted also that the amount of butane in the summer gasoline exceeds the amount of pentane by 9% in this example.

From these analyses it will be observed that starting with a stock which is satisfactory neither for winter nor summer use because it is of too low volatility for winter and too high Reid vapor pressure for summer, we have produced a winter and summer gasoline admirably suited for the requirements of these seasons. This is accomplished principally by the novel expedient of removing a large part of the pentane fraction from the summer gasoline stock and adding it to the winter gasoline stock, at the same time replacing the pentanes removed from the summer gasoline stock by butanes. The result is a winter gasoline of high volatility and relatively low vapor pressure, owing its volatility largely to pentanes; and a summer gasoline of relatively low volatility but yet quite satisfactory for summer

use, and a Reid vapor pressure sufficiently low to meet the requirements of the summer season.

We believe we have produced by our process a summer gasoline having certain desirable properties which have not been hitherto obtained. One of the outstanding properties of this gasoline is the quick starting resulting from the rapid vaporization of butane which it contains in larger proportion than any summer gasoline heretofore produced. It will be noted that the amount of butanes present actually exceeds the amount of pentanes present. Another advantage of this gasoline over ordinary gasolines owing their volatility largely to pentanes and heavier hydrocarbons lies in its lower tendency to vapor lock in hot weather when compared with ordinary summer gasolines having the same Reid vapor pressure. This advantage is apparently due to the loss of butane which occurs in handling in hot weather and which has a greater influence in reducing the Reid vapor pressure than the equivalent loss of pentanes and heavier hydrocarbons contained in ordinary summer gasolines.

There is another feature of our new summer gasoline which results from the lesser content of highly volatile hydrocarbons obtained in relation to the vapor pressure. This is the behavior in the fuel line and carburetor when subjected to elevated temperatures as in hot weather driving of automobiles. Under these conditions a lesser amount of vapor is formed, thereby resulting in less trouble or vapor lock, inasmuch as the relation of vapor pressure to percent evaporated is represented by a steeper curve than in the case of ordinary summer gasolines depending for their volatility on a large content of pentane.

In carrying out the process of this invention we may employ a distillate directly from the cracking operation, containing both lighter and heavier hydrocarbons than desired in the gasoline. In this case it is preferred to carry out the fractionation for the separation of butane and pentane under higher pressures than those described and eliminate the propane in the same operation as used to separate butane and pentane. In this case it is also convenient to employ a single fractionating column and remove the butane from a side stripper, much as shown for removal of pentane in the apparatus described herein. The wild gases, including propane and ethane, may also be rejected along with some butane to be later recovered by an absorption process from which the butane is fractionated from the propane and returned to the system. Where the pressure distillate contains hydrocarbons boiling above the desired end point, these are eliminated by a redistillation of the gasoline. This may be accomplished by flash evaporation of the stock flowing from the bottom of the fractionating tower and distillation of the remaining unevaporated stock to obtain the desired end point. This unevaporated stock may be treated with sulfuric acid or fuller's earth before final distillation for the improvement of gum stability, color etc. and antioxidants may be added to the finished gasoline.

In applying our process to the operations of a petroleum refinery it will sometimes be desirable to produce only 1 grade of gasoline at one particular season. For example, in the spring and summer it will often be desirable to produce only summer gasoline while in the fall and winter it may be desirable to produce winter gasoline only. Under these conditions we may retain in storage pentane produced in the summer gasoline manufacturing operation and draw upon this storage of pentane when it is desired to produce winter gasoline or, vice versa, we may store up butane produced in the winter gasoline manufacturing operation and retain it in storage, refrigerated or under pressure, or blended in heavier gasoline stocks until required for use in manufacturing summer gasoline. This feature of the process makes it particularly suitable for meeting varying demands of different gasolines and avoids the necessity of carrying large stocks of one gasoline or the other from one season to the next where this is not desired, as in the case of a shortage of storage capacity.

It should be understood that our invention is not limited to producing any specific vapor pressure or degree of volatility in summer and winter gasolines and we do not intend to be limited by the examples set forth. We ordinarily employ our process, however, to produce winter gasolines having a volatility of between 30 and 45% off at 158° F. and a Reid vapor pressure of between 10 and 16 lbs. The summer gasolines produced by our process will ordinarily possess vapor pressures below 10 lbs. Reid and usually between 6 and 9 lbs. Reid while the percent evaporated at 158° F. will usually be from 7 to 18%. The volatility of the winter gasoline will always be higher than that of the summer gasoline and this will be true of the vapor pressure also.

We claim:

1. The process of producing winter and summer gasolines from a single gasoline supply of relatively unvarying composition, comprising fractionating a portion of said supply gasoline to remove therefrom a fraction rich in pentane hydrocarbons and produce a gasoline deficient in pentane hydrocarbons but suitable for summer gasoline requirements characterized by having a ratio of pentanes to butanes less than 1 and more than 0.11 and a volatility of between about 7 and 18% off at 158° F., and combining said pentane-rich fraction with a further quantity of said supply gasoline to produce a gasoline having a higher concentration of pentane hydrocarbons suitable for winter gasoline requirements.

2. A motor fuel adapted for use in warm weather comprising a mixture of hydrocarbons boiling within the gasoline boiling range and containing hydrocarbons of the aliphatic series beginning with butane and pentane and substantially free from propane contamination, characterized by having a ratio of pentane hydrocarbons to butane hydrocarbons less than one and more than 0.11 and between about 7 and 18 percent evaporated at 158° F.

3. The process of producing from a single supply of gasoline of unsuitable volatility and vapor pressure characteristics for either summer or winter use, a winter gasoline having a vapor pressure of between 10 and 16 pounds Reid and a percent evaporated at 158° F. between 30 and 45 and a summer gasoline having a vapor pressure between 6 and 10 pounds Reid and a percent evaporated at 158° F. of between 7 and 18, and further characterized by having a ratio of pentanes to butanes less than 1 and more than 0.11 comprising removing pentane hydrocarbons from a portion of said initial gasoline intended for the production of said summer gasoline and blending said pentane hydrocarbons with another portion of said initial gasoline to produce said winter gasoline.

4. The method of producing satisfactory sum-

mer and winter gasoline from a single gasoline supply of relatively constant composition but unsuitable for either summer or winter use because of excessive vapor pressure for summer and insufficient volatility for winter, comprising removing pentane from one portion of said gasoline supply to reduce the pentane content substantially below the content of butane thereof, and incorporating said pentane in another portion of said gasoline supply to increase the pentane content thereof substantially above the content of butane in said other portion, said summer gasoline characterized by having a volatility of about 7 to 18% evaporated at 158° F. and by having a ratio of pentanes to butanes less than 1 and more than 0.11.

5. Improved motor fuel having a relatively low volatility and a relatively high vapor pressure adapted for summer gasoline requirements, comprising a petroleum hydrocarbon distillate boiling within the gasoline boiling range having a volatility of about 7 to 18% off at 158° F. and containing fractions boiling within the range of butanes and pentanes, the amount of said butane fraction exceeding the amount of said pentane fraction by from 1.9 to 9% of said total gasoline.

6. A motor fuel adapted for use in warm weather comprising a mixture of hydrocarbons boiling within the gasoline boiling range and containing hydrocarbons of the aliphatic series beginning with butane and pentane and substantially free from propane contamination, characterized by having a ratio of pentane hydrocarbons to butane hydrocarbons within the range of about 0.14 and 0.76 and further characterized by a volatility between about 7 and 18% evaporated at 158° F.

7. In the process of producing gasoline having volatility characteristics suitable for summer use, from a supply gasoline of substantially uniform composition, the steps which comprise removing from said supply gasoline a fraction comprising chiefly hydrocarbons of the butane boiling range, and a separate fraction comprising chiefly hydrocarbons of the pentane boiling range, leaving a blending stock deficient in both butanes and pentanes, and combining amounts of the butane boiling range fraction with said blending stock to give a product for use as a summer gasoline having a Reid vapor pressure of about 6 to 10 pounds, a volatility of about 7 to 18% off at 158° F. and a ratio of pentanes to butanes less than 1 and more than 0.11.

8. In the process of producing gasolines of widely differing volatility characteristics and suitable for winter use and summer use respectively, from a supply gasoline of substantially uniform composition but having volatility characteristics which as such are not best designed for particular climatic conditions, the steps which comprise removing from said gasoline a fraction comprising chiefly hydrocarbons of the butane boiling range, and a separate fraction comprising chiefly hydrocarbons of the pentane boiling range, leaving a blending stock deficient in both butane and pentane, combining amounts of the butane boiling range fraction with said blending stock to give a product having a ratio of pentanes to butanes less than 1 and more than 0.11, said product having a Reid vapor pressure of about 6 to 10 pounds and a volatility of about 7 to 18% off at 158° F. for use as a summer gasoline, and combining said pentane boiling range fraction with supply gasoline whereby a winter gasoline is produced which contains more pentane boiling range hydrocarbons than are contained in the supply gasoline.

9. The process of preparing from a supply gasoline a summer motor fuel and a winter motor fuel having desired volatility characteristics, which comprises the steps of removing from said gasoline two fractions of hydrocarbons, one of which contains a relatively high concentration of butane and the other a relatively high concentration of pentane and separately collecting said fractions, combining a portion of the fraction relatively high in pentane with a partly debutanized gasoline to prepare said winter motor fuel, and combining a sufficient amount of the fraction relatively high in butane with a portion of the partially debutanized and depentanized gasoline to produce a summer motor fuel with a ratio of pentanes to butanes less than 1 and more than 0.11, and a volatility of between about 7 and 18% off at 158° F.

10. The process of producing two grades of gasoline from a gasoline supply of substantially uniform composition, one of said grades of gasoline being adapted for use as a summer motor fuel, having a ratio of pentanes to butanes less than 1 and more than 0.11, and a volatility of between about 7 and 18% off at 158° F. and the other being adapted as a winter motor fuel, having a higher proportion of pentanes than butanes and a higher concentration of pentanes than that of the original supply gasoline, comprising separating from said supply gasoline a fraction boiling predominantly within the range of butanes, further separating from said supply gasoline a fraction boiling predominantly within the range of pentanes, and leaving a plurality of gasoline stocks, one of which is deficient in pentanes, combining said gasoline stock deficient in pentanes with said predominantly butane fraction to produce said summer grade of gasoline and combining another of said gasoline stocks with said predominantly pentane fraction to produce said winter gasoline.

11. In the process of adapting the pressure distillate produced by a cracking plant to the varying volatility requirements of winter and summer motor fuels having a Reid vapor pressure between about 10 and 16 pounds and a volatility of about 30 to 45% off at 158° F. and a Reid vapor pressure between about 6 and 10 pounds and a volatility of about 7 to 18% off at 158° F. respectively, the steps which comprise forming debutanized and depentanized pressure distillate from the pressure distillate supply, a fraction rich in hydrocarbons boiling within the range of butane, and a fraction rich in hydrocarbons boiling within the range of pentane, adding sufficient quantities of the fraction rich in hydrocarbons boiling within the range of butane to some of the debutanized and depentanized pressure distillate to produce a summer gasoline of the desired volatility characteristics and having a ratio of pentanes to butanes less than 1 and more than 0.11, and adding sufficient quantities of the fraction rich in hydrocarbons boiling within the pentane range to some of the undebutanized and undepentanized pressure distillate supply to produce a winter gasoline of the desired volatility characteristics.

12. In the process of adapting the pressure distillate produced by a cracking plant to the varying volatility requirements of a winter and a summer motor fuel having a Reid vapor pressure of about 10 to 16 pounds and a volatility of about 30 to 45% off at 158° F. and a Reid vapor

pressure of about 6 to 10 pounds and a volatility of about 7 to 18% off at 158° F. respectively, the steps which comprise forming a partially debutanized fraction and a partially depentanized fraction from the pressure distillate supply, a fraction rich in hydrocarbons boiling within the range of butane, and a fraction rich in hydrocarbons boiling within the range of pentane, adding sufficient quantities of the fraction rich in hydrocarbons boiling within the range of butane to the partially depentanized pressure distillate supply to produce a summer gasoline of the desired volatility characteristics having a ratio of pentanes to butanes less than 1 and more than 0.11, and adding sufficient quantities of the fraction rich in hydrocarbons boiling within the pentane range to the partially debutanized pressure distillate to produce a winter gasoline of the desired volatility characteristics.

13. The method of making seasonal gasolines from a supply gasoline of substantially constant composition which comprises making a summer gasoline of abnormally high vapor pressure with respect to its volatility by removing a sufficient amount of the fraction boiling within the range of pentane from gasolines marketed in the summer season without appreciably affecting the butane content thereof, said summer gasoline being characterized by a volatility of between about 7 and 18% off at 158° F. and a ratio of pentanes to butanes less than 1 and more than 0.11, and blending said removed pentane fraction with said supply gasoline of substantially constant composition to make a winter gasoline characterized by abnormally high volatility with respect to its vapor pressure.

14. The process of manufacturing gasoline suitable for summer and winter use from the products of a cracking operation containing gasoline and hydrocarbon gases undesirable in the gasolines, comprising eliminating said undesirable hydrocarbon gases together with butane, recovering said butane by an absorption process, separating from said products a portion of the gasoline from which pentane has not been removed, a hydrocarbon fraction boiling predominantly within the range of pentanes and a portion of gasoline from which pentane has been removed, adding said recovered butane to said portion of gasoline from which pentane has been removed to produce a summer gasoline having a ratio of pentanes to butanes less than 1 and more than 0.11, and having a volatility of about 7 percent to 18 percent evaporated at 158° F., and adding said pentane fraction to a portion of the gasoline from which pentane has not been removed to produce a winter gasoline.

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