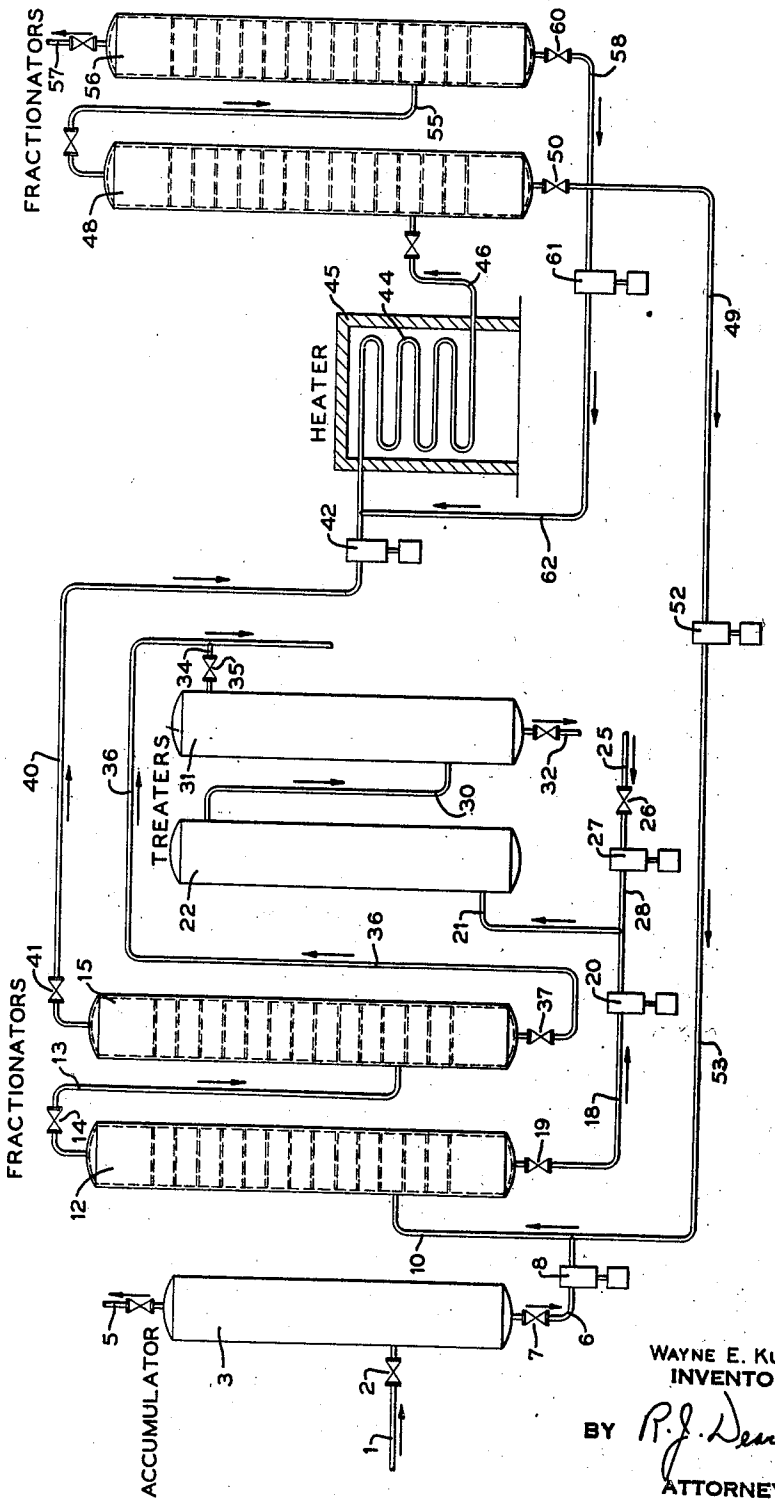
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TREATMENT OF CRACKED DISTILLATES

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TREATMENT OF CRACKED DISTILLATES

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This invention relates to the treatment of cracked distillates to produce an increased yield of high quality finished gasoline.

The invention contemplates broadly the separation of a cracked distillate into lighter and heavier fractions, subjecting the heavier fraction to a refining operation to remove impurities, separating from the lighter fraction normally gaseous hydrocarbons undesired in the finished gasoline, combining the remainder of the lighter fraction with the refined heavier fraction, subjecting said normally gaseous hydrocarbons to polymerization to form additional gasoline hydrocarbons, separating the polymer naphtha from the polymerization products and returning said polymer naphtha to the system to undergo treatment in conjunction with said cracked distillate.

More particularly, in accordance with the invention, a naphtha distillate requiring strong refining treatment is subjected, preferably after the separation of fixed gases, to fractionation to separate the naphtha into a lighter portion requiring no drastic refining treatment and a heavier portion which is subjected to rather drastic refining to remove impurities, such as sulfur compounds and unstable color and gum forming hydrocarbons. The lighter portion is thereafter fractionated to remove therefrom the more volatile constituents unsuitable for inclusion in the finished gasoline. The remainder of the light portion is then combined with the treated heavier portion to produce a finished gasoline. The more volatile materials removed from the light fraction, comprising normally gaseous hydrocarbons, are subjected to polymerization to form normally liquid hydrocarbons suitable for gasoline manufacture. These normally liquid hydrocarbons are separated from the polymerization products and returned to the system for treatment in conjunction with the cracked distillate to increase the yield and improve the quality of the finished product.

The following description of the invention should be read in connection with the accompanying drawing which shows in elevation a sketch of apparatus suitable for carrying out the process of the invention.

Referring to the drawing, a charging stock which may be a cracked distillate from an adjacent cracking still or other refinery motor fuel distillate, comprising normally gaseous hydrocarbons suitable for polymerization and gasoline constituents requiring refining treatment, as herein described, is passed through the line 1 controlled by valve 2 to accumulator 3. This accumulator may be connected with cracking stills and maintained under considerable pressure, for example around 200 pounds, and at a temperature of about 100–125° F. The product collected in the accumulator 3 ordinarily contains all or a portion of the gaseous hydrocarbons evolved in previous cracking or formation of the distillate. A portion of the gaseous materials, preferably the fixed or uncondensable gases, such as hydrocarbons of one and two carbon atoms and a portion of the hydrocarbons of three carbon atoms, are released from the top of accumulator 3 through valve controlled line 5. The distillate is then drawn from the bottom of the accumulator through the line 6 controlled by valve 7 and forced by the pump 8 through the line 10 to a fractionator 12. In this fractionator or debutanizer, a fraction comprising hydrocarbons of four carbon atoms and lighter is separated and passed through the vapor line 13 controlled by valve 14 to a secondary fractionator 15. Considerably lower pressure, for example around 75 to 100 pounds, may be maintained on the fractionator 12 than on the accumulator 3. It is intended that a lighter cut requiring no drastic chemical treatment be separated from a heavier cut requiring such drastic treatment. About 20 to 40%, preferably around 30% of such light fraction is ordinarily removed in the fractionator 12.

The heavier cut is removed from the bottom of the fractionator 12 through the line 18, controlled by valve 19. This fraction ordinarily contains impurities such as sulfur compounds and unsaturated color and gum forming hydrocarbons which are undesirable in the finished gasoline and require rather drastic treatment with refining agents to effect their removal. The treatment applied to the fraction may include one or more operations such as treatment with adsorptive materials, such as fuller's earth in the vapor or liquid phase, acid treatment, alkali washes, etc. The heavy naphtha is forced by the pump 20 through the line 21 to mixing chamber 22 wherein it is intimately mixed with a refining reagent. In the drawing I have shown an apparatus suitable for an acid treating operation although it will be understood that other types of operation, referred to heretofore, may be used. An acid such as sulfuric acid is drawn from a source of supply, not shown, through the line 25 controlled by the valve 26 and forced by the pump 27 through the line 28. Line 28 communicates with line 21 wherein the acid is conducted along with the distillate to the mixer 22. The

mixer 22 may be any suitable type of apparatus for effecting contact between the acid and the oil, such as a stirring mechanism, orifice plates, or a suitable type of apparatus for carrying out an operation involving the counter-current flow principle. Products from the mixer 22 overflow through the line 30 to settler 31 wherein the acid sludge settles out and may be withdrawn from the bottom of the settler through the valve controlled line 32. It is to be understood that one or more settlers, washing and neutralizing chambers may be employed. The acid treated product which may be previously washed, neutralized and rerun is withdrawn from the top of the settler 31 through line 34 controlled by valve 35, and combined with a lighter portion of the gasoline in the line 36. The mixture so formed may be suitable for use as a motor fuel or be further treated, for example by sweetening.

The lighter portion of the distillate, separated in the fractionator 12 and conducted to the fractionator 15, is subjected to fractionation in the fractionator or depropanizer 15 to separate the lighter normally gaseous hydrocarbons undesired in the finished gasoline. In this fractionator the hydrocarbons of three carbon atoms and all or a portion of those of four carbon atoms are separated. The remainder of the lighter cut is withdrawn from the bottom of the fractionator 15 through the line 36, controlled by valve 37, and combined with the refined heavier cut, as referred to heretofore. The normally gaseous hydrocarbon fraction, including a portion or all of butane and propane, is withdrawn from the top of the fractionator 15 through the line 40 controlled by valve 41.

It is intended that this gaseous hydrocarbon fraction be subjected to polymerization to form normally liquid hydrocarbons suitable for manufacture of gasoline. A thermal or catalytic polymerization process may be used, depending on the nature of the gases. If the gases are highly unsaturated it may be advantageous to use a catalytic polymerization operation in which the olefins are polymerized in the presence of a catalyst such as phosphoric acid. If the gases are largely saturated, it is preferable to use a thermal polymerization operation. In the drawing an apparatus intended for carrying out a thermal polymerization is shown. For this purpose, the gases in the line 40 are forced by the pump 42 to a heating coil 44 located in a heater 45. Conditions maintained in the coil 44 are those commonly used in thermal polymerization, for example pressures of 500–5000 pounds and temperatures of 900–1100° F., preferably pressures of about 2000 pounds and temperatures of around 1050° F. The reaction products are transferred through the line 46 in which may be located a heat exchanger, not shown, to fractionator 48. In the fractionator 48 the normally liquid hydrocarbons are separated as a polymer naphtha which may be withdrawn from the bottom thereof through the line 49 controlled by valve 50.

The polymer naphtha so withdrawn is forced by pump 52 located in the line 49 through the line 53 back to the system to undergo treatment in conjunction with the cracked distillate. This naphtha is preferably combined with the distillate to be treated prior to separation into the lighter and heavier fractions and may be so combined, either in accumulator drum 3 or the fractionator 12. In the drawing means are shown for combining the two in the fractionator 12. It will be understood that polymer naphtha may be introduced into the accumulator 3 and the latter may be advantageous in case appreciable amounts of fixed gases are present in this naphtha.

All or a portion of the C_3 and C_4 hydrocarbons may be retained in the polymer. However, it is preferable, particularly in a thermal polymerization operation such as carried out in the apparatus in the drawing, that the C_3 hydrocarbons and all or a portion of the C_4 hydrocarbons be separated in the fractionator 48 and withdrawn from the top thereof through the line 55 and introduced into the secondary fractionator 56. In the latter fractionator, materials lighter than the C_3 hydrocarbons are separated and released from the top of the fractionator through the valve controlled line 57. The heavier gaseous fractions comprising C_3 and C_4 hydrocarbons are withdrawn from the bottom of the fractionator through the line 58, controlled by valve 60 and recycled by the pump 61 through the line 62 back to the heating coil 44.

As an example of the operation of the invention, cracked distillate, such as that found in the accumulator drum of a cracking still used for cracking heavy oils under heat and pressure in the liquid and vapor phase, and in which the fixed gases, such as methane, ethane, ethylene and a portion of the propylene and propane have been released, is subjected to fractionation or debutanization. In the debutanization operation approximately 30% of the light constituents including C_3 and C_4 hydrocarbons are separated from the naphtha bottoms. The heavier fraction or naphtha bottoms is subjected to acid treatment with sulfuric acid and after separation of the sludge, washed, neutralized and preferably redistilled. The lighter fraction from the debutanizer is subjected to further fractionation or depropanization to separate materials lighter than C_4 hydrocarbons and as much of the C_4 hydrocarbons as required to give the proper volatility of the finished gasoline. The remainder of the lighter fraction or bottoms from the depropanizer is then combined with the acid treated heavier cut and the mixture further treated, for example by sweetening if necessary, to form a finished gasoline. The overhead from the depropanizer, comprising normally gaseous hydrocarbons chiefly of three and four carbon atoms, is then subjected to thermal polymerization under a pressure of about 2000 pounds and temperature of about 1050° F. and time of about 90 seconds, whereby a substantial amount of normally liquid hydrocarbons is formed. A polymer naphtha corresponding to over 50% conversion is separated from the polymerization products and returned to the system for retreatment. Since the polymer naphtha may require refining treatments similar to those given to the cracked distillate, this polymer naphtha is combined with the cracked distillate in the debutanizer and thereafter is subjected to the refining treatment heretofore described as given to the cracked distillate. The finished gasoline, comprises the original cracked distillate and polymer naphtha. This finished product is a high quality motor fuel having an antiknock value of 75 or higher.

The present invention provides a unitary process for treating cracked distillates to obtain a maximum yield of high quality finished gasoline. The process has the advantage of utilizing the rejected lighter materials from the cracked distillate by converting them into an additional quantity of gasoline. The polymer naphtha ob-

tained from these ordinarily rejected gaseous hydrocarbons is furthermore advantageously recombined with the cracked distillate prior to the refining treatment of the cracked distillate whereby both products are refined in one operation. In this way the gasoline constituents of both the cracked distillate and the polymer naphtha are refined and recovered as a finished gasoline while the lighter normally gaseous components are accumulated and subjected to thermal polymerization. According to the process of the invention, increased yields are obtained and the blending and treating of the products are accomplished in a more economical and facile manner. By blending the cracked distillate and polymer naphtha prior to treating, the efficiency and quality of the operation are increased because of the modifying effects obtained by the presence of the two ingredients in the mixture.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the treatment of cracked distillates, which comprises separating the distillate into lighter and heavier fractions, subjecting the heavier fraction to a refining operation to remove impurities, separating normally gaseous hydrocarbons from the lighter fraction, subjecting said gaseous hydrocarbons to polymerization, recovering a polymer naphtha and recirculating said naphtha to the first mentioned separation operation.

2. A process for the treatment of cracked distillates, which comprises separating the distillate into lighter and heavier fractions, treating the heavier fraction with a chemical refining reagent, separating normally gaseous hydrocarbons from the lighter fraction, combining the remaining lighter fraction with the treated heavier fraction, subjecting the separated normally gaseous hydrocarbons to polymerization, separating a polymer naphtha from the polymerization products and commingling said polymer naphtha with the cracked naphtha to be treated.

3. A process for the treatment of cracked distillates, which comprises separating the distillate into lighter and heavier fractions, acid treating the heavier fraction, separating from the lighter fraction less volatile portion suitable for gasoline, combining the said less volatile portion with the acid treated heavier portion, subjecting a more volatile portion of the light fraction to polymerization, recovering a polymer naphtha from the polymerization products, and combining the polymer naphtha with the cracked distillate prior to separation thereof into lighter and heavier fractions.

4. A process for the treatment of cracked motor fuel distillates, which comprises separating from the distillate fixed gases consisting mainly of hydrocarbons of one and two carbon atoms, then fractionating to separate a lighter portion amounting to around 30%, acid treating the remaining heavier portion, separating from the lighter portion normally gaseous hydrocarbons comprising C_3 and C_4 hydrocarbons and readding the remainder of the lighter portion to the treated heavier portion, subjecting said normally gaseous hydrocarbons to polymerization, recovering a polymer naphtha from the polymerization products and returning said naphtha to the system to be treated in conjunction with said cracked distillate.

5. A process for the treatment of cracked distillates, which comprises separating the distillate into lighter and heavier fractions, subjecting the heavier fraction to refining to remove impurities, fractionating the lighter fraction into a normally gaseous hydrocarbon fraction and higher boiling fraction comprising light ends of gasoline, retaining a substantial amount of C_4 hydrocarbons in said fraction comprising light ends of gasoline, blending said fraction comprising light ends of gasoline with the refined heavier fraction to obtain a product of about gasoline volatility, subjecting said normally gaseous hydrocarbon fraction to polymerization, separating a polymer naphtha, and returning said polymer naphtha to the first mentioned separation operation.

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