Nov. 23, 1937. E. H. BARLOW ET AL 2,099,835

PROCESS OF PRODUCING GASOLINE FROM CRACKED NAPHTHA

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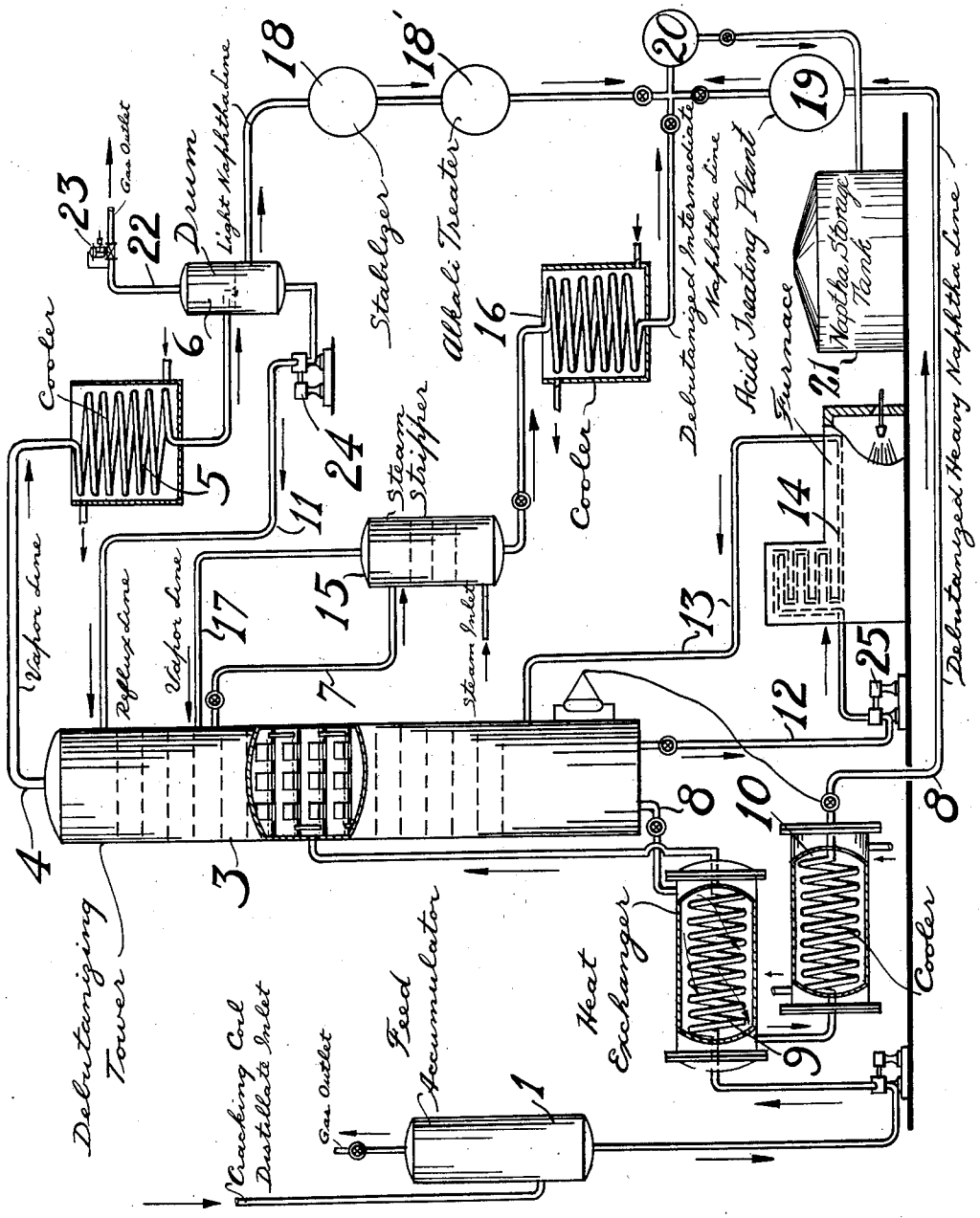


Fig. 1.

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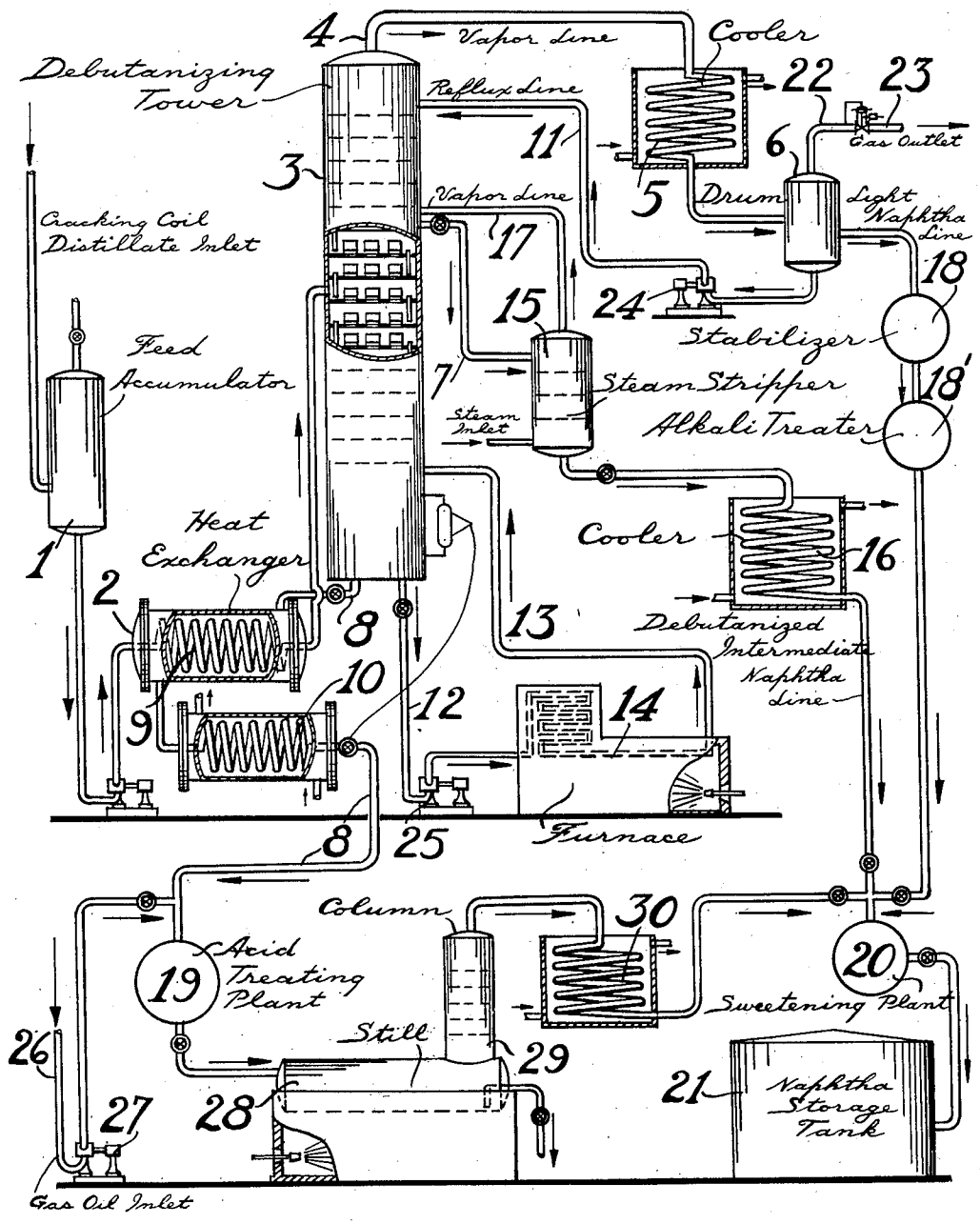


Fig. 2.

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PROCESS OF PRODUCING GASOLINE FROM CRACKED NAPHTHA

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1 Claim. (Cl. 196—23)

This invention relates to a process of producing a finished gasoline from cracked naphtha and will be understood from the following description when read in conjunction with the drawings,

Figure 1 of which is a diagrammatic side elevation, partly in section of the apparatus used for carrying out the invention, and

Figure 2 is a similar representation illustrating the improvements of rerunning the acid treated heavy naphtha.

The main object of the invention is to effect savings in the cost of producing finished gasoline by cutting an intermediate fraction which requires neither high pressure stabilization nor alkali or acid treating.

Referring now to the Figure 1, the apparatus shown will be described in conjunction with a method of operating the same. Cracked distillate from feed accumulator or tank 1 and preferably before the disengagement of very light hydrocarbon vapors, is pumped through heat exchanger 9 into an intermediate portion of a fractionating or debutanizing tower 3. In this tower, which is maintained under appropriate pressure, the raw distillate is separated by distillation and fractionation into four fractions; the overhead distillate cut, consisting of a very volatile light naphtha which is removed in vapor form through line 4, condensed in condenser 5 and collected in drum 6; the non-condensable gas which is vented from drum 6 through line 22 and pressure regulator 23; an intermediate cut which is removed in liquid form through side stream line 7; and a bottoms cut which is removed through line 8, heat exchanger 9 and cooler 10. Reflux pump back is supplied at the top of the tower from the reflux drum 6 through line 11 by means of pump 24. Part of the bottoms is continuously withdrawn through line 12 by pump 25 and returned through line 13, after heating in fired tubes 14. Other methods of heating the bottoms may also be employed. The side stream is conducted through line 7 into a steam stripper 15 and then cooled in cooler 16. The stripped vapor and steam are returned to the tower through line 17. The light naphtha from the reflux drum 6 is conducted to the naphtha stabilizer which is diagrammatically shown and designated by 18. An alkali treater 18' follows the stabilizer 18. The debutanized heavy naphtha from line 3 is led through the acid treating plant 19. The light naphtha from the stabilizer, the intermediate fraction after its passage through cooler 16, and the heavy naphtha from the acid treating plant, are combined, doctor sweetened, if necessary, in sweetening plant 20, and then stored in storage tank 21. The gas vented through line 22 may be burned or sent to an absorption plant for recovery of its gasoline constituents.

In carrying out the invention the pressure and temperature in the fractionating or debutanizing tower 3 are so regulated that the overhead distillate and gas contain at least half the hexane present in the raw distillate and substantially all the lighter components. Usually it is desirable to include slightly heavier fractions also, the desirable end point being 200°–300° F. The overhead distillate does not require acid treating but contains a sufficient amount of undesirable light components, such as propane, to require stabilization at 175–250 pounds per square inch in the high pressure stabilizer 18 in order to substantially eliminate the propane and all lighter hydrocarbons. The methods of stabilizing and caustic washing in themselves do not form part of the invention and are known in the art so that they do not need to be described in further detail.

The intermediate side stream cut will consist of progressively higher boiling naphtha fractions beginning with the lightest fractions not included in the overhead cut and limited by the highest boiling components which can satisfactorily be incorporated in the final gasoline without acid treating. This cut will consequently by-pass the acid treating operation and in addition has been freed from undesirable light ends in the stripper 15 without recourse to the more expensive high pressure stabilization process and caustic washing. The size of the cut as defined by the above limits will vary considerably for cracked distillates produced from different crudes. In the case of sour crudes, the amount of the intermediate side stream will be small as compared to the amounts of the overhead distillate and the bottoms cuts. Conversely, in the case of a sweet crude, an intermediate cut of 30% of the total distillate or even higher may be possible. In many cases a final end point of 300 to 350° F. will be suitable for the intermediate cut.

The bottoms cut will consist of all fractions not included in the above two cuts and will be substantially free of propane and butane. This fraction must be acid treated and its size will, of course, be influenced by the same factors which influence the size of the intermediate cut. After acid treating, the bottoms cut will usually be rerun so as to separate out a fraction which has no components heavier than such as can be included in the final gasoline and to remove high boiling sulfur compounds resulting from reac-

tions in acid treating. After rerunning, the bottoms cut may be doctor sweetened either separately and then blended with the intermediate and overhead distillate cuts, or first blended and then the total gasoline thus obtained is doctor sweetened. If desired the intermediate cut or a blend of the intermediate cut with the caustic washed light cut may be sweetened separately and, if desired, a gum inhibitor added immediately after sweetening.

Referring to the drawings again, Figure 2 illustrates the apparatus used in the preferred form of the present invention in which the heavy naphtha fraction is redistilled after the acid treat. It may be that the heavy naphtha fraction already contains some gas oil. If not, 5 to 10% of gas oil is added from a gas oil tank (not shown) through line **26** by pump **27**. The acid treat in the treating plant **19** is carried out in the usual way with strong sulfuric acid. Water washing and neutralizing follows the treatment with sulfuric acid as usual. The neutralized stock is then discharged into still **28** provided with a fractionating column **29**. The charge is heated until all the heavy naphtha distills off and is united with the light and intermediate naphtha fractions after being condensed in condenser **30**. The gas oil together with sulfur-containing reaction products remains as a residue in the still and is emptied therefrom after cooling. The purpose of adding the gas oil is to prevent the decomposition of the sulfur-containing reaction products and the subsequent contamination of the overhead naphtha distillate with sulfurous gases.

The principal advantage of the invention lies in the fact that the intermediate cut requires neither treatment with the usual strong sulfuric acid nor high pressure stabilization and caustic washing. Our experiments have proved that the sulfur reduction secured with the same quantity of chemicals is greater in the process of the present invention than in prior processes in which the entire cut which by-passes acid treating is submitted to washing with caustic. The sulfur reduction is also greater than in the case of prior processes in which the entire distillate is caustic washed and then acid treated. This is due to the fact that the removal of sulfur by caustic washing is most efficient when only the lighter portion of the by-passed cut is washed. It was also found that the present process offers the greatest advantages when treating high sulfur-containing distillates such as distillates containing above 0.12% sulfur as determined by the lamp method. The following example will illustrate the invention:

A cracking coil distillate of 56.7° A. P. I. gravity and .265% sulfur containing cracking coil gas dissolved under pressure and having a final boiling point (Engler) of 439° F., is fed to the apparatus. The pressure regulator (23) is set for 140 lbs. per sq. in. gauge, which is approximately therefore the operating pressure in the tower (3).

At 47.5% by volume cut of heavy distillate is withdrawn from the bottom of the tower at a temperature of 580° F. This cut has 41.9° A. P. I. gravity and its gasoline content to 392° F. has a sulfur content of 0.298%.

This heavy naphtha is acid treated and rerun to give a stock of 0.065% sulfur content.

An intermediate cut of 10.5% by volume on the feed is withdrawn at a temperature of 470° F. It is of 53.5° A. P. I. gravity and has a sulfur content of 0.23%, the Engler final boiling point being 315° F. A light distillate cut of 37.0% by volume on the feed is taken overhead, together with 5% of gas (based on the feed) at a vapor line temperature in line (4) of 280° F. and the distillate is condensed and withdrawn from the reflux drum (6) at a temperature of 80° F. This light distillate is of 80° A. P. I. and has a sulfur content of 0.225% the Engler F. B. P. being 270° F. This cut is stabilized and caustic washed to give a stock having a sulfur content of 0.1.

The stabilized and caustic washed light distillate, the untreated intermediate cut and the acid treated and rerun heavy cut are blended to give a stock of 58° A. P. I. gravity and 390° F. Engler final boiling point, with a sulfur content of 0.1%. This blend is then doctor sweetened to give a finished gasoline.

The invention may be modified in several ways, thus for example, the acid treating of the heavy cut may sometimes be replaced by treating with clay, or treating with metallic halides such as $ZnCl_2$, with mineral acids other than sulfuric acid such as HCl in the presence of a zinc bearing contact agent, with non-metallic halides such as BF_3, etc.

The figures show an apparatus in which a separate debutanizer tower is provided for obtaining the three cuts. It is evident, however, that the invention may be applied to other types of debutanizers such as for example the type which is made an integral part of the single or the secondary bubble tower of the cracking coil in which case the heat exchanger **9** and reheating circuit **12—14** may be eliminated.

Another type which may be employed is a pair of shell stills, which may operate at atmospheric pressure, the gas and light distillate cut being taken overhead in the first still, the intermediate cut in the second still, and the heavy cut taken as a bottoms from the second still. In this case the light distillate cut may require only caustic washing or may require both stabilization and caustic washing.

Other variations of the invention will be apparent to those skilled in the art. The invention is not to be limited by the example but only by the following claim in which it is our intention to claim all novelty inherent in the invention.

What we claim is:

The method of producing a finished gasoline from a cracked naphtha having a sulfur content of at least 0.12 which comprises fractionating it to remove any gas and to obtain three liquid portions, namely, a light portion having a final boiling point (Engler) of about 270° F. greatly susceptible to sulfur reduction by alkali treatment, an intermediate portion having a final boiling point (Engler) of about 315° F. only slightly susceptible to sulfur reduction by alkali treatment and greatly susceptible to sulfur reduction by treatment with sulfuric acid but also susceptible to large losses by acid treatment, and a heavy portion greatly susceptible to sulfur reduction by acid treatment with only slight treating losses, separately stabilizing the light naphtha portion and treating it with alkali, separately treating the heavy naphtha portion with sulfuric acid and redistilling it to remove polymers, blending the treated light naphtha portion and the treated heavy naphtha portion with the untreated intermediate portion and doctor sweetening the blend to obtain a finished gasoline.

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