Aug. 12, 1941. G. A. LLOYD, JR., ET AL 2,252,082

PRODUCTION OF HEATING OILS

Filed March 7, 1939 2 Sheets-Sheet 1

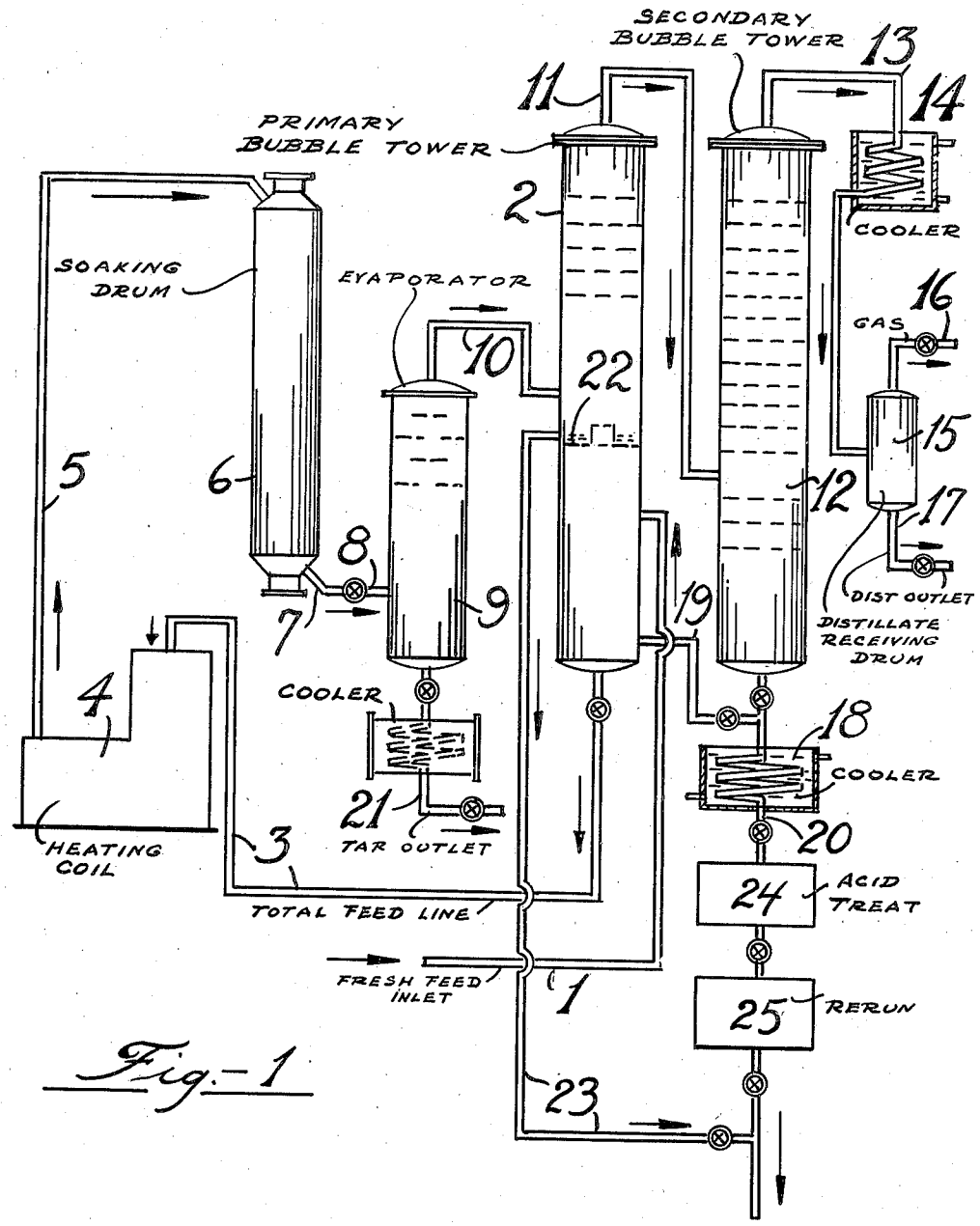


Fig.-1

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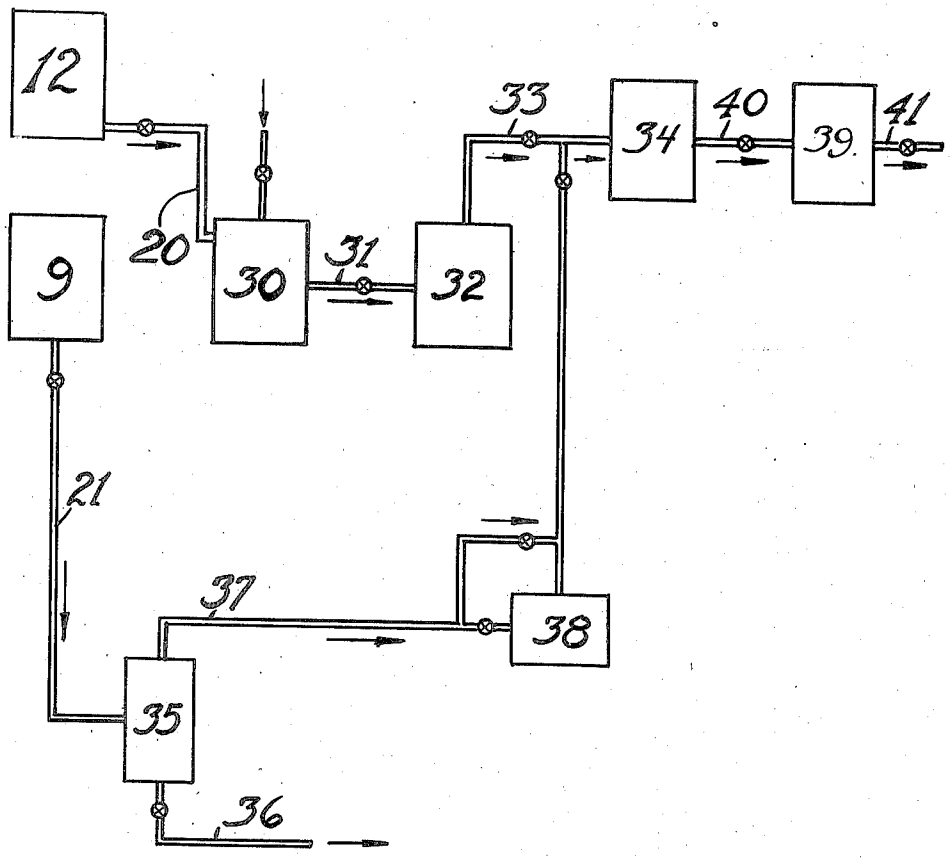


Fig. — 2

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2,252,082

PRODUCTION OF HEATING OILS

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5 Claims. (Cl. 196—40)

The present invention relates to a process for the production of high quality petroleum products boiling in the heating oil range. In accordance with the process of the present invention, the relatively unstable petroleum constituents boiling in the heating oil range are segregated from the relatively stable constituents and treated in a manner to increase their stability. The treated constituents are then subsequently blended with the by-passed relatively stable constituents.

It is well known in the art to produce petroleum products boiling in the heating oil range by various processes. For example, in order to produce heating oil products of suitable characteristics, it is known to segregate the fraction from a point in a cracking system. These heating oil fractions are usually produced when processing petroleum distillates, as for example, gas oils, furnace oils, and reduced crudes in cracking operations. It is the usual practice to pass the petroleum feed distillate, as for example, a gas oil, through a furnace under conditions adapted to cause the cracking of the feed oil. The heated distillate is then passed into a soaking drum or reaction chamber in which the oil is held under cracking conditions for a sufficient length of time to substantially complete the cracking reaction. The cracked distillate is then passed to a so-called tar separator in which tar of the desired gravity may be withdrawn. The overhead products from the tar separator are then usually led into a primary bubble tower. A cycle stock is withdrawn from the bottom of said primary bubble tower and recycled to the coil. The overhead from said primary bubble tower having an end point of about 600° F. or 700° F. is then led into a secondary bubble tower. Naphtha distillate and gas is withdrawn from the top of said secondary bubble tower while a so-called heating oil distillate is withdrawn from the bottom of said secondary bubble tower. The heating oil distillate is then acid treated, rerun, sweetened, and filtered in order to produce a suitable heating oil product.

We have now discovered a method by which it is possible to economically produce a heating oil product of higher quality and increased stability. We have discovered that the relatively lower boiling fractions of said heating oil product are relatively unstable as compared to the higher boiling constituents. These lower boiling constituents break down and deteriorate, unless treated, causing sedimentation and impairing the quality of the heating oil product. This is extremely undesirable since burners are affected and the burning efficiency of the oil is materially lowered. In order to prevent this, it has been the usual practice to treat the entire heating oil fraction. This, however, has not been entirely satisfactory since the relatively large amount of the heating oil had to be processed, thus requiring considerable quantities of treating reagents.

We have now discovered that if the relatively lower boiling constituents are segregated and treated in a manner to increase their stability, it will be unnecessary to treat the relatively higher boiling constituents. Thus, in accordance with our process, it is possible to produce a higher quality product which will not deteriorate in use or storage and to effect considerable economies in the production of heating oil products.

The process of our invention may be readily understood by reference to the attached drawings illustrating one modification of the same. Figure 1 illustrates a diagrammatical flow plan of a normal cracking operation. Figure 2 is specific to the invention and illustrates a modification in which the same may be carried out.

Referring specifically to Figure 1, for purposes of illustration, it is assumed that the feed stock is a gas oil distillate boiling in the range from about 400° F. to 700° F. and having a gravity of about 32° A. P. I. The fresh feed is introduced into the lower part of primary bubble tower 2 by means of feed line 1. The feed together with cycle oil is withdrawn from the bottom of primary bubble tower 2 by means of line 3 and is introduced into heating coil 4 in which the temperature is raised to cracking conditions. The heated oil is withdrawn from heating coil 4 by means of line 5 and introduced into soaking drum or reaction chamber 6 in which the oil is held under cracking conditions for a sufficient length of time to produce optimum conversion of the feed. The down-flow soaking drum operation is illustrated, but it is to be understood that either a down-flow or an up-flow operation may be employed. The products are withdrawn from reaction drum 6 by means of line 7 and passed through a pressure release valve 8. The products under reduced pressure are released into evaporator or tar settler 9. Tar of the desired gravity usually from about 8° to 12° A. P. I. may be withdrawn from evaporator 9 by means of line 21. The vapors pass overhead from evaporator 9 through vapor line 10 into primary bubble tower 2. Cycle stock accumulates in the bottom of primary bubble tower 2 and vapors pass overhead through vapor line 11 into secondary bubble tower 12. The temperature at the top of the primary bubble tower 2 is so adjusted to secure the desired end point in the products withdrawn from the bottom of secondary bubble tower 12. The temperature at the top of tower 12 is controlled so as to produce an overhead distillate of the desired end point which is removed by means of line 13, condensed in cooler 14 and separated from fixed gas in distillate drum 15. Fixed gas is removed from distillate drum 15 by means of line 16 while the overhead condensed distillate from 12 is removed by means of line 17. Heating oil is usually withdrawn from the bottom of the secondary bubble tower 12 by means of line 18. A portion of the heating oil, if desired, may be recycled by means of line 19. The heating oil fraction withdrawn by means of line 20 is usually acid treated, rerun, sweetened, and then filtered.

In accordance with the process of our invention, conditions are adjusted so that the relatively higher boiling stable constituents of the heating oil are condensed in side stream withdrawal accumulator 22. These relatively higher boiling constituents are removed from side stream withdrawal accumulator 22 by means of line 23 and are blended with the lower boiling constituents after said constituents are removed by means of line 20 and have been acid treated in 24 and rerun in 25 in a manner to preserve their stability.

Figure 2 illustrates another operation for carrying out the process of the present invention. In accordance with the process as illustrated by Figure 2, conditions are maintained in the cracking coil so that a relatively high gravity tar °A. P. I. is secured from the evaporator. Thus, in accordance with this process, the relatively higher boiling constituents are included with the cracking coil tar and are withdrawn from the cracking coil evaporator 9 by means of line 21. The relatively lower boiling constituents of the heating oil are withdrawn from the bottom of the secondary tower 12 by means of line 20. The lower boiling constituents are acid treated in treating unit 30 and then introduced into rerunning equipment 32 by means of line 31. The relatively lower boiling constituents of the heating oil are taken overhead from 32 by means of line 33 and introduced into sweetening unit 34. The tar withdrawn from the cracking coil evaporator 9 by means of line 21, containing the relatively higher boiling constituents of the fuel oil is introduced into fractionating unit 35. Conditions are maintained on fractionating unit 35 so that a tar of the desired gravity is withdrawn by means of line 36 and the heating oil constituents of the desired end point are removed overhead by means of line 37. With various feed oils under certain conditions, it may be desirable to rerun the heavy heating oil in rerun unit 38, although it is generally preferred to blend said constituents without rerunning with the overhead from the rerun still 32. The blend of the treated relatively low boiling heating oil constituents and by-passed relatively high boiling heating oil constituents is sweetened in sweetening unit 34, withdrawn by means of line 40, and then filtered in filtering unit 39. The finished heating oil product is withdrawn by means of line 41.

It is to be understood that the processes of the present invention may widely vary. The invention is particularly adapted for the production of heating oil petroleum products having a gravity in the range from about 25° to 40° A. P. I. and boiling in the range from about 350° F. to 750° F. It is readily applicable to the treatment of high sulfur, low sulfur gas oils, furnace oils, and the like. The amount of heating oil bypassed will depend upon the particular crude or feed stock from which the heating oil is derived and the cracking conditions, as well as upon the yield and quality of the heating oil products desired. In general, it is desirable to by-pass from about 25% to 50% of the total heating oil distillate around the acid treat. For example, it is desirable to produce from 25% to 50% of the heating oil produce from side stream withdrawal accumulator 22 or to include this quantity in the tar withdrawn from tar separator and to produce from 50% to 75% from the bottom of the secondary tower. When producing heating oil boiling in the range from 350° F. to 650° F., we have found that it is desirable to treat for stability the constituents boiling lower than about 500° F. or 550° F. The invention is particularly applicable in the production of heating oils boiling in the range from about 350° F. to 625° F. When producing a heating oil of this character, we have found that it is desirable to produce approximately 40% to 60% of the oil from the bottom of the secondary tower and to treat this fraction for stability and to separate the remainder of the relatively higher boiling heating oil constituents from either the accumulator in the primary bubble tower or to separate this quantity with the tar as described above. The temperatures and pressures maintained on the cracking system will depend upon the particular feed stocks being cracked, the yield of other products desired, as well as upon the yield and quality of heating oil desired. The following data illustrate typical operating ranges when withdrawing the entire heating oil fraction from the bottom of the secondary tower as compared to operating ranges when withdrawing the higher boiling heating fractions with the tar and from the side stream withdrawal accumulator in the primary tower.

Table 1

	Normal operation	Higher heating oil fractions withdrawn from side stream accumulator	Higher heating oil fractions withdrawn with tar
Feed stock	Gas oil	Gas oil	Gas oil
Boiling range, initial, about °F.	400	400	400
90% distilled, about °F.	700	700	700
Gravity °A. P. I.	28-33	28-33	28-33
Total feed volume per hour	18,000	18,000	18,000
Fresh feed percent	35-55	35-55	35-55
Coil outlet temperature °F.	890-940	890-940	890-940
Soaker temperature °F.	850-900	850-900	850-900
Soaker pressure pounds per sq. in.	500-1000	500-1000	500-1000
Evaporator temperature—top	650-750	650-750	600-700
Evaporator temperature—bottom	690-790	690-790	640-740
Pressure pounds per sq. in.	95-115	95-115	95-115
Tar gravity °A. P. I.	9-11	9-11	19-21
Temperature at top of primary tower	520-600	470-550	470-550
Temperature at bottom of primary tower	570-650	520-600	520-600
Primary tower pressure	90-110	90-110	90-110
Temperature at top of secondary tower	375-425	375-425	375-425
Temperature at bottom of secondary tower	425-475	425-475	425-475
Pressure pounds per sq. in.	95-105	95-105	95-105

Table 2

	Normal operation	Higher heating oil fractions withdrawn from side stream accumulator	Higher heating oil fractions withdrawn from tar
Feed stock	Reduced crude	Reduced crude	Reduced crude
Boiling range, initial, about °F.	450	450	450
50% distilled, about °F.	700	700	700
Gravity °A. P. I.	14-20	14-20	14-20
Total feed volume per hour	25,000-30,000	25,000-30,000	25,000-30,000
Fresh feed percent	60-80	60-80	60-80
Coil outlet temperature	865-910	865-910	865-910
Soaker temperature	835-880	835-880	835-880
Soaker pressure pounds per sq. in.	200-500	200-500	200-500
Evaporator temperature—top	750-825	750-825	700-775
Evaporator temperature—bottom	760-835	760-835	710-785
Pressure pounds per sq. in.	95-115	95-115	95-115
Tar gravity °A. P. I.	10-12	10-12	19-21
Temperature at top of primary tower	520-600	470-550	470-550
Temperature at bottom of primary tower	620-700	570-650	570-650
Primary tower pressure	90-110	90-110	90-110
Temperature at top of secondary tower	375-425	375-425	375-425
Temperature at bottom of secondary tower	425-475	425-475	425-475
Pressure pounds per sq. in.	95-105	95-105	95-105

The particular method of treating the heating oil to insure its stability and to prevent sedimentation and deterioration may likewise be widely varied. The usual method is to treat this fraction with from 2 to 5 pounds of sulfuric acid of from 88° to 98° concentration per barrel of oil. Thus, in accordance with the process of our invention, it is possible to save from 25% to 50% of the acid and to materially increase the overall capacity of the entire operation. The acid-treated heating oil is then rerun in order to separate higher boiling constituents and to secure the desired end point in the product. Usually, from 85% to 95% of the acid-treated heating oil is taken overhead in the rerunning unit. The overhead heating oil of the desired end point is then sweetened with caustic soda and then clay filtered in order to remove any sediment and the like.

In order to further illustrate the invention, the following example is given which should not be construed to limit the same in any manner whatsoever. In one operation, heating oil was produced by the normal operation; that is by segregating the entire fraction from the bottom of the secondary bubble tower, acid treating the same, rerunning, sweetening, and then filtering. In another operation, approximately 50% of the relatively higher boiling constituents was withdrawn from the evaporator with the tar, resulting in a tar gravity of about 20° A. P. I. The relatively lighter boiling constituents were removed from the bottom of the secondary tower in the usual manner. The tar was fractionated to separate the higher boiling constituents which were subsequently blended with the acid-treated lighter boiling fraction. The inspections of the heating oil secured by the respective processes are as follows:

Method	Current*	Split distillate**
Gravity ° A. P. I.	32.3	32.0
Initial	348	354
10% distilled at ° F.	415	416
20% distilled at ° F.	438	440
30% distilled at ° F.	454	459
40% distilled at ° F.	471	472
50% distilled at ° F.	485	488
60% distilled at ° F.	499	502
70% distilled at ° F.	516	520
80% distilled at ° F.	534	539
90% distilled at ° F.	569	577
Final boiling point	616	618
Recovery percent	98	98
Distilled at 440° F do	21	20
Total acidity units	10.4	5.5
Copper dish tests:		
Sediment	23.9	16.9
Total precipitation	39.2	35.3

*Current method.—Heating oil distillate taken from secondary tower bottom, acid treated with 2# 98% acid, rerun. Overhead sweetened and filtered.

**Split distillate.—Heating oil distillate rerun 0-10% discarded, 10-46% treated 2# 98% and rerun to a 5% bottom. The 46 to 92% cut is blended with the overhead from the treated and rerun product and the blend sweetened.

The process of the present invention is not to be limited by any theory or mode of operation but only by the following claims in which it is desired to claim all novelty insofar as the prior art permits.

We claim:

1. Process for the production of heating oils of increased stability, comprising separating from a cracked distillate boiling in the range from about 350° F. to about 650° F., about 40–60% of the relatively lower boiling constituents from the relatively higher boiling constituents, subjecting said lower boiling constituents to an acid treatment of about 2 to 5 lbs. of sulfuric acid, of from about 88 to 98% strength, per barrel of oil, without subjecting said higher boiling constituents to acid treatment, and blending the treated lower boiling constituents with the untreated higher boiling constituents.

2. Process in accordance with claim 1 in which said relatively low boiling constituents are segregated from higher boiling constituents by withdrawing said higher boiling constituents with the tar from a cracking operation.

3. Process in accordance with claim 1 in which said higher boiling constituents are segregated by withdrawing the same from a side stream withdrawal accumulator located in the middle portion of the primary tower in a cracking operation.

4. A method for treating heating oils to produce heating oils having increased stability which comprises separating a heating oil fraction boiling in the range from about 350° F. to about 650° F., into two fractions comprising a lower boiling fraction and a higher boiling fraction, subjecting the lower boiling fraction to acid treatment to remove undesirable and unstable constituents therefrom, and blending the treated lower boiling fraction with the untreated higher boiling fraction to produce a heating oil having increased stability.

5. A method in accordance with claim 4, wherein the lower boiling fraction has a boiling range of about 350° F. to 500° F. and the higher boiling fraction has a boiling range of about 500° F. to 650° F.

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