

Method for further processing of the vacuum distillation residue in a crude oil refinery

The invention relates to a method for further processing of the residue remaining after normal vacuum distillation in a crude oil refinery.

After the last step, carried out in vacuo, of the fractional distillation of the crude oil in the refinery, those substances which do not evaporate up to about 550°C (normal pressure) remain in the distillation residue. In general, depending on the provenance of the crude oil, this distillation residue corresponds to 25% of the crude oil feed. Its further processing can be carried out in practice by solvent treatment, for example by deasphalting by means of propane. As a result, the residue is separated into a first fraction containing lubricating oils and waxes soluble in the solvent, and a second fraction containing asphalts, asphaltenes and the like insoluble in the solvent. In this step, a greater quantity of the second fraction is obtained. Valuable non-fuels, such as lubricating oils and waxes, can be recovered from the first solution fraction, or the latter can be fed to a cracking installation for the recovery of low-boiling products. The solvent-insoluble second fraction or precipitate is used either for the production of bitumen or, on site, as a fuel for the refinery or, after admixture of a lighter fraction for liquefaction, is used as a heavy fuel externally, for example, for power stations.

The processing of the vacuum distillation residue by means of solvent involves various disadvantages and restrictions. The low-value asphalt-containing fraction, which remains insoluble after the solvent treatment, frequently corresponds to more than half the vacuum residue which can amount to 40% or more of the crude oil in the case of heavy crude oils. Such a large proportion exceeds the fuel requirement of the refinery. In the second possible use of the insoluble fraction, namely the production of bitumen, problems again arise, since the asphaltenes and asphalts present in a colloidal form in the crude oil are precipitated during the solvent treatment. However, complete redispersing, which is indispensable for the production of bitumen, is frequently no longer possible, so that a low-value product is obtained.

Furthermore, the lubricating oil fraction and wax fraction are not completely brought into solution by the solvent treatment and, on the contrary, high-molecular constituents are dissolved and introduced into the first fraction, which is a disadvantage for the end products then recovered and thus leads, for example, to more intense coking of the lubricating oils obtained therefrom.

In addition, the use of low-boiling solvent requires particular safety measures, in particular expensive apparatus. The recovery of the solvent requires a large amount of energy and, due to the high solvent/residue ratio, is expensive.

A method for short-path distillation of the residue from the crude oil refinery is described in European Patent Specification 0,066,790. In this case, both the evaporation pressure and the temperature of the condensation surfaces decrease from the feed to the residue take-off. To improve the energy balance, the residue from the vacuum distillation is fed to the short-path distillation without any supply of energy, so that the heat of vaporization is taken from the feed - which is at the residue temperature of the vacuum distillation residue - which necessarily leads to cooling and hence to temperatures in the short-path distillation which are lower than those during the preceding vacuum distillation.

According to German Offenlegungsschrift 3,122,650, a short-path distillation is applied within the crude oil refinery, whereby the yield of the crackable fraction is increased; at the same time, the conventional solvent extraction can be dispensed with. By lowering the working pressure, the distillation temperature can be considerably reduced, so that a mild distillation of fractions having a high atmospheric boiling point becomes possible. For heating, the residue from the vacuum distillation preceding the short-path distillation is used, from which the heat of vaporization is taken, so that the short-path distillation takes place at a temperature lower than that of the preceding vacuum distillation.

It is the object of the present invention to

propose a method for the shaft-path distillation of the residue of the vacuum distillation of crude oil, which method provides economics better than those of the methods hitherto described. Molecular distillation is not intended to be
5 comprised by the invention.

According to this invention there is provided a method for further processing the residue remaining after vacuum distillation in a crude oil refinery, characterised in that the residue is subjected to a thin-layer short-path
10 distillation in vacuo, the temperature of the evaporator surface being raised to be higher than the temperature at which the residue was treated during said distillation, and the distillate and the concentrated residue being taken off separately.

Surprisingly, it has been found that the economics of the thin-layer short-path distillation of the residue from the vacuum distillation are considerably improved by increasing the energy consumption, that is to say that a poorer energy balance entails an economic improvement.

With the invention, the increase in energy consumption is effected by raising the temperature of the short-path distillation as compared with the temperature of the preceding vacuum distillation. As a result, the feed rate and hence the distillation output are considerably increased, accompanied by a simultaneous increase in the distillation fraction at the expense of the less valuable residue.

According to the extraction method of the state of the art, the separation was effected, using an apolar solvent, on the basis of the polarity, that is to say the chemical structure of the substances. When the known short-path distillation methods are used, the vacuum residue is separated on the basis of the boiling point of the substances present. According to the invention, valuable products which, according to the state of the art, would have remained in the lower-value residue are

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recovered with the distillate as a result of the high temperature. For this reason, not only a quantitative advantage due to the greater quantity of the more valuable product but also a different composition of the fractions and hence further qualitative advantages are achieved according to the invention. A more important point than the improvement of the distillate/residue ratio is that, due to the higher temperature, the feed rate per unit time and per evaporator area can be increased many times. The economics of the method are thus improved to an extraordinary extent.

The difference of the so-called C/H ratios, that is to say the ratios of carbon to hydrogen, between the distillate and the residue is also greatly increased by the method according to the invention.

Furthermore, a greatly shortened residence time with a very low scatter, that is to say high uniformity, is ensured according to the invention.

At the same time, the higher temperature allows problem-free discharge of the residue which is enriched in high-molecular substances.

The lubricating oils obtained according to the invention can, without additives, be used in the same way as lubricating oils which are obtained by conventional vacuum distillation methods and adjusted to the desired viscosity by means of expensive additives. Moreover, the distillate is virtually free of metal-containing

constituents, whereby problems in the cracking, using catalysts sensitive to extraneous substances for the production of low-boiling substances, are eliminated. In addition, according to the invention, the polyaromatics remain in the residue, which additionally improves the quality of the distillate and stabilizes the colloidal asphaltenes in the residue.

The asphalt-containing fraction, that is to say the residue from the thin-layer short-path distillation, is here not only quantitatively reduced, as compared with the state of the art, to such an extent that its complete use as a fuel in the refinery is possible, but it is also qualitatively changed, since it can readily be redispersed in the production of bitumen. This property may, inter alia, be connected with an increased content of polar components. Another important point in the case of crude oils of high wax content is, especially in the case of use as bitumen/asphalt, that the residue virtually no longer contains any wax.

The thin-layer short-path distillation or its equipment design is known in process engineering and was used mainly for producing or purifying heat-sensitive substances under mild conditions, in order to avoid their thermal decomposition. By contrast, thermal decomposition is even desired according to the invention, since a greater quantity of the desired, more valuable distillate is thus obtained and is possible to a small extent, as

long as the vacuum can be maintained.

As a result of the method according to the invention, the hitherto last distillation residue, which cannot be further distilled and boils above about 550°C (under
5 normal pressure) in the oil refinery, is accessible to a distillation under quantitative and qualitative advantages. Products of a novel composition and in some cases novel properties are thus obtained.

Moreover, it is possible according to the invention
10 tion to recover, from heavy crude oils which contain about 50% or even more vacuum distillation residue and which are therefore hardly utilizable commercially, distillates in quantities like those in the case of usual crude oils, so that they then also become utilizable.

15 The method according to the invention can be carried out using known equipment for the thin-layer short-path distillation. This equipment is located adjoining the last stage of the refinery, namely the vacuum distillation. The temperatures in the thin-layer short-path
20 distillation are higher than in the vacuum distillation. The pressure is preferably lower, by a factor of 10 to 1000, than in the preceding vacuum distillation. According to a particular embodiment of the invention, the latter is carried out with a rising temperature pattern. For
25 the intended vacuum, under which large vapour volumes are produced, the evaporation surface and the condensation surface are preferably arranged in the closest possible proximity. In general, this is achieved by

coaxial evaporation regions and condensation regions. Advantageously, the evaporation surfaces and condensation surfaces are arranged cylindrically vertically. The material fed in can be uniformly distributed on the upper part of the heating surface and converted into a turbulent state, which can be retained until the material leaves the bottom of the heating surface by gravity. In such a case, material heated on the entire heating surface can be immediately passed to the liquid surface and the lower-boiling fraction is then evaporated.

A plurality of thin-layer short-path equipment units can be arranged in series or in parallel.

Example 1

The residue, not distillable up to 530°C (temperature data relating to normal pressure) from the vacuum distillation stage was fed to a SAMVAC thin-layer short-path distillation unit from Messrs. Buss AG. The operating data were:

Feed rate	13.1 kg/hour
Pressure	4.5×10^{-2} mbar
Heating temperature	351°C
Cooling temperature	103°C
Distillate rate	6.5 kg/hour
Distillate fraction	49.6%

The residue was continuously fed by means of a pump to the inlet of the evaporator and uniformly distributed on the inner surface by means of a rotating

distributor ring. The rotor wiper blades, which move along the evaporation surface, then pick up the material and produce a turbulent film on the heating surface. A bow wave is produced in front of the rotor wiper blades.

5 It was possible significantly to increase the throughput rate and distillate rate by increasing the heating temperature, which is to be ascribed above all to the evaporation of higher-molecular substances.

10 The data from further examples are summarized below. Examples 1 to 5 were carried out with a view to an increase in the distillate fraction, and Examples 6 to 10 were carried out with a view to increasing the feed rate.

Example	2	3	4	5
<u>Feed</u>				
Feed rate kg/hour	21.5	26.7	15.5	13.8
Stock vessel temperature °C	201	205	206	205
Feed line temperature °C	175	189	183	320
<u>Concentrate</u>				
Exit rate kg/hour	13.45	17.9	8.5	7.27
<u>Distillate</u>				
Exit rate kg/hour	8.05	8.8	7.0	6.53
Vacuum mbar	4×10^{-2}	4×10^{-2}	3.5×10^{-2}	5×10^{-2}
Heating medium inlet °C	332	329	333	350
Heating medium exit °C	312	313	319	333
Coolant inlet °C	93	95	95	103
Coolant exit °C	94	96	97	105
Distillate fraction %	37.4	33.0	45.2	47.4

Example No.	Heating temperature °C	Distillate in % of feed	Feed rate kg/hour
6	364	59	21.3
7	371	56	39.6
8	374	61	24.3
9	386	63	39.7
10	394	61.5	51.3

In these experiments, it was found that throughput rates of 225 kg/hour $\times m^2$ were readily achievable, which guarantees economical use on the refinery scale.

The invention is further illustrated by reference to Figures 1 and 2. The experimental unit, by means of which the abovementioned experiments were carried out, is shown. Purely diagrammatically,

Figure 1 shows the simplified flow diagram of the distillation tract of a crude oil refinery, and Figure 2 shows a unit for carrying out the method according to the invention.

A crude oil 1 of average quality in Figure 1 is fed to a rectifying unit 2 operating under normal pressure. After vaporization, about 50% of the crude oil fed leaves this unit in the form of separated fractions 3, 4 and 5. The residue 6 is fed to a further rectifying unit 7 operating in vacuo, about 25% of the crude oil leaving this

unit as fractions 8, 9 and 11. The non-distillable residue 12 is then fed to the further treatment according to the invention, that is to say to the thin-layer short-path distillation. In the latter, a distillate 14 and the
5 non-distillable residue 15 are obtained. The distillate 14 can either be fed to a cracking unit for the recovery of low-molecular products or can be separated further into lubricating oil and wax. The residue 15 is used as fuel in the refinery or is further processed to give tar.

10 The unit in Figure 2 for carrying out the method according to the invention has a charging vessel 21 with an agitator 22. Throughout the figure, M designates the motors belonging to the individual equipment items. The charging vessel 21 is connected via a line 24, provided
15 with a feed pump 23, to a short-path evaporator 25 which is in turn connected to a residue receiver 26 and a distillate receiver 27. Two cold traps 28 and 29 in series are also connected to the short-path evaporator 25. A Roots vacuum pump 31 is arranged between the cold traps
20 28 and 29 and, downstream of the second cold trap, a Roots vacuum pump 32 and a rotary vane-type vacuum pump 33 downstream thereof are arranged.

The residue from the vacuum rectification stage, introduced into the charging vessel 21, is fed by means
25 of the pump 23 through the line 24 into the short-path evaporator 25, where it is separated by evaporation into distillate and residue and separately collected in the

receivers 26 and 27. (A small quantity of highly volatile constituents which may be present and could be formed by thermal decomposition in the short-path evaporator 25, is collected separately in the cold traps 28 and 29.)

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The heating temperatures in the thin-layer short-path distillation according to the invention can be higher than the temperatures given in the above illustrative example. 400°C or higher temperatures are preferred.



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C L A I M S

1. A method for further processing the residue remaining after vacuum distillation in a crude oil refinery, characterised in that the residue is subjected to a thin-
5 layer short-path distillation in vacuo, the temperature of the evaporator surface being raised to be higher than the temperature at which the residue was treated during said distillation, and the distillate and the concentrated residue being taken off separately.
- 10 2. Method according to claim 1, characterised in that the temperature of the evaporator surface is higher by 50°C, preferably 80°C and especially 100°C than the temperature of the residue remaining in the vacuum distillation.
3. Method according to claim 1 or 2, characterised in
15 that the thin layer of the material to be distilled is created in the form of a turbulent film.
4. Method according to claim 3, characterised in that turbulence is imparted to the film by mechanical means.
5. Method according to claim 4, characterised in that
20 turbulence is imparted to the film by means of wiper blades.
6. Method according to any one of the preceding claims, characterised in that a vacuum distillation residue having a boiling point above 550°C under normal pressure is processed.
- 25 7. Method according to any one of the preceding claims, characterised in that it is carried out in the vacuum



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region under an absolute pressure of less than 10 mbar and above 10^{-3} mbar, preferably between 1 and 0.01 mbar.

8. Method according to any one of the preceding
5 claims, characterised in that a distillate virtually freed of asphalts is obtained.

9. Method according to any one of the preceding
claims, characterised in that it is carried out in a
plurality of equipment units which are connected in parallel
10 and to each of which a vacuum unit is assigned.

10. Method according to any one of the preceding
claims, characterised in that it is carried out at a
temperature of above 350°C , preferably above 400°C .

11. Method according to any one of the preceding
15 claims, characterised in that the feed and the heating medium are passed through in counter-current.

12. Method according to any one of the preceding
claims, characterised in that it is carried out with a rising
temperature pattern.

20 13. Method according to any one of the preceding
claims, characterised in that it is carried out under a
substantially constant pressure pattern.

14. A method of further processing the residue
remaining after vacuum distillation in a crude oil refinery,
25 substantially as hereinbefore described in the Examples
herein and/or referred to in the accompanying drawings.
