

- 1 -

PROCESS FOR THE THERMAL CRACKING OF A RESIDUAL
HYDROCARBON OIL

The present invention relates to a process for the thermal cracking of a residual hydrocarbon oil. More specifically, the present invention relates to a process for the thermal cracking of a residual hydrocarbon oil, wherein the thermal cracking is integrated with a gasification treatment of an asphaltene-rich bottom product derived from said thermal cracking.

Residual hydrocarbon oils may be obtained as the bottom product of the distillation of crude oil at atmospheric pressure ("atmospheric" or "long" residue) or at reduced pressure ("vacuum" or "short" residue).

Converting residual hydrocarbon oils by means of thermal cracking is already known for a long time. Basically, thermal cracking is an endothermic, non-catalytic process in which larger hydrocarbon molecules of residual oil fractions are broken into smaller molecules. The energy required for breaking the larger molecules into smaller ones is supplied by heating the residual hydrocarbon oil feed to a sufficiently high temperature. However, a generally recognised problem in thermal cracking operations is the formation of coke, particularly at more severe cracking conditions. There are several ways known in the art to suppress this coke formation. For instance, if the conversion level of the heavy hydrocarbons, i.e. those hydrocarbons having a boiling point of 520 °C and higher (520 °C+ hydrocarbons), is kept sufficiently low then the formation of coke may be largely prevented. Depending on the type of feedstock and severity of the thermal cracking, said conversion level (further referred to as

- 2 -

520 °C+ conversion, i.e. the weight percentage of the hydrocarbons having a boiling point of 520 °C and higher present in the feed which are converted into lower boiling components) should be kept below about 30% by weight. Another way to substantially prevent coke formation is to deasphalt the residual hydrocarbon oil prior to thermal cracking, in which case 520 °C+ conversions of 30% by weight or higher are attainable. A drawback, however, is that the asphaltenes removed can no longer contribute to the production of distillates without further upgrading separately from the deasphalted oil.

The furnace-soaker configuration is well known in the field of thermal cracking. Within the furnace, heating of the residual hydrocarbon oil feed takes place and a substantial part of the hydrocarbon oil feed is already cracked into lower boiling components. The heated oil is then fed into the soaker or "reaction chamber". In this soaker the cracking reactions continue. Since cracking in the furnace is relatively cheap and easy, the usual aim is to convert as much as possible high boiling material in the furnace and to use the soaker for further increasing the conversion level. However, the attainable conversion level in the furnace is restricted by the formation of coke. In the conventional furnace-soaker configuration, wherein a final 520 °C+ conversion of about 30% by weight can be attained, about half of the final conversion (i.e. about 15% by weight) therefore takes place in the furnace and the other half in the soaker. If the conversion level in the furnace would be higher, which implies that cracking conditions are more severe, then coke will be rapidly formed and will deposit onto the internals of the furnace, thus causing a rapid decrease in heating efficiency of the furnace and hence a decrease in the final conversion.

- 3 -

On the other hand, coke formation and consequent deposition of coke on metal parts in the soaker is also a commonly recognised problem in conventional thermal cracking processes. For this reason, the 520 °C+ conversion in the soaker is also bound to a maximum. It will be understood that too rapid a coke formation in the soaker also negatively influences the runtime of the process after each cleaning operation of the equipment.

In addition, since normally no heat is provided to the soaker, the temperature of the heated and partially converted oil decreases by about 15-30 °C during passage through the soaker. This decrease in temperature is mainly caused by the endothermic character of the cracking reactions, the evaporation of light distillates and the heat loss to the environment via the soaker walls. As a result of this temperature drop across the soaker, there is a decrease in cracking reactions in the direction of the oil flow. Accordingly, the cracking efficiency within the soaker is not at an optimum level.

In EP-A-0,328,216 a process for the thermal cracking of residual hydrocarbon oils is disclosed wherein a furnace is dispensed with and wherein the residual hydrocarbon oil feed is directly fed into a soaker together with hot synthesis gas. This synthesis gas originates from gasification of an asphaltene-rich heavy hydrocarbon oil derived from the cracked residue of thermal cracking. Accordingly, the heating of the residual hydrocarbon oil feed is attained by direct heat exchange with the hot synthesis gas. Although this process performs well and provides a very high level of integration between thermal cracking and gasification, it cannot be easily implemented in an existing refinery having thermal cracking and gasification capacity, because that would require radical changes in both refinery line-up and particularly in the thermal cracking

- 4 -

equipment. Such implementation would consequently be very expensive making the economic feasibility questionable.

The present invention aims to improve the final 520 °C+ conversion of thermal cracking processes conducted in furnace-soaker configurations to a level of at least 35% by weight. Furthermore, the present invention aims to provide a thermal cracking process which can be relatively easy and at relatively low expenses be implemented in an existing refinery having at least thermal cracking capacity and optionally gasification capacity. More specifically, the present invention aims to suppress coke formation and deposition in both furnace and soaker, while at the same time improving the cracking efficiency within the soaker, thus increasing both 520 °C+ conversion and runtime, which self evidently is beneficial from an economic point of view.

All the before mentioned objects have been met by the present invention which relates to a process for the thermal cracking of a residual hydrocarbon oil wherein a final 520 °C+ conversion of at least 35% by weight is attained, i.e. wherein at least 35% by weight of the hydrocarbons having a boiling point of 520 °C and higher present in the residual hydrocarbon oil are converted into lower boiling components, said process comprising the steps of:

(a) heating the residual hydrocarbon oil feed in a furnace to a temperature in the range of from 400 to 510 °C for sufficient time to achieve 30 to 45% of the final 520 °C+ conversion;

(b) feeding the partially converted, hot hydrocarbon oil produced in step (a) and a hot hydrogen-containing gas into a soaker, said hydrogen-containing gas having a sufficiently high temperature to maintain the temperature

- 5 -

of the hydrocarbon oil in the soaker by means of direct heat exchange at a value in the range of from 420 to 650 °C, in which soaker the remainder up to 100% of the final 520 °C+ conversion takes place; and

- 5 (c) recovering a gaseous fraction containing the hydrogen-containing gas and a cracked residue from the soaker.

Suitable residual hydrocarbon oil feeds which may be used in step (a) are heavy hydrocarbonaceous feedstocks comprising at least 25% by weight of 520 °C+ hydrocarbons, preferably more than 37.5% by weight 10 520 °C+ hydrocarbons and even more preferably more than 75% by weight of 520 °C+ hydrocarbons. Feedstocks comprising more than 90% by weight of 520 °C+ 15 hydrocarbons are most advantageously used. Suitable feedstocks thus include atmospheric residues and vacuum residues. If desired, the residual hydrocarbon oil may be blended with a heavy distillate fraction, such as e.g. a cycle oil obtained by catalytic cracking of a hydrocarbon 20 oil fraction, or with a heavy hydrocarbon oil obtained by extraction from a residual hydrocarbon oil.

In step (a) of the process according to the present invention the residual hydrocarbon is heated in the furnace to a temperature in the range of from 400 to 25 510 °C for sufficient time to achieve 30 to 45% of the final 520 °C+ conversion. The precise combination of temperature and residence time in the furnace must in any event be such that 30-45% of the final 520 °C+ conversion takes place in this furnace. Since in normal thermal 30 cracking operations involving a furnace and a subsequent soaker about 50% of the final conversion takes place in the furnace, this implies that relatively mild thermal cracking conditions are applied in the furnace, for instance those conditions usually applied in visbreaking

- 6 -

operations. The result of applying relatively mild conditions in the furnace is that less coking occurs in this furnace, thus enabling longer runtimes. It will be understood that this is economically highly attractive.

5 In order to compensate for the relatively low conversion level in the furnace, the conversion level in the soaker must be higher than usual, i.e. higher than 50% of the final 520 °C+ conversion. In the process of the present invention this is attained by introducing hot
10 hydrogen-containing gas into the soaker. In this manner the earlier mentioned temperature drop across the soaker in the direction of the oil flow is avoided and the thermal cracking reactions accordingly can proceed along the entire soaker length at a similar rate. The hot
15 hydrogen-containing gas can be introduced into the soaker at one or more of its internals and/or at the bottom of the soaker. In the event the heated hydrocarbon oil feed from the furnace is fed into the bottom of the soaker, the hot gas is preferably introduced at one or more of
20 the internals of the soaker to warrant an efficient heating. If, on the other hand, said oil feed enters the soaker at the top, the hot gas can be suitably introduced at the bottom of the soaker, as in this mode of operation the hot gas and the oil flow move in a countercurrent
25 mode through the soaker which enables an efficient heat exchange between the hot gas and the oil.

Beside its function as a heating medium, the hot gas also serves as a stripping medium for removing the lighter fractions from the cracked oil, thus increasing
30 the stability of the remaining liquid, which in return results in decreased coke formation on the metal parts inside the soaker which are in direct contact with the hot gas. In this way longer runtimes and a deeper final 520 °C+ conversion can be attained. The use of hydrogen-
35 containing gas as a stripping medium in the thermal

- 7 -

cracking process of the present invention also forms a separate aspect of the present invention. The presence of hydrogen during thermal cracking is also considered to be favourable for the stability of the remaining liquid and thus for the suppression of coke formation. Thermal cracking in the presence of hydrogen, namely, is known to reduce the formation of carbonaceous products during thermal cracking of heavy hydrocarbon oils and to be advantageous for the stability of the oils formed, such as for instance reported in JP-A-62-96589.

The hydrogen-containing gas used in step (b) in principle may be any gas which is stable at elevated temperatures and which contains hydrogen. It may for instance be pure hydrogen or a hydrogen-rich gas. Particularly in a refinery where hydrotreatment units are present, the use of such gases may be beneficial. Hot synthesis gas may also be applied as the hot hydrogen-containing gas. This is a very feasible option if the refinery involved has a gasification unit where hot synthesis gas is produced by gasification, i.e. partial oxidation, of heavy asphaltene-rich oil fractions. Furthermore, synthesis gas from a gasification unit may also contain soot. Without wishing to be bound by any particular theory, the presence of soot in the soaker may be beneficial, since it offers a surface area to deposit coke and coke precursors, thus inhibiting fouling of the metal parts in the soaker, and it may act catalytically in activating the hydrogen present in the synthesis gas due to the metals present in the soot. In this connection the presence of nickel (as nickel sulphide) is considered particularly important. It will be understood that due to its aforementioned advantageous effects in thermal cracking reactions, hydrogen may also be present in step (a) of the process according to the present invention, i.e. in the furnace.

- 8 -

In any event, the hydrogen-containing gas must be stable at such high temperatures which are necessary to maintain the temperature of the hydrocarbon oil in the soaker at a value in the range of from 420 to 650 °C, preferably 450 to 600 °C, by means of direct heat exchange. As already mentioned before, by introducing heat and hydrogen into the soaker in the form of hot hydrogen-containing gas, a temperature drop across the soaker is at least significantly reduced and coke formation on the metal parts inside the soaker being in direct contact with the hydrogen-containing gas is suppressed, as a result of which 55% or more of the final conversion can be realised in the soaker without excessive coking. Because coking is also significantly reduced in the furnace due to the milder cracking conditions, the overall result is less coke deposition on the internals of the furnace and soaker and hence longer run times can be achieved. In other words, by shifting the conversion to a certain extent and under certain conditions from the furnace to the soaker, coke formation is reduced and longer run times are attained.

The total pressure in the soaker may vary from 2 to 100 bar. For economic reasons it is, however, preferred to apply total pressures in the range of from 2 to 65 bar. At pressures above 65 bar and especially at pressures above 100 bar, the high pressure equipment needed will become so expensive that economically feasible operation of the process will become increasingly difficult.

After the thermal cracking has taken place a gaseous fraction containing the hydrogen-containing gas and a cracked residue are recovered from the soaker in step (c). The said gaseous fraction can subsequently be further separated in a fractionator into a top fraction containing methane, ethane and the hydrogen-containing

- 9 -

gas, one or more gaseous lower hydrocarbons, i.e. propane, butane and the like, and a bottom fraction. If desired, the hydrogen-containing gas can then be separated from the said top-fraction, for instance by pressure swing adsorption. The cracked residue can have different destinations. It can for instance be partially or totally recycled and blended with the furnace and/or soaker feedstock in order to be once again subjected to thermal cracking conditions. It is however preferred that the cracked residue is further separated in a subsequent step (d) into one or more asphaltene-poor fractions and an asphaltene-rich bottom fraction. This separation can suitably be performed by means of vacuum flashing or vacuum distillation. In this mode of operation the bottom fraction obtained from fractionating the gaseous fraction recovered from the soaker may optionally be vacuum flashed together with said cracked residue.

The asphaltene-rich bottom fraction can subsequently be used in several ways. It can for instance be applied in bitumen for road and roofing purposes, in emulsion fuels or in solid fuels by means of pelletizing. In a preferred embodiment of the present invention, however, the asphaltene-rich bottom fraction is partially oxidised (gasified) in an additional step (e) in the presence of oxygen and steam, usually high pressure steam, thereby producing hot synthesis gas. This synthesis gas, in return, can be applied as clean fuel gas in the refinery or for the cogeneration of power and steam, hydrogen manufacture and hydrocarbon synthesis processes. For the purpose of the present invention it is however preferred that at least a part of the hot synthesis gas produced in step (e) is introduced into the soaker in accordance with step (b) of the process according to the present invention.

- 10 -

In figure 1 an example of a refinery line-up is depicted involving a preferred embodiment of the thermal cracking process according to the present invention, i.e. a furnace-soaker configuration integrated with a gasification unit.

Residual hydrocarbon oil feed (6) is fed into furnace (2) where it is heated to a temperature of from 400 to 510 °C and where 30-45% of the final conversion takes place. The hot, partially converted hydrocarbon oil (7) leaves the furnace and is fed into soaker (3) together with hot synthesis gas (9) produced in gasification unit (1) via partial oxidation of asphaltene-rich bottom fraction (19) in the presence of oxygen/steam (8). Gaseous fraction (10) and cracked residue (15) are recovered from the soaker (3). Gaseous fraction (10) is separated in fractionator (4) into top fraction (11) -containing methane, ethane and synthesis gas-, light hydrocarbon fractions (12) and (13) and bottom fraction (14). This bottom fraction (14) is fed into vacuum flasher (5) together with cracked residue (15), where separation into the asphaltene-poor fractions (16), (17) and (18) and the asphaltene-rich bottom fraction (19) takes place. Part of the bottom fraction (19) is subsequently used as feedstock for gasification unit (1).

The invention is further illustrated by the following examples.

Example 1 and Comparative Example 1

When subjecting a Middle East short residue, having the properties as indicated in Table I, to thermal cracking, a final 520 °C+ conversion of 40% by weight can be attained when applying the process according to the present invention as illustrated by figure 1 (example 1). Under similar conditions, a conventional thermal cracking process only yields a final 520 °C+ conversion of 31% by weight (comparative example 1). Pressure in the soaker in

- 11 -

example 1 is about 10 bar. The other conditions under which both thermal cracking processes take place as well as the conversion levels in furnace and soaker and the yields of the product streams are indicated in Table II.

5 The numbers in the column "Stream/Unit No." refers to the reference numbers used in figure 1.

10 From the results given in Table II it can be concluded that in comparison with the conventional furnace-soaker thermal cracking process the process of the present invention enables a higher final 520 °C+ conversion, thus resulting in higher yields of the useful product streams boiling below 520 °C and in less residual hydrocarbons.

Table I Feedstock properties

350-520 °C fraction (% wt)	5.0
520 °C+ fraction (% wt)	95.0
Sulphur (% wt)	5.4
Conradson Carbon No. (% wt)	20.3
C7-asphaltenes (% wt)	10.2
Viscosity at 100 °C (mm ² /s)	2350
Density 70/4	0.998

- 12 -

Table II Thermal cracking experiments

	Stream/ Unit No.	Example 1	Comp. Example 1
Feed (t/d)	6	1000	1000
Feed gas (t/d)	9	255	-
Tgas (°C)	9	650	-
FOT (°C)	2	460	460
SOT (°C)	3	460	432
Product streams (t/d)			
Gas	11	288.6	25.2
0-165 °C	12	74.4	54.0
165-350 °C	13	140.7	104.1
350-520 °C	16, 17, 18	182.5	166.7
520 °C+	19	568.8	650.0
520 °C+ conv. (% wt)			
Furnace		15 (37.5%)	15 (48.4%)
Final		40	31

The abbreviations and expressions used in Table II have the following meaning:

t/d : tons/day

% wt : % by weight

5 Feed gas : synthesis gas from gasification unit

Tgas : temperature of the feed gas

FOT : Furnace Outlet Temperature

SOT : Soaker Outlet Temperature.

10 The product streams are indicated via their boiling point range and of the 520 °C+ conversion it is indicated what the final conversion is ("Final") and what part of it is attained in the furnace. The percentage between

- 13 -

brackets indicates the percentage of the final 520 °C+ conversion taking place in the furnace.

Example 2

5 A stirred autoclave of 100 ml capacity was charged with about 25 g of the same Middle East short residue used in Example 1. The filled autoclave was pressurized with synthesis gas to 50 bar. The reactor and its contents were then rapidly heated to 450 °C (within 2 minutes starting at 350 °C) and maintained at that
10 temperature for 20 minutes to allow thermal cracking reactions to occur. Thereafter the reactor was rapidly cooled to room temperature. The autoclave was subsequently depressurized and the gas and liquid were collected and sampled for analysis. The amount of coke
15 was determined by extraction with tetrahydrofuran. It was found that only 4.7% by weight of the total of gas and liquid recovered was coke. In addition, the surfaces of the autoclave and the stirrer parts in contact with the synthesis gas remained uncoked.

Comparative Example 2

20 The procedure of Example 2 was repeated only this time nitrogen was used to pressurize the filled autoclave to 50 bar instead of synthesis gas. It was found that coke constituted 7.8% by weight of the total of gas and
25 liquid recovered and that coke was formed on the surfaces of the autoclave and on the stirrer parts in contact with the nitrogen.

30 Comparing the results of Example 2, wherein the conditions in a soaker operated in accordance with the process of the present invention are imitated, with those of Comparative Example 2, shows that at thermal cracking conditions in the presence of a hot hydrogen-containing gas coke formation is significantly reduced and deposition of coke onto the metal parts inside the soaker

- 14 -

which are in direct contact with said hot gas is even completely avoided.

Example 3

A stirred autoclave of 100 ml capacity was charged with about 25 g of the same Middle East short residue as used in Example 1. The filled autoclave was pressurized with pure hydrogen gas to 10 bar. The autoclave was operated at constant pressure using a pressure controller in the outlet line of the autoclave and a continuous gas supply through the liquid residue via a hollow stirrer. Gas flow was kept constant at 200 Nl/kg.h. The residue was then preheated to a temperature of 340 °C under stirring and was held there for 15 minutes. Thereafter, it was heated at a rate of 45 °C/min to the desired reaction temperature (450 °C) and was maintained there for 15 minutes to allow thermal cracking reactions to occur. Subsequently, the autoclave was cooled to room temperature at a rate of 90 °C/min. The autoclave was subsequently depressurized and the gas and liquid were collected and sampled for analysis. The amount of coke was determined by extraction with tetrahydrofuran. It was found that only 3.5% by weight of the total of gas and liquid recovered was coke. In addition, the inner surfaces of the autoclave and the stirrer parts in contact with the hydrogen had remained uncoked.

The results of this example show that under thermal cracking conditions in the presence of hydrogen, even at such low pressure of 10 bar, coke formation is significantly reduced whilst deposition of coke onto the metal parts inside the soaker which are in direct contact with the hydrogen is completely avoided.

C L A I M S

1. Process for the thermal cracking of a residual hydrocarbon oil wherein a final 520 °C+ conversion of at least 35% by weight is attained, which process comprises the steps of:

5 (a) heating the residual hydrocarbon oil feed in a furnace to a temperature in the range of from 400 to 510 °C for sufficient time to achieve 30 to 45% of the final 520 °C+ conversion;

10 (b) feeding the partially converted, hot hydrocarbon oil produced in step (a) and a hot hydrogen-containing gas into a soaker, said hydrogen-containing gas having a sufficiently high temperature to maintain the temperature of the hydrocarbon oil in the soaker by means of direct heat exchange at a value in the range of from 420 to
15 650 °C, in which soaker the remainder up to 100% of the final 520 °C+ conversion takes place; and

(c) recovering a gaseous fraction containing the hydrogen-containing gas and a cracked residue from the soaker.

20 2. Process according to claim 1 further comprising the step of

(d) separating the cracked residue recovered in step (c) into one or more asphaltene-poor fractions and an asphaltene-rich bottom fraction.

25 3. Process according to claim 2 further comprising the step of

(e) partially oxidising the asphaltene-rich bottom fraction resulting from step (d) in the presence of oxygen and steam thereby producing hot synthesis gas.

- 16 -

4. Process according to claim 3, wherein at least a part of the hot synthesis gas produced in step (e) is used as the hot hydrogen-containing gas in step (b).

5. Use of a hydrogen-containing gas as a stripping medium in a process according to any one of claims 1 to 4.

