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PYROLYZING CRUDE OIL AND
CRUDE OIL FRACTIONS CONTAINING PITCH

The invention pertains to a process for pyrolyzing a feedstock of crude oil and crude oil fractions containing pitch in an olefins pyrolysis furnace.

5 The production of olefins, in particular ethylene, is achieved conventionally by the thermal cracking of petroleum hydrocarbon feedstocks using natural gas liquids, (NGL's) such as ethane or by using the naphtha or gas oil fractions produced from a crude distillation column operating above atmospheric pressure. More
10 recently, the trend in some regions is toward designing crackers to accommodate the use of heavier feedstocks, such as vacuum gas oils. These heavier feedstocks, however, foul tubes in convection section preheaters and downstream equipment by coke deposition. Typical process
15 temperatures at the exit of the convection section first stage preheaters range from about 200-400 °C, thereby completely vapourizing the feedstock within the convection section, or in heavy feed cases such as gas oil and vacuum gas oil, finally and completely
20 vapourizing the feedstock externally as it proceeds toward the second stage preheaters through a mix nozzle with superheated steam as described in U.S.-A-4,498,629.

U.S.-A-5,580,443 discloses a process for cracking low
25 quality feedstock such as a heavy natural gas-liquid, which is an associated oil occurring in small quantities with the production of gas from gas fields. The process is described as processing the feedstock through a first stage preheater within the convection zone to a vapour-liquid separator external to the convection zone after
30 being mixed with superheated steam, a second stage

preheater within a convection zone, and finally to the radiant zone. The feedstock is cracked by separating and removing in a vapour-liquid separator a portion of heavy fractions from the first stage preheater section, and subsequently returning the vapourized portion of the feedstock to the second stage preheater before subjecting the feedstock to pyrolysis. The temperature and pressure within the first stage preheater tubes are maintained within a range such that those fractions of the feed which would otherwise cause coking problems in the tubes are kept in liquid state, while fractions unlikely to cause coking problems are fully evaporated. Typical exit temperatures from the first preheater section range from 150 °C-350 °C in order to avoid vapourizing the coke generating fractions within the tubes.

The gas-liquid mixture exiting the first preheater section is described in U.S.-A-5,580,443 as within a ratio of 60/40 to 98/2. This ratio can be adjusted by the addition of superheated dilution steam at a point between the exit port of the first preheater section and prior to entry in a vapour-liquid separator. Once in the vapour-liquid separator, the heavy unevaporated liquid fractions are removed and discharged from the system, while the gaseous fraction is passed through a gas delivery line, mixed with superheated dilution steam again, and then passed to the second preheater. In the second preheater, the gas is heated up to a temperature just below the temperature at which cracking is promoted, after which it passes into the radiant section and is cracked.

It would be desirable to process feeds other than heavy natural gas-liquids through a pyrolysis furnace for the manufacture of ethylene. Desirable feeds include crude oil or the long residue from the bottoms of a crude oil atmospheric column. Crude oil feed is derived from

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oil fields wherein 60% or more of the production extract in liquid form is a crude oil. A heavy natural gas-liquid stream is in a gaseous or supercritical state in the ground, which condenses into a liquid as it reaches surface temperatures and pressures. Processing a crude oil feedstock or the long residue of a crude oil atmospheric column through a pyrolysis furnace under the temperature conditions described in U.S.-A-5,580,443, and in particular at a temperature ranging from 150 °C-350 °C in a first preheating stage, or at any temperature at which those fractions likely to cause coking problems remain in liquid state and those fractions unlikely to coke the tubes are fully evaporated, would be disadvantageous because at the lower temperatures at which heavy natural gas-liquids are processed, 150 °C-350 °C, insufficient fractions of vapourized crude oil or long residues are recovered, resulting in reduced yields of desirable olefin production from these feedstocks.

The heavy ends of crude oil and long residue cannot be vapourized under typical olefins pyrolysis furnace convection section conditions. The heavy ends of crude oil and long residue are normally removed by distillation, and the lighter vapourizable fractions from a distillation, most commonly the naphtha or gas oil fractions, are used as the feed for olefins pyrolysis plants. This distillation preparation step for crude oils and long residue requires additional capital and adds additional operating cost to the process.

There is now provided a process for pyrolyzing a crude oil and/or crude oil fractions containing pitch feedstock in an olefins pyrolysis furnace comprising feeding the crude oil and/or crude oil fractions containing pitch feedstock to a first stage preheater provided in a convection zone of the furnace, heating the

feedstock within the first stage preheater to an exit temperature of at least 375 °C to produce a heated gas-liquid mixture, withdrawing the heated gas-liquid from the first stage preheater to a vapour-liquid separator, separating and removing the gas from the liquid in the vapour-liquid separator, and feeding the removed gas to a second stage preheater provided in the convection zone, further heating the temperature of the gas to a temperature above the temperature of the gas exiting the vapour-liquid separator, introducing the preheated gas into a radiant zone of the pyrolysis furnace, and pyrolyzing the gas to olefins and associated by-products.

The above process can be used to process a long residue and any crude oil fractions containing pitch.

The process of the invention allows one to feed a crude oil or crude oil fractions containing pitch feedstock into the convection zone of a pyrolysis furnace without having to decoke the tubes in the convection zone any sooner than the radiant tubes of a furnace. The process of the invention extends the capability of an olefins furnace to flash a feedstock (a feed of crude oil or crude oil fraction containing pitch) at a higher temperature (e.g. 480 °C) that is not generally achievable at the bottoms of a vacuum distillation column under normal operating conditions (about 415 °C), thereby allowing one to recover a higher fraction of the crude oil or crude oil fractions containing pitch as vapour useful for cracking in the radiant heat transfer zone in a pyrolysis furnace than that recovered through atmospheric or vacuum distillation columns. The process of the invention also has the advantage of processing a crude oil or crude oil fractions containing pitch feed without having to first subject the crude oil or crude oil fractions containing pitch feed to fractionation, thereby allowing one to process a cheaper source of

feedstock in a pyrolysis furnace. Finally, the large quantity of higher boiling fractions in crude oil or crude oil fractions containing pitch, unlike heavy natural gas liquids, wet the inner surfaces of the tubes in the convection zone at suitable linear velocities under the operating temperatures described herein, thereby making crude oil or crude oil fractions containing pitch a suitable feed and minimizing the formation of coke within the convection zone tubes.

Preferably, the feedstock for use in the present invention is a feedstock wherein 85 wt.% or less of the feedstock will vapourize at 350 °C, and 90 wt.% or less of the crude oil feedstock will vapourize at 400 °C, each as measured according to ASTM D-2887.

Preferred crude oil feedstocks used in the invention have the following characteristics. Each characterization of the crude oil feedstock is measured according to ASTM D-2887:

85 wt.% or less of the crude oil feedstock will vapourize at 350 °C, and

90 wt.% or less of the crude oil feedstock will vapourize at 400 °C.

Feedstocks within the above range of characteristics minimize coking within the tubes of the convection section of a pyrolysis furnace under the operating conditions described herein. The weight percentage of lighter feedstocks, such as most heavy natural gas liquids, vapourized at 300 °C, 350 °C, or 400 °C is so high that the vapourization of the coking fraction would quickly coke the tubes within the first stage preheater at the temperatures used in this invention.

In a preferred embodiment, the crude oil specified for the feedstock has the following characteristics:

65 wt.% or less vapourizing at 300 °C, and

80 wt.% or less of the crude oil feedstock vapourizing at 350 °C, and

88 wt.% or less of the crude oil feedstock will boil at 400 °C.

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In a more preferred embodiment,

60 wt.% or less of the crude oil and long residue vapourizes at 300 °C, and

70 wt.% or less of the crude oil feedstock vapourizes at 350 °C, and

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80 wt.% or less of the crude oil feedstock will vapourize at 400 °C.

In a most preferred embodiment, the crude oil feedstock will have the following characteristics:

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55 wt.% or less of the crude oil vapourizes at 300 °C, and

65 wt.% or less of the crude oil feedstock vapourizes at 350 °C, and

75 wt.% or less of the crude oil feedstock will vapourize at 400 °C.

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Typical crude oil feedstocks will have API gravities not higher than 45.

Long residue feedstocks are the bottoms of an atmospheric distillation column used to process and fractionate desalted crude oil, also commonly known as atmospheric tower bottoms. This atmospheric distillation column separates diesel, kerosene, naphtha, gasoline, and lighter components from the crude. Long residues satisfy the above specification for suitable feeds used in the invention, and will also satisfy the following specification:

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35 wt.% or less, more preferably 15 wt.% or less, and even 10 wt.% or less, vapourizing at 350 °C, and

55 wt.% or less, more preferably 40 wt.%, and even 30 wt.% or less, vapourizing at 400 °C.

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The pressure and temperature at which the crude oil and/or long residue feedstock is fed to the inlet of the first stage preheater in the convection zone is not critical so long as the feedstock is flowable. The pressure generally ranges from between 8-28 bar, more preferably from 11 to 18 bar, and the temperature of the crude oil is generally set from ambient to below the flue gas temperature in the convection zone where it will first be heated, typically from 140 °C-300 °C. Feed rates are not critical, although it would be desirable to conduct a process at a feed rate ranging from 22,000-50,000 kg of crude oil and/or long residue feed per hour.

Figure 1 is a schematic process flow diagram of a pyrolysis furnace.

Figure 2 is an elevation view of a vapour-liquid separator.

Figure 3 is a plan view of Fig. 2.

Figure 4 is a perspective drawing of the vane assembly of the vapour-liquid separator of Fig. 2.

Figure 5 is a schematic process flow diagram of a pyrolysis furnace.

Figure 6 is a schematic process flow diagram of a pyrolysis furnace.

The invention is described below while referring to Figure 1 as an illustration of the invention. It is to be understood that the scope of the invention may include any number and types of process steps between each described process step or between a described source and destination within a process step. For example, any number of additional equipment or process steps may lie between the vapour-liquid separator and the second stage preheater, and any number of additional equipment or process steps may lie between feeding the removed gas

(from the vapour-liquid separator as the source) to a second stage preheater (the destination).

5 The olefins pyrolysis furnace 10 is fed with a crude oil or crude oil fractions containing pitch feed or a long residue feed 11 entering into the first stage preheater 12 of a convection zone A. Crude oil feedstocks are referred to throughout the specification as a feedstock of the invention, but it is to be understood that long residue feedstocks are also suitable feedstocks which may be used in lieu of or in combination with crude oil feedstocks whenever crude oil feedstocks are referred to. Further, for convenience, it is to be understood that every mention of crude oil throughout the specification includes crude oil and crude oil fractions containing pitch. Accordingly, the scope of the invention includes long residue and crude oil fractions containing pitch whenever crude oil is mentioned as a feedstock.

20 The first stage preheater 12 in the convection section is typically a bank of tubes, wherein the contents in the tubes are heated primarily by convective heat transfer from the combustion gas exiting from the radiant section of the pyrolysis furnace. Preferably, the feedstock is fed to 85 wt.% or less of the feedstock will vapourize at 350 °C, and 90 wt.% or less of the crude oil feedstock will vapourize at 400 °C, each as measured according to ASTM D-2887. In one embodiment, as the crude oil and/or long residue feedstock travels through the first stage preheater 12, it is heated to a temperature which promotes evaporation of non-coking fractions into a vapour state and evaporation of a portion of coking fractions into a vapour state, while maintaining the remainder of the coking fractions in a liquid state. We have found that with a crude oil and/or long residue feedstock, it is desirable to fully

evaporate the crude oil and/or long residue fractions which do not promote coking in the first stage preheaters, and in addition, maintain a temperature sufficiently elevated to further evaporate a portion of the crude oil and/or long residue feedstock comprised of fractions which promote coking of the tubes in the first stage preheater and/or the second stage preheater. The coking phenomenon in the first stage preheater tubes is substantially diminished by maintaining a wet surface on the walls of the heating tubes. So long as the heating surfaces are wetted at a sufficient liquid linear velocity, the coking of those surfaces is inhibited.

The optimal temperature at which the crude oil and/or long residue feedstock is heated in the first stage preheater of the convection zone will depend upon the particular crude oil and/or long residue feedstock composition, the pressure of the feedstock in the first stage preheater, and the performance and operation of the vapour-liquid separator. In one embodiment of the invention, the crude oil and/or long residue feedstock is heated in the first stage preheater to an exit temperature of at least 375 °C, and more preferably to an exit temperature of at least 400 °C. In one embodiment, the exit temperature of the feedstock from the first stage preheater is at least 415 °C.

The upper range on the temperature of the crude oil and/or long residue feedstock in the first stage preheater tubes is limited to the point at which the stability of the crude oil and/or long residue feedstock is impaired. At a certain temperature, the coking propensity of the feedstock increases because the asphaltenes in the pitch begin to drop out of solution or phase separate from the solubilizing resins in the feedstock. This temperature limit would apply to both the first stage preheater tubes and all tubes connecting

up to and including the vapour-liquid separator.
Preferably, the exit temperature of the crude oil and/or
long residue feedstock within the first stage preheater
is not more than 520 °C, and most preferably not more
than 500 °C.

Each of the temperatures identified above in the
first stage preheater are measured as the temperature the
gas-liquid mixture attains at any point within the first
stage preheater, including the exit port of the first
stage preheater. Recognizing that the temperature of the
crude oil and/or long residue feedstock inside the tubes
of the first stage preheater changes over a continuum,
generally rising, as the crude oil and/or long residue
flows through the tubes up to the temperature at which it
exits the first stage preheater, it is desirable to
measure the temperature at the exit port of the first
stage preheater from the convection zone. At these exit
temperatures, both a coke promoting fraction and a non-
coking fraction of the crude oil and/or long residue
feedstock will be evaporated into a gas phase, while
maintaining the remainder of the coke promoting fraction
in a liquid phase in order to adequately wet the walls of
all heating surfaces. The gas-liquid ratio preferably
ranges from 60/40-98/2 by weight, more preferably 90/10-
95/5, by weight, in order to maintain a sufficiently
wetted tube wall, minimize coking, and promote increased
yields.

The temperature conditions within the first stage
preheater are suitably adapted to the use of a crude oil
and/or long residue feedstock, and are not recommended
for a heavy natural gas-liquid feed. Feeding a heavy
natural gas-liquid having coking fractions through the
first stage preheater at the process conditions of the
invention could evaporate the feedstock to its dry point,
and within days to a week could coke up the furnace

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tubing in the convection section to the point where a shutdown is required.

5 The pressure within the first stage preheater 12 is not particularly limited. The pressure within the first stage preheater is generally within a range of 4-21 bar, more preferably from 5-13 bar.

10 In an optional but preferred embodiment of the invention, a feed of dilution fluid, preferably dilution gas 13 may be added to the crude oil and/or long residue feedstock in the first stage preheater at any point prior to the exit of the gas-liquid mixture from the first stage preheater. In a more preferred embodiment, dilution gas 13 is added to the crude oil and/or long residue feedstock of the first stage preheater at a point
15 external to pyrolysis furnace for ease of maintaining and replacing equipment.

20 The feed of dilution gas is a stream which is a vapour at the injection point into the first stage preheater. Any gas can be used which promotes the evaporation of non-coking fractions and a portion of coking fractions in the crude oil and/or long residue feedstock. The dilution gas feed also assists in maintaining the flow regime of the feedstock through the tubes whereby the tubes remain wetted and avoid a
25 stratified flow. Examples of dilution gases are steam, preferably dilution steam (saturated steam at its dewpoint), methane, ethane, nitrogen, hydrogen, natural gas, dry gas, refinery off gases, and a vapourized naphtha. Preferably, the dilution gas is dilution steam,
30 a refinery off gas, vapourized naphtha, or mixtures thereof.

35 The temperature of the dilution gas is at a minimum sufficient to maintain the stream in a gaseous state. With respect to dilution steam, it is preferably added at a temperature below the temperature of the crude oil

feedstock measured at the injection point to ensure that the dilution gas does not condense, more preferably 25 °C below the crude oil feedstock temperature at the injection point. Typical dilution steam temperatures at the dilution gas/feedstock junction range from 140 °C to 260 °C, more preferably from 150 °C to 200 °C.

The pressure of dilution gas is not particularly limited, but is preferably sufficient to allow injection. Typical dilution gas pressures added to the crude oil is generally within the range of 6-15 bar.

It is desirable to add dilution gas into the first stage preheater in an amount up to 0.5:1 kg of gas per kg of crude oil, preferably up to 0.3:1 kg of gas per kg of crude oil and/or long residue feedstock.

Alternatively, a feed of dilution fluid 13 (the fluid being in a liquid or mixed liquid/gas phase) may be added to the crude oil feedstock in the first stage preheater at any point prior to the exit of the gas-liquid mixture from the first stage preheater. Examples of dilution fluids are liquids that are easily vapourized along with crude such a liquid water, or naphtha in combination with other dilution liquids or gases. In general, a dilution fluid is preferred when the injection point is at a location where crude is still in the liquid phase, and dilution gases are preferred when the injection point is at a location where crude is either partially or wholly vapourized. Preferably, the process, wherein the amount of water added to the feedstock is 1 mole% or less, based on the moles of the feedstock.

In a further alternative embodiment, superheated steam can be added to the first stage preheater in line 13 to promote further evaporation of the crude oil feedstock within the first stage preheater tubes.

Once the crude oil feedstock has been heated to produce a gas-liquid mixture, it is withdrawn from the

first stage preheater through line 14, directly or indirectly to a vapour-liquid separator as a heated gas-liquid mixture. The vapour-liquid separator removes the non-vapourized portion of the crude oil and/or long residue feed, which is withdrawn and separated from the fully vapourized gases of the crude oil and/or long residue feed. The vapour-liquid separator can be any separator, including a cyclone separator, a centrifuge, or a fractionation device commonly used in heavy oil processing. The vapour-liquid separator can be configured to accept side entry feed wherein the vapour exits the top of the separator and the liquids exit the bottom of the separator, or a top entry feed wherein the product gases exit the side of the separator.

The vapour-liquid separator operating temperature is sufficient to maintain the temperature of the gas-liquid mixture within the range of 375 °C to 520 °C, preferably within the range of 400 °C to 500 °C. The vapour-liquid temperature can be adjusted by an means, including increasing a flow of superheated dilution steam to the gas-liquid mixture destined for the vapour-liquid separator as described in further detail below with respect to Figure 5, and/or by increasing the temperature of the feedstock to the furnace from external heat exchangers.

In a preferred embodiment, the vapour-liquid separator is described in copending application TH 1497 entitled, "A Wetted Wall Vapour-liquid Separator." Referring now to Figs. 2 and 3, the vapour-liquid separator 20 is shown in a vertical, partly sectional view in Fig. 2 and in a sectional plan view in Fig. 3. The conditions of the gas-liquid mixture in line 14 at the entrance of the vapour-liquid separator 20 are dependent on the feedstock 11 properties. It is preferred to have sufficient non-vapourized liquid 15

(between 2-40 vol% of the feedstock, preferably 2-5 vol% of the feedstock) to wet the internal surfaces of the vapour-liquid separator 20. This wetted wall requirement is essential to decrease the rate of, if not prevent, coke formation and deposition on the surface of the separator 20. The degree of vapourization (or vol% of non-vapourizable liquid 15) can be controlled by adjusting the dilution steam/feedstock ratio and flash temperature of the gas-liquid mixture 14.

The vapour-liquid separator 20 described herein permits separation of the liquid 15 and vapour 16 phases of the flash mixture in such a manner that coke solids are not allowed to form and subsequently foul either the separator 20 or the downstream equipment (not shown). On account of its relatively compact construction, the wetted-wall vapour-liquid separator 20 design can achieve a higher temperature flash than that in a typical vacuum crude column, thus effecting the recovery of a higher vapourized fraction 16 of the feed 11 for further downstream processing. This increases the fraction of feedstock 11 which can be used for producing higher valued products 23, and reduces the fraction of heavy hydrocarbon liquid fraction 15 having a lower value.

Referring to Fig. 2, the vapour-liquid separator 20 comprises a vessel having walls 20a, an inlet 14a for receiving the incoming gas-liquid mixture 14, a vapour outlet 16a for directing the vapour phase 16 and a liquid outlet 15a for directing the liquid phase 15. Closely spaced from the inlet 14a is a hub 25 having a plurality of vanes 25a spaced around the circumference of the hub 25, preferably close to the end nearest the inlet 14a. The vane assembly is shown more clearly in the perspective view of Fig. 4. The incoming gas-liquid mixture 14 is dispersed by splashing on the proximal end of the hub 25 and, in particular, by the vanes 25a

forcing a portion of the liquid phase 15 of the mixture 14 outwardly toward the walls 20a of the vapour-liquid separator 20 thereby keeping the walls 20a completely wetted with liquid and decreasing the rate of, if not preventing, any coking of the interior of the walls 20a. Likewise, the outer surface of the hub 25 is maintained in a completely wetted condition by a liquid layer that flows down the outer surface of hub 25 due to insufficient forces to transport the liquid 15 in contact with the surface of hub 25 to the interior of the walls 20a. A skirt 25b surrounds the distal end of the hub 25 and aids in forcing any liquid transported down the outer surface of the hub 25 to the interior of the walls 20a by depositing the liquid into the swirling vapour. The upper portion of the vapour-liquid separator 20 is filled in at 20b between the inlet 14a and hub 25 to aid wetting of the interior of walls 20a as the gas-liquid mixture 14 enters the vapour-liquid separator 20. As the liquid 15 is transported downward, it keeps the walls 20a and the hub 25 washed and reduces, if not prevents, the formation of coke on their surfaces. The liquid 15 continues to fall and exits the vapour-liquid separator 20 through the liquid outlet 15a. A pair of inlet nozzles 26 is provided below the vapour outlet tube 16a to provide quench oil for cooling collected liquid 15 and reduce downstream coke formation. The vapour phase 16 enters the vapour outlet duct 16a at its highest point 16c, exits at outlet 16a and proceeds to a vapourizer 17 for further treatment prior to entering the radiant section of the pyrolysis furnace as shown in Fig. 1. A skirt 16b surrounds the entrance 16c to the vapour duct 16 and aids in deflecting any liquid 15 outwardly toward the separator walls 20a.

The distance of the hub 25 extension below the vanes 25a was picked based on estimation of the liquid

drop size that would be captured before the drop had moved more than half way past the hub 25. Significant liquid 15 will be streaming down the hub 25 (based on observations with the air/water model) and the presence of a 'skirt' 25b on the hub 25 will introduce liquid droplets into the vapour phase well below the vanes 25a, and collection will continue below the skirt 25b of hub 25 due to the continued swirl of the vapour 16 as it moves to the outlet tube 16a.

The hub skirt 25b was sized to move liquid from the hub 25 as close as possible to the outer wall 20a without reducing the area for vapour 16 flow below that available in the vanes 25a. As a practical matter, about 20% more area for flow has been provided than is present at the vanes 25a.

The distance between the bottom of the hub 25 and the highest point 16c of vapour outlet tube 16a was sized as four times the vapour outlet tube 16a diameter. This was consistent with the air/water model. The intent is to provide area for the vapour to migrate to the outlet 16a without having extremely high radial velocities.

The distance from the entrance 16c of the vapour outlet tube 16a to the centerline of the horizontal portion of vapour outlet pipe 16a, has been chosen as roughly three times the pipe diameter. The intent is to provide distance to keep the vortex vertical above the outlet tube 16a - not have it disturbed by the proximity of the horizontal flow path of the vapour 16 leaving outlet tube 16a. The position and size of the anti-creep ring 16b on the vapour outlet tube 16a are somewhat arbitrary. It is positioned close to, but below, the lip and is relatively small to allow room for coke to fall between the outer wall 20a and the ring 16b.

Details of the separator 20 below the outlet tube 16a have been dictated by concerns outside the bounds of this

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separator. As long as nothing is done to cause liquid to jet above the inlet 16c to the outlet tube 16a, there should be no impact to separation efficiency.

Chief areas of coking concern involve sections with vapour recirculation, or metal not well washed with liquid. The area 20b inside the top head may be shaped or filled with material to approximate the expected recirculation zone. The inside of the hub 25 is another potential trouble point. If coke were to grow and fall over the inlet 16c to vapour outlet tube 16a, a significant flow obstruction could occur (such as a closed check valve). For this reason, a cage or screen 25c of either rods or a pipe cap may be used. This would not prevent the coke from growing, but would hold most of it in place so that a large chunk is not likely to fall. Areas under the vane skirts and the skirts 16b on the vapour outlet tube 16a are also 'unwashed' and coke growth in these areas is possible.

The gaseous vapourized portion 16 of the crude oil and/or long residue feedstock 11 fed to the vapour-liquid separator 20 as a gas-liquid mixture from the first stage preheater 12 is subsequently fed through a vapourizer mixer 17, in which the vapour mixes with superheated steam 18 to heat the vapour to a higher temperature. The vapour is desirably mixed with superheated steam in order to ensure that the stream remains in a gaseous state by lowering the partial pressure of the hydrocarbons in the vapour. Since the vapour exiting the vapour-liquid separator is saturated, the addition of superheated steam will minimize the potential for coking fractions in the vapour to condense on inner surfaces of the unheated external piping connecting the vapour-liquid separator to the second stage preheater. The source of the superheated steam is a steam feed 18 into the convection section of the pyrolysis furnace between the first and second stage

preheaters. The flue gases from the radiant section preferably act as the heating source for increasing the temperature of the steam to a superheated state.

5 Suitable superheated steam temperatures are not particularly limited at the high end, and should be sufficient to provide a measure of superheating above the dew point of the vapour. Generally, the superheated steam is introduced to the vapourizer mixer 17 at a temperature ranging from about 450 °C to 600 °C.

10 The vapourizer mixer 17 is preferably located external to the pyrolysis furnace, again for ease of maintenance. Any conventional mix nozzle may be used, but it is preferred to use a mix nozzle as described in U.S.-A-4,498,629, to further minimize the coking
15 potential around the inner surfaces of the mix nozzle. The preferred mix nozzle as described in U.S.-A-4,498,629 comprises a first tubular element and a second tubular element surrounding the first tubular element to form an annular space. The first tubular element and the second
20 tubular element have substantially coinciding longitudinal axes. Preferably, superheated steam is combined with the removed gas prior to entry into the second stage preheater. Therefore, a first inlet means is provided for introducing the vapourized crude oil and/or
25 long residue or long residue feedstock into the first tubular element and a second inlet means is provided for introducing superheated steam into the annular space. The first tubular element and the second tubular element are each provided with an open end for the supply of the
30 superheated steam as an annulus around a core of the vapour feed, the open ends terminating in openings arranged in a plane, substantially perpendicular to the longitudinal axes. The apparatus also includes a frustoconically shaped element at one end connected to
35 the open end of the second tubular element, provided with

a longitudinal axis substantially coinciding with the longitudinal axes of the tubular elements and diverging in a direction away from the second tubular element, the frustoconically shaped element having an apex angle of at most 20 degrees. The arrangement of a slightly diverging frustoconically shaped element behind the location where the superheated steam meets the feed prevents the contact of liquid droplets with the wall of the element thereby minimizing the risk of coke formation in the mix nozzle.

The superheated steam/gas mixture exits the vapourizer mixer 17 through line 19, is fed to the second stage preheater 21 and is heated in the second stage preheater through tubes heated by the flue gases from the radiant section of the furnace. In the second stage preheater 21, the mixed superheated steam-gas mixture is fully preheated to near or just below a temperature at which substantial feedstock cracking and associated coke laydown in the preheater would occur. The mix feed subsequently flows to the radiant section B through line 22 of the olefins pyrolysis furnace where the gaseous hydrocarbons are thermally cracked to olefins and associated by products exiting the furnace through line 23. Typical inlet temperatures to the radiant zone B are above 480 °C, more preferably at least 510 °C, most preferably at least 537 °C, and at least 732 °C at the exit, more preferably at least 760 °C, and most preferably between 760 °C and 815 °C, to promote cracking of long and short chain molecules to olefins. Products of an olefins pyrolysis furnace include, but are not limited to, ethylene, propylene, butadiene, benzene, hydrogen, and methane, and other associated olefinic, paraffinic, and aromatic products. Ethylene generally is the predominant product, typically ranging from 15 to 30 wt.%, based on the weight of the vapourized feedstock.

In an optional embodiment, superheated steam may be added to the first stage preheater 12 in the convection section through line 13 in lieu of dilution steam as shown in Fig. 1, or may be added between the exit port of the first stage preheater and the vapour-liquid separator as shown in Fig. 5, for the purpose of further elevating the temperature of the gas-liquid mixture so desired, thereby increasing the fractions and weight percentage of vapour recovered from the crude oil and/or long residue feedstock.

The percentage of vapourized components in a gas-liquid mixture within the first preheater may be adjusted by controlling the flash temperature, the quantity of optional dilution steam added, and the quantity and temperature of optional superheated steam added to the crude oil and/or long residue feedstock in the first stage preheater 12. The amount of vapour recovered from the crude oil and/or long residue feedstock should not exceed the stated gas-liquid ratio, that is, no greater than 98/2, in order to minimize coking.

The process of the invention can inhibit coke formation within the vapour-liquid separator 20, the vapourizer mixer 17, and in the second stage preheater 21, by continually wetting the heating surfaces within the first stage preheater and the vapour-liquid separator. The process of the invention achieves high recovery of crude oil and/or long residue fractions not otherwise obtainable at first stage preheater temperatures of 350 °C or less, while simultaneously inhibiting coke formation.

The pyrolysis furnace may be any type of conventional olefins pyrolysis furnace operated for production of lower molecular weight olefins, especially including a tubular steam cracking furnace. The tubes within the convection zone of the pyrolysis furnace may be arranged

as a bank of tubes in parallel, or the tubes may be arranged for a single pass of the feedstock through the convection zone. At the inlet, the feedstock may be split among several single pass tubes, or may be fed to one single pass tube through which all the feedstock flows from the inlet to the outlet of the first stage preheater, and more preferably through the whole of the convection zone. Preferably, the first stage preheater is comprised of one single pass bank of tubes disposed in the convection zone of the pyrolysis furnace. In this preferred embodiment, the convection zone comprises a single pass tube having two or more banks through which the crude oil and/or long residue feedstock flows. Within each bank, the tubes may arranged in a coil or serpentine type arrangement within one row, and each bank may have several rows of tubes.

To further minimize coking in the tubes of the first stage preheater and in tubes further downstream and within the vapour-liquid separator, the linear velocity of the crude oil and/or long residue feedstock flow is preferably selected to reduce the residence time of coking fraction vapourized gases in the tubes. An appropriate linear velocity will also promote formation of a thin uniform wetted tube surface. While higher linear velocities of crude oil and/or long residue feedstock through the tubes of the first stage preheater reduce the rate of coking, there is an optimum range of linear velocity for a particular feedstock beyond which the beneficial rates of coke reduction begin to diminish in view of the extra energy requirements needed to pump the feedstock and the sizing requirements of the tubes to accommodate a higher than optimum velocity range. In general, crude oil and/or long residue linear velocity through the tubes of the first stage preheater in a convection section ranging from 1.1-2.2 m/s, more

preferably from 1.7-2.1 m/s, and most preferably from 1.9-2.1 m/s, provide optimal results in terms of reducing the coking phenomenal balance against the cost of the tubes in furnace and the energy requirements.

5 One means for feeding a crude oil and/or long residue feedstock at a linear velocity within the range of 1.1-2.2 m/s is through any conventional pumping mechanism. In a preferred embodiment of the invention, the linear velocity of the crude oil and/or long residue
10 feedstock is enhanced by injecting a small amount of liquid water into the crude feed prior to entry within the first stage preheater, or at any point desired within the first stage preheater. As the liquid water vapourizes in the crude oil and/or long residue
15 feedstock, the velocity of the feed through the tubes increases. To achieve this effect, only small quantities of water are needed, such as 1 mole% water or less based on the moles of the feedstock through the first stage preheater tubes.

20 In many commercial olefins pyrolysis furnaces, the radiant section tubes accumulate sufficient coke every 3-5 weeks to justify a decoking operation on those tubes. The process of the invention provides for the preheating and cracking of a crude oil and/or long residue feedstock
25 in a olefins furnace without having to shutdown the furnace for decoking operations any more often than the furnace would otherwise have to be shutdown in order to conduct the decoking treatment in the radiant section tubes. By the process of the invention, the convection
30 section run period is at least as long as the radiant section run period.

35 In another embodiment of the invention, the convection section tubes are decoked on a regular scheduled basis at a frequency as required, and in no event more frequent than the frequency of radiant section

decoking. Preferably, the convection section is decoked at a frequency at least 5 times longer, more preferably from at least 6 to 9 times longer than the radiant section decoking schedule. Decoking of a tube may be conducted with a flow of steam and air.

In yet another embodiment of the invention, a flow of superheated steam is added to the first stage preheater tubes and/or between the exit point from the first stage preheater convection section and the vapour-liquid separator via a mix nozzle. Thus, there is provided an embodiment where a flow of superheated steam enters the convection zone, preferably between the first and second stage preheaters, thereby superheating the flow of steam to a temperature within a range of about 450 °C-600 °C. As shown in Fig. 5 and Fig. 6, the source of superheated steam may be split by a splitter to feed a flow of superheated steam to the vapour-liquid separator 6 and a flow of superheated steam to a mix nozzle 5 located between the exit of the first stage preheater comprising the tube banks 2, 3, and 4 and the vapour-liquid separator 6.

In yet a further embodiment of the invention, the feedstock may optionally be split by a splitter 1a as shown in Fig. 6, between heat exchangers 2 and 3, or between any other heat exchangers in the first preheater section of the convection section of the furnace. Such a splitter may be desirable when the feedstock contains a high weight percentage of pitch and is heated to a high temperature within the heat exchanger 1 in order to control its flowability, thereby obviating the need to process all of the feedstock through the first heat exchanger in the first preheater section of the convection zone.

The following prophetic example illustrates one of the embodiments of the invention and is not intended to

limit the scope of the invention. This example is derived from the modeling program Simulated Sciences ProVision Version 5.1. Reference is made to Figure 5 to illustrate this embodiment. In each case, the vapour-liquid mixture exiting the convection zone is at a temperature which exceeds 375 °C. Under the pressure/temperature conditions described in the examples, lighter feeds such as heavy natural gas liquid would vapourize cracking fractions, causing the convection section to coke up at a much faster rate than the coking rate in a furnace processing the feedstocks under the conditions described below.

Prophetic Example 1

A crude oil feed, having the properties listed below, is used as the feedstock:

API Gr.	37.08
ASTM D-2887 TBP	
Wt. %	Deg. C
1%	24
10%	111
20%	170
30%	225
40%	269
50%	309
60%	368
70%	420
80%	477
90%	574
97%	696

This crude oil feedstock which has an API gravity 37.08, and an average molecular weight of 211.5, is fed

at a temperature of 27 °C and a rate of 38,500 kg/hr to an external heat exchanger 1 to warm the crude oil to a temperature of 83 °C at a pressure of 15 bar prior to entry into the first bank of convection section heater tubes 2. The heated crude oil feedstock, still being all liquid at this point, is routed through the single pass first bank of tubes 2 having eight rows of tubes, each row spatially arranged in a serpentine fashion, and there is heated to a temperature of 324 °C and exits at a pressure of 11 bar. At this stage the liquid weight fraction is 0.845, and the liquid is flowing at a rate of 32,500 kg/hr. The density of the liquid is 612 kg/m³ and its average molecular weight is 247.4. The vapour phase flows at a rate of 5950 kg/hr and has an average molecular weight of 117.9 and a density of 31 kg/m³.

The vapour-liquid mixture exits the first bank of tubes 2 and is fed to a second bank of tubes 3 identical to the first bank, where the vapour-liquid mixture is further heated to a temperature of 370 °C and exits at a pressure of 9 bar. The liquid weight fraction exiting this second bank of tubes is 0.608. The liquid now has a density of 619 kg/m³ and has an average molecular weight of 312.7, and flows at a rate of 23,400 kg/hr. The vapour phase flows at a rate of 15,100 kg/hr and has an average molecular weight of 141.0 and a density of 27.4 kg/m³.

The vapour-liquid mixture is subsequently fed to a third bank of tubes 4 identical to the first and second bank of tubes, wherein the vapour-liquid mixture is further heated to a temperature of 388 °C, and exits the third bank and the convection zone at that temperature and at a pressure of about 7 bar. At the third bank of tubes 4, a flow of 1359 kg/hr of dilution steam, stream 3.5, is fed to the third bank of tubes 4 at 10 bar

and at 182 °C. The liquid weight fraction exiting the third bank of tubes 4 is now reduced down to 0.362. The average molecular weight of the liquid phase at the exit of the third bank of tubes is increased to 419.4 and it has a density of 667 kg/m³ flowing at a rate of 14,400 kg/hr. The vapour phase flows at a rate of 25,400 kg/hr, has an average molecular weight of about 114.0 and a density of 14.5 kg/m³.

The vapour-liquid mixture exits the third bank of tubes 4 in the convection section of the ethylene furnace and flows to the Mix Nozzle 5. A flow 5a of about 17,600 kg/hr of steam superheated to 594 °C at a pressure of 9 bar is injected into the vapour-liquid mixture exiting the convection zone through the Mix Nozzle 5.

The resulting vapour-liquid mixture flows to a vapour-liquid separator 6 at a rate of 57,500 kg/hr, at a temperature of 427 °C, and at 6 bar. The average molecular weight of the liquid phase now has further increased to 696.0. The liquid weight fraction is now 0.070 due to the addition of superheated steam.

The vapour-liquid mixture is separated in the vapour-liquid separator 6. The separated liquids exit through the bottom of the separator. The separated vapour 7 exits the vapour-liquid separator at the top or through a side draw a rate of 53,500 kg/hr and at a temperature of about 427 °C and a pressure of 6 bar. The average molecular weight of the vapour stream is about 43.5, and it has a density of 4.9 kg/m³. The liquid bottom stream exiting the vapour-liquid separator is regarded as pitch and may be treated accordingly. The rate of pitch flow is about 4,025 kg/hr, and exits at a temperature of about 427 °C at 6 bar. This liquid has a density of 750 kg/m³ and an average molecular weight of 696.

5 The vapour stream 7 is combined with steam 8a heated
in a bank of tubes 8. The steam through line 8a flows at
a rate of about 1360 kg/hr and is superheated to a
temperature of 593 °C at a pressure of 9 bar. It flows
through a Mix Nozzle 9 where it is combined with vapour
stream 7 to produce a vapour stream 9a flowing at a rate
of 54,800 kg/hr at a temperature of 430 °C and a pressure
of about 6 bar to the convection zone second stage
preheater 9b, where it is further heated and passed to a
10 radiant zone, not shown. The average molecular weight of
the vapour stream 9a is 42.0 and its density is
4.6 kg/m³.

15 The vapour stream subsequently flows back to the
convection zone and into the radiant zone of the ethylene
furnace to crack the vapour.

Prophetic Example 2

20 A long residue stream derived from crude oil which
originates as the bottoms stream of an atmospheric crude
distillation column and has the properties listed below,
is used as the feedstock:

API Gr.	25.85
ASTM D-2887 TBP	
Wt. %	Deg. C
0%	220
10%	356
20%	391
30%	414
40%	432
50%	447
60%	467
70%	492
80%	536
90%	612
98%	770

This long residue feedstock which has an API gravity
 of 25.85 and an average molecular weight of 422.2 and is
 fed at a temperature of 38 °C and a rate of 43,000 kg/hr
 to an external heat exchanger(s) 1 to warm the long
 residue to a temperature of 169 °C at a pressure of
 18 bar prior to entry into the first bank of convection
 section heater tubes 2. The long residue feedstock,
 still being all liquid at this point, is routed through
 the single pass first bank of tubes 2 having eight rows
 of tubes, each row spatially arranged in a serpentine
 fashion, and there is heated to a temperature of 347 °C
 and exits as a liquid at a pressure of 13 bar.

The long residue has a density of 710 kg/m³ as it
 exits the first bank of tubes 2 and is fed to a second
 bank of tubes 3 identical to the first bank, where it is
 further heated to a temperature of 394 °C and exits at a
 pressure of 10 bar. No vapourization takes place and

entire stream exits as a liquid flowing at a rate of 43,000 kg/hr with density is 670 kg/m^3 .

5 The long residue is subsequently fed to a third bank of tubes 4 identical to the first and second bank of tubes, wherein it is further heated to a temperature of 410 °C, and exits the third bank and the convection zone at that temperature and at a pressure of about 7 bar. At the third bank of tubes 4, a flow of 1360 kg/hr of dilution steam, stream 3.5, is fed to the third bank of
10 tubes 4 at 10 bar and at 182 °C. It leaves the third bank of tubes 4 as a vapour-liquid mixture having a liquid weight fraction of 0.830. The average molecular weight of the liquid phase at the exit of the third bank of tubes is 440.5 and it has a density of 665 kg/m^3
15 flowing at a rate of 36,850 kg/hr. The vapour phase flows at a rate of 7540 kg/hr, has an average molecular weight of about 80.5 and a density of 9.6 kg/m^3 .

The vapour-liquid mixture exits the third bank of tubes 4 in the convection section of the ethylene furnace and flows to the Mix Nozzle 5. A flow 5a of about
20 17,935 kg/hr of steam superheated to 589 °C at a pressure of 9 bar is injected into the vapour-liquid mixture exiting the convection zone through the Mix Nozzle 5. The resulting vapour-liquid mixture flows to a
25 vapour-liquid separator 6 at a rate of 62,330 kg/hr, at a temperature of 427 °C, and at 6 bar. The average molecular weight of the liquid phase now has further increased to 599.0. The liquid weight fraction is now 0.208 due to the addition of superheated steam.

30 The vapour-liquid mixture is separated in the vapour-liquid separator 6. The separated liquids exit through the bottom of the separator. The separated vapour 7 exits the vapour-liquid separator at the top or through a side draw at a rate of 49,400 kg/hr and at a temperature

of about 427 °C and a pressure of 6 bar. The average molecular weight of the vapour stream is about 42.9, and it has a density of 4.84 kg/m³. The liquid bottom stream exiting the vapour-liquid separator is regarded as pitch and may be treated accordingly. The rate of pitch flow is about 13,000 kg/hr, and exits at a temperature of about 427 °C at 6 bar. This liquid has a density of 722 kg/m³ and an average molecular weight of 599.

The vapour stream 7 is combined with steam 8a heated in a bank of tubes 8. The steam through line 8a flows at a rate of about 1360 kg/hr and is superheated to a temperature of 589 °C at a pressure of 9 bar. It flows through a Mix Nozzle 9 where it is combined with vapour stream 7 to produce a vapour stream 9a flowing at a rate of 50,730 kg/hr at a temperature of about 430 °C and a pressure of about 6 bar to the convection zone second stage preheater 9b, where it is further heated and passed to a radiant zone, not shown. The average molecular weight of the vapour stream 9a is 41.3 and its density is 4.5 kg/m³.

The vapour stream subsequently flows back to the convection zone and into the radiant zone of the ethylene furnace to crack the vapour.

C L A I M S

1. A process for pyrolyzing a crude oil and/or crude oil fractions containing pitch feedstock in an olefins pyrolysis furnace comprising feeding the crude oil and/or crude oil fractions containing pitch feedstock to a first stage preheater provided in a convection zone of the furnace, heating the feedstock within the first stage preheater to an exit temperature of at least 375 °C to produce a heated gas-liquid mixture, withdrawing the heated gas-liquid from the first stage preheater to a vapour-liquid separator, separating and removing the gas from the liquid in the vapour-liquid separator, and feeding the removed gas to a second stage preheater provided in the convection zone, further heating the temperature of the gas to a temperature above the temperature of the gas exiting the vapour-liquid separator, introducing the preheated gas into a radiant zone of the pyrolysis furnace, and pyrolyzing the gas to olefins and associated by-products.
2. The process of claim 1, wherein 85 wt.% or less of the feedstock will vapourize at 350 °C, and 90 wt.% or less of the crude oil feedstock will vapourize at 400 °C, each as measured according to ASTM D-2887.
3. The process according to claim 1 or 2, wherein the feedstock is fed to the first stage preheater at a pressure ranging from 11 to 18 bar and at a temperature ranging from 140 °C-300 °C.
4. The process according to any one of claims 1-3, wherein the feedstock in the first stage preheater is heated to an exit temperature of at least 400 °C.
5. The process according to any one of claims 1-4, wherein the gas-liquid ratio ranges from 60/40 to 98/2.

6. The process according to any one of claims 1-5, wherein dilution gas is added to the feedstock in the first stage preheater.

5 7. The process according to any one of claims 1-6, wherein superheated steam is combined with the removed gas prior to entry into the second stage preheater.

8. The process according to any one of claims 1-7, wherein the olefins comprise ethylene in an amount ranging from 15 to 30 wt.%, based on the weight of the
10 vapourized feedstock.

9. The process according to any one of claims 1-8, wherein a dilution fluid, which fluid is in a liquid or mixed liquid/gas phase, is added in the first stage preheater.