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PROCESS FOR THE RECOVERY OF HEAT FROM HOT GASES

Claes Wilhelm Pilo, Stockholm, and Sven Wilhelm Dahlbeck, Djursholm, Sweden

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The present invention relates to a method of utilising the heat content of hot gases by direct heat exchange with a liquid flowing in the same direction or in the opposite direction thereto. If desired, the treatment of the gas may be carried out with the liquid flowing partly in the same direction and partly in the opposite direction thereto, or by the so-called cross-current method, that is to say in a method in which the directions of flow of the gas and the liquid are not parallel to one another.

By "heat content" of the gases, the quantity of heat is hereinafter meant which is contained as sensible heat in the gas, in addition to the quantity of heat which is present in the form of latent heat, for example in the form of heat of evaporation of vapours which are constituents of the gas. The constituent most frequently present in technical gases containing latent heat is, for example, steam. As is well known, steam contains not only sensible heat corresponding to its vapour temperature but at the same time the heat of evaporation which must be expended to convert the liquid phase into the vapour phase without an increase in temperature.

In industry, a number of gases are formed at a temperature of about 200–250° C. and are then generally either discharged through chimneys or fed to coolers in which the heat content of these gases is destroyed. Such gases are, for example, the flue gases from a steam boiler installation which have passed through the feed-water preheater, as also the flue gases from coke ovens and gas works which, after having given up a large proportion of their sensible heat in the heating walls of the coke ovens, are passed through regenerators for the purpose of utilising further portions of their sensible heat, but which leave the latter while still at a temperature of 200–250° C. The useful gases formed in the gasification of coke in producers also belong to this group of gases. This so-called "producer gas" is generally fed to a cooling scrubber after leaving the producer, and is simultaneously purified and cooled therein.

Many attempts have been made to utilise profitably the heat content of such gases, more especially of waste gases of the aforesaid type. For this purpose, two different methods may fundamentally be employed. The gas may be indirectly cooled in a cooler, in which case the gas flows on one side and the cooling medium, generally water, on the other side of the cooling surfaces. Alternatively, the gas may be cooled directly with water, in which case the gas and the cooling medium come into contact with one another while flowing in the same direction or in opposite directions, while if desired the cooling medium may be introduced into the gas in finely divided form. The first-mentioned method of indirect cooling has the disadvantage that it entails the recovery of heat which is of relatively low value owing to its low temperature level and the cooling surfaces must be made uneconomically large, because it is necessary to work with small temperature differences in the heat exchanger owing to the low heat transfer coefficients on the gas side.

The second method of direct cooling with a liquid has the considerable disadvantage that the cooling water cannot be heated to a temperature higher than the dew point of the gas to be cooled because water has practically always been employed as cooling liquid. Even if a counter-current method of the most favourable possible form is employed for the direct cooling the cooling water generally cannot be heated above 45°–55° C. if, for example, the gas has a temperature between 150° and 250° C. Water at a temperature of 45°–55° C. generally cannot be technically utilised, while in addition the water has generally been contaminated by contact with the gas and therefore cannot be directly employed, but must first give up to the pure water, through an indirect heat exchanger, the heat which it has absorbed from the gas, which process naturally entails a further loss of useful heat.

The inventor's experiments have shown that the heat content of hot gases may be technically and economically utilised even with direct cooling by a cooling medium if the direct cooling is carried out in the following novel manner. According to the invention, the gas to be cooled is brought into direct heat exchange with a non-aqueous cooling liquid which is of such nature that its boiling point at normal pressure is considerably higher than 100° C. and its partial pressure at a temperature which the liquid assumes in the neighbourhood of its entry into the direct cooler is substantially zero, and that the cooling liquid heated by direct heat exchange with the gas to a temperature close to that of the entering gas gives up at least the greater part of its heat to water or another liquid or gas, whereafter the cooling liquid is returned preferably to the direct cooler, if desired after having been freed from dust and other impurities.

If the gas to be cooled contains steam and it is cooled to below its dew point for steam, the properties of the cooling liquid employed for the direct cooling must in addition be such that it does not dissolve water in appreciable quantities and has no special tendency to form emulsions with water. In addition, the cooling liquid must in this case have a specific gravity which differs so greatly from that of water that the water and the cooling liquid are separated from one another by simple means, preferably by settling.

Such liquids are in fact known and a number of them exist. The most suitable for this purpose are fractions of aliphatic hydrocarbons, aromatic hydrocarbons or naphthenes. If desired, mixtures of such hydrocarbons and mixtures of organic compounds with inorganic compounds may be successfully employed. One example of such liquids is tetradecane, which is a liquid hydrocarbon of the paraffin series which contains fourteen carbon atoms. The physical properties of tetradecane will be more fully described in the example hereinafter given.

In carrying out the process according to the invention, in which the counter-current principle is above all of particular advantage, the cooling liquid may actually be heated to a temperature which is only lower by a relatively small amount, for example 10° C., than the temperature of the gas to be cooled which enters the cooling arrangement. The cooling liquid may then yield the heat absorbed from the gas, for the greater part by means of an indirect heat exchange, to pure water which, if the heat exchanger is suitably dimensioned, nevertheless assumes a temperature which, although somewhat lower than the temperature of the cooling liquid, is so high that technical utilisation, for example for the generation of steam or for the production of hot water, is possible. After having given up the heat absorbed from the gas to pure water and thus having been cooled, the cooling liquid is returned into the circuit for the purpose of cool-

ing further quantities of gas, preferably after having been freed from dust or other impurities which it has absorbed from the gas.

If the gas contains no appreciable quantities of steam, that is to say, has a comparatively low dew point, or provided that its temperature does not fall below its dew point in the cooling of a steam-containing gas having a relatively high dew point, the method according to the invention may be carried out in a particularly simple manner with a single circulation of cooling liquid, in which case the gas is introduced into the cooler at the bottom and withdrawn from the top, while the cooling liquid is introduced at the top of the cooler and withdrawn from the bottom. The nature of the coolers employed is in principle immaterial. Coolers may be employed which are provided with packing elements or hurdles or which have bubble-trays or the like. Direct coolers having rotating internal fittings have proved highly suitable for this purpose, in which the cooling liquid is accelerated to relatively high speeds by centrifugal forces and come into contact with the gas in counter-current.

However, it is desirable in most cases, and especially if the dew point of the gas is relatively high, for example 40° or 50° C., to cool the gas to below the dew point and thus to utilise not only the sensible heat of the gas but also the heat of evaporation which is liberated in the condensation of the steam contained in the gas, but in this case the cooling medium circuit must be divided into two substantially separate circuits intercommunicating through the gas stream to be cooled, in order to achieve the desired result. The latter step, the details of which will hereinafter be more fully described, is necessary because the water produced in the cooler when the temperature falls below the dew point of the gas flows together with the non-aqueous cooling liquid into that part of the cooler to which the hot, still uncooled gas is fed. If the penetration of water to this point were not prevented by other steps, water would again evaporate at this point and the heat of evaporation required for this purpose would be extracted, not only from the sensible heat of the gas, but also from the sensible heat of the cooling liquid, so that the cooling liquid would leave the cooler, together with water, at a temperature considerably below that desirable and necessary for an economical utilisation.

In accordance with a further feature of the invention, the water of condensation collecting on an appropriately fashioned intermediate plate in the central part of the direct cooler in such a case is at least partly withdrawn from the said central part, preferably together with the entire quantity or a part of the cooling liquid. The water of condensation is preferably withdrawn from the cooler at a point at which the gas to be treated is at a temperature in the neighbourhood of the dew point of the gas fed to the cooler, that is to say, slightly below or above the said dew point.

If there are completely withdrawn from the cooler at a point between the bottom and the top both the water of condensation which has been formed up to this point and the cooling liquid which has reached this point—and the inventor prefers this embodiment of the invention—the cooling medium must be returned into the cooler when it has been separated from the entrained water outside the cooler, this preferably taking place at a point lying behind the point of discharge of the cooling liquid and the condensed water, as seen in the direction of flow of the cooling liquid in the cooler.

More particularly, the last embodiment of the invention may be performed by dividing the cooling liquid, after separation of the condensed water, into two component streams, one of which is fed to the top of the cooler after utilisation of the sensible heat and the other to the central part of the cooler, that component stream which is fed to the top of the cooler after utilisation of the sensible heat being heated only to a temperature in

the neighbourhood of the dew point of the gas to be treated, while the second component stream, after having been returned into the cooler, is heated therein to a temperature higher than the dew point and withdrawn from the bottom of the cooler and, after utilisation of the sensible heat, returned to the centre of the cooler.

The sensible heat of the first-mentioned component stream may be utilised in various ways. For example, the sensible heat of the cooling liquid may be employed to produce hot water. Alternatively, the sensible heat of the cooling liquid may be utilised with the aid of a heat pump. The sensible heat of the second component stream, on the other hand, will be employed as far as possible to produce hot water or steam owing to the considerably higher temperature of the cooling liquid.

The cooling stages thus produced, which are characterised by substantially separate cooling medium circuits, need not necessarily be situated in a single scrubber housing. It is alternatively possible first to cool the gas in one or more direct coolers to a temperature in the neighbourhood of the dew point and thereafter to cool it in one or more similarly or differently constructed direct coolers connected in series with the first-mentioned coolers to a temperature below the dew-point of the gas to be treated.

An embodiment of the invention is diagrammatically illustrated in the drawing. The gas to be treated, for example flue gas resulting from the combustion of coke oven gas with air, enters the direct cooler 2 at a temperature of about 250° C. by way of the duct 1 and leaves it at a temperature of about 30° – 35° C. by way of the duct 3. The cooler consists substantially of two cooling stages I and II which are separated from one another on the liquid side by the intermediate plate 4, but are connected together in series on the gas side. The various cooling stages contain packing elements of the known type, for example Raschig rings or the like. Cooling liquid is uniformly distributed over the packing elements by atomiser nozzles 5. The gas is so cooled in the cooling stage I that the temperature does not fall appreciably below its dew point, if at all, so that no appreciable quantities of water of condensation are formed in this cooling stage. The cooling liquid is heated to a temperature of about 10° – 20° C. lower than the temperature of admission of the gas. The cooling liquid is drawn from the bottom of the cooler 2 through the duct 6 and fed through the pump 7 to a steam generator 8 in which steam at 125° C. (2.4 atmospheres absolute) is generated by indirect heat exchange with water flowing through the duct 9, the said steam being withdrawn through the duct 10. The cooling liquid cooled to a temperature of about 130° C. in the steam generator 8 thereafter flows through the duct 11 into the indirect heat exchanger 12, in which it gives up a further part of its sensible heat to the water, which is converted into steam in the steam generator. The cooling liquid is thus cooled to about 55° C. and flows back into the cooler 2 through the duct 13. Since the liquid has absorbed dust and certain impurities from the gas in the cooling stage I while in contact therewith, a part of the cooling liquid is withdrawn from the duct 13 through the duct 13a and purified and thereafter returned into the circuit at a point which will hereinafter be defined.

The gas cooled in the cooling stage I to a temperature in the neighbourhood of the dew point then passes through the gas-permeable intermediate plate 4 into the next cooling stage II, to which comparatively cold cooling liquid—at about 30° C.—is admitted through the duct 14. A part of the steam is condensed and is collected on the intermediate plate with the cooling liquid which is descending and thus being heated. From the said intermediate plate, the cooling liquid mixture is withdrawn through the duct 15 and fed to a separating container 16 in which the two liquids are separated by reason of their

different specific gravities. The heavier water is removed from the system through the duct 17, while the lighter cooling medium flows through the duct 18 into the pump 19. The duct 20 guides the cooling medium, which is at a temperature of about 55° C., through the indirect heat exchanger 21, from which it returns through the duct 14 into the cooling stage II after having been cooled to about 30° C. in the heat exchanger. Water at normal temperature which flows to the heat exchanger 21 through the duct 22 is heated in the said exchanger to a temperature of about 45° C. This heated water is withdrawn through the duct 23 and may be fed through the duct 24 for use for any desired purpose. A part of this hot water flows through the duct 25 into the direct heat exchanger 12, in which it is preheated to a temperature of about 125° C. Some of the hot water leaving the heat exchanger 12 is fed to the duct 26 for use for any desired purpose, the remainder flowing through the duct 9 into the steam generator 8.

Since a part, although small, of the cooling liquid is inevitably always carried away in the form of steam with the cooled gas through the duct 3 and is thus lost, a quantity of fresh cooling medium must be continuously or intermittently introduced into the system. This is effected through the duct 27, through which that part of the cooling medium which has been withdrawn through the duct 13a may also be returned into the system after having been purified.

Since a relatively great quantity of cooling liquid flows from the cooling stage I into the cooling stage II in the form of steam and is then discharged from this cooling stage by way of the duct 15, a reduction of the quantity of cooling medium in the cooling stage I would occur. Therefore, a proportion of the cooling medium is branched off from the cooling medium circuit of the cooling stage II beyond the pump 19 and returned through the duct 28 into the duct 13 and thus into the cooling medium circuit of the cooling stage I.

Example

The method according to the invention will be assumed in the following example to be applied to the quantity of waste gas formed when 2,000 tons of coal are carbonised daily in a horizontal coke-oven battery heated by blast furnace top gas.

Blast furnace top gas has a lower heating value of about 940 large calories per cubic metre. About 49,700 cubic metres at normal temperature and pressure are required per hour to carbonise the aforesaid quantity of coal. The combustion of the blast furnace gas requires 45,200 cubic metres of air at normal temperature and pressure per hour and gives a waste gas quantity of 87,000 cubic metres at normal temperature and pressure per hour. The composition of the waste gas is as follows:

	Percent
N ₂ -----	75.72
CO ₂ -----	20.81
O ₂ -----	1.82
H ₂ O—steam-----	1.65

After leaving the regenerators of the coke oven battery, the waste gas still has a temperature of 250° C. This temperature is to be reduced to 35° C. by means of the method according to the invention. The dew point of the waste gas amounts to about 21.5° C., taking into account the moisture contained in the combustion air.

It is proposed to effect the cooling of the waste gas with a cooling liquid having the chemical formula C₁₄H₃₀ (tetradecane). This liquid has the following physical properties:

Molecular weight-----	198
Density-----	0.7645
Vapor pressure:	
At 230° C-----	mm. Hg-- 400
At 60° C-----	mm. Hg-- 0.3
At 55° C-----	mm. Hg-- 0.2
At 50° C-----	mm. Hg-- 0.1
At 40° C-----	mm. Hg-- 0.04
At 35° C-----	mm. Hg-- 0.02
Boiling Point-----	° C-- 252.5
Melting point-----	° C-- 5.5

The specific heat at constant pressure (c_p) is as follows:

- 15 In the 230°–60° C. range: 0.59 cal./kg. in degrees C.
In the 60°–40° C. range: 0.50 cal./kg. in degrees C.

20 In the cooling stage I, the temperature of the waste gas is lowered from 250° C. to 60° C. With a mean specific heat of the waste gas of 0.34 in this temperature range, the quantity of heat to be taken up by the cooling liquid is 5,620,000 large calories per hour, which is withdrawn from the cooling medium in the heat exchanger 12 and the steam generator 8. With an end temperature of the cooling liquid of 230° C. and an end temperature of the waste gas of 55° C. in this stage, the cooling medium required in this stage is 53,800 kg. per hour. The loss of cooling liquid in this stage, that is to say, the quantity of cooling liquid transferred into the next stage together with the waste gas, then amounts to 0.18 grammes per cubic metre at T. B. of waste gas, that is to say, 16.5 kg. per hour in all.

30 In the cooling stage II, the temperature of the waste gas is further lowered from 60° C. to 35° C. No steam is condensed in the waste gas, because the dew point of the waste gas for steam is 21.5° C. The quantity of heat which must be taken up by the cooling liquid in this cooling operation amounts, with a specific heat of the waste gas of 0.33 in this temperature range, to a total of 717,000 cal. per hour, which is withdrawn from the cooling medium in the heat exchanger 21. The quantity of cooling liquid required for this purpose is 57,400 kg. per hour. The loss of cooling liquid carried out of the cooling stage II in vapour form together with the cooled gas and thus absolutely lost amounts to 1.65 kg. per hour.

45 Taking into consideration unavoidable losses due to heat radiation and the like, about 6,287,000 cal. per hour in all can be recovered from the waste gas (calculated on water at 20° C.), which is divided as follows:

Steam (125° C.): 6,480 kg./h. with 4,060,000 cal./h.
Hot water (125° C.): 21,020 kg./h. with 2,200,000 cal./h.
Warm water (45° C.): 1,100 kg./h. with 27,600 cal./h.

55 If coke oven gas (calorific value 4,352 cal. per cubic metre at N. T. P.) is employed instead of blast furnace gas to heat the coke oven battery, 5,990,000 cal. per hour can be covered from the waste gas by the method according to the invention, which is divided as follows:

60 Steam (125° C.): 4,700 kg./h. with 2,950,000 cal./h.
Hot water (125° C.): 15,300 kg./h. with 1,610,000 cal./h.
Warm water (55° C.): 40,800 kg./h. with 1,430,000 cal./h.

65 The considerably larger quantity of warm water is due to the fact that the waste gas emanating from the combustion of coke oven gas or other hydrogen-containing gases, for example producer gas or water gas, has a fairly high steam content (dew point 57° C. in the case of coke-oven gas and 38.5° C. in the case of producer gas), so that a very much larger quantity of heat in the form of heat of condensation can be recovered in the cooling stage II, naturally with the aid of a correspondingly larger cooling medium circulation in this cooling stage and a correspondingly large quantity of water in the heat

exchanger 21, in which the absorbed heat is extracted from the cooling medium.

As has already been stated, two cooling medium circuits are not actually essential for cooling a gas which contains no appreciable quantities of steam or is not to be cooled below its dew point, but since the undergrate firing gas is frequently changed in coke-oven batteries, sometimes strong gas and sometimes weak gas, for example blast furnace gas, being employed, the arrangement for the recovery of heat according to the invention will always be so designed that any waste gases, including gases having a high steam content, may be treated, that is to say, the arrangement will be provided with a double cooling medium circuit.

We claim:

1. A method of utilizing the heat content of hot gases containing water vapor by heat exchange with a liquid comprising the steps of passing said hot gases mainly in counter current with and in direct heat exchanging relation with a first liquid in a first direct heat exchanger so as to heat said liquid to a temperature close to that of the gas entering said direct heat exchanger, while cooling said gas to a temperature not appreciably below the dew point of said gas, withdrawing said heated liquid substantially free from water condensate and passing said heated liquid in indirect heat exchanging relation with a second liquid in an indirect heat exchanger so as to give up at least the major portion of its heat contents to said second liquid, said first liquid being non-aqueous and having a boiling point at normal pressure considerably higher than 100° C., and the pressure of the vapor phase above said first liquid being approximately zero at the temperature prevailing in the liquid at the place where said gas escapes from and said first liquid enters said direct heat exchanger.

2. A method as claimed in claim 1 wherein after said gas is cooled not appreciably below its dew point, it is thereafter cooled below its dew point in at least one additional direct heat exchanger.

3. A method of utilizing the heat content of hot gases containing water vapor by heat exchange with a liquid comprising the steps of passing said hot gases mainly in counter current with and in direct heat exchanging relation with a first liquid in a first direct heat exchanger so as to heat said liquid to a temperature close to that of the gas entering said direct heat exchanger, while cooling said gas to a temperature below the dew point of the gas so as to condense at least some of said water vapor, separating the water condensate thus formed from said first liquid and passing said heated liquid in indirect heat exchanging relation with a second liquid in an indirect heat exchanger so as to give up at least the major portion of its heat content to said second liquid, said first liquid being non-aqueous and having a boiling point at normal pressure considerably higher than 100° C. and the pressure of the vapor phase above said first liquid being approximately zero at the temperature prevailing in the liquid at the place where said gas escapes from and said first liquid enters said direct heat exchanger.

4. A method as claimed in claim 3 wherein said condensate is withdrawn from the central part of said first direct heat exchanger.

5. A method according to claim 3, characterised in that tetradecane is employed as said first liquid.

6. A method according to claim 3, characterised in that the condensate is withdrawn from the said first heat exchanger at a point at which the gas to be treated is at a temperature in the neighbourhood of the dew point of the gas fed to the said first heat exchanger.

7. A method according to claim 3, characterised in that at least some of the said first liquid is withdrawn from said first heat exchanger together with the condensate, is separated from the water and is at least partially fed back to the direct heat exchanger at a point behind the point of discharge for cooling liquid and said con-

densate as seen in the direction of flow of the liquid in said heat exchanger.

8. A method according to claim 3, characterised in that the said first liquid is divided into two component streams when the condensate has been separated off, one component stream being fed to the top of said heat exchanger after utilisation of the sensible heat and the other component stream being fed to the central part of said heat exchanger, so that while the component stream fed to the top of said heat exchanger after the utilisation of the sensible heat is heated only to a temperature in the neighbourhood of the dew point of the gas to be treated, the second component stream, after having been returned into said heat exchanger, is heated therein to a temperature higher than the dew point and is thereafter returned into said heat exchanger after utilisation of the sensible heat.

9. A method according to claim 8, characterised in that the sensible heat of the part of the liquid which has been heated in said heat exchanger only to a temperature in the neighbourhood of the dew point of the gas is utilised with the aid of a heat pump.

10. A method for utilizing the heat of hot gases containing water vapor which comprises flowing said hot gases serially through a two-stage direct heat exchanger, flowing a non-aqueous liquid counter-current to said gases and in two streams through said heat exchanger, said non-aqueous liquid having a boiling point substantially above 100° C. and a vapor pressure approximately zero at the exit temperature of the gas, flowing the first of said streams through the second of said stages, wherein said gas is cooled below the dew point and the water vapor content thereof is condensed, withdrawing said first stream from the bottom of said second stage and cycling the non-aqueous liquid therein back to the top of said second stage after separation of condensed water therefrom, said recycling bringing said non-aqueous liquid in a first indirect heat exchange relation with a heat-transfer liquid prior to the re-introduction of said non-aqueous liquid into said second stage, the second of said streams flowing through said first stage wherein said gas is cooled but there is substantially no condensation of the water vapor content thereof, and withdrawing said second stream of non-aqueous liquid at the bottom thereof substantially free from condensed water, flowing this withdrawn non-aqueous liquid through a second indirect heat exchanger so as to heat said heat-transfer liquid cycled from said first heat exchange to said second indirect heat exchanger to a vaporizing temperature and thereafter recycling said non-aqueous liquid to the top of said second stage.

11. A method of utilizing the heat content of hot gases containing water vapor wherein said hot gases are passed through a direct heat exchanger having at least two stages in counter-current flow and in direct heat exchanging relation with a non-aqueous liquid having a boiling point considerably higher than 100° C. and a vapor pressure of approximately zero at the exit temperature of said gas on leaving said heat exchanger, said process comprising introducing a first stream of said non-aqueous liquid into the top of the second of said stages and flowing said first stream counter-current to said gas passing into said second stage from a first stage of said heat exchanger, thereby cooling said gases below the dew point, and condensing said water vapor, withdrawing said first stream from the bottom of said second stage, separating condensed water therefrom, and recycling the separated non-aqueous liquid to the top of said second stage, further passing a second stream of said non-aqueous liquid to the top of said first stage and flowing said second stream counter-current to said hot gases introduced into the bottom of said first stage, thereby cooling said hot gases to a temperature not substantially below the dew point, and thereafter passing said cooled gases to said second stage, withdrawing said second stream sub-

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stantially free from water condensate and at a temperature not substantially below that of said introduced hot gases from the bottom of said first stage, passing it in indirect heat exchange relation with a heat transfer liquid and thereafter recycling said second stream to said first stage.

12. A method for heating a heat-transfer liquid to a vaporizing temperature by utilizing the heat from hot gases containing water vapor, wherein a non-aqueous liquid having a boiling point substantially above 100° C. and a vapor pressure approximately zero at the exit temperature of the gas, is passed in counter-current flow to said hot gases through a two-stage direct heat exchanger, the temperature of the first of said stages being not substantially below the dew point and the temperature of the second of said stages being below the dew point of said gases so that the water vapor content is condensed therein, which comprises introducing a first stream of said non-aqueous liquid at the top of said second stage at a temperature approximately the same as the cooled gases exiting therefrom, passing said first stream through said second stage counter-current to said hot gases entering from said first stage, and withdrawing said first stream

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from the bottom of said second stage and separating said non-aqueous liquid from the condensed aqueous phase, recycling the former to the top of said second stage through an indirect heat exchange means wherein said heat-transfer liquid is first heated, introducing a second stream of said non-aqueous liquid into the top of said first stage, withdrawing said second stream heated to a temperature substantially that of the entering gases and substantially free from water condensate from the bottom thereof, cycling this second stream through a second indirect heat exchange means wherein said heat-transfer liquid is heated to a vaporizing temperature and thereafter recycling said second stream to the top of said first stage.

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