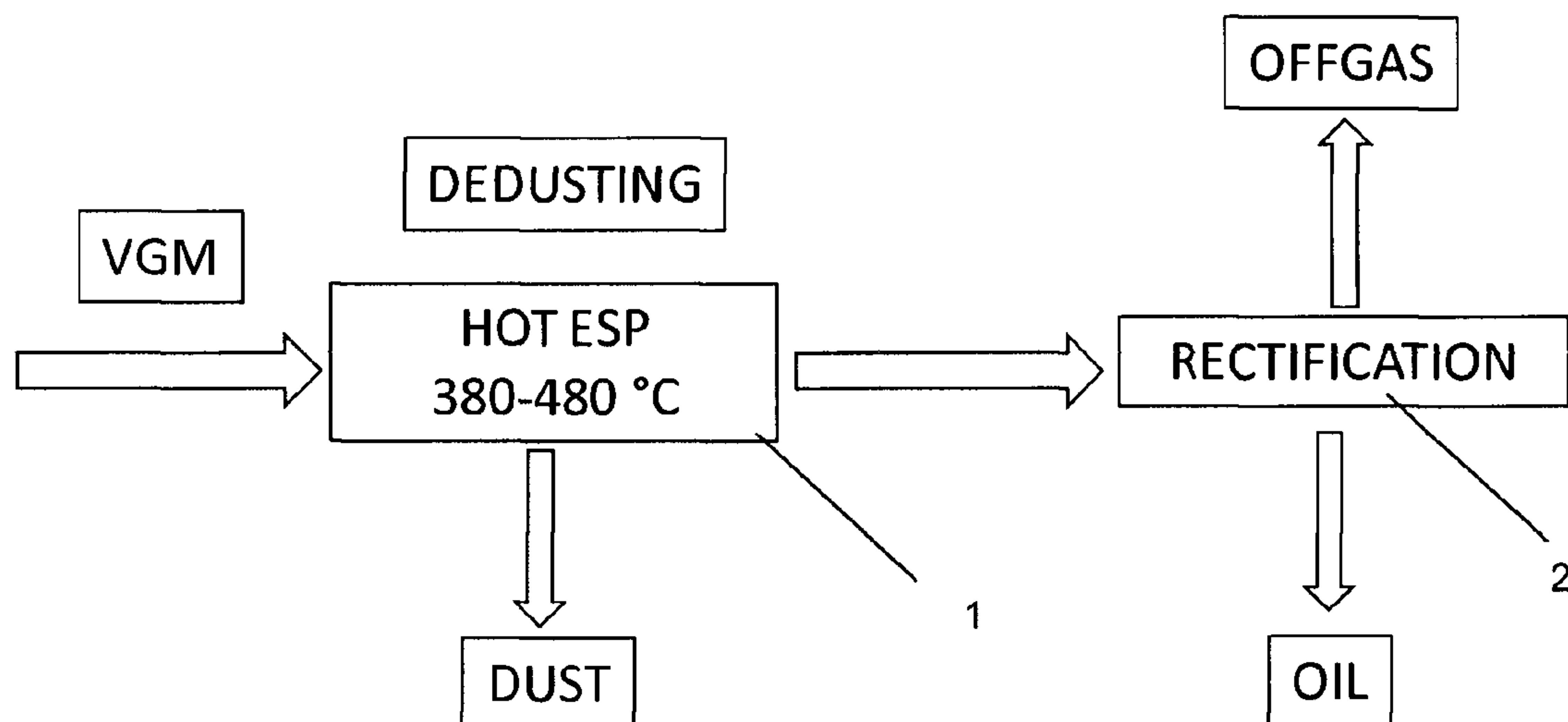




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(72) **Inventeurs/Inventors:**
SIEGER, HERMANN, DE;
BINDER, CHRISTIAN, DE;
ANASTASIJEVIC, NIKOLA, DE;
ORTH, ANDREAS, DE
(73) **Propriétaire/Owner:**
ENEFIT OUTOTEC TECHNOLOGY OU, EE
(74) **Agent:** ROBIC

(54) **Titre : PROCÉDE ET APPAREIL PERMETTANT DE DEPOUSSIERER UN MELANGE VAPEUR-GAZ**
(54) **Title: PROCESS AND APPARATUS FOR DEDUSTING A VAPOR GAS MIXTURE**



(57) **Abrégé/Abstract:**

In a process for dedusting a dust laden vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, in particular oil shale, the dust laden VGM is treated in a dry electrostatic precipitator at a temperature of 380 to 480 °C to separate dust from the VGM.



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(71) Applicant (for all designated States except US): **ENEFIT OUTOTEC TECHNOLOGY OÜ** [EE/EE]; Laki 24, EE-12915 Tallinn (EE).

(72) Inventors; and

(71) Applicants (for US only): **SIEGER, Hermann** [DE/DE]; Nieder-Ramstädter Strasse 231, 64285 Darmstadt (DE). **BINDER, Christian** [DE/DE]; Neuhofstrasse 34, 60318 Frankfurt am Main (DE). **ANASTASIJEVIC, Nikola** [RS/DE]; Zum Niddersteg 11, 63674 Altenstadt (DE). **ORTH, Andreas** [DE/DE]; Obere Römerhofstrasse 132, 61381 Friedrichsdorf (DE).

(74) Agent: **KEIL & SCHAAFHAUSEN PATENT- UND RECHTSANWÄLTE**; Cronstettenstrasse 66, 60322 Frankfurt am Main (DE).

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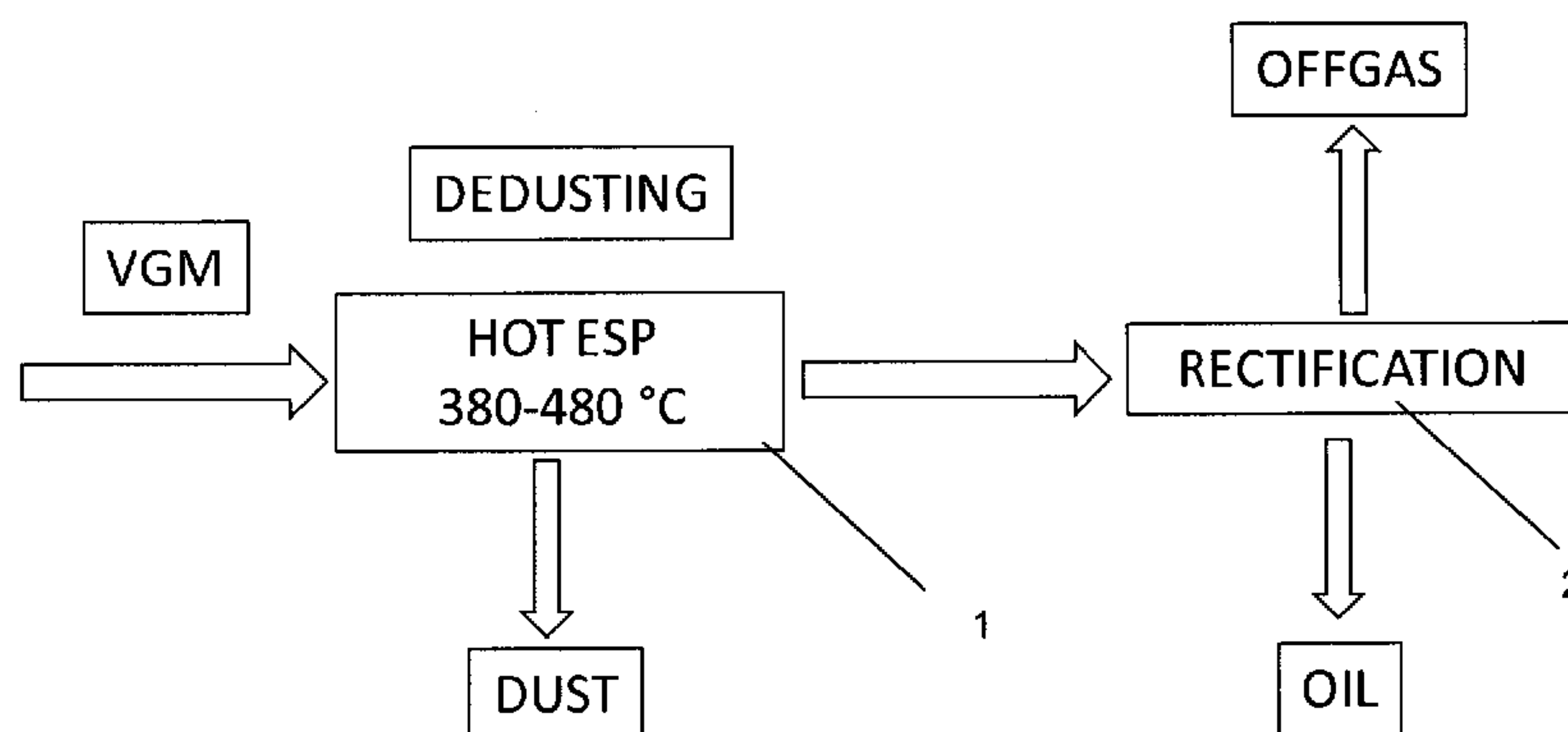


Fig. 1

(57) Abstract: In a process for dedusting a dust laden vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, in particular oil shale, the dust laden VGM is treated in a dry electrostatic precipitator at a temperature of 380 to 480 °C to separate dust from the VGM.

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Process and apparatus for dedusting a vapor gas mixture

5 The present invention is directed to a process and an apparatus for dedusting a dust laden vapor gas mixture obtained by the pyrolysis of preferably solid material containing hydrocarbons, in particular oil shale.

10 In order to obtain oil from oil shale, the oil shale is directly heated by a hot heat carrier (ash) to a temperature of about 500°C in a rotary kiln. Hereby, oil evaporates from the oil shale forming the so called vapor gas mixture (VGM). The vapor gas mixture (a gas containing also fine particles) is then quenched in a condensation unit for winning the oil. This oil contains particulate material (fines), which are very hard to separate from the oil and prevent a further improvement of its quality due to e.g. catalyst deactivation. Traditionally, such
15 separation has been done by using a scrubber. The dust particles collected by droplets produced in the scrubber can be found in the cooled oil at the scrubber bottom. If a venturi scrubber is used, there is a high pressure loss, which requires corresponding high pressures in the rotary kiln and thereby increases the equipment costs. Further, dust laden heavy oil is recycled to the pyrolysis zone
20 and thus cannot be used directly as a product. The removal of fine dust particles from oil is a very expensive procedure and a technical challenge which has not yet been completely solved.

25 According to US patent 4 548 702 A raw oil shale is fed into a specified surface retort followed by solid heat carrier material at 1000 to 1400°C. The withdrawn product stream is partially dedusted in a cyclone or filter. Further dust is removed in a fractionator, scrubber or quench tower. The oil fraction then is fed into a hydroprocessor followed by a catalyst and hydroprocessing gas. The dust removed from the oil fraction and the water stream of sludge containing the dust

is used together with the retorted shale as a fuel to heat the heat carrier material and to retort the raw oil.

5 From document DE 196 11 119 C2 a process for purifying hot waste gases containing dust and tar and obtained during the production of calcium carbide in an arc furnace is known, which comprises dedusting the waste gas at 200 to 900°C using a ceramic filter and subsequently removing the tar at 50 to 200°C using a gas scrubber or electro filter. At such temperatures substantial condensation of heavier oil fractions would have to be expected so that this
10 process is not suitable for dedusting VGM.

It is the object of the present invention to provide for a more efficient production of oil from oil shale or the like. In particular, the removal of dust from the vapor gas mixture obtained by pyrolysis shall be optimized.

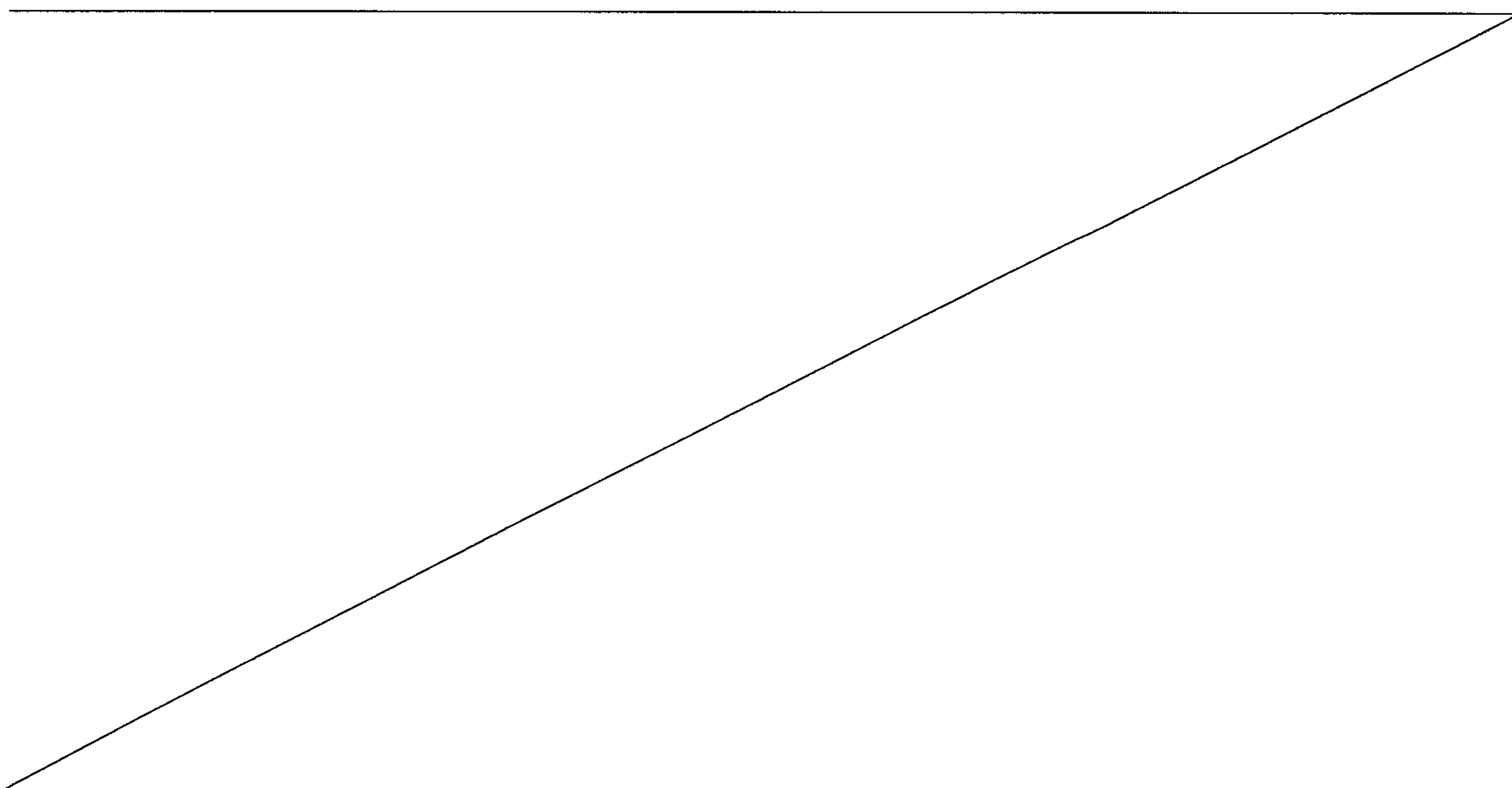
15 In accordance to a particular embodiment, the invention relates to a process for dedusting a dust laden vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, in particular oil shale, wherein the dust laden VGM is treated in a dry electrostatic precipitator at a temperature of 380 to 480 °C
20 to separate dust from the VGM and wherein subsequent to the dust removal in the electrostatic precipitator the VGM is cooled and directed to at least one further electrostatic precipitator where it is treated at a temperature suitable to separate a desired fraction of the oil.

25 The electrostatic precipitator is operated in a dry state at a temperature above the condensation temperature of the oil so that the dust is separated without any condensation of oil. This substantially reduces the contamination of the product (pyrolysis oil). This is particularly important for the subsequent oil upgrading requiring oils having very low dust loads.

2a

In accordance to another particular embodiment, the invention relates to an apparatus for dedusting a vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, and for performing a process according to the present invention and as described above, comprising at least one electrostatic precipitator operating at 380 to 480°C and a first cooler provided downstream of the at least one electrostatic precipitator, characterized in that a rectification means (2) is provided downstream of the at least one electrostatic precipitator, wherein the rectification means (2) comprises one or more electrostatic precipitator(s) each in combination with another cooler for adjusting the temperature of the VGM entering the respective electrostatic precipitator.

An electrostatic precipitator (ESP) is a particulate collection device that removes particles from the VGM using the force of induced electrostatic charge. It, thereby, is a highly efficient filtration device that minimally impedes the flow of gases through the precipitator and can easily remove fine dust particles from the VGM. For implementing the present invention, the electrostatic precipitator may be a tube, plate or chamber precipitator, wherein a tube precipitator is preferred.



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It should be noted that instead of oil shale other hydrocarbon containing materials, such as oil sand, biomass, plastics, oil wastes, waste oils, animal fat containing materials, or vegetable oil containing materials may be used for the process of the present invention as long as a vapor gas mixture containing oil can be produced by the pyrolysis of said material. Preferably, the hydrocarbon material contains 8 to 80 % by weight of hydrocarbons.

According to a preferred embodiment of the present invention the vapor gas mixture comprises 40 to 90% by weight of C₅₊ hydrocarbons, 4.5 to 40% by weight of C₄₋ hydrocarbons, 0.01 to 30% by weight of non condensable fractions (i.e. gases like H₂, N₂, H₂S, SO₂, NO, etc.) and 5 to 30% by weight of water. Preferably, the composition of the vapor gas mixture is as follows: 55 to 85% by weight of C₅₊ hydrocarbons, 7 to 25 % by weight of C₄₋ hydrocarbons, 0.1 to 15% by weight of non condensable fractions and 7 to 20% by weight of water, more preferably the composition of the vapor gas mixture is as follows 60 to 80% by weight of C₅₊ hydrocarbons, 13 to 22% by weight of C₄₋ hydrocarbons, 0.3 to 10% by weight of non condensable fractions and 7 to 15% by weight of water.

20

The dust content of the dust laden vapor gas mixture preferably is 3 to 300 g/Nm³, more preferably 20 to 150 g/Nm³.

25

In order to improve the dust separation, at least two successive electrostatic precipitators are provided, in which the dust laden vapor gas mixture is treated at a temperature of 380 to 480 °C.

30

As the condensation of oil is substantially avoided, the dust separated in the electrostatic precipitator can be mechanically removed by rapping or vibrating the precipitator.

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It is within the present invention to cool the vapor gas mixture to a temperature of 310 to 360°C subsequent to the treatment in the electrostatic precipitator. Thereby, an extra heavy oil stream can be separated from the VGM by condensation which has an ash content of < 80 ppm and can be used as a recycle stream or as product. If the VGM is cooled to room temperature (about 23°C) all oil fractions of the pyrolysis oil can be condensed.

The cooling preferably is done by indirect cooling with air or water or by injecting additional oil (direct cooling).

In a quite preferred embodiment of the present invention, subsequent to the cooling step the VGM is treated in a wet electrostatic precipitator at the temperature defined by the cooler, i.e. between 310 and 360°C, or at another temperature suitable to separate the desired oil fraction. In the wet electrostatic precipitator further portions of the heavy or other oil fraction may be separated from the VGM and recycled or used as a product.

Subsequent to the dust removal in the electrostatic precipitator, the cleaned VGM is treated in a rectification means to separate various desired oil fractions. In a preferred embodiment, the cleaned VGM is directed to at least one further electrostatic precipitator where it is treated at a temperature suitable to separate a desired fraction of the oil. Several electrostatic precipitators operating at various temperatures may be successively provided to obtain the desired oil fractions based on their condensation temperature.

Thereby, different low dust product oil fractions are obtained, comprising less than 30 ppm of dust.

- 5 -

The invention also is directed to an apparatus for dedusting a vapor gas mixture obtained by the pyrolysis of a material containing 8 to 80% by weight of hydrocarbons, in particular oil shale, which is suited for performing a process as described above. The apparatus comprises at least one electrostatic precipitator
5 operating at 380 to 480°C.

Preferably, a cooler is provided downstream of the electrostatic precipitator. In a further embodiment, a wet electrostatic precipitator may be provided downstream of the cooler.

10

Downstream of the dry and/or wet electrostatic precipitator a suitable rectification means may be provided for separating various oil fractions.

In a preferred embodiment the rectification means comprises one or more electrostatic precipitator(s) each in combination with a cooler for adjusting the temperature of the VGM entering the respective precipitator to a value suitable to separate (condense) the desired oil fraction.

15

The invention now will be described in more detail on the basis of preferred
20 embodiments and the drawing.

In the drawing:

Fig. 1 is a schematic view of an apparatus according to a first embodiment of the present invention,
25

Fig. 2 is a schematic view of an apparatus according to a second embodiment of the present invention and

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Fig. 3 is a schematic view of an apparatus according to a third embodiment of the present invention.

In the first embodiment of the present invention as shown in Fig. 1 depicting the basic concept of the invention, a vapor gas mixture (VGM) obtained by the pyrolysis of oil shale or any other suitable material and having a dust content of 3 to 300g/Nm³ is introduced into a hot electrostatic precipitator 1 operated at a temperature of 380° to 480°C. In the electrostatic precipitator the dust is separated from the oil vapor and settles on the tube walls from where it can be removed by rattling/rapping.

The cleaned (dedusted) oil vapor then is conducted to a rectification means 2, e.g. a standard rectification column, for separating various product oil fractions based on their condensation temperature. The oil fractions may be obtained by standard processes and have a dust content of < 30 ppm.

In the somewhat more detailed embodiment according to Fig. 2 the VGM obtained by oil shale pyrolysis in a rotary kiln 3 or any other suitable pyrolysis device enters a first electrostatic precipitator 4.1. As shown in Fig. 2, two electrostatic precipitators 4.1 and 4.2 are provided in series and successively passed by the VGM. Both electrostatic precipitators 4.1 and 4.2 are operated as dry precipitators at a temperature of 380 to 480°C, preferably 400 to 460°C, which basically corresponds to the exit temperature of the rotary kiln 3 and is well above the condensation temperature of the oil so that a condensation even of heavy oil fractions can be avoided. The temperature of the electrostatic precipitators 4.1 and 4.2 is maintained by respective electrical trace heaters 5.1 and 5.2 or any other suitable heating device. By means of electrodes 6.1 and 6.2 a suitable voltage of e.g. 5 kV to 120 kV, preferably 10 kV to 30kV is provided to separate the dust which is withdrawn through lines 7.

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Subsequent to the electrostatic precipitators 4 a cooler 8 is provided to cool the dedusted VGM to a temperature close to the ambient temperature, in particular about 23°C before the VGM enters a wet electrostatic precipitator 9 also operating at this temperature. The wet precipitator is operated at a temperature below the condensation temperature of hydrocarbons contained in the gas. As the VGM is cooled, small condensed droplets are formed which are dispersed as aerosols in the gas stream. The main part of the condensed droplets is collected at the cooler surface, the droplets remaining in the gas stream, being small enough, pass through the cooler. After charging them via the electrode, they are separated at the counter-electrode. Thereby, the wet electrostatic precipitator precipitates all wet/condensed components from the gas. In the wet electrostatic precipitator 9 the generated oil aerosols are separated so that oil can be withdrawn through line 10. As there already is some condensation of extra heavy oil fractions in the cooler 8 this condensate can also be withdrawn and combined with the pyrolysis oil withdrawn from the wet electrostatic precipitator 9.

In the embodiment according to Fig. 3 an additional cooler 11 is provided between the two electrostatic precipitators 4.1 and 4.2.

In the first electrostatic precipitator 4.1 the dust is separated and withdrawn. As in the second embodiment, the electrostatic precipitator 4.1 is operated at a temperature of 380 to 480°C, preferably 400 to 460°C. The VGM then enters the cooler 11, in which it is preferably indirectly cooled with air to a temperature of 310 to 360 °C. Extra heavy fractions of the oil may be condensed and withdrawn through line 12. In this embodiment the second electrostatic precipitator 4.2 is operated as a wet electrostatic precipitator at a lower temperature between 310 and 360°C basically corresponding to the exit temperature of the cooler 11.

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After the second electrostatic precipitator 4.2 an additional cooler 8, preferably indirectly cooled with water, is provided which cools the VGM to the ambient temperature, preferably about 23 °C, prior to introducing it into the wet electrostatic precipitator 9 where the pyrolysis oil is separated and may be withdrawn
5 as product or for further processing. The offgas is discharged through line 13.

The invention will now be further explained by way of examples which are based on research plants according to Fig. 2 and 3, respectively.

10 **Example 1 (based on Fig. 2)**

Table 1: Vapor gas mixture VGM

VGM at 430°C before dedusting		
Composition of VGM before electrostatic precipitator (4)		
H ₂	3,4	g/h
Methane	16	g/h
CO	28	g/h
CO ₂	7	g/h
Ethylene + Ethane	19	g/h
Propylene + Propane	16	g/h
HC ₄ to HC ₆	30	g/h
water	220	g/h
Pyrolysis oil, condensable at 23°C	550	g/h
Dust content	approx. 52	g/h

15

The vapor gas mixture (VGM) is produced by pyrolysis of oil shale type I. The mass flow of main components of VGM is found in table 1. The VGM stream enters at 430°C two successive tubular type electrostatic precipitators, 4.1 and 4.2. The dimensions of the tubes of both ESPs are Ø60.3x2.9mm, the material
20 is stainless steel. Both tubes are electrically earthed. The applied voltage to the

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electrodes 6.1 and 6.2 is controlled between 5 kV to 20 kV. The tubes of the ESPs are heated from the outside by electrical trace heaters 5.1 and 5.2, respectively and the wall temperature is controlled at 430°C. Every 15 min the ESPs are cleaned by mechanical rapping and the separated dust is collected in a glass bottle. The dust collected during the test was 52 g/h. After the VGM was cleaned from dust by the two electrostatic precipitators, it is cooled down by indirect water cooling (cooler 8) to 23°C and final oil mist is separated from the gas stream by a wet electrostatic precipitator (9). The pyrolysis oil stream of 550 g/h is collected in a glass bottle. The dust content of the oil was measured and is 30 ppm (=0.003 wt.-%).

Example 2 (based on Fig. 3)

Table 2: Vapor gas mixture VGM

VGM at 430°C before dedusting		
Composition of VGM before electrostatic precipitator (4)		
H ₂	2,3	g/h
Methane	16	g/h
CO	7	g/h
CO ₂	40	g/h
Ethylene + Ethane	21	g/h
Propylene + Propane	19	g/h
HC ₄ to HC ₆	21	g/h
water	205	g/h
Pyrolysis oil, condensable at 23°C	440	g/h
dust content	approx. 37	g/h

The vapor gas mixture (VGM) is produced by pyrolysis of oil shale type II. The composition of the VGM is found in table 2. The VGM stream enters the first tubular type electrostatic precipitator 4.1 at 430°C. The applied voltage to the electrodes is controlled between 5 kV and 30 kV. The tube of the first electro-

– 10 –

static precipitator 4.1 is heated from the outside by an electrical trace heater 5.1 and the wall temperature is controlled to 430°C. Every 15 min the ESP 4.1 is cleaned by mechanical rapping and the separated dust is collected in a glass bottle. The dust collected during the test was 37 g/h.

5

After the first ESP 4.1 the VGM is cooled down by an indirect air cooler 11 to a temperature of 315°C. The VGM enters then a second ESP 4.2. The tube of the second ESP 4.2 is heated from outside by the electrical trace heater 5.2 and the wall temperature is controlled at 315°C. The oil mist and the remaining dust which was not collected by the first ESP 4.1 are separated in the second ESP 4.2. The second ESP is operated as a wet ESP. The oil fraction together with remaining dust flows down the ESP tube and is collected in a glass bottle. No mechanical rapping is required for the second ESP 4.2. An extra heavy fraction of pyrolysis oil of 30 g/h (7 wt.-% of total collected oil) with dust content of 100 ppm was collected from ESP 4.2. After the second ESP 4.2 the VGM is cooled down by indirect water cooling 8 to 23°C and final oil mist is separated from the remaining gas stream by a wet ESP 9 operated at 23°C. The pyrolysis oil stream of 410 g/h (93 wt.-% of total collected oil) is collected in a glass bottle. The dust content of this oil stream was measured and is < 10 ppm (< 0.001 wt.-%).

20

Reference numbers

	1	electrostatic precipitator
	2	rectification means
5	3	rotary kiln
	4	electrostatic precipitator
	5	electric trace heater
	6	electrodes
	7	line
10	8	cooler
	9	wet electrostatic precipitator
	10	line
	11	cooler
	12	line
15	13	line

ESP electrostatic precipitator

VGM vapor gas mixture

Claims:

1. Process for dedusting a dust laden vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, wherein the dust laden VGM is treated in a dry electrostatic precipitator at a temperature of 380 to 480 °C to separate dust from the VGM and wherein subsequent to the dust removal in the electrostatic precipitator the VGM is cooled and directed to at least one further electrostatic precipitator where it is treated at a temperature suitable to separate a desired fraction of the oil.
2. The process according to claim 1, characterized in that the VGM is obtained by the pyrolysis of a material containing 8 to 80 % by weight of hydrocarbons.
3. The process according to claim 1 or 2, characterized in that the VGM comprises 40-90 % by weight of C₅₊ hydrocarbons, 4.5-40 % by weight of C₄₋ hydrocarbons, 0.01-30 % by weight of non condensable fractions and 2-30 % by weight of water.
4. The process according to any one of claims 1 to 3, characterized in that the dust content of the dust laden VGM is 3 to 300 g/Nm³.
5. The process according to any one of claims 1 to 4, characterized in that the at least one further electrostatic precipitator comprises at least two successive electrostatic precipitators, in which the VGM is treated at a temperature of 380 to 480 °C.

6. The process according to any one of claims 1 to 5, characterized in that subsequent to the treatment in the at least one further electrostatic precipitator, the VGM is cooled to a temperature of 310 to 360 °C.
7. The process according to claim 1, characterized in that the VGM is cooled by indirect cooling or by introducing additional oil.
8. The process according to claim 6, characterized in that subsequent to the cooling step the VGM is treated in a wet electrostatic precipitator at a temperature between 310 and 360 °C.
9. The process according to any one of claims 1 to 7, characterized in that in the cooling step and/or in the wet electrostatic precipitator a heavy oil fraction is separated from the VGM.
10. The process according to any one of claims 1 to 9, wherein the material containing hydrocarbons is oil shale.
11. Apparatus for dedusting a vapor gas mixture (VGM) obtained by the pyrolysis of a material containing hydrocarbons, and for performing a process according to any one of claims 1 to 10, comprising at least one electrostatic precipitator operating at 380 to 480°C and a first cooler provided downstream of the at least one electrostatic precipitator, characterized in that a rectification means (2) is provided downstream of the at least one electrostatic precipitator, wherein the rectification means (2) comprises one or more electrostatic precipitator(s) each in combination with another cooler for adjusting the temperature of the VGM entering the respective electrostatic precipitator.

12. The apparatus according to claim 11, characterized in that a wet electrostatic precipitator (4.2, 9) is provided downstream of the first cooler.

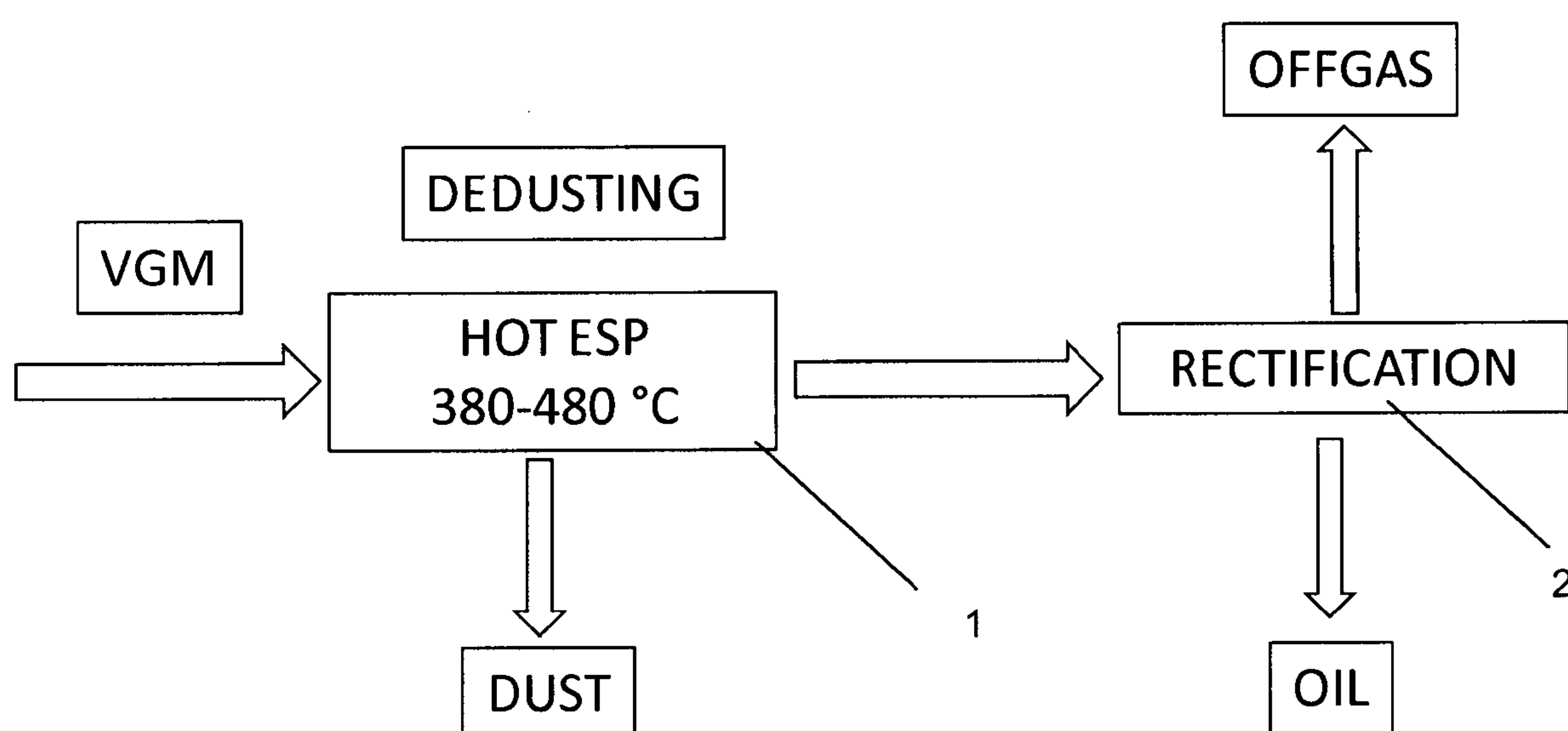


Fig. 1

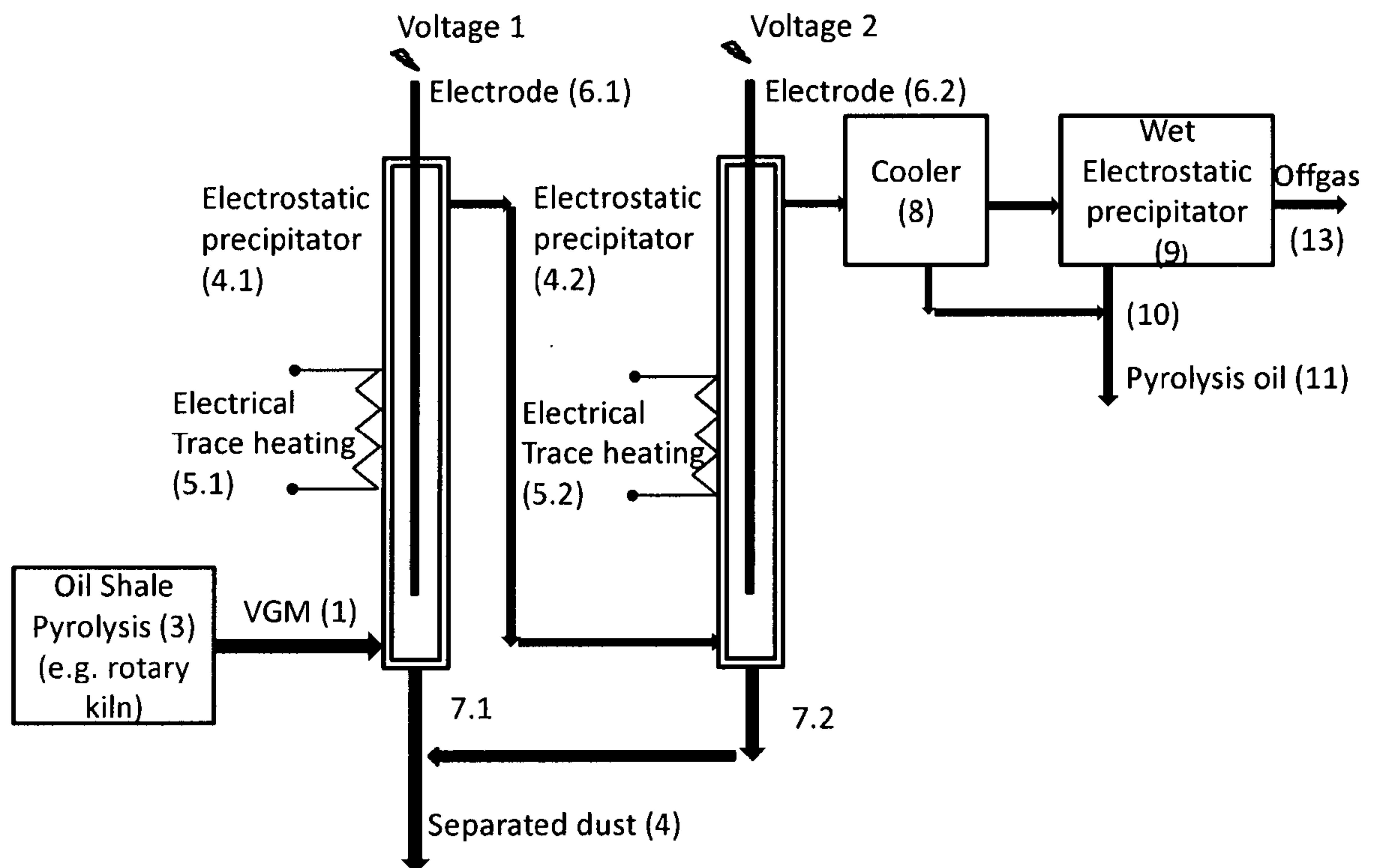


Fig. 2

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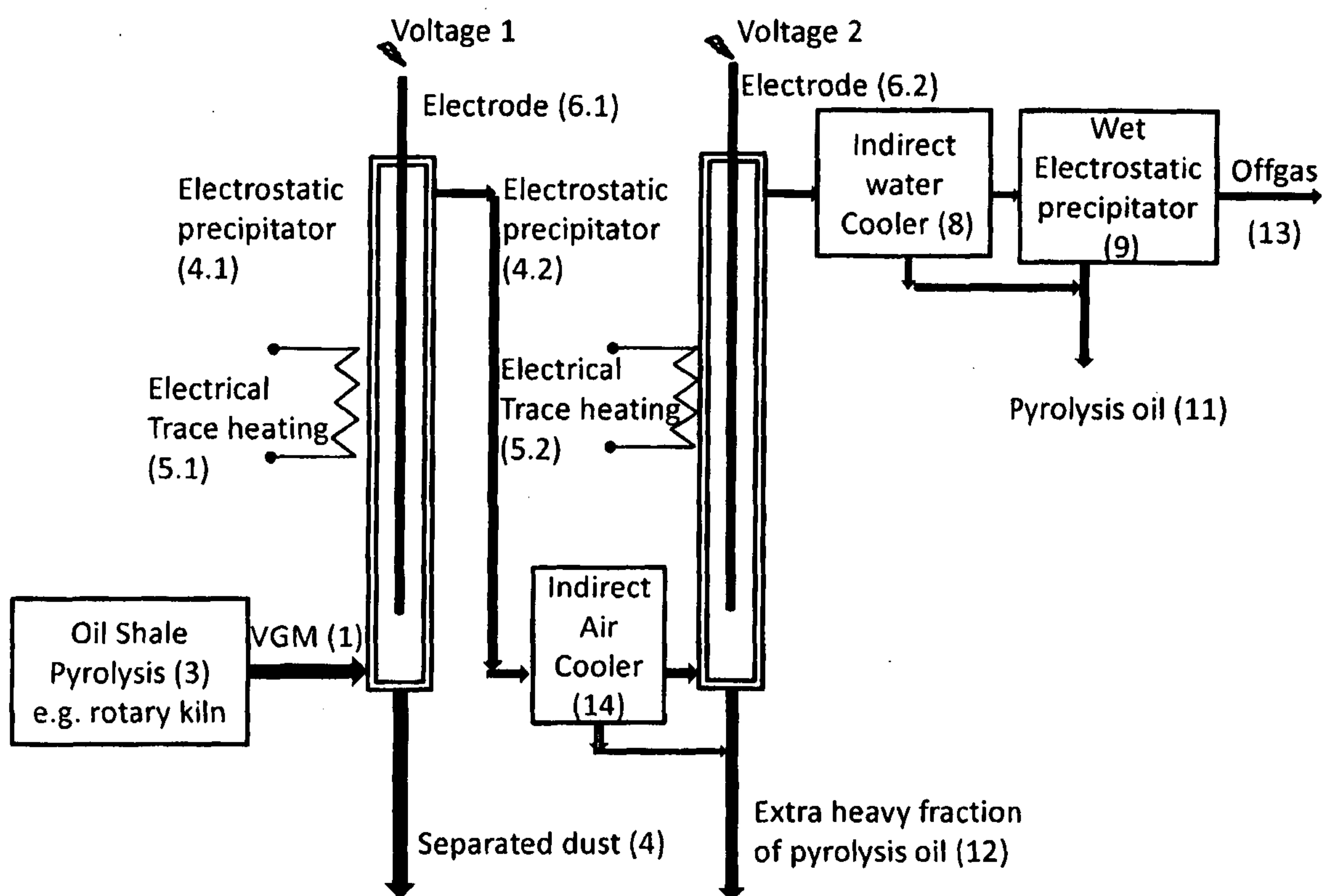


Fig. 3

