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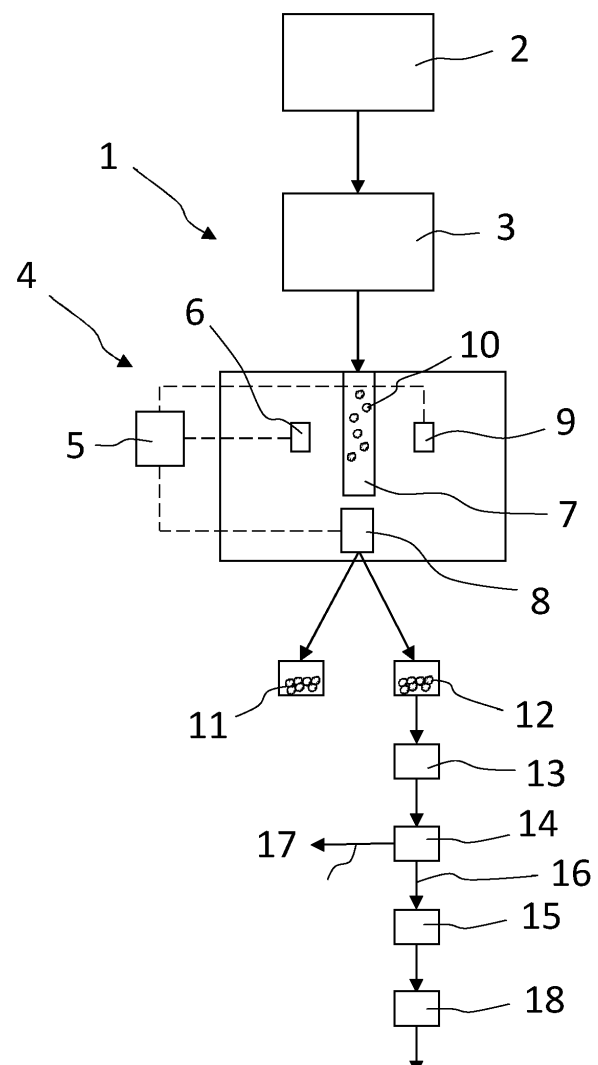
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(54) **METHOD AND ARRANGEMENT FOR PROCESSING LIMESTONE ROCK MATERIAL**

(57) The invention describes a method and arrangement for processing kerogen-containing limestone rock material obtained from oil shale mining. The rock material is comminuted into rock particles (10) and the rock particles (10) are classified to a particle size in a range of 5 to 300 mm. The rock particles (10) are sorted into first rock particles (11) having higher kerogen content and second rock particles (12) having lower kerogen content using a sensor-based sorting device (4).



Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method and arrangement for processing kerogen-containing limestone rock material obtained from oil shale mining.

BACKGROUND OF THE INVENTION

[0002] There are two kinds of oil shale in Estonia, both of which are sedimentary rocks laid down during the Ordovician geologic period. Graptolitic argillite is the larger oil shale resource, but, because its organic matter content is relatively low, it is not used industrially. The other is kukersite, which has been mined for more than a hundred years. Historically, most of mined oil shale was used for electricity generation. About half of mined oil shale is used to produce phenolic-based products, such as dicarboxylic acids, and shale oil, a type of synthetic oil extracted from oil shale by pyrolysis. In addition, oil shale and its products are used in Estonia for district heating and as a feedstock material for the cement industry.

[0003] Kukersite is a light-brown marine-type Late Ordovician oil shale formed some 460 million years ago. Oil shale is a sedimentary rock comprising organic matter, i.e. kerogen, and inorganic matter. Kukersite has an exceptionally high organic matter content, varying from 15% to 55%, and averaging over 40%. The conversion ratio of its organic content into usable energy (shale oil and oil shale gas) is between 65 and 67%. Organic substance in kukersite is mainly kerogen.

[0004] The mining and processing of oil shale in Estonia has over time generated and accumulated approximately a billion tons of solid waste, consisting of more than 200 million tons of disposed oil shale mine tailings (waste rock). The oil shale mine tailings contains mainly mineral materials and smaller amounts of organic material, mostly kerogen. The beneficiation of the oil shale mine tailings has not been done on an industrial scale so far.

OBJECT OF THE INVENTION

[0005] An object of the present invention is to provide a method and arrangement by which kerogen-containing limestone rock material obtained from oil shale mining can be processed.

SUMMARY OF THE INVENTION

[0006] The object of the invention can be achieved by a method according to claim 1 and an arrangement according to claim 14.

[0007] In the method according to the invention, kerogen-containing limestone rock material is comminuted into rock particles, rock particles are classified to a particle size in a range of 5 to 300 mm, and the rock particles

are sorted into first rock particles having higher kerogen content and second rock particles having lower kerogen content using a sensor-based sorting device.

[0008] According to the embodiment of the invention, the rock particles are sorted into the first rock particles having a kerogen content greater than a predetermined threshold value and into the second rock particles having a kerogen content not more than the predetermined threshold value.

[0009] According to the embodiment of the invention, the sensor-based sorting device comprises at least one sensor by which the rock particles are monitored, and a processing unit by which data received from the at least one sensor is processed to determine at least one property indicative of or proportional to the kerogen content of the rock particles, and the rock particles are sorted based on said at least one property into the first rock particles and the second rock particles.

[0010] According to the embodiment of the invention, the at least one property comprises X-ray absorption rate the rock particles.

[0011] According to the embodiment of the invention, the sensor-based sorting device comprises at least one sensor by which the rock particles are monitored, and a processing unit by which data received from the at least one sensor is processed to differentiate the elements contained in the rock particles, and the rock particles are sorted based on their composition into the first rock particles and the second rock particles.

[0012] According to the embodiment of the invention, the sensor-based sorting device comprises an X-ray source, from which X-ray radiation is emitted through the rock particles, and intensity of X-ray radiation passing through the rock particles is detected by the at least one sensor, and the rock particles are sorted based on their X-ray absorption rate into the first rock particles and the second rock particles.

[0013] According to the embodiment of the invention, the at least one sensor comprises an X-ray transmission (XRT) sensor and/or a dual energy X-ray transmission (DE-XRT) sensor.

[0014] According to the embodiment of the invention, the rock material to be processed is run-of-mine oil shale and/or oil shale mine tailings, such as kukersite run-of-mine oil shale and/or kukersite oil shale mine tailings.

[0015] According to the embodiment of the invention, the sensor-based sorting device comprises transfer member, such as a belt conveyor or a sloping chute, by which rock particles are transferred onwards in the sensor-based sorting device while being detected with the sensor(s).

[0016] According to the embodiment of the invention, the second rock particles are fed to a further sensor-based sorting device by which the second rock particles are sorted based on their qualities.

[0017] According to the embodiment of the invention, the second rock particles are sorted into third rock particles and fourth rock particles by the further sensor-based

sorting device, wherein calcium carbonate content of the third particles is greater than that of the fourth particles.

[0018] According to the embodiment of the invention, the second rock particles and/or third rock particles (16) are comminuted.

[0019] According to the embodiment of the invention impurities are separated from the third rock particles using flotation method.

[0020] The arrangement according to the invention comprises a comminution device for comminuting the kerogen-containing rock material into smaller particles, a classifying apparatus for classifying the rock particles to a particle size in a range of 5 mm to 300 mm, and a sensor-based sorting device configured to sort the rock particles into first rock particles having higher kerogen content and second rock particles having lower kerogen content.

[0021] Significant advantages can be achieved by means of the invention. The method and arrangement according to the invention enable converting oil shale mine tailings into various qualities of recycled raw materials, such as industrial minerals and functional fillers (calcium carbonate) and kerogen concentrate, which can be utilized in number of applications, e.g. as raw materials in chemical and cement industry. This significantly contributes to the circular economy. Moreover, the amount of oil shale mine tailings can be significantly reduced, which frees the land occupied by the mine tailings heaps to be used for other purposes.

[0022] The method according to the invention may also be used to process or enrich run-of-mine oil shale, which enables the separation and pre-concentration of kerogen-containing rock material from mined material, already in the mining area.

BRIEF DESCRIPTION OF THE DRAWING

[0023] In the following, the invention will be described in more detail by the aid of examples with reference to the attached drawing, which shows a schematic diagram of a processing arrangement according to an embodiment of invention.

DETAILED DESCRIPTION

[0024] The drawing shows a processing arrangement 1 by which kerogen-containing limestone rock material 10 obtained from oil shale mining is processed and/or enriched. The kerogen-containing limestone rock material to be processed may be run-of-mine oil shale and/or oil shale mine tailings (waste rock). Oil shale is a sedimentary rock comprising organic matter, mostly kerogen, and inorganic matter.

[0025] The run-of-mine oil shale may be so-called kukersite oil shale, which is found in the Baltic Oil Shale Basin in Estonia. Kukersite oil shale has an organic content varying from 15 to 55 wt%, with average more than 40 wt%. Kukersite has 65-67% conversion ratio into shale

oil and/or oil shale gas. The organic material in run-of-mine oil shale is mainly kerogen. Run-of-mine oil shale also contains mineral materials, such as calcium carbonate (CaCos), dolomite (CaMg(CO₃)₂) and quartz (SiO₂), and clay.

[0026] The oil shale mine tailings may be solid waste rock originating from the mining and/or processing of oil shale, such as kukersite oil shale. The oil shale mine tailings contains organic material, mainly kerogen, and carbonate minerals, such as calcium carbonate (CaCos) and dolomite (CaMg(CO₃)₂) and quartz (SiO₂), and clay.

[0027] The total organic carbon content of the oil shale mine tailings is typically 2-11 wt%. Kerogen content of the oil shale mine tailings is typically 2-11 wt%. Calcium carbonate content of the oil shale mine tailings is typically 40-55 wt%, dolomite content 15-40 wt% and clay content 5-15 wt%.

[0028] The processing arrangement 1 is configured to process/enrich kerogen-containing limestone rock material obtained from oil shale mining. The processing arrangement 1 may comprise a comminution device 2, by which the feedstock, i.e. kerogen-containing limestone rock material, is comminuted into smaller rock particles 10. The comminution device 2 may be a crusher, such as an impact crusher. The comminution splits the rock material into smaller particles at boundaries of different constituents. Thus, it is possible to obtain rock particles 10 containing mainly specific constituents, such as kerogen or mineral material(s). The rock material is comminuted to a particle size in a range of 5 mm to 300 mm, typically 20 mm to 120 mm.

[0029] The processing arrangement 1 may further comprise a classifying apparatus 3, such as a screen, by which the comminuted rock particles 10 are classified. The particles are classified to a particle size in a range of 5 mm to 300 mm, typically 20 mm to 120 mm. The rock particles 10 may be classified into one or several different size fractions. The ratio of minimum and maximum particle size within a fraction is typically at most 1/3.

[0030] The processing arrangement 1 further comprises a sensor-based sorting device 4 configured to sort the rock particles 10 into first rock particles 11 and second rock particles 12. Kerogen content of the first rock particles 11 is greater than that of the second rock particles 12. It is possible that the second particles 12 contain no kerogen at all. The sensor-based sorting device 4 may utilize density separation, in which the sorting is based on atomic densities or atomic density differences of the rock particles 10.

[0031] Sensor-based sorting may be performed using one or a combination of technologies, including X-Ray transmission (XRT), dual energy X-ray transmission (DE-XRT), X-ray fluorescence (XRF), X-ray luminescence, laser-induced breakdown spectroscopy (LIBS), optical color (RGB), short-wave infra-red (SWIR), near infra-red (NIR), and/or prompt gamma neutron activation analysis (PGNAA). The technology or the combination of technologies to be used may depend on the effectiveness of the

technologies' selectivity for respective kerogen-containing limestone rock material.

[0032] The sensor-based sorting device 4 comprises one or more sensors 6, by which the rock particles 10 are monitored. The sensor-based sorting device 4 further comprises a processing unit 5 configured to receive data from the sensor(s) 6. The processing unit 5 comprises a data processing algorithm, which is configured to process and/or evaluate data received from the sensor(s) 6 to identify the first rock particles 11 and the second rock particles 12. As the main elements of the rock particles 10 and their average contents in the rock particles 10 are known, the data processing algorithm can determine the kerogen content of rock particles 10 based on the measurement data of the sensor(s) 6. A suitable data processing algorithm may be determined, for example, experimentally and/or by simulation.

[0033] The data received from the sensor(s) 6 is processed by the processing unit 5 to determine at least one property indicative of or proportional to the kerogen content of the rock particles 10. Thereafter, the rock particles 10 are sorted based on said at least one property into the first rock particles 11 and the second rock particles 12.

[0034] The at least one property may comprise X-ray absorption rate of the rock particles 10. In that case, the sensor-based sorting device 4 comprises an X-ray source 9 configured to emit X-radiation towards the rock particles 10 to be sorted and at least one sensor 6 configured to measure the intensity of the X-ray radiation passing through the rock particles 10. The sensor(s) 6 may comprise an X-ray transmission (XRT) sensor(s) and/or dual energy X-ray transmission (DE-XRT) sensor(s). The X-radiation absorption rate of the rock particle 10 is the difference between X-radiation emitted by the X-ray source 9 and measured by the sensor 6. The X-ray absorption rate of the material making up the rock particle 10, signifies the relative density of the material making up the rock particle 10.

[0035] There is a relation between atomic density/elemental composition of the rock particle 10 and the intensity of X-radiation passing through or absorbed by the rock particle 10. The intensity of X-radiation passing through the rock particles 10 may be measured at two different energy levels (DE-XRT sensor). By using two X-ray beams of different energies, it is possible to measure the material's absorption of X-rays at different energy levels, allowing for more accurate identification and separation of different materials. For example, one X-ray beam may be optimized for detecting low-density materials, while the other X-ray beam may be optimized for detecting high-density materials.

[0036] As X-rays are absorbed differently depending on the rock particle material's composition and atomic density, with the appropriate data processing algorithm, the elements contained in the rock particles 10 can be differentiated based on the X-ray absorption rate of the rock particles 10. As a result, the rock particles 10 can be identified as the first particles 11 and second particles

12, and sorted accordingly. The data processing algorithm used in the processing system 5 can be determined experimentally or by simulation. Materials may also be sorted on the basis of an association with a mineral which is easily detectable and associated/related with another mineral, as both minerals appear mostly jointly in the rock particle material.

[0037] In addition to or instead of X-ray transmission technology, other technologies may be utilized in the sensor-based sorting. Such technologies may comprise X-ray fluorescence (XRF), X-ray luminescence, laser-induced breakdown spectroscopy (LIBS), optical color (RGB), short-wave infra-red (SWIR), near infra-red (NIR), and/or prompt gamma neutron activation analysis (PGNAA). The sensor-based sorting device 4 comprises sensor(s) 6 suitable for the technology to be used.

[0038] Each individual rock particle 10 is sorted into first rock particles 11 and second rock particles 12. The rock particles 10 may be sorted into first particles 11 having a kerogen content greater than a predetermined threshold value and into the second rock particles 12 having a kerogen content not more than the predetermined threshold value.

[0039] The sensor-based sorting device 4 further comprises a transfer member 7, by which the rock particles 10 are transferred onwards in the sensor-based sorting device 4 while being detected with the sensor(s) 6. The transfer member 7 may be a belt conveyor, on which the rock particles 10 are conveyed, or a sloping chute, into which the rock particles 10 are fed.

[0040] The sensor-based sorting device 4 further comprises a sorting member 8, such a compressed air nozzle, configured to perform the sorting of the rock particles 10 into first rock particles 11 and second rock particles 12. The sorting member 8 is placed downstream of scanning region of the sensor(s) 6, for example at the downstream end of the transfer member 7. The processing unit 5 is configured to operate the sorting member 6 based on the data received from the sensor(s) 6 so that rock particles 10 having higher kerogen content are sorted into first rock particles 11 and the rock particles having lower kerogen content are sorted into second rock particles 12. The first rock particles 11 may be sorted into a first container and the second rock particles 12 into a second container.

[0041] The first rock particles 11 having higher kerogen content may be combusted to generate heat and/or electricity and/or utilized as a raw material for chemical industry. The second rock particles 12 may be used as raw material for cement industry and/or fed to further processing steps 12-14.

[0042] The further processing steps may comprise a second comminuting step 13, in which the second rock particles 12 are comminuted into smaller particles. Alternatively or additionally, the further processing steps may comprise a second sensor-based sorting step 14, in which the second rock particles 12 are monitored with sensor(s) to determine at least one property, e.g. average

atomic density, indicative of or proportional to calcium carbonate content of the second rock particles 12. Thereafter, the second particles 12 are sorted based on said at least one property into third rock particles 16 and fourth rock particles 17. The calcium carbonate content of the third rock particles 16 is higher than that of the fourth rock particles 17. The second sensor-based sorting step 14 may be performed with a similar sensor-based sorting device as described above.

[0043] Impurities in the third rock particles 16 may be separated from calcium carbonate by means of flotation process using at least one flotation cell 18. Prior to the flotation step 18, the third rock particles 16 are milled 15 (wet or dry milling) to the appropriate particle size, which allows separation by flotation.

[0044] The fourth rock particles 17 may be used as cement replacement or as a raw material for geopolymer production.

[0045] It is obvious to the person skilled in the art that the invention is not limited solely to the embodiments presented above, but that it can be varied within the scope of the claims presented below.

Claims

1. A method for processing kerogen-containing limestone rock material obtained from oil shale mining, **characterized in that**

- rock material is comminuted into rock particles (10),
- the rock particles (10) are classified to a particle size in a range of 5 to 300 mm, and
- the rock particles (10) are sorted into first rock particles (11) having higher kerogen content and second rock particles (12) having lower kerogen content using a sensor-based sorting device (4).

2. The method according to claim 1, **characterized in that** the rock particles (10) are sorted into the first rock particles (11) having a kerogen content greater than a predetermined threshold value and into the second rock particles (12) having a kerogen content not more than the predetermined threshold value.

3. The method according to any of the preceding claims, **characterized in that** at the sensor-based sorting device (4) comprises at least one sensor (6) by which the rock particles (10) are monitored, and a processing unit (5) by which data received from the at least one sensor (6) is processed to determine at least one property indicative of or proportional to the kerogen content of the rock particles (10), and the rock particles (10) are sorted based on said at least one property into the first rock particles (11) and the second rock particles (12).

4. The method according to claim 3, **characterized in that** the at least one property comprises X-ray absorption rate the rock particles (10).

5. The method according to any of the preceding claims, **characterized in that** the sensor-based sorting device (4) comprises at least one sensor (6) by which the rock particles (10) are monitored, and a processing unit (5) by which data received from the at least one sensor (6) is processed to differentiate the elements contained in the rock particles (10), and the rock particles (10) are sorted based on their composition into the first rock particles (11) and the second rock particles (12).

6. The method according to any of the preceding claims, **characterized in that** the sensor-based sorting device (4) comprises an X-ray source (9), from which X-ray radiation is emitted through the rock particles (10), and intensity of X-ray radiation passing through the rock particles (10) is detected by the at least one sensor (6), and the rock particles (10) are sorted based on their X-ray absorption rate into the first rock particles (11) and the second rock particles (12).

7. The method according to any of the preceding claims, **characterized in that** said at least one sensor (6) comprises an X-ray transmission (XRT) sensor and/or a dual energy X-ray transmission (DE-XRT) sensor.

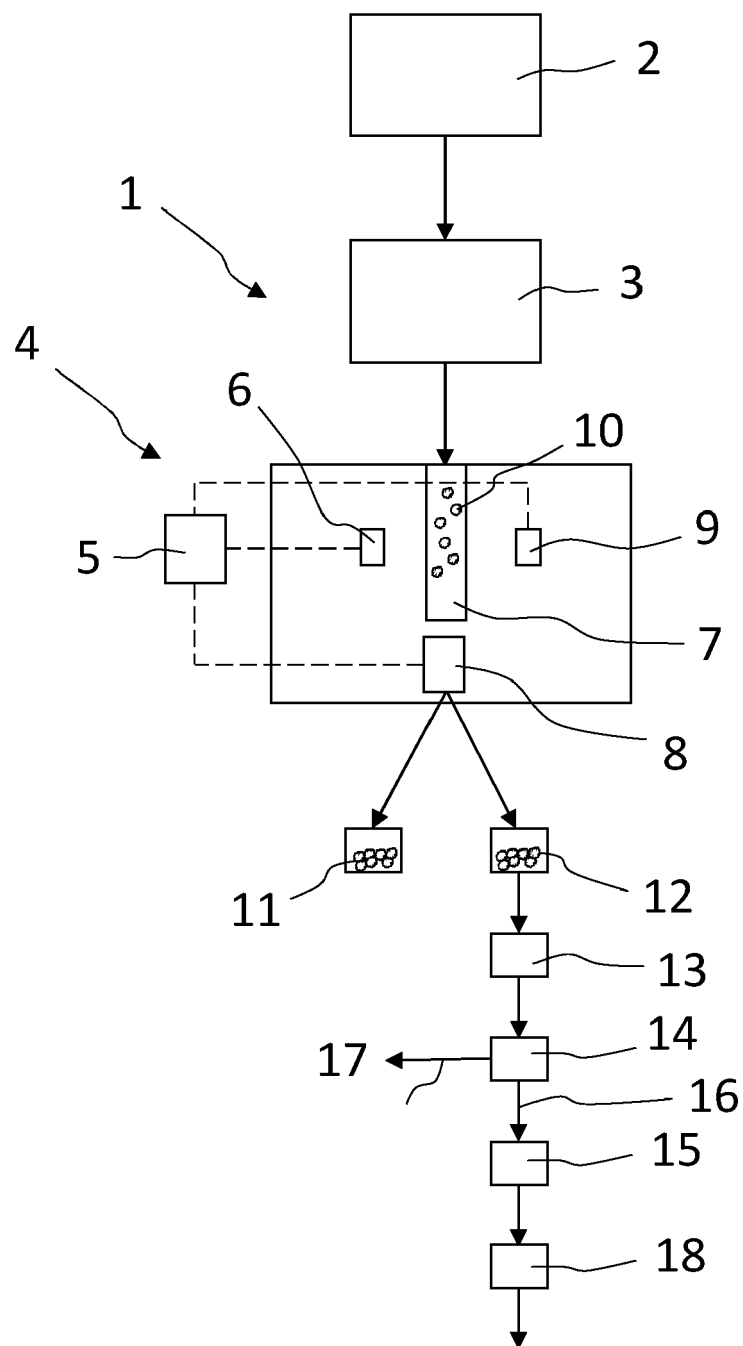
8. The method according to any of the preceding claims, **characterized in that** the rock material (10) to be processed is run-of-mine oil shale and/or oil shale mine tailings, such as kukersite run-of-mine oil shale and/or kukersite oil shale mine tailings.

9. The method according to any of the preceding claims, **characterized in that** the sensor-based sorting device (4) comprises transfer member (7), such as a belt conveyor or a sloping chute, by which rock particles (10) are transferred onwards in the sensor-based sorting device (4) while being detected with the sensor(s) (6).

10. The method according to any of the preceding claims, **characterized in that** the second rock particles (12) are fed to a further sensor-based sorting device (14) by which the second rock particles (12) are sorted based on their qualities.

11. The method according to claim 10, **characterized in that** the second rock particles (12) are sorted into third rock particles and fourth rock particles by the further sensor-based sorting device (14), wherein calcium carbonate content of the third particles is greater than that of the fourth particles.

12. The method according to claim 11, **characterized in that** the second rock particles (12) and/or third rock particles (16) are comminuted.
13. The method according to claim 11 or 12, **characterized in that** impurities are separated from the third rock particles (16) using flotation method. 5
14. An arrangement (1) for processing kerogen-containing limestone rock material (10) obtained from oil shale mining, **characterized in that** the arrangement (1) comprises a comminution device (2) for comminuting the rock material (10) into smaller particles, a classifying apparatus (3) for classifying the rock particles to a particle size in a range of 5 mm to 300 mm, and a sensor-based sorting device (4) configured to sort the rock particles (10) into first rock particles (11) having higher kerogen content and second rock particles (12) having lower kerogen content. 10 15 20
15. Use of an arrangement according to claim 14 in processing kerogen-containing limestone rock material (10) obtained from oil shale mining. 25
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EUROPEAN SEARCH REPORT

Application Number

EP 23 17 2713

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	* Summary of invention and figure 5 * -----	10-13	
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			TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
Munich		31 August 2023	Laurim, Jana
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T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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