

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978**PUBLICATION PARTICULARS AND ABSTRACT**

(Section 32(3)(a) – Regulation 22(1)(g) and 31)

OFFICIAL APPLICATION NO.

LODGING DATE

ACCEPTANCE DATE

21	01	2002/1747
----	----	-----------

22	1 MAR 2002
----	------------

43	3.3.2003
----	----------

INTERNATIONAL CLASSIFICATION

NOT FOR PUBLICATION

51	B01D
----	------

CLASSIFIED BY: WIPO

FULL NAMES OF APPLICANT

71	INEOS FLUOR HOLDINGS LIMITED
----	------------------------------

FULL NAMES OF INVENTORS

72	1. CORR, STUART 2. DOWDLE, PAUL ALAN 3. LOW, ROBERT ELLIOTT 4. MURPHY, FREDERICK THOMAS 5. MORRISON, JAMES DAVID
----	--

EARLIEST PRIORITY CLAIMED

COUNTRY

NUMBER

DATE

33	GB
----	----

31	9920943.9
----	-----------

32	6 SEP 1999
----	------------

TITLE OF INVENTION

54	APPARATUS AND METHODS FOR REMOVING SOLVENT RESIDUES
----	---

57	ABSTRACT (NOT MORE THAN 150 WORDS)
----	------------------------------------

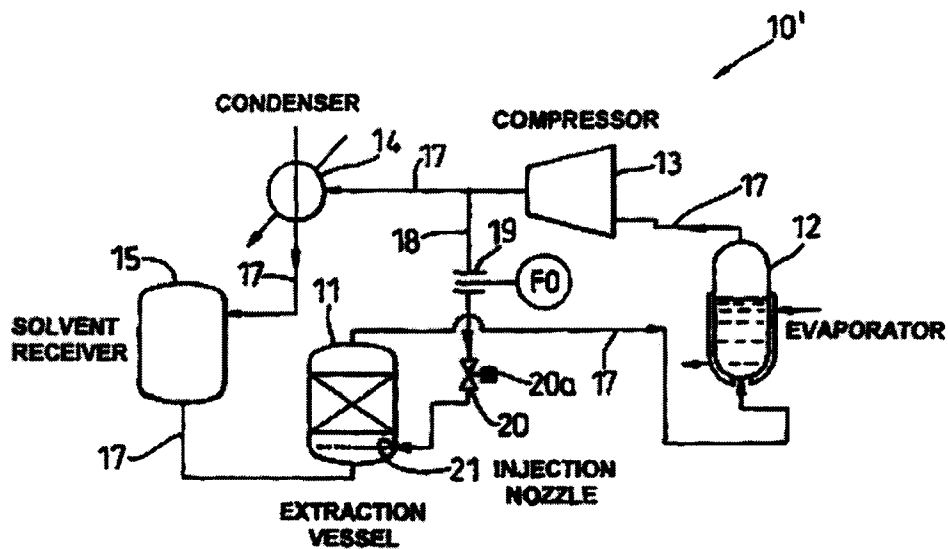
NUMBER OF SHEETS	38
------------------	----

If no classification is finished, Form P.9 should accompany this form.
The figure of the drawing to which the abstract refers is attached.

43

Abstract

In biomass extraction apparatuses there is a need for improvements in the efficiency of recovery of solvent, such as R-134a, from spent biomass. An apparatus for extracting biomass includes an extractor (11), evaporator (12), compressor (13) and condenser (14) connected in series by pipework (17) to define a closed loop extraction circuit. A transfer line (18) selectively supplies hot solvent vapour from the outlet side of the compressor (13) to the interior of the extractor (11), where the solvent vapour heats the biomass. This causes stripping of solvent from the biomass. The transfer line (18) includes control elements (19, 20) for controlling the flow of solvent vapour.



APPARATUS AND METHODS FOR REMOVING SOLVENT RESIDUES

This invention concerns apparatus and methods for removing solvent
5 residues in particular after "extraction" of biomass. Biomass extraction is
the extraction of flavours, fragrances or pharmaceutically active
ingredients from materials of natural origin (these materials being referred
to as "biomass").

10 Examples of biomass materials include but are not limited to flavoursome
or aromatic substances such as coriander, cloves, star anise, coffee,
orange juice, fennel seeds, cumin, ginger and other kinds of bark, leaves,
flowers, fruit, roots, rhizomes and seeds. Biomass may also be extracted
in the form of biologically active substances such as pesticides and
15 pharmaceutically active substances or precursors thereto, obtainable e.g.
from plant material, a cell culture or a fermentation broth.

There is growing technical and commercial interest in using near-critical
solvents in such extraction processes. Examples of such solvents include
20 liquefied carbon dioxide or, of particular interest, a family of chlorine-free
solvents based on organic hydrofluorocarbon ("HFC") species.

By the term "hydrofluorocarbon" we are referring to materials which
contain carbon, hydrogen and fluorine atoms only and which are thus
25 chlorine-free.

Preferred hydrofluorocarbons are the hydrofluoroalkanes and particularly
the C₁₋₄ hydrofluoroalkanes. Suitable examples of C₁₋₄ hydrofluoroalkanes
which may be used as solvents include, inter alia, trifluoromethane (R-

23), fluoromethane (R-41), difluoromethane (R-32), pentafluoroethane (R-125), 1,1,1-trifluoroethane (R-143a), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1,2-tetrafluoroethane (R-134a), 1,1-difluoroethane (R-152a), 1,1,1,2,3,3-hexafluoropropane (R-236ea), heptafluoropropanes and particularly 1,1,1,2,3,3,3-heptafluoropropane (R-227ea), 1,1,1,2,2,3-hexafluoropropane (R-236cb), 1,1,1,3,3,3-hexafluoropropane (R-236fa), 1,1,1,3,3-pentafluoropropane (R-245fa), 1,1,2,2,3-pentafluoropropane (R-245ca), 1,1,1,2,3-pentafluoropropane (R-245eb), 1,1,2,3,3-pentafluoropropane (R-245ea) and 1,1,1,3,3-pentafluorobutane (R-365mfc). Mixtures of two or more hydrofluorocarbons may be used if desired.

R-134a, R-227ea, R-32, R-125, R-245ca and R-245fa are preferred.

15 An especially preferred hydrofluorocarbons for use in the present invention is 1,1,1,2-tetrafluoroethane (R-134a)

It is possible to carry out biomass extraction using other solvents such as chlorofluorocarbons ("CFC's") and hydrochlorofluorocarbons ("HCFC's"), and/or mixtures of solvents. CFC's and HCFC's are not approved for food use and consequently are rarely employed in extraction processes in which the depleted biomass residue is intended as e.g. an animal feed.

25 Known extraction processes using solvents are normally carried out in closed-loop extraction equipment. A typical example 10 of such a system is shown schematically in Figure 1.

In this typical system, liquefied solvent is allowed to percolate by gravity

in downflow through a bed of biomass held in vessel 11. Thence it flows to evaporator 12 where the volatile solvent is vaporised by heat exchange with a hot fluid. The vapour from evaporator 12 is then compressed by compressor 13. The compressed vapour is next fed to a condenser 14
5 where it is liquefied by heat exchange with a cold fluid. The liquefied solvent is then optionally collected in intermediate storage vessel 15 or returned (line 16) directly to the extraction vessel 1 to complete the circuit.

10 One of the key areas of concern relating to the use of solvents such as are used in biomass extraction processes is the level of residual solvent on the biomass material after extraction is complete. High levels of residual HFC (or other) solvent may be regarded as undesirable from a number of aspects:

15

- loss of HFC to atmosphere
- loss of HFC from the recycle process potentially increasing top-up costs
- landfill, incineration, composting and other biomass disposal
20 regulatory issues
- suitability of depleted biomass for use as an animal feed supplement.

When an extraction is completed it is customary to allow as much as
25 possible of the solvent to drain from the extraction vessel 11 to the solvent evaporator, whether by gravity or by imposed pressure difference between the extractor 11 and evaporator 12. This does not however guarantee the complete removal of liquid solvent: some may be trapped in the voids of the extractor bed and some will be chemically adsorbed onto the surface of

the biomass.

Any liquid solvent which is not removed from the biomass prior to the vessel being opened for cleaning will obviously be lost from the system.

5 This is undesirable from a financial viewpoint. It also means that the solvent is emitted to the environment, either by direct vaporisation on opening, or by slow desorption and vaporisation from the biomass which is also undesirable. If the biomass is disposed of by incineration, and the solvent contains fluorine, this may attract an additional cost penalty for
10 incineration because most commercial incineration plant can only handle fluorine-containing wastes by blending with other material.

In order to improve the rate of solvent extraction, the biomass is usually chopped or ground in some manner in order to increase the surface area in
15 contact with the extraction solvent. Whilst beneficially increasing the rate of extraction of the desired components during biomass extraction, this increased surface area acts to increase the quantity of solvent that can remain adsorbed onto and in the biomass after extraction. Clearly some cost-effective method of achieving acceptable residual HFC solvent levels
20 in the exhausted biomass would be of significant value in the development of the technology.

One way to remove residual solvent from a bed of biomass is to supply heat. This forces evaporation/desorption and therefore allows substantial
25 removal of the residue. This can be accomplished conventionally by admission of heated air or steam, or by supply of external heat to the walls of the packed bed extractor vessel 11.

Methods involving heat supply are however not very efficient for the

following reasons:

In the case that hot air is used to remove the solvent, the solvent is driven off as a low concentration of condensable vapour in an inert air vent. The recovery of solvent from such vents is a well known problem in the chemical process industry: owing to the boiling points of most volatile solvents the refrigeration equipment required to condense and recover solvent from such vents is rarely economically justified at small scale, yet most extraction equipment for the flavour and fragrance industry is at relatively small scale. Thus although the biomass is cleaned of solvent, this solvent is still lost to the user and still represents an emission to the environment.

When steam is used as a heat source, recovery of solvent is possible: in this case the steam would first be condensed, leaving a vent of mostly solvent, then a second refrigerated condenser could be used to condense the solvent vent. However this too is potentially costly in terms of additional equipment. Furthermore the condensed steam will be contaminated with solvent, the condensed solvent will be contaminated with water, and there will probably still be losses of solvent to the atmosphere.

If heat is supplied to the external wall of the extractor 11 as the final stage of the extraction process, then some vaporisation of solvent can be expected. In this case any solvent vaporised will be recovered in the normal way and thus is not lost from the system. The problem with this approach is that the thermal conductivity of a packed bed of material (biomass and solvent) which is substantially free of liquid will be very low - approaching the thermal conductivity of the solvent vapour. This means

that the rate at which heat can be transmitted radially into the vessel will be low and consequently the time taken to raise the whole bed temperature to a level which is effective for desorption will be large. This time represents a loss of potential processing time and is therefore an economic
5 penalty.

A combination of evacuation and heat (e.g. using a heating jacket surrounding extraction vessel 11 and additional components to evacuate the vessel 11) may also act to reduce the levels of residual solvent in the
10 biomass over a period of time. This method however has a number of potential disadvantages including:

- prolonged evacuation time to achieve low residue levels
- poor heat transfer into the packed bed of biomass from the vessel
15 jacket resulting in uneven heating and possible thermal deterioration of the biomass (charring, caramelisation etc.)

Such charring and caramelisation are particularly undesirable since they may adversely affect the commercial value of the biomass extracts.

20

According to the invention in a first aspect there is provided apparatus as defined in Claim 1.

This apparatus advantageously permits the efficient supply of heat to the
25 spent biomass and solvent in the extractor, thereby improving the efficiency of solvent recovery.

Preferably the transfer line supplies hot solvent vapour from the outlet of the compressor to the solvent in the extractor. Such vapour is, of course,

under high pressure, so a means of reducing this pressure is desirable.

On passing through the biomass/solvent mixture in the extractor the hot gas gives up its heat thereby acting as a heat source for
5 vaporisation/desorption of residual liquid. The vapour thus produced flows back to the compressor through the normal solvent pipework and so over time the trapped solvent can be removed and recovered via the main solvent condenser.

10 Practical features of the extractor of the apparatus of the invention are defined in Claims 3 and 4.

Preferably the control elements include one or more of a flow restrictor; and an isolation valve.

15

The flow restrictor advantageously ensures that despite the bleeding of solvent vapour from the outlet side of the compressor the pressure of fluid exiting the compressor remains sufficiently high to permit effective condensation in the condenser.

20

The isolation valve permits the transfer line to be selectively opened and closed. In preferred embodiments of the invention the transfer line is normally closed.

25 One preferred form of the flow restrictor is or includes an adjustable orifice plate connected in line in the transfer line whereby hot fluid passing to the solvent in the extractor passes through the orifice plate. An alternative flow restrictor is or includes a length of capillary tubing connected in line in the transfer line whereby hot fluid passing to the

solvent in the extractor passes along the capillary tubing. Other forms of flow restrictor are possible and are within the scope of the invention.

5 The control elements referred to hereinabove may optionally be replaced or augmented by a modulating control valve. Such valves combine the functions of the flow restrictor and the isolation valve in a single device.

10 Conveniently the apparatus includes a controller as defined in Claim 9. In preferred embodiments the controller is e.g. a programmable microprocessor such as a sequential batch controller.

In particularly preferred embodiments the controller operates as defined in Claim 10. This advantageously ensures that the hot fluid transfer does not commence until completion of a biomass extraction cycle.

15

More preferably the apparatus includes a detector as defined in Claim 11 and in particular as defined in Claim 12. Such arrangements are advantageously simple, and provide an automatic indication of when biomass extraction is complete.

20

According to a second aspect of the invention there is provided a method as defined in Claim 14.

25 This method may advantageously be practised using apparatus according to the invention.

Advantageous features of the Claim 14 method are defined in Claims 15 and 16.

According to a third aspect of the invention there is provided a method as defined in Claim 17.

Advantageous features of the Claim 17 method are defined in Claims 18
5 and 19.

The methods of Claims 17 to 19 may also conveniently be practised using the apparatus according to the invention.

10 The invention also resides in solvent recoverable by the methods defined herein; and in biomass extract obtainable by the methods defined herein.

There now follows a description of preferred embodiments of the invention, by way of non-limiting example, with reference being made to
15 the accompanying drawings in which:

Figure 1 is a schematic representation of a prior art closed loop biomass extraction circuit; and

Figure 2 is a schematic representation of apparatus according to the
20 invention.

Referring to Figure 2 there is shown apparatus 10', for extracting biomass, according to the invention. Several of the components of apparatus 10' of Figure 2 are of similar function and/or construction to
25 corresponding components in the apparatus 10 of Figure 1. Such corresponding components are denoted by the same reference numerals in Figure 2 as in Figure 1.

Apparatus 10' is a closed loop circuit including, operatively connected in

series, an extractor 11, an evaporator 12, a compressor 13, a condenser 14 and an optional solvent receiver 15.

Apparatus 10' includes pipework 17 operatively interconnecting the various components to complete the closed loop. In some embodiments solvent receiver 15 may be dispensed with and a single length of the pipework 17 used directly to interconnect the condenser 14 and the extractor 11.

In the embodiment shown the extractor 11 is an upright, hollow substantially closed cylinder that may be packed with a bed of biomass to be extracted.

Preferably the bed of biomass is densely packed and completely occupies the interior cross-section of extractor 11 over a portion of its axial length.

Regardless of the precise nature of the biomass bed, the extractor permits a solvent such as but not limited to R-134a to contact biomass to effect extraction.

20

In Figure 2 the solvent is supplied at the base of extractor 11 and flows upwardly through the biomass therein by virtue of suction of the compressor 13. However other arrangements, such as a gravity flow of solvent as shown in Figure 1; or pumping or sucking solvent through the biomass in another direction or flow pattern, are possible.

The evaporator operates, by heating, to separate the solvent and any biomass extract entrained therewith from one another. The biomass extract in the extractor is drained for further commercial use.

The compressor and condenser respectively compress and condense the solvent from which biomass extract has been separated, whereby the solvent is available for re-use in the extractor 11, optionally after
5 collecting in receiver 15.

Apparatus 10' includes a transfer line 18 interconnecting the outlet (high pressure) side of compressor 13, remote from extractor 11, and the interior of extractor 11. Transfer line 18 serves selectively to supply hot
10 fluid in the form of hot, compressed solvent vapour, to the interior of extractor 11

Transfer line 18 is for the most part a hollow pipe of similar construction to the pipework 17.

15

Transfer line 18 includes one or more control elements for controlling the flow of hot fluid. In the embodiment shown the control elements are in the form of a flow restrictor 19, described in more detail below; and an isolation valve 20, connected in series.

20

In Figure 2 the flow restrictor is an adjustable orifice plate of *per se* known construction that may be adjusted, by replacement with differently sized plates between extraction cycles.

25 As an alternative to the adjustable flow restrictor 19, the flow restrictor may be non-adjusting, e.g. in the form of a length of capillary tubing (not shown in Figure 2 but of *per se* known construction) connected in line in transfer line 18.

Other forms of flow restrictor are possible within the scope of the invention. The primary function of the flow restrictor is to permit transfer of hot solvent vapour to the extractor 11 while maintaining the vapour pressure in the pipework 17 interconnecting the compressor 13 and
5 condenser 14.

Isolation valve 20 is adjustable e.g. by means of a rotary member 20a to open and close the transfer line 18.

10 The rotary member 20a may in some embodiments be operated manually if desired. Alternatively the actuators in the apparatus may be powered by motors acting under the control of a controller such as a programmable batch controller in the form of e.g. a microprocessor.

15 The flow restrictor 19 and isolation valve 20 may if desired be replaced or augmented by a modulating control valve (not shown in Figure 2 but of *per se* known design) installed in line in transfer line 18.

A modulating control valve is known which combines the flow restrictor
20 and isolator (ON-OFF) functions of the restrictor 19 and valve 20 of Figure 2.

The modulating control valve may be manually operated or motor actuated, any actuating motors optionally operating under the control of a
25 controller as described hereinabove.

When present the controller controls the or each controllable control element in transfer line 18 to prevent flow of hot solvent vapour to the extractor 11 while biomass extraction takes place. The controller permits

such flow after completion of a period of biomass extraction.

The apparatus 10' may include a detector for detecting the completion of a said period, the detector optionally being in the form of a sensor, whose
5 output is an input to the controller, for sensing the rate of condensation of solvent in the circuit (e.g. at the condenser 14). When the sensor detects that the rate of condensation has fallen to below a predetermined rate the controller then operates to permit the flow of hot solvent vapour to the extractor 11.

10

The apparatus includes a nozzle 21 connected to the end of transfer line 18, inside extractor 11 at the base thereof. Nozzle 21 allows even distribution of gas across the transverse cross-section of the biomass bed, thereby ensuring good separation of solvent from the biomass residue.

15

In use of the apparatus 10' the extractor 11 is packed with biomass as aforesaid, the pipework 17 is charged with solvent as necessary and the evaporator 12, compressor 13 and condenser 14 operated as necessary to achieve biomass extraction.

20

During this process the transfer line 18 is closed by means of the isolation valve 20 and/or the modulating control valve (if present). Biomass extract is drained as desired from evaporator 12.

25 At the end of the extraction process (determined e.g. by the detector, or on the basis of timings) the isolation valve 20 and/or the modulating control valve open and, optionally, the flow restrictor is adjusted to achieve a desired flow of hot solvent vapour, output from the compressor, through the biomass. Hot solvent vapour can then pass through the bed,

heating the contents as it goes and thereby causing vaporisation of residual solvent. This delivers heat across the whole radial profile of the bed and therefore is superior to heating from the external wall only.

- 5 After the hot solvent vapour has passed through the biomass bed for a sufficient period substantially all of the solvent trapped therein is liberated and flows around the main flow loop 17, to the receiver 15 (if present) or back to the extractor 11 (if the receiver is absent). The isolating valve 20 and/or modulating control valve may then be closed as part of preparing
10 the apparatus 10' for further use to extract biomass.

The precise nature of the control (whether it is manual or determined by an automatic controller as described) will depend on the biomass being extracted. It is necessary to develop appropriate operating procedures for
15 each biomass as the amount of solvent held up will vary from biomass to biomass.

Summary of Benefits of the Invention

- 20 • Improved removal of solvent from biomass prior to emptying/cleaning/disposal of spent biomass
- Improved recovery of valuable solvent compared to e.g. air stripping or steam cleaning operations
- Reduced heating time compared to introduction of heat through
25 external wall
- Little additional equipment or complexity of control required compared to alternative means of effecting solvent removal and recovery

CLAIMS

1. Apparatus for extracting biomass, comprising a closed loop circuit including, operatively connected in series,
 - 5 an extractor, for containing biomass, that permits a solvent or a solvent mixture to contact biomass to effect extraction;
 - an evaporator for separating solvent and biomass extract from one another;
 - a compressor for compressing gaseous solvent; and a condenser for
 - 10 condensing pressurised solvent for return to the extraction vessel, wherein the apparatus includes a fluid transfer line for supplying hot fluid from a part of the closed loop circuit, remote from the extractor, to solvent in the extractor; and
 - one or more control elements for controlling the supply of hot fluid
 - 15 via the transfer line.
2. Apparatus according to Claim 1 wherein the transfer line supplies hot solvent vapour from the outlet of the compressor to the solvent in the extractor.
- 20 3. Apparatus according to Claim 1 or Claim 2 wherein the extractor is an upright, hollow vessel and the transfer line supplies hot fluid to the base of the hollow vessel.
- 25 4. Apparatus according to Claim 3 when containing a bed of biomass.
5. Apparatus according to any preceding claim wherein the control elements include one or more of:
 - a flow restrictor;

operating the evaporator to separate solvent and biomass extract from one another;

compressing solvent in the compressor; and

condensing solvent in the condenser, the method further including
5 the step of transferring hot solvent vapour from a part of the circuit, remote from the extractor, to the extractor to heat biomass and solvent therein and thereby separate biomass and solvent in the extractor from one another.

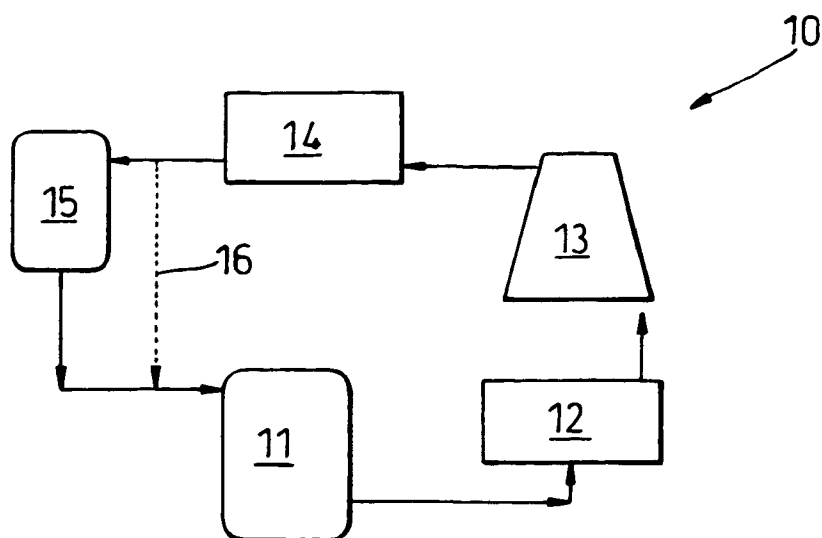
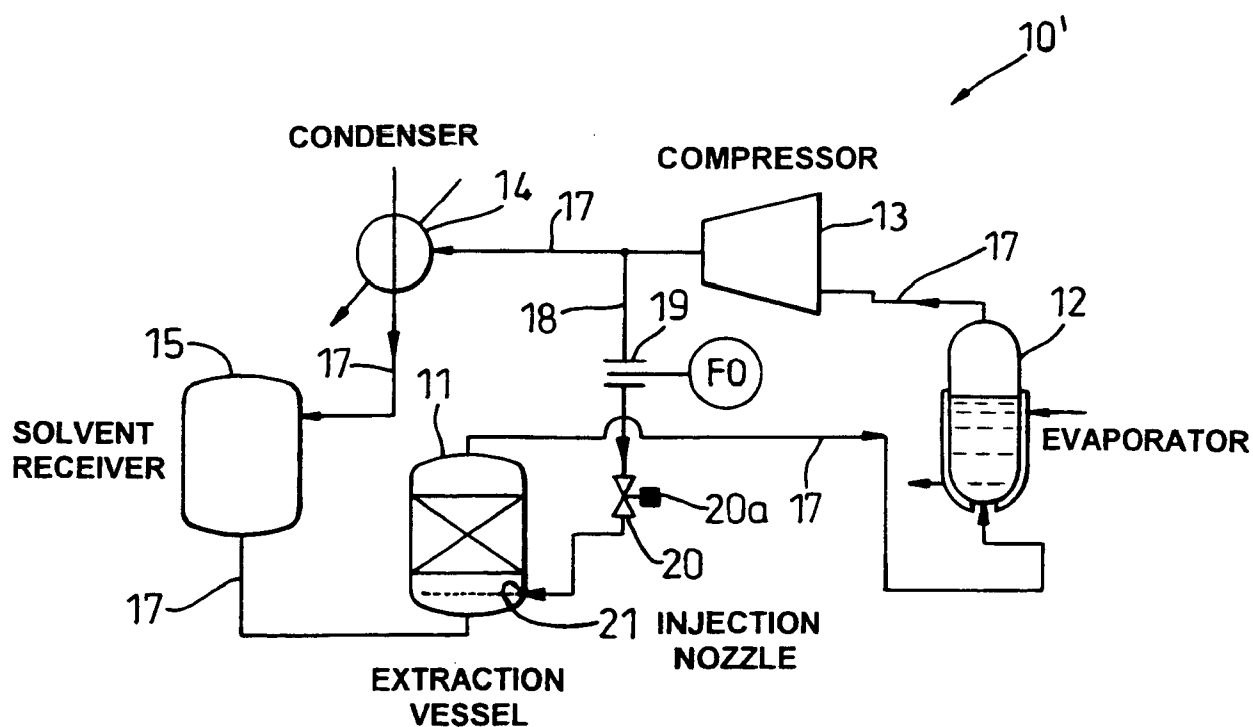
10 18. A method according to Claim 17 wherein the transfer of hot vapour occurs via a transfer line that is selectively openable and closeable to control the transfer of hot solvent vapour to the extractor, the method including the step of controlling the said transfer using the transfer line.

15 19. A method according to Claim 18 including the steps of preventing transfer of hot vapour via the transfer line while the rate of condensation of solvent in the circuit exceeds a predetermined rate; and permitting transfer of hot vapour via the transfer line when the rate of condensation of solvent in the circuit falls below the predetermined rate thereby
20 signifying substantial completion of biomass extraction.

20. Solvent recoverable by the methods of any of Claims 14 to 19.

21. Biomass extract obtainable by the methods of any of Claims 14 to
25 19.

1/1

*Fig. 1**Fig. 2*