

ELIMINATION OF CHLOROHYDRINS FROM LIQUID HYDROLYZATES

1 This invention relates to a process for the pro-
duction of a seasoning in which vegetable proteins are
hydrolyzed with concentrated hydrochloric acid, the
hydrolyzate is neutralized, first insolubles are separated
5 therefrom and, after standing, second insolubles are
separated therefrom, and to a steam distillation apparatus
for carrying out this process.

Recent studies have shown that non-decoloured liquid
seasonings prepared by hydrolysis of vegetable proteins
10 with concentrated hydrochloric acid contain a considerable
quantity of chlorohydrins, including in most cases a
dominant proportion of 1,3-dichloro-propan-2-ol. The
problem of their elimination arises. Various processes
may be considered for eliminating these components.

15 It has been found in particular that the pastes
obtained by concentrating these seasonings by evaporation
or those versions of these seasonings decoloured with
active carbon have distinctly lower concentrations of
chlorohydrins. However, concentration by evaporation
20 involves a considerable consumption of energy. Similarly,
decolouration with active carbon in filter presses, for
example, not only involves high outlay on the necessary
operations and plant, it also considerably modifies the
organoleptic qualities of the seasoning which loses its
25 characteristic taste while retaining its flavour enhancing
power.

Another possibility is to hydrolyze a starting material
which does not contain any fats, glycerol being precisely

1 the precursor which enables chlorohydrins to be formed with
hydrochloric acid. Now, on the one hand, starting materials
such as these are more or less commercially unobtainable
and, on the other hand, would significantly modify the
5 organoleptic qualities of the seasoning.

Hydrolysis could also be carried out with a chlorine-
free mineral acid, such as sulfuric acid or phosphoric
acid. However, such a modification of the traditional
process would also have adverse affects upon the organo-
10 leptic qualities of the seasoning obtained.

Yet another possibility is to separate a fraction of
the hydrolyzate containing the chlorohydrins by
rectification. However, a process such as this involves
at least two separation steps if it is desired to
15 retain in particular in the end product components which
perform an important organoleptic function but which
are more volatile than the chlorohydrins.

The object of the present invention is to provide a
process for the production of a seasoning which enables
20 the chlorohydrins and, in particular, the 1,3-dichloro-
propan-2-ol to be eliminated therefrom simply and effectively
without modifying the density or the aminoacid composition
or the organoleptic qualities of the seasoning.

The present invention provides a process for the
25 production of a seasoning in which vegetable proteins are
hydrolyzed with concentrated hydrochloric acid, the
hydrolyzate is neutralized, a first insoluble fraction is
separated therefrom, the hydrolyzate is allowed to stand to
produce a second insoluble fraction which is then also
30 separated therefrom, characterised in that, after a
separation of said first or second insolubles, the
hydrolyzate is subjected to steam distillation under
reduced pressure while keeping the density of the
hydrolyzate at a substantially constant value in order to
35 eliminate 1,3-dichloro-propan-2-ol present.

The present invention also relates to a steam distillation apparatus for carrying out the process of the present invention, comprising a distillation column consisting of a head, a cylindrical body filled with contact elements and a sump; a gas pumping units connected to said head; a pipe

1 for the introduction of hydrolyzate connected to said
column between said body and said head; a steam injection
pipe connected to said column between said sump and said
body; and a pipe for the removal of hydrolyzate connected
5 to said sump, characterized in that it additionally comprise
an arrangement for regulating the temperature of the
hydrolyzate connected to said introduction pipe and in
that the diameter of said head is larger than
the diameter of said body.

10 It has surprisingly been found that it is thus
possible to eliminate virtually all the 1,3-dichloro-
propan-2-ol from the hydrolyzate in a single step following
the separation of said first or said second insolubles,
that this elimination may thus be carried out while
15 keeping the density of the hydrolyzate at a substantially
constant value and that the aminoacid composition and
the organoleptic qualities of the liquid seasoning thus
obtained remain substantially unchanged in relation to
those of the seasoning obtained by the traditional process.

20 Throughout the remainder of the present specification,
the abbreviation DCP is used to denote 1,3-dichloro-
propan-2-ol. As mentioned above, a seasoning produced
by hydrolysis of vegetable proteins with concentrated
hydrochloric acid may contain other chlorohydrins than
25 DCP, more especially 3-chloro-propan-1,2-diol and 2,3-
dichloro-propan-1-ol. On the other hand, however, the
concentration of these chlorohydrins in the seasoning is
generally lower than that of DCP while, on the other
hand, it has been found that these other chlorohydrins are
30 also substantially eliminated at the same time as the DCP
during the process according to the invention. Thus,
it is sufficient to determine the DCP content of the
seasoning in order validly to determine whether or not
the chlorohydrin content of this seasoning exceeds a
35 certain limit.

1 Similarly, in the present specification, the term
"eliminate" is used in such expressions as "eliminating the
DCP from the condiment" to signify that the major part
of this substance is removed to leave only an
5 insignificant fraction. It should be noted in this
regard that the analytical method used to determine the
DCP content of the seasoning, i.e. the concentration of
DCP in the seasoning, plays a decisive part in regard to
the reproducibility of the result. Thus, a particularly
10 reliable method which even enables concentrations below
one tenth of a ppm to be safely determined has been
developed within the scope of the present invention.
This method is described in detail hereinafter just
before the Examples.

15 To carry out the process according to the invention,
vegetable protein sources of various origins may be used
as starting material. For example, it is possible to
use oil seed cakes, cereal gluten or defatted soya flour.

Accordingly, concentrated hydrochloric acid may be
20 used for hydrolysis. For example, it is possible to
use a 4N to 8N and preferably 6N hydrochloric acid, i.e.
a hydrochloric acid having a concentration of approxi-
mately 15-25% and preferably 20% by weight. Hydrolysis
may be carried out in enamelled tanks by stirring the
25 starting material slowly in the acid at a temperature
of from 70 to 120°C over a period of several hours, for
example 6-13 h. A dark-coloured hydrolyzate containing a
high proportion of so-called humic insoluble substances,
referred to in the present specification as the first
30 insolubles, is generally obtained in this stage of the
process. The hydrolyzate may be neutralized with a
concentrated base, preferably sodium carbonate in dry or
paste-like form, to a pH-value of approximately 5.0-6.0.
The neutralized hydrolyzate may then be filtered to
35 eliminate said first insolubles therefrom. The hydrolyzate

1 may be subjected to said steam distillation in this
second stage or after having been allowed to stand. The
hydrolyzate may be left standing for a more or less long
time, for example for a few days to a few weeks, depending
5 on the application for which it is intended, in order to
allow separation of slowly crystallizing substances and
slowly agglomerating colloidal particles referred to in
the present specification as the second insolubles. Said
second insolubles may be separated by filtration. Finally,
10 the hydrolyzate may be subjected to said steam distillation
in this third stage unless it was carried out after the
separation of said first insolubles. A dark-coloured liquid
hydrolyzate is obtained of which the quality is considered
as being better the higher its density. Accordingly,
15 the above stages of the process are preferably carried
out in such a way as to obtain a density of the hydrolyzate
of from 1.250 to 1.265 g/cm³.

After separation of said first or said second in-
solubles, the hydrolyzate is subjected to steam distillation
20 under reduced pressure while keeping the density of the
hydrolyzate at a substantially constant value in order to
eliminate the DCP therefrom. It has been found to be
important to carry out any steam distillation step under
moderate temperature conditions which keep the organo-
25 leptic qualities of the hydrolyzate intact and under
working conditions which allow virtually no dilution of
the hydrolyzate and thus provide for maximum effectiveness
of the process for removal of the DCP.

This steam distillation process is preferably carried
30 out at a temperature of from 45 to 70°C under a pressure
of 100-320 mbar by contacting an ascending stream of
10-20 parts by weight/h steam with a descending stream of
100 parts by weight/h hydrolyzate over a contact zone
5-15 m in height filled with contact elements. It has
35 been found that it is preferable not to allow the distil-

1 lation temperature to exceed 70°C if it is intended not
to cause in particular any modification of the organo-
leptic qualities of the hydrolyzate. It is preferred to
work at temperatures towards the upper end of the above-
5 mentioned range in order not unnecessarily to increase
the consumption of energy necessary for reducing the
pressure in the column on the one hand and for condensing
the steam charged with DCP on the other hand.

The above-mentioned pressure of 100-320 mbar sub-
10 stantially corresponds to the pressure of steam at 45
to 70°C. Accordingly, it is preferred to work under
such conditions that the hydrolyzate and the distillation
steam are substantially in thermal equilibrium over the
entire height of said contact zone, the hydrolyzate showing
15 virtually no increase in its boiling point in relation
to water.

The respective quantities of hydrolyzate and steam
brought into contact depend in particular upon the residual
DCP content of the hydrolyzate which it is desired to
20 obtain, on the height of the contact zone and on the
available contact surface in said zone. The ratio between
the quantities of hydrolyzate and steam and the height
of the contact zone as indicated above enable the concen-
tration of DCP in the seasoning to be reduced by a factor
25 of approximately 10-100. In other words, they enable a
concentration of DCP in the hydrolyzate of 1-10 ppm for
example to be reduced to less than 0.2-0.5 ppm. For a
desired reduction factor, it is thus possible to use only
the minimum necessary quantity of steam and hence to
30 expend only a minimum of energy. The absolute values
of the quantities of steam and hydrolyzate contacted per
h, in other words the throughputs, may be selected so as
to ensure a DCP transfer level approaching the optimum
level over a relatively broad range limited at its upper
35 end by the risks of entrainment of considerable quantities

1 of hydrolyzate by an excessively violent stream of steam.

In regard to the contact surface available in said zone, it is preferably as large as possible and designed adequately to avoid the formation of preferential pathways for the steam while ensuring ready flow of the hydrolyzate. To this end, therefore, the contact zone is filled with contact elements. Although contact elements designed to be loosely arranged, such as spirals or tube sections are also suitable, it is preferred to use contact elements arranged in a predetermined order, such as for example corrugated metal sheets drilled with holes and applied to one another across the corrugations. With contact elements such as these, it is possible to obtain a contact surface per unit volume of the contact zone as large as 250 m²/m³ for example. They also enable the inevitable pressure difference between the top and bottom of the contact zones, i.e. between the head and sump of the column, to be limited to a few tens of mbar. This difference should preferably not exceed approximately 100 mbar so that, if the temperature of the hydrolyzate and the steam is, for example, 60°C at the top of the contact zone, it does not exceed 70°C at the bottom of the contact zone.

In one preferred embodiment of the process according to the invention, the temperature of the hydrolyzate before steam distillation is kept at a value higher by 1-5°C than that of the hydrolyzate above the contact zone. It has been found that it is thus possible to compensate a slight dilution of the hydrolyzate caused by the condensation of a small quantity of steam along the contact zone. This condensation is difficult to eliminate completely, a certain amount of heat being lost despite everything through insulation to be provided between the contact zone and the outside.

35 In one particular embodiment of the process according

1 to the invention, the density of the hydrolyzate is
kept at a substantially constant value by regulating the
temperature of the hydrolyzate before distillation according
to the density of the hydrolyzate after distillation. This
5 embodiment is particularly intended for the case where
the hydrolyzate is subjected to said steam distillation
after the separation of said second insolubles. This is
because, in this case, the density of the hydrolyzate may
vary in particular according to the time for which it was
10 left standing. If hydrolyzate is taken from different
tanks to arrive at a suitable mixture before bottling for
example, this embodiment enables the density to be
automatically adjusted to a precise desired value. In
cases where, in any event, it is intended to regulate the
15 temperature of the hydrolyzate before distillation, this
temperature regulation may be effected around a desired
value imposed automatically according to the density of
the hydrolyzate after distillation. If the measured
density is slightly too low, the desired temperature will
20 be slightly increased so that the hydrolyzate undergoes
a slight concentration by evaporation under said reduced
pressure. Conversely, if the measured density is too
high, the desired temperature will be slightly lowered so
that the hydrolyzate undergoes a slight dilution by
25 condensation of the distillation steam under said reduced
pressure. This principle of regulation has proved to be
particularly simple, safe and effective in practice where
the density of the liquid condiment in its retail form has
to satisfy very stringent requirements.

30 So far as the steam distillation apparatus for carrying
out the process according to the invention is concerned,
it is thus constituted and characterized as described
above. With regard to the distillation column, it is
made up of a head, a cylindrical body filled with contact
35 elements and a sump. It is preferably completely

1 surrounded by an insulating jacket intended to minimize
the losses of heat from inside to outside. The cylindrical
body delimits said contact zone. It may be filled with
5 as spirals or tube sections for example. It is preferably
filled with contact elements arranged in a predetermined
order.

The head of the column has a diameter considerably
larger than the diameter of the body. This is because it
10 has been found that this larger diameter of the head of
the column enables the problem of foaming of the hydrolyzate
introduced into the column to be largely resolved. If the
head of the column were to have the same diameter as the
column itself, the foam produced by the gases expanding
15 and leaving the hydrolyzate when it is introduced into
the column where said reduced pressure prevails would be
in danger of ascending too high in said head while the
steam issuing from the column would be in danger of taking
with it a considerable quantity of hydrolyzate.

20 Accordingly, in a preferred embodiment of said
apparatus, the head of the column is connected to the
body by a frustoconical neck, a cylindrical expansion
collar having at least one flow orifice is arranged
concentrically against the inner wall of said neck,
25 said pipe for the introduction of hydrolyzate opens into
an annular space delimited by said frustoconical neck
and said expansion collar, and a distributor for hydrolyzate
is arranged below said expansion collar. This embodiment
represents an improvement which also assists in resolving
30 said problem of foaming of the hydrolyzate. Thus, not
only does the foam have a wider space in which to collapse
before ascending too high, the hydrolyzate introduced
into the column also has a larger space which promotes
a less violent expansion of the gases present therein and,
35 hence, the production of a smaller amount of foam. The

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- 1 expansion collar has at least one flow orifice through
which the largely degassed hydrolyzate is able to flow
to a distributor intended to distribute it uniformly
among the contact elements over the entire cross-section
5 of the cylindrical body.

Said gas pumping unit is intended to create and
to maintain said reduced pressure and is preferably con-
nected to said head in its upper part in order not to
aspirate the foam produced by the expansion of the gases
10 present in the hydrolyzate introduced into the column.
This pumping unit preferably consists of a mechanical pump,
such as a vane pump, for example, for removing the air
and a condenser for condensing the steam charged with DCP
connected in series. In one preferred embodiment, the
15 apparatus according to the invention comprises an arrangement for
regulating said reduced pressure comprising a pressure
gauge disposed at the top of said head, a valve for
regulating the flow of auxiliary air connected to the
gas pumping unit after said condenser and before said
20 mechanical pump and an electronic control circuit
electrically connected to said gauge and to said valve.
This arrangement has proved to be particularly advan-
tageous because it has a much shorter reaction time than
an arrangement based on regulation of the temperature of
25 the condenser for example. In addition, a device for
the removal of DCP from the condensate may be connected to
the condenser. A device such as this may consist simply
of a buffer vessel placed between the condenser and a
wastewater collector intended to collect the condensate
30 flowing from the condenser and to enable it to be over-
neutralized. This is because it has been found that the
30-50 ppm of DCP which the condensate may contain can be
destroyed by overneutralization, particularly by addition
of sodium hydroxide.

- 35 The sump of the column forms the lower part of

1 the column. It is intended to collect the hydrolyzate
which has passed through the cylindrical body filled with
contact elements. The steam injection pipe is connected
5 into a nozzle intended to distribute it uniformly among
the contact elements over the entire cross-section of the
cylindrical body. The pipe for the removal of hydrolyzate
is connected to the sump, preferably at its lowest point.
In one preferred embodiment, the apparatus according to
10 the invention also comprises a device for regulating
the level of hydrolyzate in the sump connected to the
removal pipe. This device may consist for example of
a level detector arranged in the sump below the steam
15 injection nozzle, a flow regulating valve installed in
series in the removal pipe and an electronic control
circuit electrically connected to this detector and to
this valve.

As mentioned above, the apparatus according to the
invention additionally comprises an arrangement for
20 regulating the temperature of the hydrolyzate connected
to the pipe for the introduction of hydrolyzate into the
column. This arrangement may itself comprise a heat
exchanger connected in series on the one hand with said
introduction pipe and on the other hand with an auxiliary
25 circuit for the circulation of a heat-carrying liquid,
a steam heating circuit for the heat-carrying liquid
connected to the closed circuit, a valve for controlling
the flow of heating steam, an element for measuring the
temperature of the hydrolyzate arranged on the introduction
30 pipe downstream of the heat exchanger and an electronic
circuit for regulating the temperature of the hydrolyzate
electrically connected to this element and to this valve.
This arrangement for regulating the temperature of the
hydrolyzate may be electrically connected by an electronic
35 temperature control circuit to a cell for measuring the

1 density of the hydrolyzate connected to the removal pipe.

In one preferred embodiment, the apparatus according to the invention additionally comprises an arrangement for regulating the flow of hydrolyzate connected to the introduction pipe and electrically connected by an electronic flow control circuit to an arrangement for regulating the flow of steam connected to the injection pipe. These flow regulating arrangements may each comprise a flow measuring cell, a flow regulating valve and an electronic regulating circuit electrically connected to this cell and to this valve. The electronic flow control circuit may impose a preset value for the flow rate of steam according to the flow rate of hydrolyzate. A preset value for a ratio to be maintained between the two flow rates may be manually fed into this control circuit after having been predetermined according to the DCP content of the hydrolyzate before distillation and the acceptable residual content after distillation.

The steam distillation apparatus for carrying out the process according to the invention is described in the following with reference to the accompanying drawing which diagrammatically illustrates a preferred embodiment thereof.

The apparatus illustrated comprises a distillation column 1 consisting of a cylindrical body 2 filled with contact elements 3, a head 4 and a sump 5. The column 1 is completely surrounded by an insulating jacket 22. The head 4 has a considerably larger diameter than the body 2 to which it is connected by a frustoconical neck 17. A gas pumping unit consisting of a condenser 8 cooled with cold water and a vane pump 9 is connected to the head 4 in its upper part. In the embodiment illustrated, the apparatus comprises an arrangement for regulating the reduced pressure comprising a pressure gauge 23 arranged at the top of the head 4, an electropneumatic valve 24

1 for regulating the flow of auxiliary air connected to
the pumping unit after the condenser 8 and before the
pump 9 and an electronic control circuit 25 electrically
connected to the gauge 23 and to the valve 24. A certain
5 quantity of auxiliary air is continuously pumped by the
pump 9. If the pressure measured by the gauge 23 is
below a preset pressure fed manually into the control
circuit 25, the control circuit 25 will cause the valve 24
to open to a greater extent to increase the flow of
10 auxiliary air introduced into the pumping unit and
vice versa. In addition, the condenser 8 is connected
to a wastewater collector 26 by a means for the removal
of DCP from the condensate consisting primarily of a
buffer vessel 27 equipped with a stirrer 48 in which the
15 condensate may be overneutralized.

A cylindrical expansion collar 18 is arranged
concentrically against the frustoconical neck 17 with
which it defines an annular space 20. A pipe 7 for the
introduction of hydrolyzate connected upstream to at least
20 one hydrolyzate tank or dwell tank by a pump (not shown)
opens into the annular space 20. At least one flow
orifice 19 is provided at the bottom of the expansion
collar 18 to allow the hydrolyzate to flow from the
bottom of the annular space 20 to a distributor 21
25 situated beneath the expansion collar 18 and above contact
elements 3 filling the cylindrical body 2.

The sump 5 of the column is intended to collect the
hydrolyzate which has passed through the cylindrical body 2.
A steam injection pipe 6 connected upstream to a means
30 for generating saturated steam under pressure (not shown)
is connected to the column between the sump 5 and the body
2. The pipe 6 opens through a nozzle 28 beneath the
contact elements 3. A pipe 10 for the removal of hydro-
lyzate is connected to the sump 5 at its lowest point. A
35 discharge pump 29 is connected in series with the pipe 10.

1 In the embodiment illustrated, the apparatus comprises
an arrangement for regulating the level of hydrolyzate in
the sump. This arrangement comprises a level detector 30
5 arranged in the sump 5 below the nozzle 28, an electro-
pneumatic valve 31 for regulating the flow of hydrolyzate
removed connected in series with the pipe 10 and an
electronic control circuit 32 electrically connected to
the detector 30 to the valve 31.

The apparatus additionally comprises a temperature
10 regulating arrangement 11 which itself comprises a
heat exchanger 35 connected in series on the one hand
with the pipe 7 for the introduction of hydrolyzate and on
the other hand with an auxiliary circuit 33 in which a
heat-carrying liquid circulates under the effect of a
15 pump 34; a circuit for heating the heat-carrying liquid
comprising a steam feed pipe 36, an electropneumatic
valve 37 for regulating the flow of steam, a nozzle 38 for
injecting steam into the auxiliary circuit 33 and a
pipe 39 for the removal of condensate provided with an
20 excess pressure valve 49; an element 40 for measuring the
temperature of the hydrolyzate arranged on the pipe 7
downstream of the exchanger 35; and an electronic control
circuit 41 electrically connected to the element 40 and to
the valve 37. In the embodiment illustrated, the
25 apparatus also comprises an electronic temperature control
circuit 15 electrically connected on the one hand to a
cell 16 for measuring the density of the hydrolyzate
connected to the removal pipe 10 and on the other hand
to the electronic control circuit 41 in which it
30 automatically imposes a preset temperature value according
to the density of the hydrolyzate removed.

In the embodiment illustrated, the apparatus also
comprises an arrangement 12 for regulating the flow of
hydrolyzate introduced into the column and an arrangement
35 14 for regulating the flow of steam injected into the

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1 column. Each of these arrangements comprises a flow
measuring cell 42, 43, an electropneumatic flow regulating
valve 44, 45 and an electronic control circuit 46, 47
electrically connected to the cell 42, 43 and to the
5 valve 44, 45. The electronic circuit 46 is intended to
regulate the flow of hydrolyzate around a preset value
fed in manually and is electrically connected to the
electronic control circuit 47 by an electronic flow control
circuit 13. The control circuit 13 is intended
10 automatically to impose a preset value for the flow of
steam according to the flow of hydrolyzate in the control
circuit 47. A preset value for a ratio to be maintained
between the two flows may be fed manually into the control
circuit 13.

15 The following Examples are intended to illustrate
the process according to the invention. In these
Examples, the percentages and parts are by weight, unless
otherwise indicated. As mentioned above, these Examples
are preceded by a description of the method developed
20 within the scope of the invention to determine the DCP
content of the present hydrolyzates, condensates and
seasonings.

Method of determination of the DCP content

25 Principle: The method comprises adsorption of the product
to be analyzed onto a column, elution of the DCP with a
mixture of ether and pentane, quantitative analysis by
gas-phase chromatography on a capillary column and
detection by electron capture.

30

Reagents:

1. Eluent: mixture of 85 parts by volume of pentane
and 15 parts by volume of diethylether.
2. 4 µg/ml solution of trichlorobenzene in the eluent.
- 35 3. Mixed standard solutions having identical concen-

- 1 trations of 0.1 $\mu\text{g/ml}$ of trichlorobenzene, but graduated concentrations of 0.125; 0.25; 0.5 and 1 $\mu\text{g/ml}$ of DCP in the eluent.

4. 20% solution of NaCl in distilled water.

5

Apparatus

- Gas phase chromatography on a capillary column with a slot injector and a detector operating by electron capture (ionization of a "reactive" gas consisting of 95 parts argon and 5 parts methane using β -rays emitted by ^{63}Ni).
- Integrator and/or recorder

Samples

- The samples of which the DCP content is assumed to be above 2 ppm are diluted with the 20% NaCl solution (reagent 4).
- Similarly, 20% NaCl are added to the condensates.

Elution

- 20 g of samples are introduced into the upper part of a small column or vertical cylindrical cartridge containing a granular filling.
- The sample is allowed to permeate the filling for a period of 15 minutes.
- 3 x 20 ml eluent (reagent 1) are then poured into the column and approximately 40 ml of eluate are collected in approximately 20 minutes at the lower end of the column.
- 1 ml of trichlorobenzene solution (reagent 2) is added to these 40 ml of eluate.

Chromatography

- The column used is a capillary column of fused silica 50 m long and 0.2 mm in diameter coated with a 0.2 μm thick layer of polyethylene glycol having a degree

- 1 of polymerization of 20,000.
- The column is brought to a temperature of 200°C 24 h beforehand.
 - The sample is subjected to a heating program
- 5 comprising keeping it at 115°C for 10 minutes, then increasing its temperature to 200°C at a rate of 30°C/min. and then keeping it at 200°C for 12 minutes.
- The injector is brought to a temperature of 250°C and the opening of its slot is adjusted to 1:10.
- 10 - The volume of sample injected is adjusted to 1.5 µl (of which only 1/10th permeates the column).
- Hydrogen under a pressure of 1.4 bar is used as the carrier gas.
 - The detector is brought to a temperature of 300°C
- 15 24 h beforehand.
- A mixture of argon and of methane in a ratio of 95:5, dried beforehand by passage through a molecular sieve, is used as the reaction gas in a quantity of 30 ml/minute.
- 20 - The retention times are approximately 5.9 minutes for the trichlorobenzene and approximately 8.5 minutes for the DCP.

Results

- 25 - The height and/or area of the peaks obtained for the sample and for the standard mixed solutions (reagent 3) are compared.
- For the mixed standard solution which comes closest to the sample, a ratio is formed between the heights and/or
- 30 areas of the peaks corresponding to the DCP and to the trichloroethylene.
- The corresponding ratio is formed for the peaks of the sample.
 - The quotient of the two ratios enables the DCP
- 35 content of the sample to be established.

1 Limits of the method

The concentration limit detectable by the present method is situated at around 0.05-0.1 ppm (0.05-0.1 mg of DCP per kg sample).

- 5 The percentage removal of DCP achieved by the present method is in excess of 90%.

EXAMPLE 1

- 10 Peanut cake is hydrolyzed with 6 N hydrochloric acid for 13 hours at 107°C. Humic substances, so-called first insolubles, are then separated therefrom by filtration. A hydrolyzate having a DCP content of 6-7 ppm is obtained.

- 15 The hydrolyzate is subjected to steam distillation in an apparatus of the type illustrated in the drawing, completely automated and controlled by a computer, in which the head of the column has a diameter of 2 m and a height of 3 m, the body of the column has a diameter of 1 m and is filled with contact elements over a height of 20 6 m and the column has a total height of 11.5 m. The contact elements are corrugated metal sheets drilled with holes and applied to one another across the corrugations (contact surface $250 \text{ m}^2/\text{m}^3$).

- 25 Over a period of 1 week without interruption, 8000 kg/h of hydrolyzate having a density of 1.260 g/cm^3 and a temperature of 62°C are introduced into the column. A pressure of 200 mbar is maintained in the head of the column. 1440 kg/h of saturated steam, for example under a pressure of 2 bar, is injected in countercurrent into 30 the column. The temperature in the sump is 63°C. 8000 kg/h of hydrolyzate having a density of 1.260 g/cm^3 and a DCP content below 0.1 ppm are removed from the column. In addition, the DCP is eliminated from the condensate, coming from the condenser by increasing its 35 pH to at least 11 by addition of NaOH.

1 The hydrolyzate is left standing for 2 weeks, after
which substances which have crystallized slowly and
colloidal particles which have agglomerated slowly, so-
called second insolubles, are separated therefrom by
5 filtration. A dark-coloured liquid seasoning is obtained
of which the DCP content is below 0.1 ppm, although its
density, aminoacid composition and organoleptic qualities
are no different from those of a seasoning obtained in
the same way but without subjecting the hydrolyzate to
10 steam distillation after separation of the first or
second insolubles.

EXAMPLE 2

 Wheat gluten is hydrolyzed with 6 N hydrochloric acid
15 for 12 h at 100°C. Humic substances, so-called first
insolubles, are then separated therefrom by filtration.
A hydrolyzate having a DCP content of approximately 5 ppm
is obtained.

 The hydrolyzate is subjected to steam distillation
20 in an apparatus of the type illustrated in the drawing,
completely automated and controlled by a computer, in
which the head of the column has a diameter of 0.9 m and
a height of 2 m, the body of the column has a diameter
of 0.4 m and is filled with the same contact elements
25 as in Example 1 over a height of 6 m and the column
itself has a total height of 11 m.

 Over a period of 1 week without interruption,
2000 kg/h of a hydrolyzate having a density of 1.262 g/cm³
and a temperature of 64°C are introduced into the column.
30 A pressure of 200 mbar is maintained in the head of the
column. 300 kg/h saturated steam, for example under a
pressure of 2 bar, are injected in countercurrent into
the column. The temperature in the sump is 63°C.
2000 kg/h of hydrolyzate having a density of 1.262 g/cm³
35 and a DCP content below 0.1 ppm are removed from the

1 column. In addition, the DCP is eliminated from the condensate coming from the condenser by increasing its pH to at least 11 by addition of NaOH.

5 The hydrolyzate is left standing for a few days and the second insolubles are separated therefrom by filtration. A dark-coloured liquid seasoning is obtained of which the DCP content is below 0.1 ppm, although its density, aminoacid composition and organoleptic qualities are no different from those of a seasoning obtained in the same
10 way, but without subjecting the hydrolyzate to steam distillation after separation of the first or second insolubles.



CLAIMS

1. A process for the production of a seasoning in
5 which vegetable proteins are hydrolyzed with concentrated
hydrochloric acid, the hydrolyzate is neutralized, a first
insoluble fraction is separated therefrom, the hydrolyzate
is allowed to stand to produce a second insoluble fraction
10 which is then also separated therefrom, characterised in
that, after a separation of said first or second
insolubles, the hydrolyzate is subjected to steam
distillation under reduced pressure while keeping the
density of the hydrolyzate at a substantially constant
15 value in order to eliminate 1,3-dichloro-propan-2-ol
present.

2. A process as claimed in Claim 1, characterized in
that the hydrolyzate is subjected to steam distillation at
a temperature of from 45 to 70°C under a pressure of 100-
320 mbar by contacting an ascending stream of 10-20 parts
20 by weight/h steam with a descending stream of 100 parts by
weight/h of hydrolyzate over a contact zone 5-15 m in
height filled with contact elements.

3. A process as claimed in Claim 2, characterized in
that the temperature of the hydrozylate before distillation
25 is kept at a value higher by 1 to 5°C than that of the
hydrozylate above the contact zone.

4. A process as claimed in Claim 1, characterized in
that the density of the hydrozylate is kept at a
substantially constant value by regulating the temperature
30 of the hydrozylate before distillation according to the
density of the hydrozylate after distillation.

5. A process as claimed in Claim 1, characterized in
that the density of the hydrozylate is maintained at a
substantially constant value from 1.250 to 1.265 g/cm³.

35 6. A process as claimed in Claim 1, wherein the
apparatus for steam distillation comprises a distillation
column (1) consisting of a head (4), a cylindrical body (2)
filled with contact elements (3) and a sump (5); a gas
pumping unit (8,9) connected to said head; a pipe (7)



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for the introduction of hydrolyzate connected to said column between said body and said head; a steam injection pipe (6) connected to said column between said sump and said body; and a pipe (10) for the removal of hydrolyzate connected to said sump, characterized in that it additionally comprises an arrangement (11) for regulating the temperature of the hydrolyzate connected to said introduction pipe (7) and in that the diameter of said head (4) is larger than the diameter of said body (2).

7. A process as claimed in Claim 6, characterized in that the apparatus additionally comprises an arrangement (12) for regulating the flow of hydrolyzate connected to said introduction pipe (7) and electrically connected by an electronic flow control circuit (13) to an arrangement (14) for regulating the flow of steam connected to said injection pipe (6).

8. A process as claimed in Claim 6, characterized in that in the apparatus said arrangement (11) for regulating the temperature of the hydrolyzate is electrically connected by an electronic temperature control circuit (15) to a cell (16) for measuring the density of the hydrolyzate connected to said removal pipe (10).

9. A process as claimed in Claim 6, characterized in that in the apparatus said head (4) is connected to said body (2) by a frustoconical neck (17), a cylindrical expansion collar (18) having at least one flow opening (19) is arranged concentrically against the inner wall of said neck, said pipe (7) for the introduction of hydrolyzate opens into an annular space (20) defined by said frustoconical neck (17) and said expansion collar (18) and a distributor (21) for hydrolyzate is arranged below said expansion collar and above contact elements (3).
