

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

0 087 195**A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 83200237.2

(51) Int. Cl.³: **F 23 G 7/00**

(22) Date of filing: 16.02.83

(30) Priority: 18.02.82 NL 8200650

(43) Date of publication of application:
31.08.83 Bulletin 83/35(84) Designated Contracting States:
AT BE CH DE FR GB IT LI NL SE(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)(84) Designated Contracting States:
BE CH DE FR IT LI NL SE AT(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P O Box 68
London EC4P 4BQ(GB)(84) Designated Contracting States:
GB(72) Inventor: **Segers, Jacobus Cornelis**
Finsestraat 17
NL-2912 TG Nieuwerkerk a/d IJssel(NL)(74) Representative: **de Jonge, Aeilko Pieter, Dr. et al,**
Unilever N.V., Patent Division Olivier van Noortlaan 120
P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) Method for processing of by-products of the refining of oils and fats.

(57) To avoid environmental objections in discarding by-products of refining and processing of fatty oils, fats or mineral oils, especially those containing alkali metal ions or salts, such by-products are combusted with excess air or oxygen, preferably in a fluidized bed oven, using a bed material having a low silicon content, particularly those consisting mainly of titanium, calcium and/or aluminium oxides, at 600-950°C, preferably 800-850°C. The organic materials in the by-products are thereby converted into products which can be discharged without problems; the exhaust gases contain only low amounts of carbon monoxide and nitrogen oxides. By passing the combustion gases through a heat-exchanger, the heat generated can be used, e.g. to preheat the excess air for the process or to generate steam or heated water, which can be used economically in other parts of the plant. The process is particularly suitable

for the combustion of soapstock, the water content of which has been reduced, e.g. by evaporation, if necessary.

EP 0 087 195 A2

METHOD FOR PROCESSING OF BY-PRODUCTS OF THE REFINING OF
OILS AND FATS

The invention relates to a process for the processing of by-products of the refining of fatty oils, fats and mineral oils.

5 Crude fatty oils and fats and mineral oils contain, apart from triglycerides and hydrocarbons, numerous other substances in smaller amounts, which commonly are removed in a refining process to obtain the valuable purified raw materials, e.g. triglyceride oils and fats,
10 suitable for further processing.

Crude fatty oils and fats contain free fatty acids formed by hydrolysis of triglycerides. They also contain small amounts of other components such as colorants,
15 sugars, sterolglucosides, waxes, partial glycerides, proteins, phosphatides and metals.

By-products that are obtained in the removal of such contaminants and in the further processing of the oils
20 and fats are e.g. soapstock, lecithin sludge, tank foots, spent active carbon and bleaching and catalyst earth, wastes of oil seeds remaining after extraction of the oils, etc.

25 By-products that are obtained in the refining of mineral oils are e.g. polymerized oils, spent bleaching clay and catalyst, that may be contaminated with sulphur-containing compounds, cycle stock from the catalytic cracking of oil and distillation residues.

30

Such by-products have to be disposed of, possibly after isolating valuable materials therefrom, which may give rise to environmental problems.

For instance, for a long time it has been usual to remove the free fatty acids from fatty oils and fats by the action of alkaline materials, particularly of an aqueous solution of sodium hydroxide, through which they
5 are converted into water-soluble salts (soaps) and as such separated from the oil or the fat. Hereby many of the above-mentioned materials are also removed. The by-product formed hereby is usually referred to with the term "soapstock".

10

The soapstock is processed in different manners. It can be discharged as such. Also, the fatty acids, after acidification, e.g. with sulphuric acid, can be released therefrom and worked up.

15

These methods give rise to environmental objections. Discharge of soapstock as such changes the pH of the surface water into which it is released. After isolation of the fatty acids, the products still contain many
20 organic materials and electrolytes which, upon disposal, in addition to influencing the pH unfavourably also decrease the oxygen content of the surface water (increase of biological oxygen demand).

25 It is clear that authorities, wielding environment legislation, can charge industry to take measures other than disposal.

Naturally, it is possible to apply biological pre-
30 purification, but this is a costly procedure.

It has now been found that by-products of the refining or processing of fatty oils, fats and mineral oils, which by-products contain organic matter, can be processed by sub-
35 jecting them, after reduction of the water content if necessary, to a high temperature in the presence of air or oxygen, thereby converting the organic materials by com-

bustion into water and carbon dioxide, carbonate and small amounts of other salts.

In this way, e.g. the soapstock can be processed,
5 through combustion, to products which can be discharged without objection.

If materials to be combusted contain relatively high amounts of water, the combustion may be affected adversely.
10 ly. The volume may then first be reduced, e.g. by evaporation, to a concentration acceptable for the process, e.g. to a content of 40% total fatty matter or more. The water content is preferably such that the material is still thin enough to be satisfactorily conveyed into the
15 combustion chamber, but on the other hand it should be not so high that the combustion is affected adversely.

Liquid materials to be combusted can be brought into the fluidized bed through a pipe, which may have been provided with means to divide the stream of liquid into
20 thin spouts or drops. Care should be taken, however, that such means are not obstructed by small solid particles occurring in the liquid material. Essentially solid materials can be brought into the oven by means of
25 a slowly rotating screw, in a manner known in the art.

The combustion is carried out with an excess of air or oxygen and at a temperature between 600° and 950°C, preferably at 800-850°C, so that the organic material is
30 completely burnt.

An advantage of such moderate temperatures is that the production of nitrogen oxides is limited. Typically, the carbon monoxide and nitrogen oxides contents of the combustion gases are below 200 and 60 ppm, respectively.
35

The water present in the material, e.g. soapstock, evaporates and is discharged as water vapour with the

orates and is discharged as water vapour with the exhaust gases. The carbonates and other salts formed are discharged as ash (when sodium hydroxide is used for the neutralization, soda is formed which can be used for all kinds of purposes).

The combustion of the aforementioned by-products preferably takes place in a fluidized bed oven, of which the bed material is chosen in a way such that neither sintering nor melting of the materials formed, such as the carbonate, occurs. Nor should the particle size be reduced quickly by the friction in the fluidized bed.

Some of the by-products, especially the soapstock, contain substantial amounts of alkali metal ions or salts. For the combustion of such by-products a bed material should be used having a low silicon (silicon oxides, silicates) content.

Combustion of materials containing alkali metal ions or salts in fluidized bed ovens with bed materials having high contents of silicon oxides or silicates, e.g. the commonly used sand, causes substantial sintering to occur, thereby preventing a stable combustion process.

A bed material, suitable for the combustion of products comprising alkali metal ions or salts, is titanium dioxide or a material consisting mainly thereof. Other materials that can also be used are e.g. calcium or aluminium oxides or mixtures thereof, or mixtures of these oxides with products consisting mainly of titanium oxides. The total silicon content should be less than 8%, preferably less than 4% by weight of the bed material.

For the combustion of sulphur-containing products, such as certain catalyst earths, a bed material containing a substantial amount of calcium oxide is particularly

suitable. The calcium oxide reacts with the sulphur compounds, thereby preventing discharge of sulphur oxides into the atmosphere together with the exhaust gases.

- 5 For the combustion of soapstock having a high water content, e.g. 70% or more, the volume of the soapstock may be reduced, before the combustion, by evaporation.

Alternatively, the soapstock may be mixed with another
10 essentially organic waste material having a lower water content. Also, the soapstock may be burnt as such, but if the combustion process cannot maintain itself, it should be supported, e.g. by combustion of oil or gas simultaneously.

15

The bed material and the solid combustion products formed can be entrained with the combustion gases and separated outside the oven. The solid materials collected may be entirely or partially recirculated and fed
20 back into the fluidized bed.

Preferably, however, the particle size and the density of the fluidized bed material and the construction of the oven are chosen such that, after the combustion,
25 separation is effected by the velocity of the combustion gases, which entrain the solid combustion products and leave the bed material behind.

The feed-in velocity of the air or oxygen and that of
30 the material to be burnt are adjusted to each other such that the temperature over the fluidized bed is reasonably homogeneous, that only a little carbon monoxide forms and that the content of nitrogen oxides is kept limited, i.e. that the contents of carbon monoxide and
35 nitrogen oxides in the combustion gases are below about 200 and 60 ppm, respectively.

The exhaust gases loaded with the solid combustion products formed can be cooled in an effective heat-exchanging system, whereby the heat discharged can be used to generate steam, to obtain heated water, and/or
5 to pre-heat the feed-in gases and by-products.

The solid combustion products are separated from the combustion gases in a filter system and, without there being environmental objections raised, can be discharged
10 in the usual way.

By-products of the refining of fatty oils, fats and mineral oils that can be processed in a manner as described above, are e.g. soapstock, polymerized oils,
15 wastes of oil seeds remaining after extraction of the oil, lecithin sludge, tank foots, spent active carbon and bleaching and catalyst earth and mixtures thereof, and even spent fuel oil. Also, waste products such as essentially organic house-hold refuse can be combusted
20 according to the process of the invention. However, material having a higher silicon content, such as bleaching earth, should not be mixed with products containing substantial amounts of alkali metal ions or salts, such as soapstock, but should be burnt separately.

25

In particular, products having a high content of organic materials and containing a substantial amount of alkaline materials can be suitably combusted by the process of the invention in a fluidized bed oven having a
30 bed material with a low content of silicon oxides and silicates. By this process the organic materials are converted into products that are not a burden to the environment and that can be discharged without problems. Moreover, the heat generated in the process can be made
35 use of in other parts of the plant, thereby reducing the overall energy costs of the plant.

Example 1

Raw fish oil is neutralized in a known manner by treatment with an aqueous solution of sodium hydroxide. The
 5 soapstock obtained is reduced by evaporation until it contains 45% total fatty matter.

This soapstock is subjected to combustion in a fluidized bed oven. The bed material used in this oven is a ground
 10 blast-furnace slag obtained from the iron preparation. The slag material comprises:

		<u>% by weight</u>
	H ₂ O	2
	TiO ₂ + Ti ₂ O ₃	72
15	Fe + FeO	12
	Al ₂ O ₃	5
	SiO ₂	5
	CaO	1
	V ₂ O ₅	0.6
20	Cr ₂ O ₃	0.2
	MnO	0.3

The particle size of the bed material is 0.9-1.5 mm.

25 The fluidized bed oven is heated to a temperature of 800°C by combustion of oil.

The soapstock is thereafter fed into the fluidized bed, in thin spouts. The amounts of air and soapstock are
 30 chosen such that, on the one hand, the organic material is completely burnt and, on the other hand, the temperature in the part where the combustion takes place remains at about 800°C.

35 The combustion gases loaded with the soda particles are discharged at the top of the oven (the bed material remains behind in the oven) and are conducted through a

so-called spent gas boiler, in which the exchanged heat converts water into steam, which is made use of elsewhere in the factory.

- 5 The cooled gases are separated from the soda particles in a conventional fly ash filter system.

The combustion gases, consisting mainly of water vapour and carbon dioxide, are discharged into the atmosphere
10 via a chimney and the soda is collected.

The soda obtained is free of organic material and can be used for all kinds of purposes.

15 Example 2

Lecithin sludge and soapstock, obtained from the refining of crude soybean oil, are mixed in a weight ratio of 2:1. The total content of organic material is
20 about 55%.

This mixture is pre-heated to 80°C and fed into a fluidized bed oven which contains calcium oxide as bed material. The bed height is 0.5 m. The oven has so-
25 called membrane walls, i.e. the walls contain pipes through which cooling water is circulated. The oven has been pre-heated to 750°C. When the mixture of lecithin sludge and soapstock and excess air are fed into the oven, the temperature in the fluidized bed rises to
30 850°C. Then the amounts of the mixture fed into the oven and of the heat withdrawn by the membrane walls are adjusted such that the complete combustion of the organic material, as indicated by a carbon monoxide content of the exhaust gases of at most 150 ppm, is ensured and
35 that the temperature remains constant at about 850°C. The amount of nitrogen oxides in the exhaust gases is about 50 ppm. The combustion gases are led through a

water-operated heat-exchanger; the heated water is used to pre-heat the aforementioned mixture and can further be used elsewhere in the factory.

CLAIMS

1. A process for the processing of by-products obtained by the refining or processing of fatty oils, fats and mineral oils, characterized in that by-products containing organic matter, after reduction of the water
5 content if necessary, are subjected to a high temperature in the presence of air or oxygen, whereby the organic materials are converted into water and carbon dioxide, carbonate and small amounts of other salts.
- 10 2. A process according to claim 1, characterized in that the by-products are products containing alkali metal ions or salts.
3. A process according to claim 2, characterized
15 in that the by-product is soapstock obtained by alkaline neutralization of glyceride oil.
4. A process according to claims 1-3, characterized in that the combustion is carried out at a temperature of 600-950°C.
20
5. A process according to claim 4, characterized in that the combustion is carried out at a temperature of 800-850°C.
25
6. A process according to claims 1-5, characterized in that the combustion takes place in a fluidized bed oven.
- 30 7. A process according to claim 6, characterized in that a bed material is used that contains less than 8% by weight of silicon.
8. A process according to claims 6-7, characterized
35 in that titanium dioxide or a material con-

taining titanium dioxide is used for the fluidized bed material.

9. A process according to claims 6-8, characterized in that the solid combustion products formed are
5 blown out of the fluidized bed by the combustion gases, are subsequently cooled and separated from the spent gases in a filter system.
- 10 10. A process according to claims 1-9, characterized in that the conversion products are cooled in a heat-exchanger, whereby the heat discharged is used for the heating of water or the generation of steam.