Complex biomass technologies. Biorefinery for clover, oats and barley as non-waste technology.

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In general I don't see biomass and specifically phytomas as a fuel source, but as a new basic raw material for the chemical industry, which for the German chemistry in the past was coking coal and limestone.

Later it was diesel as the foundation for the entire petrochemical industry. Today it can be also a renewable resource. Thus, biomass, specifically fytomasss.

Fytomass processing technology can be economically viable, only if the fytomasss will be processed and used complexly.

Orientation for ethanol production from starch grain is economically disadvantageous.

For the grain is about 65% starch, during saccharification, fermentation, isolation ethanol losses occur.

It can easily happen that we effectively utilize only ¼ materials. As with the first generation of biofuels. Biofuels should not be the only product, but one of a series of complex products processing of fytomass. Phytomass contains two main components: the polysaccharide - cellulose and derivative of α - phenylpropane -lignin. It is clear that the plants grown by farmers, such as grasses and herbs are lignocellulosic materials. While trees are cellulose and lignin contain more lignin.

But processing phytomass is different, if it is a raw material mainly cellulose or lignin material.

Cellulose can be further processed by biotechnology.

In case of lignin it can not be successfully done yet.

So the basis for processing phytomass is converting the basic raw material.

This can be done in two ways:

a) hydrolysis;

b) thermally.

Example should be hydrolysis of phytomass. This can be done by the effect of strong acids or bases at high temperatures and high pressures. It is outdated, classical and expensive way.

Starch hydrolysis may also be done by malt diastasis, as it is commonly done in each distillery or by a fungal or bacterial amylase.

We obtain sugar solutions, but only from the starch, not from cellulose. This means that is used only about 15% of the mass of potato and max. 30-35% of the mass of grains.

New technologies are characterized by complex use of fytomass in processes where the composition of primary agricultural commodities ceases to be significant.

We can handle whatever is grown.

Not only canola oil in the manufacture of MEŘO, or a sugar and starch in the manufacturing proccess of ethanol from sugar beet, cereals and other starchy crops.

The advantage of the new technologies is greater economic efficiency.

Support for intensive agricultural production in the case of relative abundance of food in the world capable of payment.

The rapid development of the product spectrum of the chemical industry and its development on the basis of sufficient new basic material - fytomass.

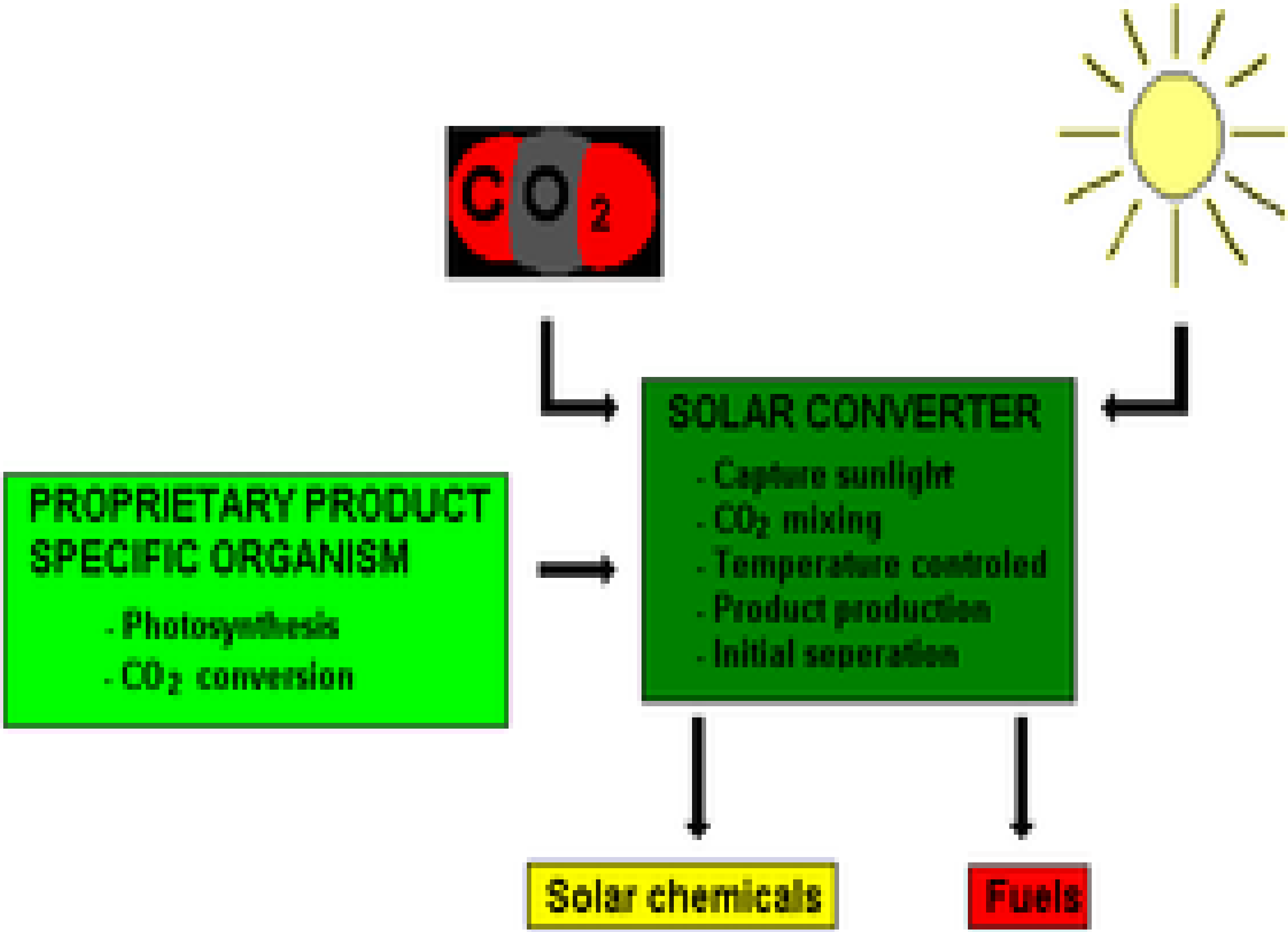
Phytomass has to be converted, the essence of which is the release of sugars from lignocellulose or where there is a release of gaseous products with a predominance of CO, CO_2 + H_2 of cellulose – lignin fytomass.
Cellulose – lignin phytomass, ie wood can be gasified in the generator and get the generator gas.
When water stream is injected into the generator, can obtain water gas mixture $CO + H_2 + CO_2$. That is the current known technology. Already 70 years ago came Fischer and Tropsch in Germany on the idea that the water gas can be hydrogenated at a temperature of about 190°C and pressure of 1-15 atm on the catalyst composed of CoO and ThO_2 and obtain a mixture of saturated hydrocarbons paraffins. In the literature it is possible to meet a variety of new technologies. Production of ethanol from cellulose. The experimental operation of the Canadian company Iogen in Ottawa.

For the production of ethanol is used tropical fungus, which is genetically modified to produce the enzyme cellulase, cleaving cellulose.
The advantage of using fungal cellulases lies in the ability to use all forms of fytomass.
At the Edmonton University in Alberta, Faculty of Engineering is working group of students who call themselves "The butanerds". They prepared genetically modified *Escherichia coli* capable of producing butanol.
Scientists from University of California made an intervention into the genome of the enteric bacteria *Escherichia coli* using genetic modification. They created producer of compounds with a longer carbon chain, such as isobutanol, 1-butanol, 3-methyl-1-butanol, 2-phenylethanol and 2-methyl-1-butanol.

Genetically modified *Escherichia coli*

The company Joule Unlimited in Cambridge, Massachusetts, developed a process Helioculture [TM] which is based on generating a hydrocarbon-based fuel.
The process uses brackish water, nutrients, photosynthetic organisms, CO_2 and sunlight to create fuel by C*yanobacteria*.
In 2011 it produced equipment for the production of more than 20,000 gallons (1 gallon = 3,785 l) of fuel per acre (1 acre = 0.405 ha) per year.
HeliocultureTM process using photosynthetic organisms, but in other way than in the production of fuel from algae.
Oils of marine or freshwater algae usually have to be extracted and purified to fuel.
HeliocultureTM produces fuel directly, namely ethanol or other hydrocarbons without the need for refining.

The process scheme of *Helioculture* [TM]



System Helioculture™ with photosynthetic organisms to produce fuel

The process is made possible by the discovery of genes coding for enzymatic mechanisms that enable the direct synthesis of alkanes, olefins, ethanol, and other key molecules.

Joule Unlimited claims that its product will be competitive with crude oil at 50 US dollars per barrel. (Note to 5.5 2016 price of a barrel of Brent crude oil fell to US $ 45.09, WTI Crude Oil Crude Oil $ 44.33 US).

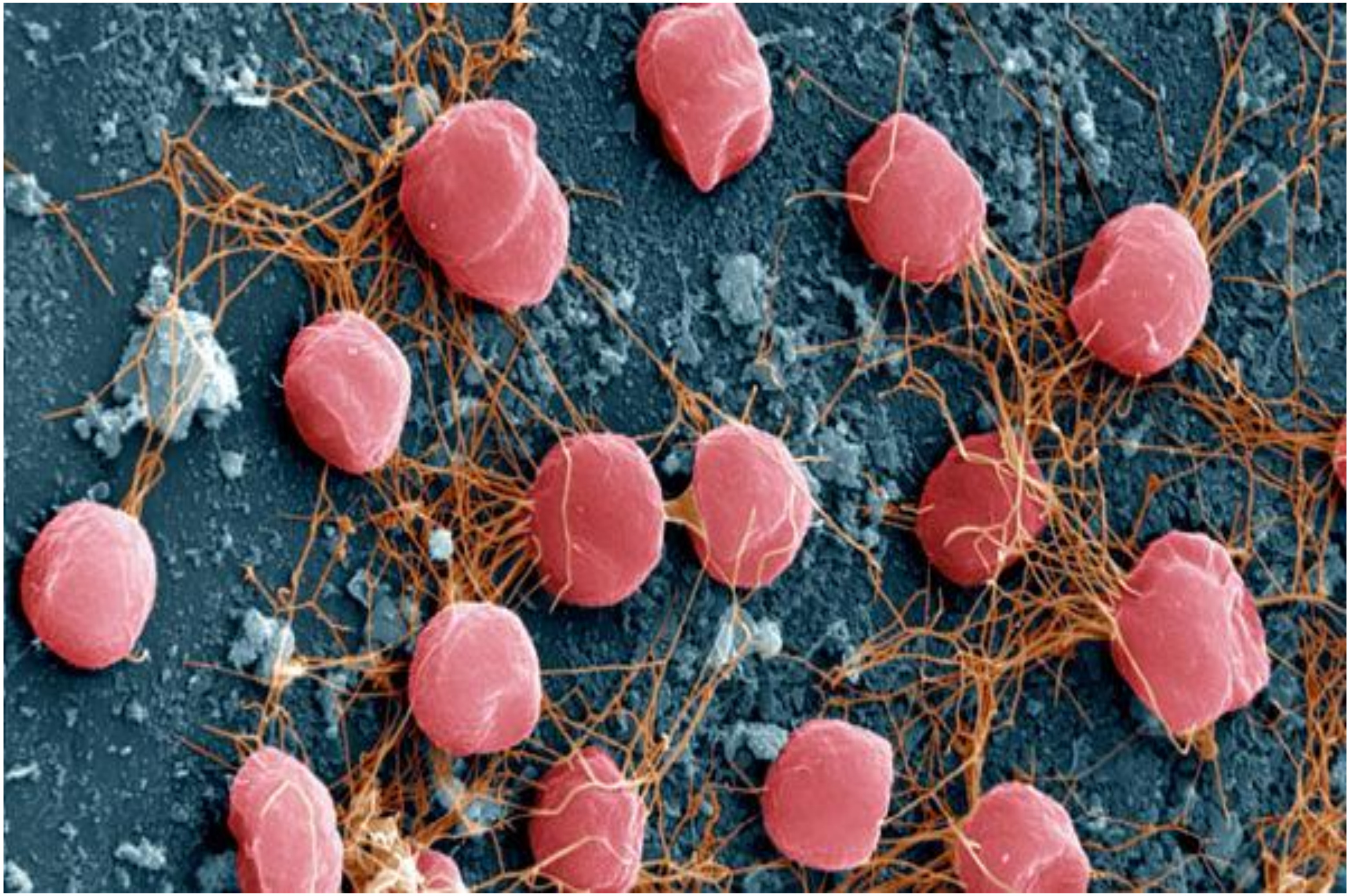
The company also states that using the technology can deliver all transport fuel to an area the size of Texas.

The base of production is patent on genetically modified C*yanobacteria* and numerous other patents.

Archaea produce fuel from the air.
Researchers from the University of Georgia, US sees air as feedstock.
Carbon dioxide in the atmosphere is generally considered a problem.
Their new technology is based on the development of a micro-organism that transforms atmospheric CO_2 to fuel.
In fact they discovered a way to create a microorganism which does the same thing with CO_2 as plants.
He absorbs it and produce from it something useful. The discovery with promising industrial application described a professor of biochemistry and molecular biology Michael Adams from Franklin Faculty.

Genetically modified archaea

Pyrococcus furiosus



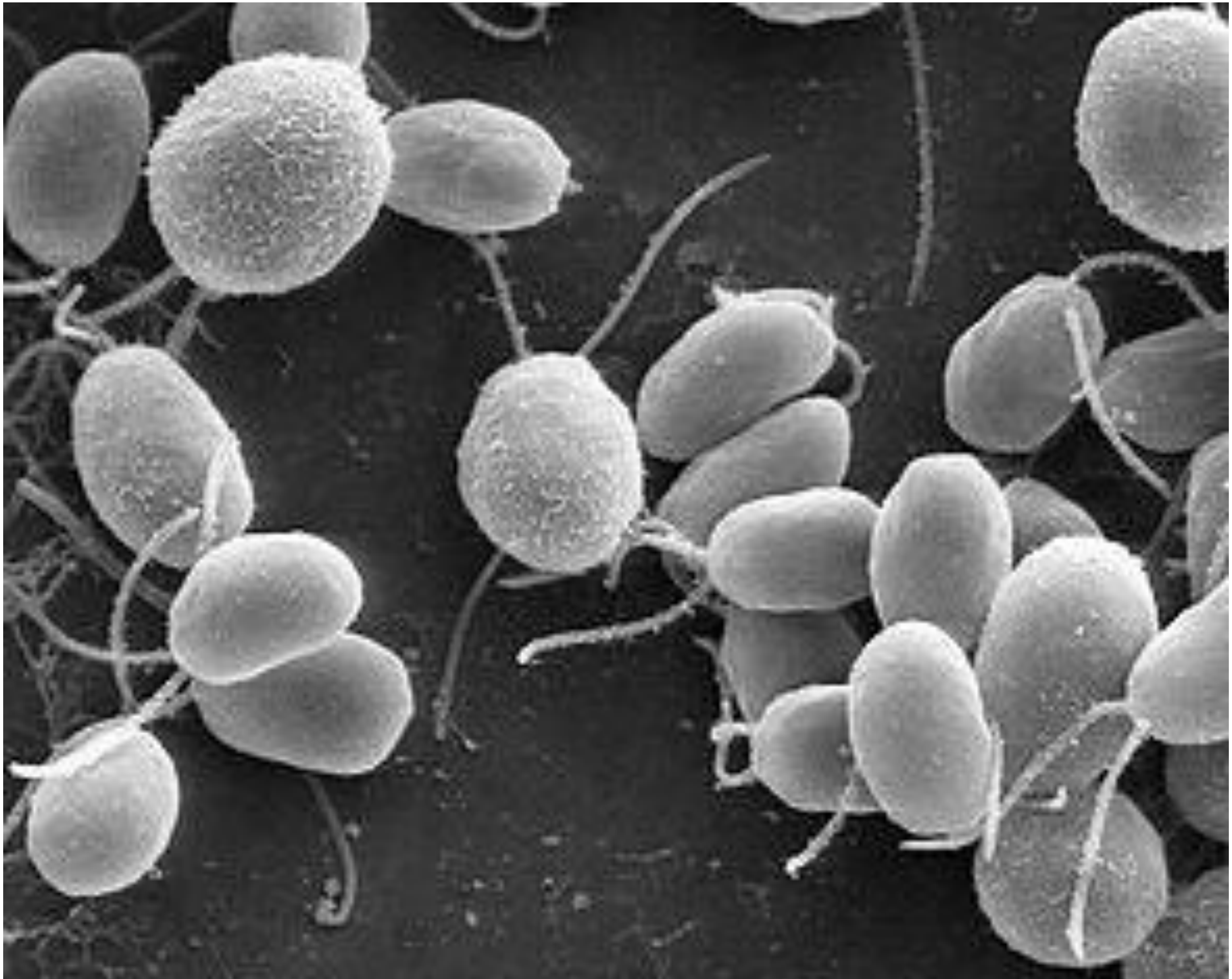
During photosynthesis, plants convert solar energy using water and CO_2 into sugars, which serve them to nourish. These sugars plants burn similarly like people calories from food.

Thanks to the discovery can be removed the plants as a mediator. It is possible to take CO_2 directly from the atmosphere and convert it to useful products such as fuel or chemicals.

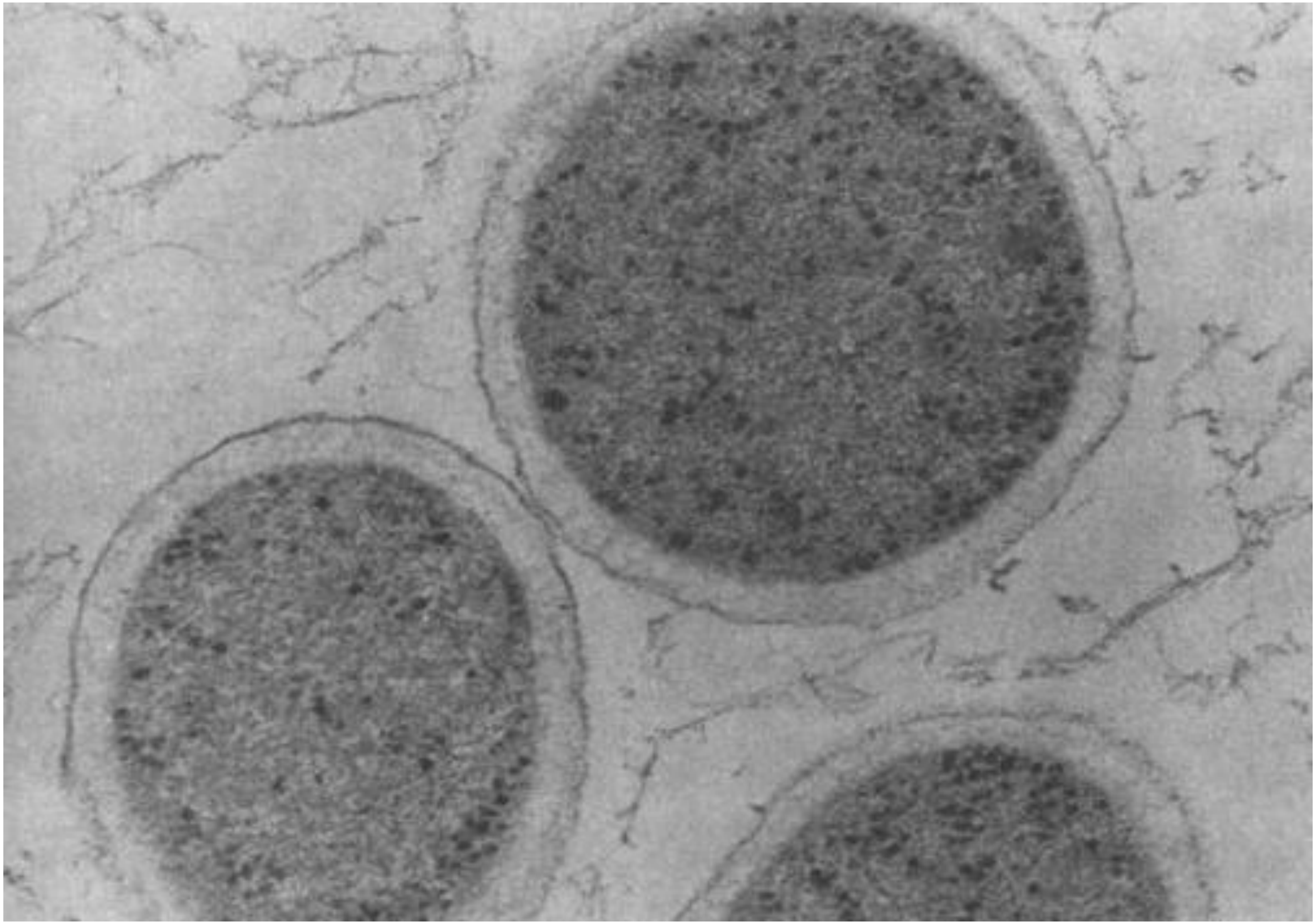
Archaea *Pyrococcus furiosus* with 1.5 micrometers in diameter, known by experts as a " wild fireball " lives nearby geothermal resources in the oceans at temperatures of around 100°C. Artificially modified microorganism was persuaded by scientists to feed with CO_2 at lower temperatures

With the addition of hydrogen starts a team in a microorganism a chemical reaction that will incorporate carbon dioxide into 3-hydroxypropionic acid, which is used for example for the production of acrylates and other industrial materials. Another mutation of the microorganism produce other chemicals, including fuel.
Hydrogen production with the help of algae *Chlamydomonas reinhardtii* was implemented in laboratories at the University of California at Berkeley. On the base of patent company develops Melis Energy technical equipment using this algae for commercial production of hydrogen.
Scientists from Brookhaven National Laboratory in Upton working on development of hydrogen technology acquisition with the help of facultative anaerobic bacteria *Thermatoga Neapolitana*.

Chlamydomonas reinhardtii



Thermatoga neapolitana



Bacteria at a temperature between 70-85°C can produce from glucose, economically interesting amount of hydrogen which. The peculiarity of Bacteria is that it does not require a strictly anaerobic environment.

Professor of biological systems engineering Zhang managed with xylose, the second most abundant plant simple sugar, the production of large amounts of hydrogen with a method that can be realized with any source of biomass. Produces very pure hydrogen under mild reaction conditions at 122°C and at normal atmospheric pressure.

Among biocatalysts used to release the hydrogen are groups of enzymes isolated from various microorganisms that thrive in extreme temperatures. This eco-friendly way of hydrogen production using renewable natural resources and almost does not emit greenhouse gases, does not require expensive heavy metals.

Czech agricultural system is limited by fear of overproduction of food as much as possible. We fertilize the soil at least from all the allied countries of Europe, 50% of agricultural land was included in the Less Favoured Areas (LFA), where agriculture has fulfill only secondary functions. We have only 0.28 of big livestock units (BLU)/1 ha , while in developed European countries it is more than 1 BLU. In the Czech Republic there is not managed 0.5 mil. ha of arable land and about 0.5 mil. ha of meadows and pastures. Agricultural systems of Europe and the world, including Canada and the USA, have huge reserves. Applying already known and proven working practices would allow (especially on fertile soils in the world and favorable climatic conditions) a sharp increase in agricultural production on the sole condition - the existence of payments of capable buyer of agricultural production.

Comprehensive waste-free processing of red clover

Not only in this country but in other countries it is agricultural land largely made up of so-called Less Favoured Areas (LFA), which are not suitable for intensive agricultural production, but are suitable for cultivation of grassland, particularly perennial forage crops that enable to maintain of soil fertility and are yet unpretentious.

The shift of the agriculture to a raw material reservoir for energetics and industry in combination with agricultural subsidy policy would contribute to preserve the fertility of agricultural land resources and to the sustainable development of these areas.

Clover is a very significant multi-year crop in crop rotation.

They form the base of feed and livestock production significantly affects soil fertility due to numerous root residues and harvest residues, representing a significant proportion of labile organic matter entering into the soil under crop rotation. Sustainability of Czech agriculture is currently limited by the lack of production of high-quality organic fertilizer, manure, slurry, etc.., Because of the small number of livestock. Positive balance of organic matter (OM) and sufficient supply of organic matter to the soil (9 OM t dry matter per hectare per year), is possible to provide with increasing proportion of clover in crop rotation and with the use of surplus clover as a raw material for green biorefineries.

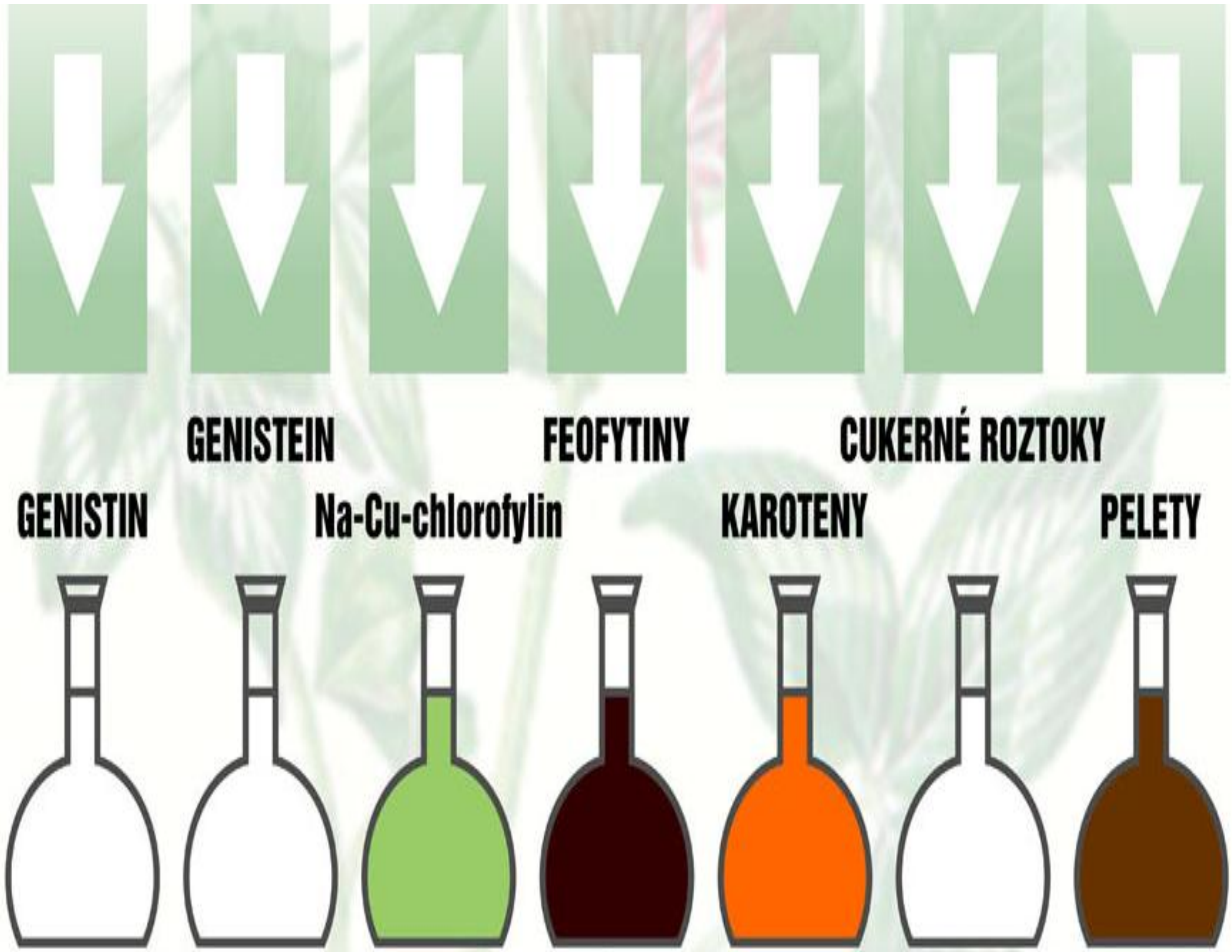
When processing clover in green biorefineries we can get a lot of interesting products. In our patented technology, CZ 302596, it is proposed eight products.
The technology provides a method for processing of the extracted biomass of red clover (*Trifolium pratense* L.) for the purpose of industrially viable isolation of genistin or genistein, a green pigment Na-Cu-chlorophyllin, carotenes and phaeophytins. Genistein is a phytoestrogen is used to produce drugs for alleviating menopause of women. Other substances are useful as colorants in food processing or cosmetic industry. A process for obtaining the substances can be used advantageously as parallel processing technology to clover on sugar processing for bioethanol and molasses, and for solid biofuels according to patent CZ 301956

Zpracování jetele lučního (Trifolium pratense L.)

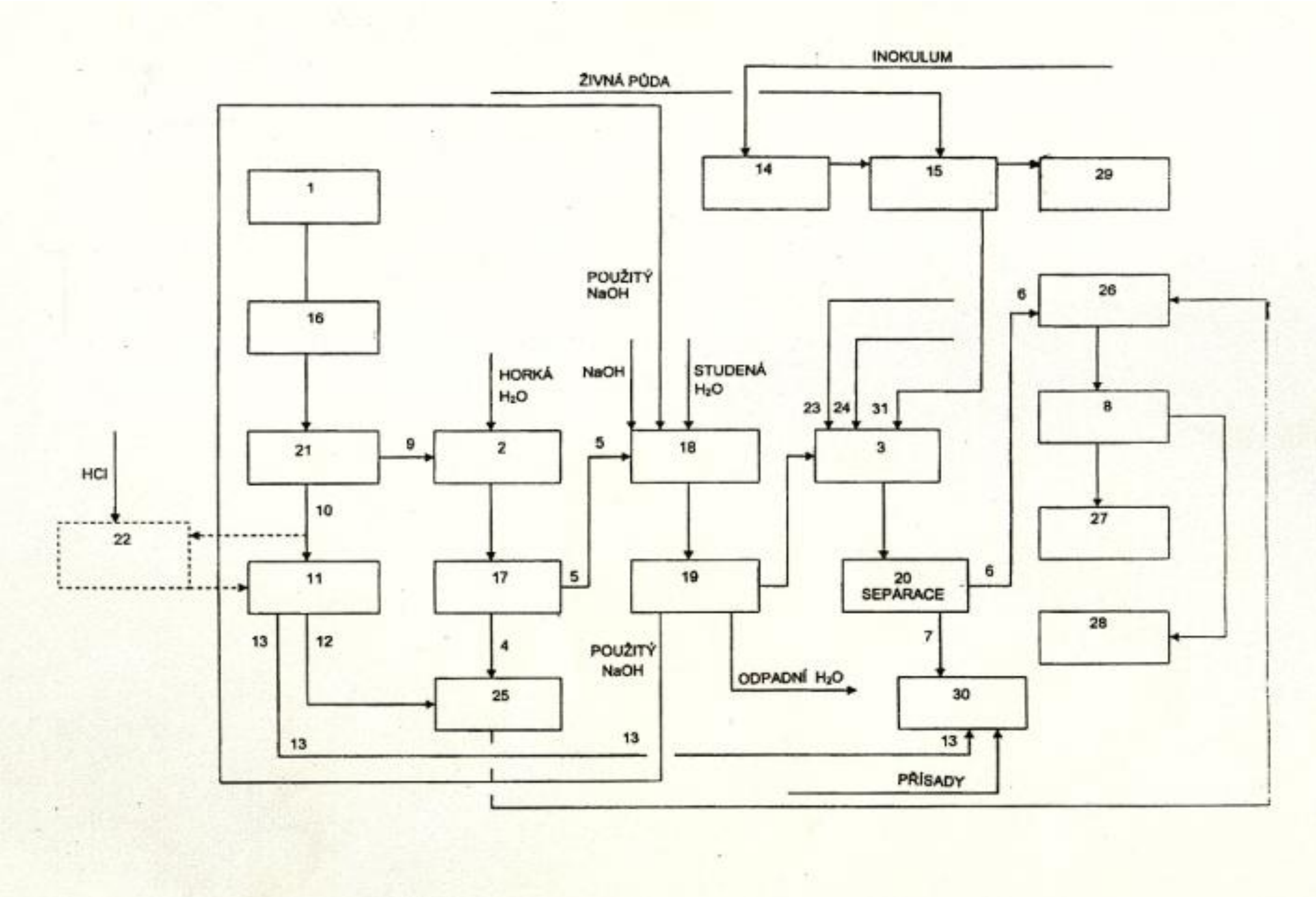
na genistin, genistein, Na-Cu-chlorofylin, feofytiny, karoteny, cukerné roztoky a pelety biopaliva pro peletkové kotle

Prof. Ing. L. Kolář, DrSc., prof. Ing. S. Kužel, CSc.

Součást řešení problémového okruhu 02-04: "Nepotravinářské využití biomasy ze zemědělské produkce", výzkumného záměru MSM 6007665806 (koordinátor prof. Ing. J. Frelich, CSc).


GENISTEIN
FEOFYTINY
CUKERNÉ ROZTOKY
GENISTIN
Na-Cu-chlorofylin
KAROTENY
PELETY

Scheme of biorefinery of clover



Comprehensive waste-free processing of oats

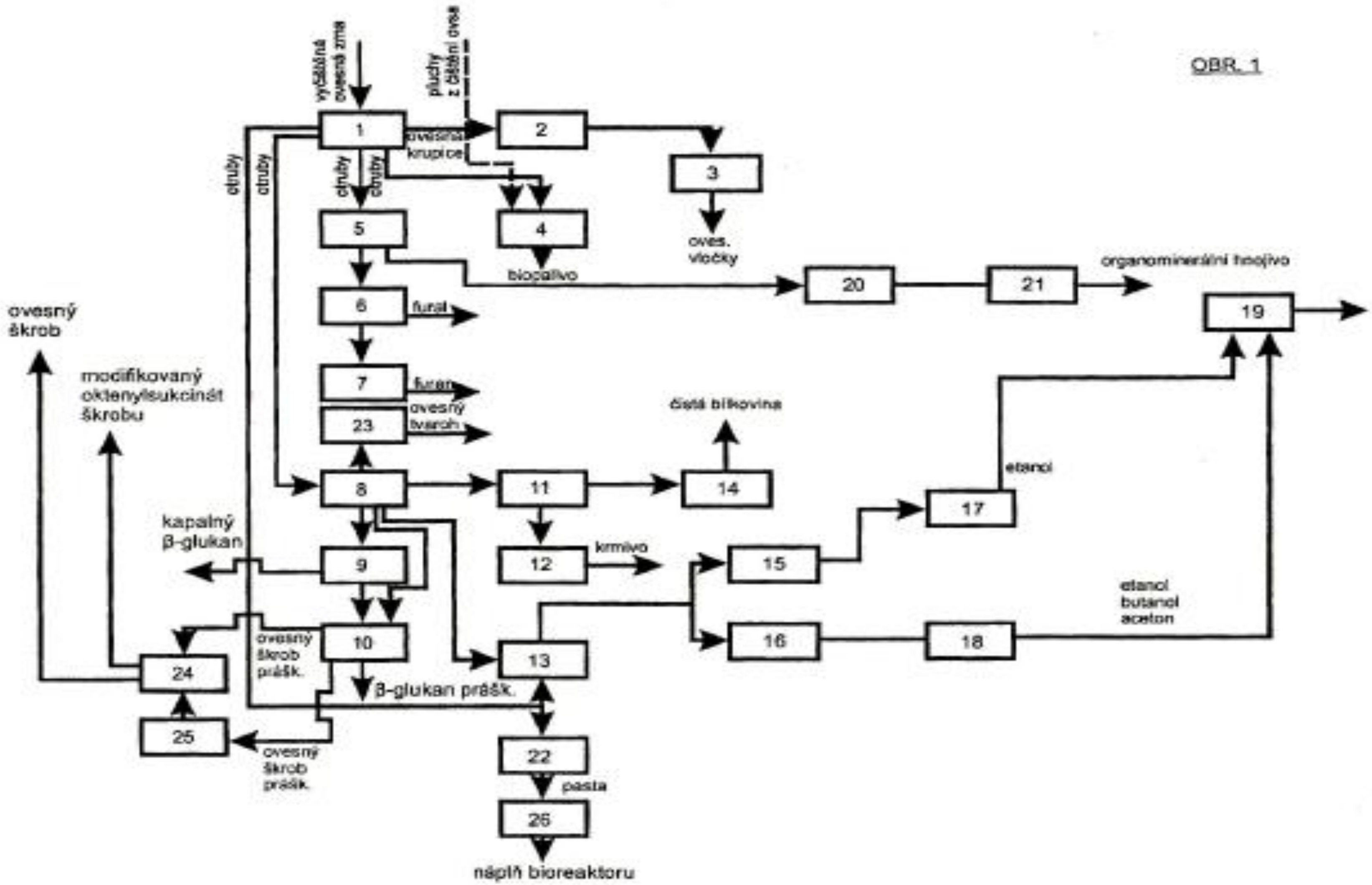
Oats is a crop that is in agricultural production LFA areas together with red clover paramount importance if the processing will be complex, independent on sales in the food and feed industries, and waste-free. Expected oat biorefineries products: β-glucans of oats are among the so-called anti-nutritional factors. In feed they cause lowering of nutrient utilization of ingested food.

For human consumption, this effect can be very effectively utilized in the production of so-called. "Slimming diets". Indeed, obesity threatens the life of a modern, but too comfortable civilized man's with the relationship to diseases that cause most deaths. The vascular system diseases and tumors develop.

Products from oat biorefineries

- Pellets biofuels
- Fural
- Lipase paste
- β-glucans (powder)
- Energetic bioethanol
- Butanol
- Crude oat starch
- Oat cheese
- Oat syrup (emulsifier)
- Oat drink with fruit
- Oat ice
- Organomineral fertilizers
- Furan
- Solution of β-glucans
- Pure oat protein (isolate),
- Acetone
- Octenylsuccinate of oat starch,
- Protein feed
- Oat mayonnaise
- Oat cream
- Oat pudding

Scheme of oat biorefinery



From the production of β-glucans can be isolated extremely fine oat starch as a substitute for mineral carriers (talc) in cosmetics. This product will be only perfectly washed with water and then carefully dried. As the final product will be offered for the cosmetic industry. From the production of β-glucans can be isolated further oat protein fraction β- glucans free, from the antinutritional feed point of view.
It possible to use this protein fraction in the production of protein feed. When preparing raw oat material are separeated the hulls and impurities that can be well processed via current production of oatmeal in Vestec into biofuel pellets. In case of little interest for biofuel is contemplated utilizing this fraction of the feedstock which contains up to 29% pentosan (arabans and xylans) together with a part of oat bran for the manufacture of furfural.

From decarbonylation fural to CaO at 300°C can be produced furan, whose hydrogenation with hydrogen on nickel can be obtained tetrahydrofuran. It is an important solvent and raw material for the technology of numerous organic compounds and plastics.

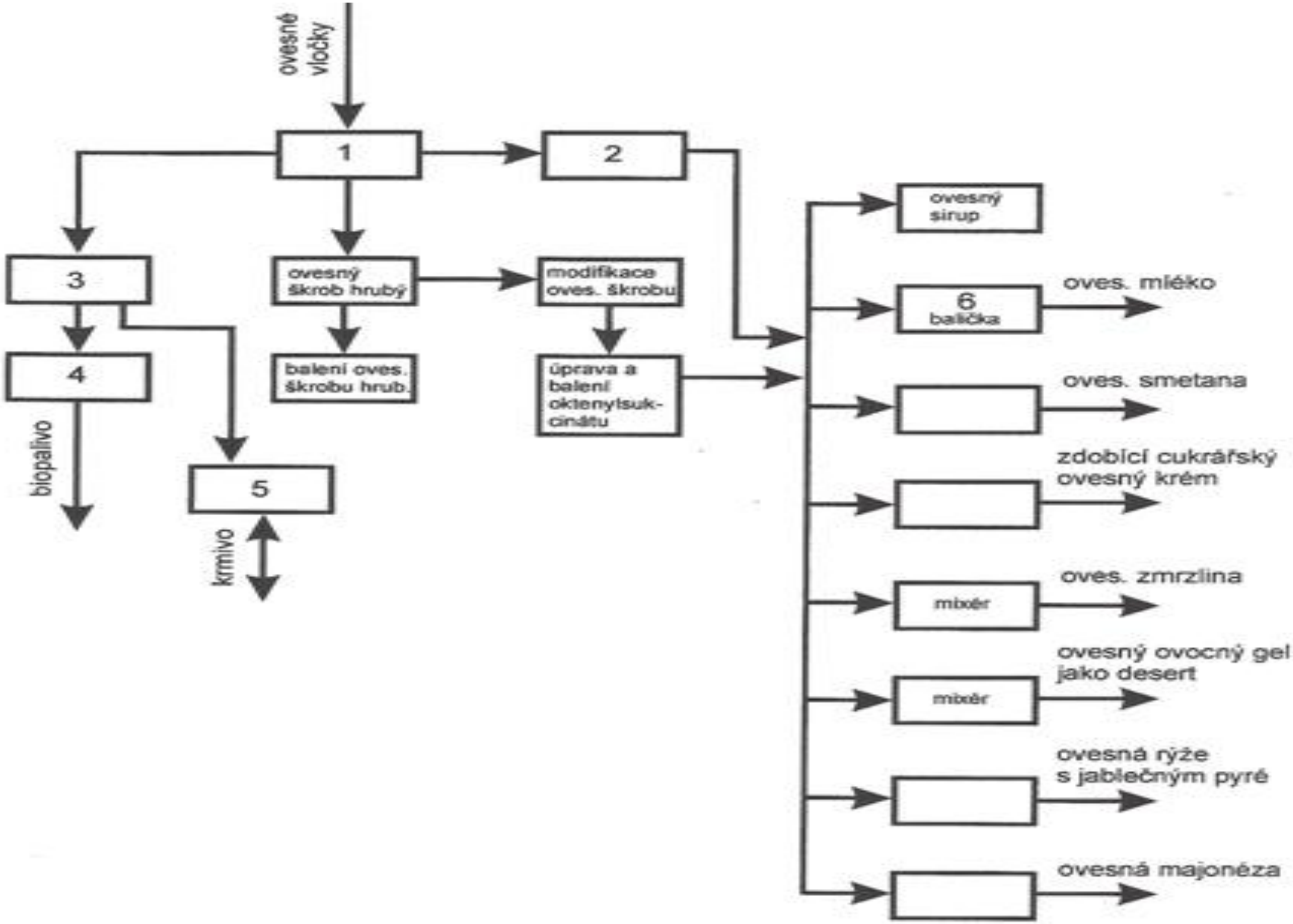
Part of the oat raw material in the form of bran is designed for use in the production of lipase cleaning paste fats clogged pipes. Oats generates a substantial amount of the enzyme lipase, which digests fats to glycerol and fatty acids. Oat bran contains 69% of the total lipase oats. The paste is a mixture of bran and the respective buffer in conjunction with modified starch.

Oat material after separation β-glucans, parts of starch and protein is unsuitable for the production of oatmeal because their nutritional quality is low. However, it contains plenty of carbohydrates, which can be well used.

It is designed mash preparation of this material with processing into fermentable sugars via long distiller malt. Mash are fermented with cold Nýdrle brewer's yeast made from lager production and from the fermented mash containing 8-10% of ethanol is distilled alcohol. This is a common distillery production. It is also possible to mash ferment with anaerobes *Granulobacter butyricum* at 38°C for 28-36 hours to distill from fermented mash 2-3% of a mixture which contains 60% butanol, 30% acetone and 10% ethanol. From the mixture can then be separated by distillation, acetone for the needs of the chemical and painter industry and and ethanol and butanol as an energy source e.g. for mixing with gasoline. Separate solid waste from all stages of the production is exported on compost where are homogenized with the waste from the production of fural with black humic substances.

It is mixed with a buffering material - ground limestone and clay suspensions of brick clay and water. Than is added the concentrate of trace elements in the solution, the source of N, K, P and S. The homogenized material is placed in the bioreactor, with temperature of 55°C which falls within 5 days on 35°C. Generator is heated with waste heat from the regenerator or recuperator of heat from the production of oat flakes. The product is mineral fertilizers. Oatmeal as an existing product remain. To increase sales of this traditional product is designed to use hydrocolloid properties of oat mucus, commonly called "oat gum" with plenty of β-glucans and emulsifying properties of oat protein of oat flakes, for the manufacture of new products: oat milk, oat cream,

Scheme of using oatmeal on functional foods

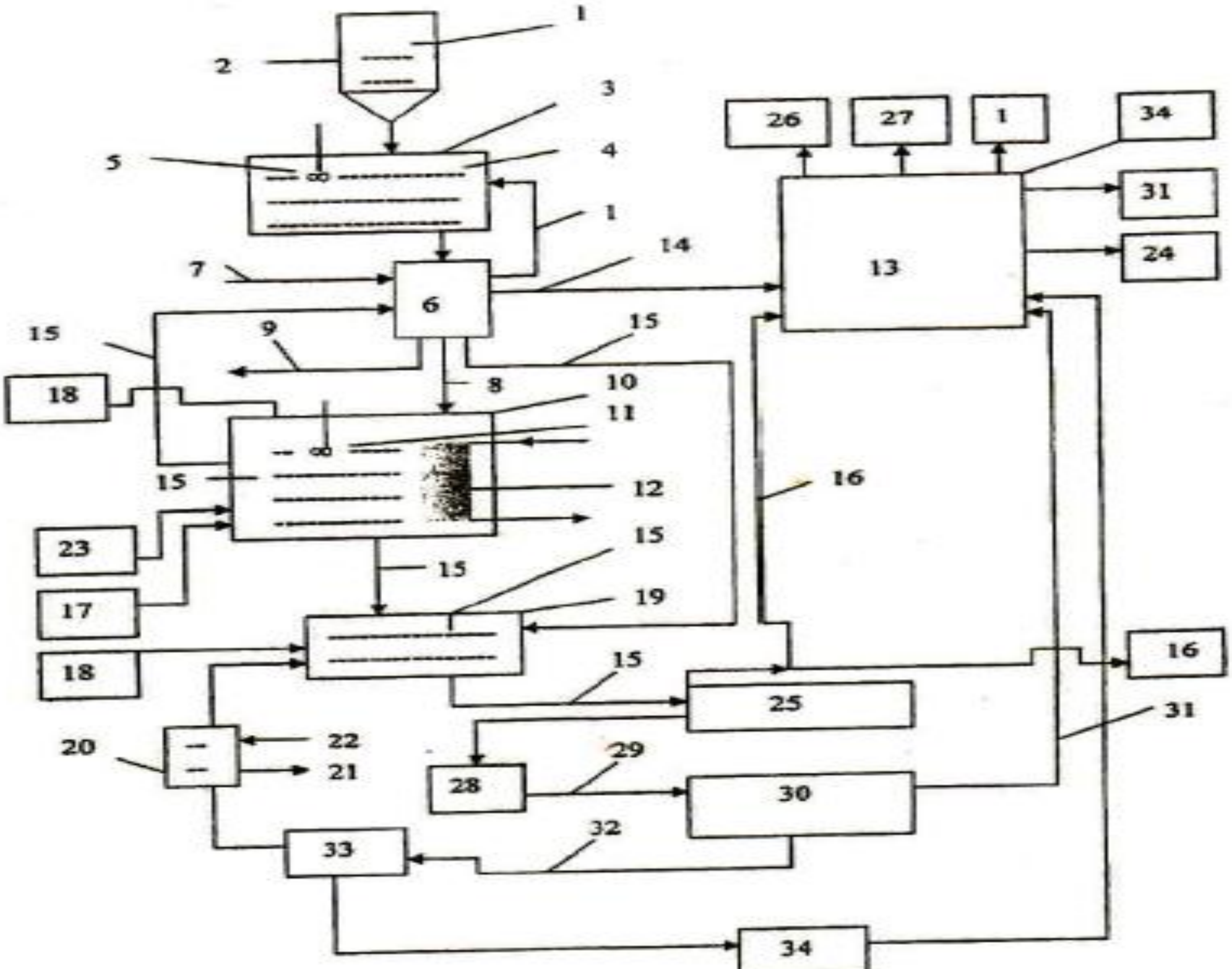


oat pudding, oat cream with fruit, oat cheese, oat mayonnaise and oat strawberry syrup against constipation. The principle of the manufacture is emulsification of fats extracted by oat proteins whose emulsifying capability can be enhanced by modifications of oat starch to octenylsuccinate, with which they are mixed. Isolated oat starch is modified octenylsukcinanhydrid in a weakly alkaline medium in an aqueous suspension.In current pressure for milk production price increase these products provide a cheap and nutritionally valuable substitutes for dairy products.

Comprehensive waste-free processing of barley (Hordeum vulgare) is processed in patent no. 304017 and utility models UV 19 912; UV 20030; UV 20058; UV 20855; UV 21609; UV 22445; UV 22457

The best feedstock for processing in bio-refineries are barley, known as food barley because they have a higher content of fiber and β-glucans.
There are less suitable varieties of barley that are classified in the group industrial barleys (to produce whiskey, starch, ethanol) and malting barley.
The worst raw material are feed barleys, with high protein and low content of β-glucans.
The product of 13.4% by dry weight of the original amount of ground barley contains 81.1% protein and 18.9% β-glucan.
The daily required dosage of this product is 15.9 grams on day for one adult.

Scheme of biorefinery for barley processing.



Use barley flour from lemma-free lines of food barley because in lemma-free varieties is higher amounts of hemicelluloses from the category of non-starch polysaccharides or barley flour of crossbred wax type of food barley, because it is a barley with wax (soft) type endosperm, which is the main source of β-glucan or barley flour from lemma varieties of food barley, because they have higher yields than lemma-free varieties and they are in the Czech Republic easily accessible.

List of patents and utility models (U) from barley, oats and clover biorefinery

CZ 305395 A food intermediate product for the preparation of protein dietary functional food and method of its production

CZ 304945 Food supplement with cereal and fungal β-glucans and arabinoxylans and method for its production

CZ 304017 A method of processing of lemma varieties of barley and apparatus for performing this method

CZ 303813 A method for processing oat, apparatus for implementing this method and use of oat bran to isolate valuable ingredients

CZ 302596 method of processing biomass of red clover

CZ 302295 A method for processing oat flakes, food products obtained by this process, apparatus for implementing this method

CZ 301951 pelletized or briquetted biofuel, composition for its manufacture, method for its production and use of native rye flour for its production.

CZ 22445 U Equipment for processing barley
CZ 20058 U Dietary food supplement containing β-glucans
CZ 20030 U Protein functional food for diet
CZ 20001 U Fruit cream designed as a protein functional food for diet
CZ 19959 U Food intermediate product for the preparation of protein dietary functional foods
CZ 19912 U Food ingredient in cooked and breaded functional foods
CZ 18793 U paste for cleaning of grease-clogged pipes and equipment for its production
CZ 18792 U Refill of bioreactor for biogas production and apparatus for its production

CZ 18791 U Pelleted biofuel containing oat parts and equipment for its manufacturing

CZ 18790 U Organo-mineral fertilizers from oats and equipment for its production

CZ 18789 U Oat cheese and apparatus for its production

CZ 18788 U Equipment for the production from oat

CZ 18765 U Products from oat flakes and equipment for their production

CZ 18803 U Nutritionally modified oat flakes and equipment for the production of nutritionally modified oat flakes and other oat products

CZ 17229 U Equipment for processing biomass of grasses, especially perennial forage crops, into sugar raw material for the production of bioethanol and / or feed

CZ 17228 U Pelleted or briquetted biofuel, its composition, and a binder for its manufacture