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(54) Title: PROCESS AND SYSTEM FOR PRODUCTION OF ORGANIC SOLVENTS

(57) Abstract: The present invention relates to a process for production of organic solvents, mainly butanol, using the anaerobic fermentation by butanol, acetone, and ethanol-producing bacteria, also the invention relates to a system for carrying out of the process and product obtained by the process. The claimed process comprises pretreating plant raw material, saccharifying the pretreated material with enzymes which degrade or convert the material into sugar solution, fermenting the sugar solution by butanol, acetone, ethanol producing bacteria in a fermentor, removing organic solvents and fermentation gases, recovering end product. Moreover the pretreatment comprises a coarse milling and then a fine milling, an enzyme complex is used for the saccharification, and the enzyme complex is matched to polysaccharide components of the raw material; the fermentation is carried out with predominant production of butanol by periodic pressure reduction in the fermentor and simultaneous removal of organic solvents and fermentation gases.



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## Process and system for production of organic solvents

### TECHNICAL FIELD OF THE INVENTION

The present invention relates to a process for production of organic solvents, particularly acetone, butanol, ethanol using the anaerobic fermentation by butanol, acetone, and ethanol-producing bacteria, also the invention relates to a system for carrying out of the process.

### BACKGROUND OF THE INVENTION

Butanol fermentation, also called acetone butanol ethanol (ABE) fermentation is one of the oldest fermentation processes. Butanol is the most valuable of the produced solvents.

Butanol is an important industrial chemical and is currently used as solvency enhancer in the formation of nitrocellulose lacquers, synthetic resins; as a feedstock chemical in the plastics industry and as a food grade extractant in the food and pharmaceutical industry. As it turned out butanol has excellent fuel characteristics. Compared to the currently popular fuel additive ethanol, butanol is more miscible with gasoline and diesel fuel, has a lower vapor pressure, and is less miscible with water, qualities that make butanol a superior fuel extender than ethanol. Use of butanol as fuel will contribute to clean air by reducing smog-creation compounds, harmful emissions (carbon monoxide).

The present invention is focused mainly on butanol production in ABE fermentation.

Currently butanol is produced chemically by either the oxo process starting from propylene (with H<sub>2</sub> and CO over rhodium catalyst or nickel-cobalt catalyst) or the aldol process starting from acetaldehyde.

The recent trend of using butanol as biofuel has revived research efforts aimed at obtaining liquid fuels by anaerobic fermentation.

In order to make butanol fermentation an economically viable option, various laboratories around the world identified the following factors to impact the economics of butanol fermentation: high cost of substrate; low product concentration (<20 g/l); low reactor productivities (<0.5 g/l/hour); low ABE yields (0.29-0.33) and an escalated cost for butanol recovery by distillation, which is the classical approach for solvent recovery (Food biotechnology, Second Edition, edited by Kalidas Shetty, et al., CRC Press, 2006, p.527).

Therefore the main directions of ABE process development are metabolic engineering of *Clostridium*, improvements in the process productivity and research of new techniques of solvent recovery.

Traditionally ABE fermentation was performed (and still is in some cases) by a wild microorganism of *Clostridium acetobutylicum* isolated from the natural environment (soil, lake sediments, etc.). Then the bacteria was subsequently modified by conventional strain

improvement strategies, using physical and chemical mutagenesis (US5192673, US4757010, EP0973929). Several processes developed in the last 20 years have involved recombinant microorganisms and genetic engineering technology has increasingly been used to improve established strains. Recombinant DNA technology has allowed specific gene sequences to be transferred from one organism to another and allows additional methods to be introduced into strain improvement schemes. This can be used to increase the product yield by removing metabolic bottle-necks in pathways and by modifying specific metabolic steps (US 2007259410, WO 2007050671, etc.).

There are many efforts to increase the productivity of the ABE process through providing the optimum conditions for fermentation and development of effective methods of solvent recovery from the fermentation broth.

SU 1604852 discloses a method for anaerobic fermentation of starch based feedstock by *Clostridium acetobutylicum* wherein, the fermentation broth containing the amylolytic enzymes was taken off in 24 hours of fermentation process and the starch based feedstock was liquefied with this broth at 70-75 °C for 15-20 minutes. Total solvent yield is 19g/l.

US 5753474 describes a process for the manufacture of butanol and like volatile organic compounds by fermenting carbohydrates, mainly polysaccharide, with microorganisms which convert carbohydrates into mainly butyric acid and other acids. The acids are subsequently transferred to solventogenesis production stage using a different strain of bacteria which continuously produces butanol via multistage fermentation process that is stable, high yielding (weight product per unit weight carbohydrate) and productive (faster throughput). By employing one microbe (the first) in the major pathway to produce the acid of choice specifically and faster and provide for another microbe (the second) with unique property to convert the acid to a solvent, carbohydrates are not wasted on ancillary product. The unique advantage of the second microbe is that it has capability of converting acids into solvents.

RU 2044773 discloses a method for fermentation of carbohydrate-containing medium with bacteria which produce butanol, acetone, ethanol and/or isopropanol. The method is carried out in two steps. The first step involves growth of bacteria, at the second step bacteria are immobilized on porous carrier. Products are recovered by extraction with higher alcohols or higher fatty acids or by diffuse evaporation through membrane.

US 2005089979 discloses a continuous process for production of solvents, particularly acetone-butanol-ethanol using fermentation of solventogenic microorganisms and gas stripping. Generally gas stripping involves passing a flow of stripping gas through a liquid to form a

stripping gas enriched in one or more of the volatile components from the liquid. The volatile components are then removed using means known in the art, for example condensation.

The cited patent documents do not make efforts to solve all above mentioned problems of ABE fermentation, and generally are focused on overcoming one of drawbacks, e.g., butanol toxicity or selective butanol removal from the fermentation broth.

Summarizing the aforesaid, a need exists for an improved process for production of organic solvents by anaerobic fermentation that is able to overcome the combination of problems, i.e. there is a need in an improved process wherein

- the raw material is low-cost and readily available lignocellulosic material (which in many cases is obtained from wastes);
- the pretreatment of the raw material does not require use of chemicals;
- high productivity of the enzymatic hydrolysis of lignocellulosic material to soluble sugars;
- high productivity of ABE fermentation process through providing the optimum conditions for fermentation;
- energy saving (in comparison with the distillation) recovery technology of ABE.

#### BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a process for production of organic solvents, mainly butanol, comprising:

- pretreating plant raw material,
  - saccharifying the pretreated material with enzymes which degrade or convert the material into solution of sugars,
  - fermenting the solution by butanol, acetone, ethanol producing bacteria in a fermentor at a nutrient medium,
  - removing organic solvents and fermentation gases,
  - feeding of carbohydrate and mineral salts solution for the fermentation,
  - recovering the target product, wherein
- the pretreatment comprises a coarse milling and then a fine milling,
- an enzyme complex is used for the saccharification, and the enzyme complex is matched to polysaccharide components of the raw material;
- the fermentation is carried out with predominant production of butanol by periodic pressure reduction in the fermentor and simultaneous removal of organic solvents and fermentation gases.

The present invention also relates to a system for carrying out of the process comprising a device for a coarse milling of plant material, an extractor, a device for fine milling, an agitation tank for mixing of the fine raw material with water, a tank for the saccharification of the obtained suspension, a fermentor, a vacuum-pump, a post-fermentor, a concentrator and a device for separating of the target products.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic representation of a system for carrying out the claimed process of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

It is known that the cost of substrate/raw material is one of the most influential factors impacting the economics of fermentation-derived liquid fuels. In order to reduce production cost, it has been attempted to produce butanol from renewable agricultural resources including wheat, corn and sugar beet, but the production of biofuels from edible substrates, such as starch or sucrose, would not be appropriate because of food shortage. Prominent among the economic factors is the current surplus of agricultural waste, waste wood that can be utilized as inexpensive fermentation substrates. Billions of tonnes of these materials currently go to waste each year, which could be converted into chemical energy or useful fermentation products.

In accordance with the present invention plant material (biomass) includes various agricultural residues (straws, hulls, stems, stalks); deciduous and coniferous woods and herbaceous energy crops (swathgrass, Bermudagrass). The compositions of these materials vary. The major component is cellulose (35-50%), followed by hemicellulose (20-35%), and lignin (10-25%). Proteins, oils, and ash make up the remaining fraction of plant material. In a preferred aspect, the plant material is wood chips. The term "wood chips" refers to shavings, sawdust, flakes and other such solid wood in the form of particles. It is possible to use the coniferous wood chips as the plant material. One of advantages of the present invention is processing of agricultural residues, and forestry residues. Such cheap substrate results in very low costs of produced solvents.

An important limitation of plant biomass utilization comes from the pretreatment and the hydrolysis. The goal of pretreatment is to prepare biomass to facilitate bioconversion. For butanol production any loss of carbohydrates in the pretreatment process must be minimized (provided the associated cost is economically justified) to maximize production. Pretreatment refers to a process that converts plant biomass from its native form, in which it is recalcitrant to enzyme systems, into a form for which cellulose hydrolysis is effective. Compared to untreated biomass, effectively pretreated plant materials are characterized by an increased surface area

(porosity) accessible to enzymes, and solubilization of lignin. Increased porosity results mainly from a combination of disruption of cellulose crystallinity, hemicellulose disruption and lignin redistribution and/or solubilization.

There are a lot of methods of pretreatment that include physical, chemical, and biological techniques. For example, physical pretreatment techniques can include various types of milling, crushing, irradiation, steaming/steam explosion. Chemical pretreatment techniques can include pretreatment with dilute acid, alkaline, organic solvent, ammonia, sulfur dioxide, carbon dioxide, ionic liquid. Biological pretreatment can involve applying lignin-solubilizing microorganisms. Biological pretreatments appear to have the advantages of requiring no chemicals (if nutrient supplementation is not required) and low energy input. However, biological pretreatments are relatively slow processes, and most lignin-solubilizing microorganisms also solubilize or consume hemicellulose and cellulose (David M. Mousdale, *Biofuels: biotechnology, chemistry and sustainable development*, CRC Press, 2008, pp. 56-63).

It should to be noted that because of the increased awareness of, and emphasis on, human health and environmental protection, effective pretreatment that use few or no (hazardous) chemicals are likely to gain research, development, and deployment momentum. This trend is believed to be crucial in guiding future research and development efforts (Handbook on Bioethanol: production and utilization, Edited by Charles E. Wyman, Applied Energy Technology series, p.194). Therefore the inventor efforts have been focused on development of effective pretreatment technique using no chemicals.

It is known that milling can greatly increase the susceptibility to enzymic depolymerization of cellulose but we have discovered surprisingly that in result of two-stage milling process of the plant material cellulose crystallinity index is decreased from 65-70% to 10-20%. Also the time of saccharification of such milled material at pH 5-6 and temperature of 50 °C is only 12-13 hours, and in column process 3-7 hours. The sugars yield is 50% from the weight of wood chips.

The coarse milling of plant material is carried out in mills, preferably in ball-mills to particles ranging in size from 1 mm to 2 mm with simultaneous drying by air blowing. The process gives option to dry the raw material and prepare it for the fine milling.

The fine milling is carried out to particles ranging in size from 1  $\mu$ m to 5  $\mu$ m. Preferably, the fine milling is carried out in vibro energy, colloid, jet or impeller mill that provides the shearing force. It should to be noted that the fine wood powder has specific properties; particularly it is watered rapidly and goes down immediately compared to conventional wood chips that float awash. It is clear that such properties allow to enzymes to contact efficiently

with cellulose material. Also the saccharification process of such activated material takes less water, and it is very important on an industrial scale. It gives option to improve the mixing with water, using ratio 1:6 (in case of untreated raw material 1:10). The up-to-date mills produce the ultrafine powder in few seconds without significant energy consumption.

In one preferred embodiment, the plant material is coniferous wood chips. In this case naturally-occurring wood extractives (pitch and volatile organic compounds) are found in both resin canals within the structure of the wood, as well as within the parenchyma cells of the wood. In the embodiment the removal of pitch is preferable before the fine milling. More particularly, according one embodiment of invention, wood chips are subjected to a solvent extraction process, preferably with acetone or ethanol (plant material: solvent ratio is 1:7 – 1:10).

It is known that the processes for hydrolysing plant material include biological and non-biological methods of depolymerization. The biological methods involve the use of enzymes. The oldest and best known non-biological method of producing sugars from plant material is the use of acid hydrolysis. Saccharification of the plant biomass can readily be achieved by treatment with  $H_2SO_4$ . However, this acid-catalyzed reaction leads to the degradation of glucose to hydroxyl methyl furfural (HMF) and xylose to furfural at the temperature of hydrolysis, resulting in inhibition of the ABE fermentation by these degradation products. Also there is a need in acid-resistant equipment. Therefore the enzymatic hydrolysis was selected as the subsequent stage of the process.

The enzymatic hydrolysis of plant material to soluble sugars is catalyzed by several enzymes. In plant cell walls, cellulose fibrils occur in close association with xylans (monocotyls) or xyloglucans (dicotyls). The enzymatic conversion of cellulose/xylans is a complex process involving the concerted action of exo/endocellulases and cellobiases yielding glucose and xylanases yielding xylooligomers and xylose. Filamentous fungi are a source of cellulases and hemicellulases, as well as other enzymes useful in the enzymatic hydrolysis of major polysaccharides. In particular, strains of *Trichoderma* sp. and *Penicillium* sp. have previously used to hydrolyze crystalline cellulose.

Taking into account the different composition of plant material (e.g. different components of deciduous and coniferous wood chips), there is a need to choose an enzyme complex that is matched to polysaccharide components of the raw material. It is one of the important features of the present invention. Preferably strain of fungi *Penicillium verruculosum* can be used in the process of the saccharification, for the different sorts of plant material different strains of *Penicillium verruculosum* are used. We have discovered that such approach

allows to digest the polysaccharides completely. Preferably the saccharification is carried out at  $\text{pH} = 4.5 - 6.0$  and temperature =  $50 - 55^\circ\text{C}$ .

Preferably lignin is removed before the saccharification. Then the sugar solution is concentrated to 25-40% to avoid the contamination.

The obtained solution is used as substrate in the fermentation with butanol, acetone, ethanol producing bacteria. Butanol, acetone, ethanol producing bacteria includes species of *Clostridium*, including *Clostridium beijerinckii* and *Clostridium acetobutylicum*, as well as another bacteria known in the art. Other fermentation conditions such as temperature, pH are easily chosen by ordinary skill in the art without undue experimentation.

As noted above the most important solvent is butanol. We have discovered that high butanol productivity can be achieved if the process is carried out with periodic pressure reduction. At the period of pressure reduction the solvent produced for the fermentation are removed from a fermentor. The pressure reduction is set up when butanol concentration in the fermentor is approaching to toxic for producing bacteria, it means when butanol concentration in the fermentor is 8-9 g/l. The pressure reduction is kept on until butanol concentration in the fermentor is 5-2 g/l. The pressure in the fermentor during the removal is - 0.90 -0.94 kg/cm<sup>2</sup>. The improved process results in high carbohydrate utilization and a high butanol yield as compared to current processes.

Without wishing to be bound by theory of operation, the reason of this effect is the action of periodic pressure into biological systems, probably it causes the irregularity (disturbance) of mass transfer processes through membranes, change in fermentative processes in cell, initiation and development of repair reactions accompanied by novel synthesis (Akopyan V.B., Korzhevenko G.N., Shangin-Berezovskiy G.N., The buried reserve of growth and development of live system, Vestnik selskohozyastvennoy nauki, 1988, No 4 (380), p 69-105).

It should to be noted that only such combination of techniques of the present process leads to high productivity of ABE fermentation and promotes the complex resolution of typical shortcomings of the process.

The process may be more easily understood with reference to FIG.1, where the schematic view of the system for carrying out of the claimed process is shown. The plant raw material, preferably wood chips are processed in a device for a coarse milling 1, which can be a ball-mill. Then optionally 1-2 mm particles of wood chips from the device 1 are charged to an extractor 2 to remove pitch. The extracted particles are subjected to fine milling in a device for fine milling 3, which can be a vibro energy, colloid or jet mill. The obtained powder is mixed with water in an agitation tank 4. The process of saccharification of the obtained suspension is

carried out in a tank 5, the formed lignin is removed and the solution of sugars is transferred into a fermentor 6. The standard mixture of minerals (mineral salts, vitamins) was added into the fermentor 6. Then the medium was inoculated with cells of *Clostridium acetobutylicum* (e.g. VKM B-2531D) with density of 1-2 milliard/ml. 30 min after inoculation the intensive fermentation gas formation began, in 5-6 hours the organic acids production took place, in 10-12 hours the intensive production of organic solvents, the rate of solvent production was maximal to 28-36 hours. At this moment the cell concentration was also peak -  $3 \cdot 10^9$  cells/ml of suspension. At the same time the pressure in the fermentor 6 was reduced by a vacuum-pump 10 to remove the solvents to concentration 5-2 g/l from the fermentation broth and simultaneous feeding of the carbohydrate and mineral solution was carried out, maintaining the carbohydrate concentration in the fermentor about 8-12 g/l at a flow rate of about 0.025 – 0.035 l/hour. The process was allowed to proceed in the continuous mode for 500 hours, although there is almost no limitation of growth and solvent production. Then the product is transferred into a post-fermentor 7, a concentrator 8. The solvents are separated by rectification in a rectifying column 9. Pumps 11 are used for liquid communication in the system.

The invention may be further understood by the following non-limiting examples.

#### **Example 1**

The known process of biosynthesis

A four-liter fermentor containing 2.4 l water with 120 g wholemeal flour was inoculated with 300 ml of inoculum of *Clostridium acetobutylicum* VKPM B-4786 with density of 1-2 milliard/ml. The fermentation was allowed to proceed in the batch mode for 72 h. The temperature was maintained at 37 °C. In 72 hours the solvent vapors were taken off. The ABE vapors were cooled in a condenser and in result 250 ml of solution, containing 5% butanol, 1.5% acetone and 0.5% ethanol was obtained. Productivity was 3 g/l/day.

#### **Example 2**

A four-liter fermentor containing 2.4 l water with 120 g wholemeal flour was inoculated with 300 ml of inoculum of *Clostridium acetobutylicum* VKPM B-4786 with density of 1-2 milliard/ml. The fermentation was allowed to proceed at 37 °C.

When butanol concentration approached 6 g/l, the pressure in the fermentor was reduced to - 0.94 kg/cm<sup>2</sup> for 0.5 hour. It results to changing of ABE ratio from the classical one 30:60:10 to 15:80:5. In 8 hours the procedure of pressure reduction was repeated and ABE ratio was 9:90:1. The ABE vapors were cooled in a condenser and in result 250 ml of solution, containing 6.5% butanol, 2% acetone and 0.75% ethanol was obtained (ABE ratio 15:80:5).

After the ABE vapors and fermentation gases removal the nutrient medium containing 50 g/l of glucose was added into the fermentor. Total time of process is 48-52 hours. Productivity was 8.5 g/l/day.

### Example 3

Wood chips are milled in the ball mill (AS-2M, Novosibirsk) to size of 1-2 mm and are dried on hot air to humidity no more than 10%. The obtained wood chips are milled in the activation mill (OGO-3, Novosibirsk) to the size of 1-5 $\mu$ m. The obtained mixture is suspended in water and the complex of hydrolytic enzyme (cellulase, xylanase, cellobiase) is added to the suspension in the ratio 2.5 g per 1 kg of the pulverized wood chips. The saccharification was allowed to proceed at 37 °C, pH 5 and in 12 hours the process is completed. 40% of carbohydrates are in the suspension and lignin is removed from the sugar solution by centrifugation.

A four-liter fermentor containing 2.5 l of 4% obtained carbohydrate solution was inoculated with 300 ml of inoculum of *Clostridium acetobutylicum* VKM B-2531D with density of 1-2 milliard/ml. The fermentation was allowed to proceed at 37 °C.

When butanol concentration approached 10 g/l, the pressure in the fermentor was reduced to - 0.90 kg/cm<sup>2</sup> for 1 hour. It results to changing of ABE ratio from the classical one 30:60:10 to 21:70:9. In 6 hours the procedure of pressure reduction was repeated and ABE ratio was 9:90:1. The ABE vapors were cooled in a condenser and in result 250 ml of solution, containing 6.5% butanol, 2% acetone and 0.75% ethanol was obtained (ABE ratio 9:90:1).

The procedure of pressure reduction was repeated every time when the butanol concentration approached 10 g/l. After the ABE vapors and fermentation gases removal the nutrient medium containing 50 g/l of glucose was added into the fermentor. One time in three days 28 g of yeast autolyzate was added into the fermentor. Productivity was 10 g/l/day.

### Example 4

Wood chips are milled in the ball mill (AS-2M, Novosibirsk) to size of 1-2 mm and are dried on hot air to humidity no more than 10%. The obtained wood chips are extracted with ethanol (ratio 1:10). The wood chips are separated from extractant by centrifugation and the rest of solvent are removed by dry vapour.

The obtained wood chips are milled in the activation mill (OGO-3, Novosibirsk) to the size of 1-5 $\mu$ m. The obtained mixture is suspended in water and the complex of hydrolytic enzyme (cellulase, xylanase, cellobiase) is added to the suspension in the ratio 2.5 g per 1 kg of the pulverized wood chips. The saccharification was allowed to proceed at 37 °C, pH 5 and in

12 hours the process is completed. 40% of carbohydrates are in the suspension and lignin is removed from the sugar solution by centrifugation.

A four-liter fermentor containing 2.5 l of 4% obtained carbohydrate solution was inoculated with 300 ml of inoculum of *Clostridium beijerinckii* KM MSU (Moscow State University) No 101 with density of 1-2 milliard/ml. The fermentation was allowed to proceed at 37 °C.

When butanol concentration approached 12 g/l, the pressure in the fermentor was reduced to - 0.90 kg/cm<sup>2</sup> for 1 hour. It results to changing of ABE ratio from the classical one 30:60:10 to 21:70:9. In 6 hours the procedure of pressure reduction was repeated and ABE ratio was 9:90:1. The ABE vapors were cooled in a condenser and in result 250 ml of solution, containing 6.5% butanol, 2% acetone and 0.75% ethanol was obtained (ABE ratio 9:90:1).

The procedure of pressure reduction was repeated every time when the butanol concentration approached 12 g/l. After the ABE vapors and fermentation gases removal the nutrient medium containing 50 g/l of glucose was added into the fermentor. One time in three days 28 g of yeast autolyzate was added into the fermentor. Productivity was 10 g/l/day.

Therefore the claimed process, system and product have got the following advantages:

- the raw material is low-cost and readily available lignocellulosic material (which in many cases is obtained from wastes);
- the pretreatment of the raw material does not require use of chemicals;
- high productivity of the enzymatic hydrolysis of lignocellulosic material to soluble sugars;
- high productivity of ABE fermentation process through providing the optimum conditions for fermentation;
- energy saving (in comparison with the distillation) recovery technology of ABE.

## CLAIMS

1. A process for production of organic solvents, mainly butanol, comprising:

- pretreating plant raw material,
- saccharifying the pretreated material with enzymes which degrade or convert the material into solution of sugars,
- fermenting the solution by butanol, acetone, ethanol producing bacteria in a fermentor at a nutrient medium,
- removing organic solvents and fermentation gases,
- feeding of carbohydrate and mineral salts solution for the fermentation,
- recovering the target product, wherein

the pretreatment comprises a coarse milling and then a fine milling,

an enzyme complex is used for the saccharification, and the enzyme complex is matched to polysaccharide components of the raw material;

the fermentation is carried out with predominant production of butanol by periodic pressure reduction in the fermentor and simultaneous removal of organic solvents and fermentation gases.

2. The process of claim 1 wherein the coarse milling is carried out to particles ranging in size from 1 mm to 2 mm with simultaneous drying by air blowing.

3. The process of claim 1 wherein the fine milling is carried out to particles ranging in size from 1  $\mu\text{m}$  to 5  $\mu\text{m}$ .

4. The process of claim 1 wherein the fine milling is carried out in vibro energy, colloid or jet mill.

5. The process of claim 1 wherein the plant raw material are wood chips.

6. The process of claim 5 wherein the wood chips are coniferous wood chips.

7. The process of claim 1, further comprising removal of pitch before fine milling.

8. The process of claim 7 wherein the removal of pitch is carried out by extraction with organic solvents, preferably acetone or ethanol in ratio 1:7 - 1:10.

9. The process of claim 1 wherein the culture liquid obtained by growth of *Penicillium verruculos* is used as the enzyme complex, and the saccharification is carried out at pH = 4.5 – 6.0 and temperature = 50 – 55 °C.

10. The process of claim 1 wherein lignin is removed before the saccharification.

11. The process of claim 1 wherein the sugar solution is concentrated to 25-40% before the fermentation.

12. The process of claim 1 wherein the pressure reduction is set up when butanol concentration in the fermentor is approaching to toxic for producing bacteria.

13. The process of claim 12 wherein the pressure reduction is set up when butanol concentration in the fermentation broth is 8-9 g/l.

14. The process of claim 1 wherein the pressure reduction is kept on until butanol concentration in the fermentation broth is 5-2 g/l.

15. The process of claim 1 wherein the pressure in the fermentor during removal is -0.90 -0.94 kg/cm<sup>2</sup>.

16. The process of claim 1 wherein said butanol, acetone, ethanol producing bacteria is *Clostridium acetobutylicum*.

17. The process of claim 1 wherein solvent separation is carried out by the rectification.

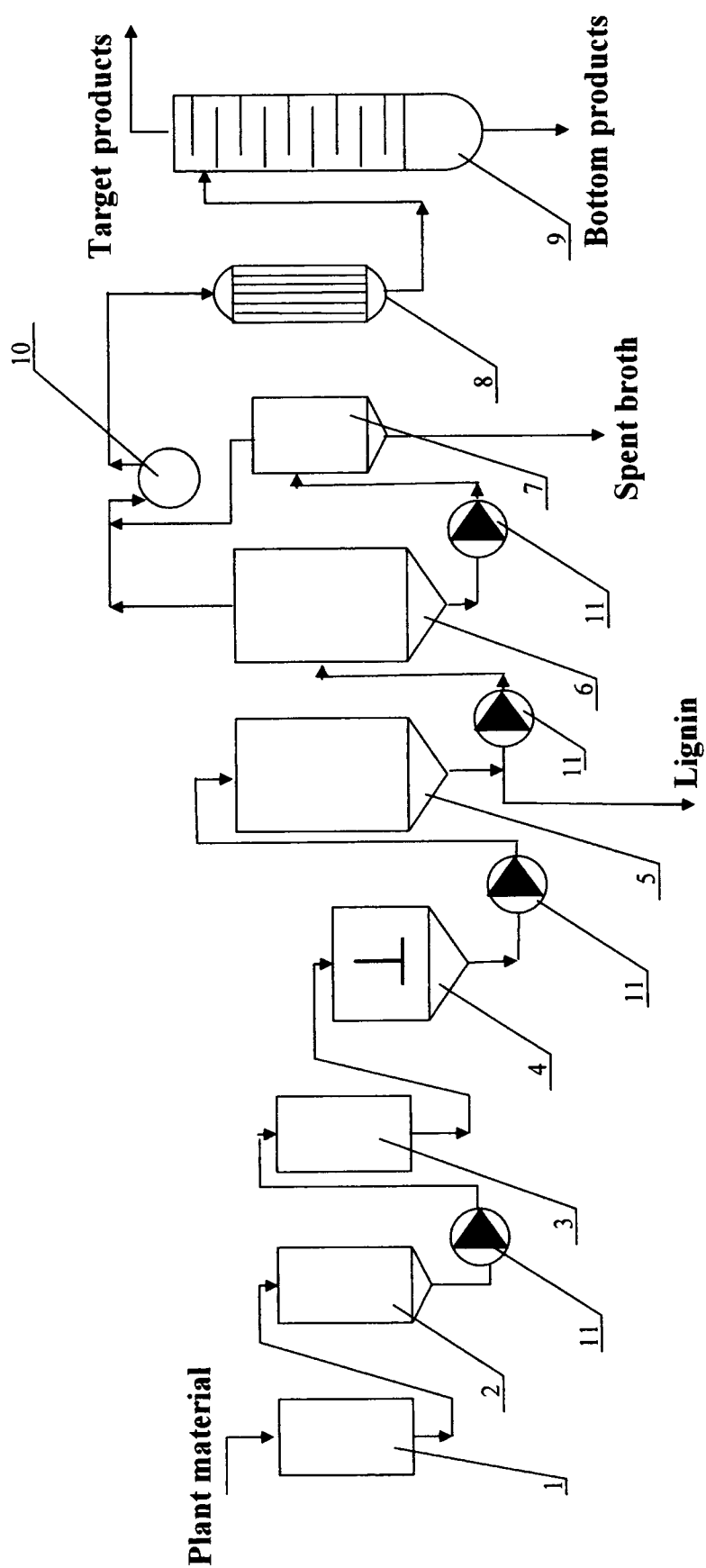
18. A system for carrying out of the process comprising a device for a coarse milling of plant material, an extractor, a device for fine milling, an agitation tank for mixing of the fine raw material with water, a tank for the saccharification of the obtained suspension, a fermentor, a vacuum-pump, a post-fermentor, a concentrator and a device for separating of the target products.

19. The system of claim 18 wherein the device for a coarse milling of plant material is a ball-mill provided with hot air blowing.

20. The system of claim 18 wherein the device for fine milling is a vibro energy, colloid or jet mill.

21. The system of claim 18 wherein the device for solvent separating is a rectifying column.

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**FIG.1**