

METHOD FOR PRODUCING HYDROCARBONS AND OXYGEN-CONTAINING COMPOUNDS, FROM BIOMASS

Technical field of the invention

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The present invention generally relates to biochemical and chemical industry, and more particularly to a method which can be used in fermenting carbohydrate substrates of plant origin for producing C₁-C₅ alcohols, and for synthesis of higher alcohols, other oxygen-containing compounds and hydrocarbons as well as for the production of motor
10 fuel components from biomass. Since C₆ and higher alcohols, ethers, acetals, and higher hydrocarbons are not obtainable by a direct biochemical route, it is proposed to synthesize these using known chemical reactions, wherein by-products of fermentation are as raw materials for said synthesis.

15 Background art

Obtaining alcohols and other oxygen-containing compounds by fermentation of carbohydrates is known since long ago [Brief Chemical Encyclopaedia, Moscow, 1967] and used industrially mainly for producing ethanol. However, even the most advanced process for biochemical production of ethanol allows for conversion of only about half of the
20 source carbohydrate substrate into the final commercial alcohol. The remaining part of carbohydrates is used for maintaining the vital functions of microorganisms and is converted into carbon dioxide. When it comes to other alcohols or other oxygen-containing compounds, such as ketones or acids [H.G. Schlegel. Allgemeine Mikrobiologie, 1985], the known biochemical processes allow conversion of raw materials into
25 the final products to an even lesser extent. Considerable part of the carbohydrate substrate in these processes is converted into by-products. The obtaining of hydrocarbons by means of biochemical methods is also well known since long ago [H.G. Schlegel. Allgemeine Mikrobiologie, 1985]. However, biogas obtained in fermentation of the waste of
30 livestock farming or in decomposition of biomass by bacteria contains mainly methane. Production of hydrocarbons and oxygen-containing compounds from synthesis gas, which in turn originates from biomass, also seems problematic. At present there is no industrial process for producing hydrocarbons and oxygen-containing compounds using synthesis gas obtained from biomass. Synthesis gas obtained from coal, petroleum

and natural gas is used industrially for producing oxygen-containing compounds [Reaction of hydroformylation, Kirk-Othmer Encyclopaedia, 3rd edition, v. 19, N.Y., 1982]. These processes are widely used by the industry for producing aldehydes, alcohols and many other oxygen-containing compounds originating from said materials. Methods for
5 producing hydrocarbons from synthesis gas are also well known and used industrially [Fisher-Tropsch reaction, Kirk-Othmer Encyclopaedia, 3rd edition, v. 19, N.Y., 1982]. However nothing is known about using synthesis gas obtained from biological raw materials in these processes.

- 10 There are various methods for intensifying the production of ethyl alcohol, such as by introducing new types of microorganisms, characterized by a higher speed of fermentation and wider range of utilization of the carbohydrates substrates, by using continuous processes of fermentation or processes of cell immobilizing, or by effective processing of new and traditional types of raw material, providing widening of the range of the
15 raw materials and deeper assimilation of the raw-material components. The productivity of the fermentation process in these methods can reach up to 10-15 litres of ethanol per cubic meter of the fermentor volume per hour, and specific speed of fermentation can reach up to 2.5-3.0 litres of ethanol per 1 gram of the yeast biomass per hour, with a yield of ethanol from the fermented carbohydrates in terms of weight of up to 49-50%
20 (the theoretic value is 51%).

The prior art discloses a method for preparation of the grain starch-containing raw material for alcohol fermentation (RU 2145354, C12P7/06, 1998). The method includes cleaning of the grain from admixtures, mixing with water, thermal treatment, adding of
25 enzymes, acid, and saccharification. After cleaning the grain is divided into the floury kernel and husk. Further processing of the raw material is carried out in two streams: the floury kernel is mixed with water to reach 19-21% mass part of humidity and treated thermally by extrusion. Then, after mixing with water, amylolytic enzymes and acid are added in an amount providing optimal pH value for the particular enzyme
30 used. This is followed by saccharification, after which the husk is mixed with water to 21-23% of the mass water content and at least 2% by mass of alkali is added. The material is then treated thermally with addition of the acid in an amount providing the optimum pH value for the specific enzyme used. Then the cellulolytic enzymes are added

and saccharification is carried out. Thereafter, both streams are brought together and directed to the fermentation.

- There is a known method for producing ethyl alcohol from grain raw material (RU 2127760, C12P7/06, 1997). The method specifies the following steps: the grain is cleaned of husk, crushed, mixed with the liquid fraction, treated thermally, then the amylolytic enzymes carrying out the enzymatic hydrolysis of starch are added, the mass is sterilized, cooled down, enzymatic complex is added, followed by saccharification and cooling down to the fermentation temperature. The obtained wort-mash is distilled to obtain ethyl alcohol and distillery dreg. The total amount of the distillery dreg obtained is divided into two streams, one of which is further separated into two streams, one of which is re-directed to the stage of thermal processing of the grain separated from husk, where it is used as a liquid phase in the mixture with water; the other stream, after 15-16 hours after the start of fermentation, is directed to each of the fermentors fermenting the mass at the fermentation stage in separate streams in the amount of 15-20% of the volume of the fermenting medium. The remaining stream of the distillery dreg is taken out of the process in the mixture with the separated husk for using as a fodder product.
- Disadvantages of the above-described methods are their low specific speed of fermentation (1.5-2.0 l/kg*h) and low C₃-C₅ alcohols yield. C₃-C₅ alcohols (fusel oil) are by-product of ethanol production from the plant raw material. The yield of C₃-C₅ alcohols in the production of ethanol by known methods is 0.2-0.6% of ethanol. In the production of a food-grade ethanol C₃-C₅ alcohols are an unwanted admixture and should be thoroughly removed by rectification and purification. All technologic means in the process of a food-grade ethanol production, starting from the raw material preparation and finishing with the rectification, aim at minimizing the formation of fusel oil or at its maximum removal.
- Collecting and storing fusel oil for the subsequent qualified processing and using is non-expedient due to its low yield. Modern methods for utilization of fusel oil propose either its incineration in a burner in admixture with fuel oil (Klimovski D.I, Smirnov V.N. "Alcohol Technology, Moscow, 1967) or using fusel oil as a raw material for producing isoamyl alcohol by distillation in a rectification unit (Russian patent RU

2109724, C07C 31/125, 1996). Recently, the methods for producing fuel-grade ethanol from carbohydrates of plant origin have gained a great importance. There are different known methods for using the products of fermentation of carbohydrate substrates of plant origin: ethyl alcohol and C₃-C₅ alcohols as a motor fuel or components of motor
5 fuels for internal combustion engines. In this case ethyl alcohol is mainly used as a fuel component, while C₃-C₅ alcohols are used as an octane-boosting additive for the fuel, or as a component in chemical synthesis for obtaining diesel fuel (Russian Patent 2155793, C10L1/18, 2000 "High octane additive for obtaining automotive gasoline", Russian Patent RU 2106391, C10L 1/18, 1995 "Composition of hydrocarbon fuel").

10 In the light of the above, ethyl alcohol production with an increased yield of C₃-C₅ alcohols would offer a possibility to widen the range of various types of motor fuels produced by processing "green" carbohydrate raw material. The total yield of fusel oil obtained in fermentation depends on the quality of carbohydrate substrate and the
15 method of fermentation and is generally 0.2-0.6% of absolute ethyl alcohol.

Summary of invention

20 We have developed a new method for obtaining hydrocarbons and oxygen-containing compounds from biomass or products originating from biomass. The process is carried out in several steps and includes also biosynthesis of methane, carbon dioxide, acetaldehyde, acetone, lower C₁-C₅ alcohols, and glycerine for producing unsaturated hydrocarbons from said alcohols, obtaining of synthesis gas, including using methane and carbon dioxide, interaction of unsaturated hydrocarbons with synthesis gas, condensa-
25 tion of the obtained aldehydes, hydrogenation of the obtained unsaturated aldehydes into alcohols, and converting saturated alcohols into saturated hydrocarbons. Besides that, the aldehydes can be used for obtaining acids, which are then converted into esters. The aldehydes can also be used for the synthesis of acetals. The alcohols can also be converted into ethers. Moreover, C₁-C₅ alcohols and glycerine obtained in biosynthe-
30 sis can first be converted into aldehydes, which are then condensed into higher unsaturated aldehydes, which in turn are hydrogenated into higher saturated alcohols.

The present invention relates to biochemical and chemical industry and can be used in the methods for fermenting carbohydrate substrates of plant origin for producing C₁-C₅

alcohols, and for synthesis of higher alcohols, other oxygen-containing compounds and hydrocarbons as well as for the production of motor fuel components from biomass. Since C₆ and higher alcohols, ethers, acetals, and higher hydrocarbons are not obtainable by a direct biochemical route, it is proposed to synthesize these using known

5 chemical reactions, wherein the source raw materials for said synthesis are:

- Synthesis gas produced from carbon dioxide obtained in biomass fermentation and from methane obtained in fermentation of the amino acids-containing distillery dreg after extraction of alcohol, and/or from various products and wastes obtained in biomass processing, including processing of wood, production of
- 10 grain, or production of vegetable oils;
- C₁-C₅ alcohols produced by the inventive method using amino acids as a biocatalyst at the fermentation stage. The amino acids include leucine, isoleucine, valine, or a mixture of amino acids extracted from the yeast autolysate after separation of asparagine and ammonium;
- 15 - Glycerine produced by the inventive method and/or by saponification of fats. It is proposed to use the glycerine for producing higher hydrocarbons and oxygen-containing compounds to increase the extent of utilization of the renewable raw material, including for the purpose of motor fuel production;
- Acetaldehyde and acetone produced by the inventive method.

20 It is proposed to use carbon dioxide or a mixture of carbon dioxide and oxygen in the processes of alcohol oxidation into aldehydes and aldehydes into fatty acids. At the stage of aldehydes condensation and to increase the yield of the higher hydrocarbons we propose to use besides the aldehydes obtained from alcohols the furfural obtained

25 by hydrolysis of the pentosane-containing raw material. At the stage of etherification and to increase the yield of higher esters we propose to use along with the fatty acids, obtained from aldehydes, C₂-C₆ fatty acids produced by biosynthesis, as well as the acids obtained in the saponification of fats and extracted from the tall oil. To increase the yield of higher esters we also propose to use terpenes at the etherification stage.

30 To increase the extent of the biomass conversion in the synthesis of hydrocarbons and oxygen-containing compounds we propose to produce methanol using carbon dioxide obtained in the enzymatic processing of biomass or a mixture of carbon dioxide and

hydrogen. Methanol obtained from carbon dioxide is then directed to the production of higher hydrocarbons and oxygen-containing compounds.

To increase the extent of the biomass conversion in the synthesis of hydrocarbons and oxygen-containing compounds it is proposed to use carbon dioxide obtained in the enzymatic processing of biomass. Besides carbon dioxide the said carbon oxide production can use wastes of the grain production, wood processing, turf, and lignin obtained in hydrolysis of the cellulose-containing raw material.

Production of synthesis gas can use as a raw material wastes of the production of grain, vegetable oils, wastes of wood processing, including pulp and wood coal, as well as by-products and wastes obtained in C₁-C₅ alcohols biosynthesis, biosynthesis of glycerine, acetaldehyde, acetone, C₂-C₆ acids, and by-products obtained in the chemical processing of the aforesaid oxygen-containing compounds. The following can be used for producing synthesis gas: gaseous and liquid products obtained in biomass pyrolysis, furfural, turpentine, colophony, tall oil, fusel oil, vegetable oils, and wastes obtained in the processing of said products.

It is also proposed to use carbon oxide obtained by the inventive method from the stage of fermentation, or from various types of biomass, and hydrogen, obtained from water by known methods, for the production of synthesis gas.

It is proposed to use synthesis gas produced by the inventive method for obtaining hydrocarbons and oxygen-containing compounds by the Fisher-Tropsch method and by methods based on hydroformylation.

Of course, the inventive method for producing hydrocarbons and oxygen-containing compounds from biomass or products originating from biomass allows using some source compounds of non-biologic origin. For example, in the production of synthesis gas along with carbon dioxide obtained in biosynthesis can be used hydrogen originating from petroleum, natural gas or coal. However the greatest effect is achieved when the source compounds are substances originating from renewable raw material. This is a possibility to obtain products needed for vital activities of humans from the raw mate-

rials currently not used to a full extent, but continuously reproduced by nature in contrast to petroleum, gas and coal, the reserves of which decrease continuously.

The present invention aims at solving the following problems:

- 5 - To increase the yield of C₃-C₅ alcohols;
- To increase the specific speed of carbohydrate substrates fermentation;
- To utilize the protein-containing waste of the alcohol production;
- To produce higher oxygen-containing hydrocarbons and non oxygen-containing hydrocarbons, including those having C₄ and more carbon atoms in the mole-
- 10 - To produce higher oxygen-containing hydrocarbons and non oxygen-containing hydrocarbons, including those having C₄ and more carbon atoms in the mole-
- To utilize in the said production carbon dioxide obtained in biosynthesis of lower alcohols, acids and hydrocarbons; glycerine obtained in saponification of fats; furfural obtained in hydrolysis of the pentosane-containing raw material; fatty
- 15 acids obtained in biosynthesis, fat saponification and extracted from tall oil, resin and gases obtained in pyrolysis of wood;
- To increase the rate of direct utilization of biomass for synthesis of higher alcohols, other oxygen-containing compounds, and higher hydrocarbons for motor fuel production from biomass.

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Detailed description of the invention

The inventive method for fermentation of carbohydrate substrates allows to increase the yield of C₃-C₅ alcohols to a level of 0.65–3.1% of ethyl alcohol with a simultaneous

25 increase of the specific speed of fermentation of carbohydrate substrates to 4.0 l/kg*h. This is accomplished as follows.

While carrying out the alcohol fermentation it is necessary to add to the carbohydrate substrate the sources of mineral nutrition, i.e. nitrogen-containing and phosphorus-

30 containing salts. These additives are necessary elements of the yeast nutrition and take part in the build-up of the biomass' cells growing in the course of fermentation.

Conventionally, the concentration of nitrogen in the substrate is from 50 to 600 mg/l and depends on concentration of carbohydrates. In the prior art, mineral salts such as

ammonium sulphate, ammophos, or urea are used as the nitrogen nutrition of the yeast for carrying out the alcohol fermentation.

5 The present inventors have found that the yeast assimilates nitrogen of amino acids faster than nitrogen of mineral salts, which determines rapid development of the yeast culture and high speed of the alcohol fermentation.

10 The inventive method for fermentation of carbohydrate substrates of plant origin is characterized in that the amino acids leucine, isoleucine or valine, or a mixture thereof is used as a nitrogen-containing component for the preparation of the carbohydrate substrate in an amount providing a content of the amino nitrogen in the substrate of 120-420 mg/l. The method is further characterized by subsequent fermentation of the carbohydrates of the substrate with a specific speed of alcohol fermentation of up to 4.0 l/kg/hour and a yield of C₃-C₅ alcohols in an amount of from 0.65% to 3.1% of ethyl
15 alcohol. The carbohydrate substrate used is beet or cane molasses, acid or enzymatic hydrolysate of starch-containing or cellulose-containing plant materials.

20 The alcohol yeast, obtained in the fermentation of the molasses' carbohydrates, is condensed to a dry substance content of 5-10%, washed with water during the process of condensation and treated by autolysis at 45-55°C during 24-48 hours. The obtained autolysate with amino nitrogen content of 3000-8000 mg/l containing the amino acids valine, leucine and isoleucine is used as a nitrogen nutrition source for the yeast for fermenting the carbohydrate substrates.

25 Suspended substances of the distillery dreg, after extraction of alcohol, obtained in the fermentation of starch-containing plant materials can be condensed to a dry substance content of 5-10%, followed either by enzymatic hydrolysis of proteins of the distillery dreg free of alcohol at pH=2-pH=8 and a temperature of 30-60°C using proteolytic enzymatic preparations, such as proteases, including exopeptidases: aminopeptide-
30 aminoacide hydrolases, carboxypeptide-aminoacidohydrolases; and endopeptidases: dipeptidhydrolases and peptide-peptidehydrolases, or by acid hydrolysis of proteins of the distillery dreg free of alcohol at 40-90°C using 0.2-0.5% sulphuric or hydrochloric acid. The amino-acid hydrolysate obtained containing amino-acids valine, leucine and

isoleucine with amino nitrogen content of 2000-6000 mg/l can then be used as nitrogen nutrition of the yeast in the fermentation of carbohydrate substrates.

Alternatively, combined acid hydrolysis of the cellulose-containing plant material and of the microorganisms' biomass in the ratio of cellulose to biomass of 20:1-100:1 can be carried out. The obtained hydrolysate containing 3-20% of carbohydrates and 50-600 mg/l of amino nitrogen is used for the alcohol fermentation of carbohydrates.

Water-soluble substances of the distillery dreg, after extraction of alcohol, can be used for the aerobic cultivation of the yeast; the obtained yeast is condensed to a dry substance content of 5-10% and treated by autolysis at 45-55°C during 24-48 hours. The obtained autolysate containing the amino acids valine, leucine and isoleucine with an amino-nitrogen concentration of 3000-8000 mg/ is used as nitrogen nutrition of the yeast in the fermentation of carbohydrate substrates.

The amino acid autolysate of the yeast, containing the amino acids valine, leucine, and isoleucine in an amount providing a content of amino nitrogen in the carbohydrate substrate of from 120 to 420 mg/l, which autolysate has been obtained in the aerobic cultivation of the yeast with pentose-containing distillery dreg, after extraction of alcohol, can be used as nitrogen nutrition in the fermenting of carbohydrate substrates. Pentose-containing distillery dreg, after extraction of alcohol, can be used for the aerobic cultivation of the yeast; the obtained yeast is condensed to a dry substance content of 5-10%, washed with water during the condensation and treated by autolysis at 45-55°C during 24-48 hours. The autolysate thus obtained, containing 3000-8000 mg/l of amino nitrogen, is used as nitrogen nutrition of the yeast in the fermentation of carbohydrate substrates.

After extraction of asparagine and ammonium salts, the autolysate of the yeast protein, the acid or enzymatic hydrolysates of the protein of the distillery dreg are used as nitrogen nutrition in the fermentation of the carbohydrate substrates.

Formation of C₃-C₅ alcohols is a result of active functioning of the process of deamination of amino acids in the yeast cells with formation of free ammonia. We have demonstrated that formation of C₃-C₅ alcohols in the process of alcohol fermentation is

determined by assimilation of nitrogen from the amino acids valine, leucine, and isoleucine by the growing cells. The yield of C₃-C₅ alcohols reached 3.1% of ethanol when pure valine, isoleucine, and leucine were the sole source of nitrogen nutrition of the yeast in the inventive fermentation process. Moreover, the maximum formation of C₃-C₅ alcohols in the inventive process of alcohol fermentation occurred at pH=6.0 of the medium and at 38°C (standard conditions of alcohol fermentation pH 4.5-5.5; temperature 28-34°C).

It has been found that presence in the substrate of asparagine and ammonium ions, in addition to the amino acids valine, leucine, and isoleucine, inhibits formation of C₃-C₅ alcohols. Other amino acids do not inhibit the process of C₃-C₅ alcohols formation. The inhibition constant for the system leucine - ammonium sulphate is 750 mg/l, leucine - asparagine 730 mg/l, valine - asparagine 650 mg/l.

When amino acid autolysate of the yeast was used, the maximum yield of C₃-C₅ alcohols reached 1.1-2.1% of ethanol, and when the amino acid protein hydrolysate of the distiller's grains were used, the maximum yield of C₃-C₅ alcohols was 0.65-0.8% of ethanol. The relatively low yield of C₃-C₅ alcohols, when using the yeast autolysate or distillery dreg protein hydrolysate, is a result of the presence of asparagine.

Wastes of the production of ethyl alcohol from carbohydrate substrates are: biomass of the alcohol yeast, which is increased during the process of fermentation; non-fermentable soluble organic components of the substrate, such as pentose sugar, organic acids, hexose and ethanol residues; non-soluble protein components of grain, etc.

There are known methods for utilisation of said wastes for producing baking yeast, fodder protein and amino acid products.

Biomass of the alcohol yeast or the yeast obtained in aerobic cultivation using non-fermentable organic components of the substrate can be used for obtaining amino acids by known methods of autolysis. Non-soluble protein waste of the ethyl alcohol production can be also used for obtaining amino acids by known methods of enzymatic or acid hydrolysis of protein.

Extraction of ammonia and asparagine from the amino acid mixture by known methods of ion exchange can be used in order to increase the yield of C₃-C₅ alcohols in terms of ethanol, when using yeast autolysate or hydrolysate, and acid or enzymatic hydrolysate of the distillery dreg as nitrogen nutrition of the yeast in the process of carbohydrate
5 substrates fermentation.

The total content of C₃-C₅ alcohols increases from 0.8-2.1% to 2.2-2.95% of ethanol when yeast autolysate free of ammonia and asparagines, or yeast hydrolysate and acid or enzymatic hydrolysate of the distillery dreg protein is used as nitrogen nutrition in
10 the process of carbohydrate substrates fermentation in the production of ethanol.

In the processes of acetone and glycerine biosynthesis it is proposed to use a method similar to that used according to the invention in the biosynthesis of ethanol to increase the yield of C₃-C₅ alcohols, that is to use at the stage of carbohydrate substrate
15 preparation as a nitrogen-containing component the amino acids leucine, isoleucine, valine or mixtures of said acids, including those extracted from the yeast or distillery dreg protein.

To increase the extent of biomass conversion in the synthesis of hydrocarbons and oxygen-containing compounds it is proposed to use for methane biosynthesis distillery
20 dreg, after extraction of alcohol, containing excess amino acids produced in the autolysis or hydrolysis of the yeast. Methane should be obtained under anaerobe conditions using methane-producing bacteria.

To increase the yield of C₁-C₅ alcohols it is proposed to process glycerine, obtained in the biosynthesis and from the saponification of fats, into n-propanol. To increase the yield of higher alcohols it is proposed to use vegetable and animal fats in addition to glycerine obtained as a result of biosynthesis in the processing of said glycerine into n-propanol by hydrogenation. The process of hydrogenation of the mixture of glycerine
25 and vegetable and/or animal fats into a mixture of n-propyl alcohol, higher C₆-C₂₀ alcohols and C₆ and higher hydrocarbons can be performed in the presence of copper-chromium, zinc-chromium, nickel-chromium catalysts at 300±100°C and a pressure of
30 10-30 MPa by hydrogen obtained from biomass. This process can be also carried out in

the presence of catalysts comprising precious metals, such as Pt, Pd, Re, Ru, Rh at 200±50°C and a pressure of 5-20 MPa.

It is proposed to condensate C₁-C₅ alcohols produced by the inventive method into
5 higher alcohols, esters and acids. The condensation can be carried out at a temperature of 100-400°C and a pressure of 0.1-10 MPa in the presence of alcoholates of alkali metals or caustic alkali.

To increase the extent of biomass conversion in the synthesis of hydrocarbons and oxygen-containing compounds it is proposed to use carbon dioxide, obtained in the enzymatic processing of biomass or a mixture of carbon dioxide and hydrogen, for producing methanol. It is also proposed to use hydrogen obtained from biomass and/or from the water obtained in the processing of alcohols obtained in biosynthesis. Water conversion can be carried out by means of known methods. Synthesis of methanol using
15 the raw materials originating from biomass can be carried out at a temperature of 350-450°C in the presence of ZnO-Cr₂O₃ catalyst or at a pressure 4-6 MPa and a temperature of 220-280°C in the presence of CuO-ZnO-Al₂O₃ (Cr₂O₃). Methanol obtained from carbon dioxide is then directed to the processes for production of higher hydrocarbons and oxygen-containing compounds.

To increase the extent of biomass conversion in the synthesis of hydrocarbons and oxygen-containing compounds we propose to use carbon dioxide obtained in the enzymatic processing of biomass for producing carbon oxide. Besides carbon dioxide aforesaid production can use gaseous products of biomass pyrolysis including wood, lignin, turf,
25 solid waste of grain production and wood processing, and lignin obtained in the hydrolysis of cellulose-containing raw material. This process can be carried out in industrial gas generators with boiling or pseudo-liquefied layer of solid particles or in gas generators of other types. The source gas is a mixture of carbon dioxide and oxygen. The reaction temperature is 1000-1500°C. If needed the process of carbon dioxide production can be carried out at a pressure 2-6 MPa. Carbon oxide obtained from the biologic raw material is subsequently mixed with hydrogen obtained from biomass and/or
30 with hydrogen obtained from the water obtained in dehydration of alcohols obtained in biosynthesis or from the water obtained in condensation of aldehydes obtained from said alcohols. Conversion of the water is carried out by known methods. This gas mix-

ture is then used for synthesis of hydrocarbons, including higher alcohols, and other oxygen-containing compounds.

For the oxidation of alcohols into aldehydes it is proposed to use carbon dioxide obtained in the process of biosynthesis. Oxidation of alcohols into aldehydes is carried out at a temperature of 450-650°C and a pressure of 0.05 MPa in the presence of a silver catalyst Ag-Al₂O₃. In contrast to the known processes the steam-gaseous mixture of C₁-C₅ alcohols and carbon dioxide heated to 180-200°C is directed to the oxidation. The use of this mixture gives a possibility to use for the oxidation oxygen or a mixture of oxygen and carbon dioxide. We propose to carry out the condensation of aldehydes, obtained from lower alcohols, with furfural in the alkali medium at 0-10°C. It is further proposed to hydrogenate unsaturated aldehydes obtained in croton condensation of aldehydes, which are obtained in oxidation of lower C₁-C₅ alcohols, and also unsaturated aldehydes, obtained in condensation of furfural with lower C₁-C₅ aldehydes, by hydrogen obtained from biomass and/or by hydrogen obtained from the water obtained in oxidation of alcohols or in condensation of aldehydes. Conversion of the water is carried out by known methods.

For oxidation of aldehydes into fatty acids we propose to use carbon dioxide obtained in biosynthesis. Oxidation of aldehydes into fatty acids is carried out at a temperature of 50-250°C and a pressure of 0.05-0.5 MPa in the presence of a manganese acetate catalyst. In contrast to the known methods the steam-gas mixture of aldehydes and carbon dioxide heated to 50-150°C is supplied to the oxidation. Utilization of said mixture gives a possibility to use for the oxidation oxygen or a mixture of oxygen and carbon dioxide. For etherification of the fatty acids obtained by the inventive method we propose to use a mixture of C₁-C₅ alcohols produced by the inventive method, or to use a mixture of unsaturated C₂-C₅ hydrocarbons obtained from said alcohols. Furthermore, to increase the yield of higher esters we propose to use at the stage of etherification fatty acids, obtained by the inventive method, C₂-C₆ fatty acids obtained by biosynthesis, and also acids obtained in the saponification of the fats and extracted from tall oil. We propose to perform the etherification in the gas phase at a temperature of 100-200°C and a pressure of 0.5-2.5 MPa in the presence of sulphocationite catalyst or in the liquid phase at a temperature of 50-200°C and a pressure of 0.1-0.5 MPa in the presence of non-organic acids as a catalyst.

- For obtaining acetals and ketals it is proposed to use acetaldehyde, acetone, glycerine, and a mixture of C₃-C₅ alcohols produced by the inventive method, acetaldehyde obtained in oxidation of ethanol produced by biochemical method, and formaldehyde obtained in oxidation of methanol synthesized from carbon dioxide produced by biochemical method.. It is proposed to carry out the process of acetals and ketals production in the liquid phase at a temperature of 0-50°C and a pressure of 0.1-0.5 MPa using hydrochloric or sulphuric acids or salts of these acids as a catalyst.
- 10 For producing synthesis gas wastes of the grain production, vegetable oils, wood processing, including pulp production and production of wood coal, and also by-products and wastes obtained in biosynthesis of C₁-C₅ alcohols, glycerine, acetaldehyde, acetone, C₂-C₆ acids, and by-products and wastes obtained in chemical processing of the aforesaid oxygen-containing compounds can be used. For the production of synthesis gas it is also proposed to use biogas obtained in the fermentation of the various types of biomass and carbon dioxide obtained at the fermentation stage of the same production or carbon dioxide obtained in the biosynthesis of other bio-products. For producing synthesis gas, besides carbon dioxide obtained in biosynthesis, it is also possible to use the gases and resins obtained in the pyrolysis of wood, furfural, turpentine, colophony, tall oil, fusel oils, vegetable oils and wastes of the production of aforesaid products. The process of synthesis gas production is carried out at a temperature of 800-1100°C and a pressure of 0.1-3 MPa in the presence of an Al₂O₃ supported NiO catalyst or at 1450-1550°C and a pressure of 2-10 MPa without a catalyst. It is proposed to use synthesis gas obtained by the inventive method for producing hydrocarbons and oxygen-containing compounds by the Fisher-Tropsch method and by processes based on the reaction of hydroformylation.

It is proposed to carry out the production of hydrocarbons by the Fisher-Tropsch method from synthesis gas, obtained by the inventive method, at a temperature of 200-350°C and a pressure of 2.0-2.5 MPa in the presence of ferrous catalyst promoted by oxides of alkali metals or at 170-200°C and a pressure of 0.1-1.0 MPa in the presence of cobalt-thorium-magnesium catalyst. The process of production of the oxygen-containing compounds by the Fisher-Tropsch method from synthesis gas obtained by our inventive method should be carried out at a temperature of 180-250°C and a pres-

sure of 1.0-3.5 MPa in the presence of a ferrous-copper catalyst promoted by oxides of aluminium, calcium, zinc, magnesium, and alkaline agents, such as compounds of alkaline metals, which when dissolved in water produce an alkaline reaction.

- 5 For producing unsaturated hydrocarbons, which are subsequently directed to hydroformylation or alkylation, it is proposed to dehydrate the mixture of C₂-C₅ alcohols, obtained in biosynthesis, and/or glycerine, as well as the glycerine obtained by saponification of fats. Dehydration is carried out at a temperature of 200-400°C and a pressure of 0.1-3 MPa in the presence of an Al₂O₃ catalyst. The mixture of alcohols and/or glycerine can be also dehydrated by heating with sulphuric acid.

- 15 It is proposed to alkylate unsaturated hydrocarbons obtained in dehydration of lower C₂-C₅ alcohols by using isobutane and isopentane obtained from the corresponding isoalcohols, and also using terpenes, which have previously been heated to a temperature of 200±50°C. The result of alkylation, which is carried out at 0-10° and a pressure of 0.5-1 MPa in the presence of 90-100% sulphuric acid as a catalyst, is the obtaining of the mixture of C₆-C₁₅ hydrocarbons. The alkylation can be also carried out in the presence of an AlCl₃ catalyst at a temperature of 50-60°C and a pressure of 1-2 MPa.

- 20 It is proposed to perform the process of hydroformylation of unsaturated hydrocarbons obtained in dehydration of lower C₂-C₅ alcohols using synthesis gas, obtained from biomass, at a temperature of 160±20°C and a pressure of 30±10 MPa in the presence of cobalt carbonyl catalyst; or at a temperature of 175±25°C and a pressure fo 7.5±2.5 MPa in the presence of a cobalt catalyst modified by phosphorus compounds; or at 25 90±10°C and a pressure of 2±1 MPa in the presence of a cobalt-rhodium catalyst.

- 30 It is proposed to hydrogenate the aldehydes, obtained in hydroformylation of unsaturated hydrocarbons, and/or acrolein, obtained in dehydration of glycerine into saturated alcohols, by hydrogen obtained from biomass and/or by hydrogen produced from the water obtained in dehydration of alcohols obtained from biosynthesis. Conversion of the water is carried out by known methods. It is proposed to hydrogenate saturated and unsaturated aldehydes into saturated alcohols at a temperature of 50-150°C and a pressure of 1-2 MPa in the presence of an Al₂O₃ supported NiO catalyst or at a tem-

perature of 200-250°C and a pressure of 5-20 MPa in the presence of a CuO-Cr₂O₃ catalyst.

Thus, the inventive method for production of higher hydrocarbons, including oxygen-
5 containing compounds, from biomass offers a solution to the following problems:

- To produce higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having four and more carbon atoms in the molecule, from biomass using the raw material obtained by biochemical methods;
- 10 - To considerably increase the yield of C₃-C₅ alcohols in the process of their biosynthesis by fermenting the carbohydrate substrates;
- To increase by 1.5-2.0 times the productivity of the fermentation stage for the technology of C₁-C₅ alcohols production;
- To utilize the protein-containing waste and other bio components of the distillery dreg after extraction of alcohol within the frame of the technology for C₁-C₅ alcohols production, including for the purpose of methane production;
- 15 - To utilize in the production of hydrocarbons, including oxygen-containing compounds, carbon dioxide obtained in the biosynthesis of C₁-C₅ alcohols, and also carbon dioxide obtained in the biosynthesis of other lower hydrocarbons;
- 20 - To utilize in the production of hydrocarbons, including oxygen-containing compounds, fats, glycerine obtained in the saponification of fats, furfural obtained in hydrolysis of pentosane-containing raw material, C₂-C₆ fatty acids obtained by biosynthesis, acids obtained in the saponification of fats and extracted from tall oil, resins, turpentine, colophony and tall oil obtained in the wood processing;
- 25 - To increase the rate of the direct use of biomass for synthesis of higher alcohols and other oxygen-containing compounds, and also higher hydrocarbons;
- To use hydrocarbons, including oxygen-containing compounds, obtained from biomass by the inventive method as a component for motor fuels.

30 The invention is further illustrated by the below non-limiting examples demonstrating the feasibility of the inventive process.

EXAMPLE 1

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of enzymatic hydrolysis the concentration of carbohydrates in the substrate reached 16%. To the substrate were added: superphosphate in an amount providing a content of P_2O_5 of 200 mg/l, and the amino acid leucine in an amount of 4000 mg/l (amino nitrogen 420 mg/l). Starter yeast biomass *S. cerevisiae* was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0.

The speed of fermentation was 3.0 l/g*h, the ethanol concentration at the end of fermentation was 8.9% by vol., and the isopentanol concentration 2300 mg/l or 3.1% of the volume of ethanol..

EXAMPLE 2

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glucoamylase Glucozym L-400C (pH 5.0; 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA were used. As a result of the enzymatic hydrolysis the concentration of carbohydrates in the substrate reached 16%. To the substrate were added: superphosphate in an amount providing a P_2O_5 content of 200 mg/l, and the amino acid valine in an amount of 3000 mg/l (amino nitrogen 360 mg/l). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in an amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0.

The fermentation speed was 2.8 l/g*h, the ethanol concentration at the end of fermentation was 8.9% vol., and the isobutanol concentration 1810 mg/l or 2.5% of the ethanol volume..

EXAMPLE 3

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch) and in the
5 second stage glucoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA were used. As a result of the enzymatic hydrolysis the carbohydrate concentration in the substrate reached 16%. To the substrate were added: superphosphate in an amount
10 providing a P_2O_5 content of 200 mg/l, and the amino acid isoleucine in an amount of 4000 mg/l (amino nitrogen 420 mg/l). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the concentration of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0. The speed of fermentation was 3.0 l/g*h, the ethanol concentration at the end of fermentation reached 8.9%, the isopentanol
15 concentration 2120 mg/l or 2.8% of the ethanol volume.

EXAMPLE 4

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermo-stable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch) and in the
20 second stage glucoamylase Glucozym L-400C (pH 5.0; 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the carbohydrates concentration in the substrate has reached 16%. Superphosphate was added to the substrate in an
25 amount providing a P_2O_5 content of 200 mg/l, the amino acid leucine was added in an amount of 1000 mg/l, the amino acid isoleucine in the amount of 1000 mg/l, and the amino acid valine in the amount 1500 mg/l. The yeast starter biomass *S. cerevisiae* was added to the substrate in the amount of 5 g/l. The fermentation was carried out at
30 a temperature of 38°C and a pH=6.0.

The fermentation speed was 3.5 l/g*h, the ethanol concentration at the end of the fermentation was 8.8% vol., the isopentanol's concentration 1290 mg/l, and the isobu-

tanol concentration 910 mg/l, or the total content of C₄-C₅ alcohols was 3% of the ethanol volume.

EXAMPLE 5

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch) and in the second stage glucoamylase Glucozym L-400C (pH 5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the carbohydrate concentration in the substrate reached 16%. To the substrate were added: superphosphate in an amount providing a P₂O₅ content of 200 mg/l, and liquid autolysate of the alcohol yeast in an amount of 50 ml/l (amino nitrogen 320 mg/). The yeast starter biomass *S. cerevisiae* was added to the substrate in an amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH 6.0. The speed of the fermentation was 4.0 l/g*h, the ethanol concentration at the end of fermentation was 8.8% vol., the isopentanol concentration 480 mg/l, and the isobutanol concentration 270 mg/l. The total content of C₃-C₅ alcohols was 1.1% of the volume of ethanol.

EXAMPLE 6

Beet molasses with a saccharose concentration of 46% was diluted with water to a saccharose concentration of 18%, acidified by sulphuric acid to pH 5.5, then the alcohol yeast autolysate was added in an amount of 50 ml/l (350 mg/l of the amino nitrogen) and the yeast starter biomass *S. cerevisiae* in the amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and pH 5.5. The fermentation speed was 3.8 l/g*h, the ethanol concentration at the end of fermentation was 8.6% vol., the isopentanol concentration 490 mg/l, the isobutanol concentration 290 mg/l, and the total content of C₃-C₅ alcohols was 1.1% of the volume of ethanol while the concentration of the alcohol yeast biomass was 6.2 g/l.

The alcohol yeast was separated from the liquid culture by filtration and washed with water. The obtained yeast was used for preparation of the suspension with a dry sub-

stance content of 12%. Autolysis of the yeast was carried out and the suspension was let to stand in a thermostat at a temperature of 48°C for 36 hours. The content of amino nitrogen in the autolysate obtained was 7000 mg/l, and the amount of the obtained autolysate was 55 ml/l of the medium. The obtained autolysate was used for
5 preparing the source medium for fermentation of the molasses substrate.

EXAMPLE 7

Sugar cane molasses with a saccharose concentration of 46% was diluted with water to
10 a saccharose concentration of 18%, acidified by sulphuric acid to pH 5.5, and then the alcohol yeast autolysate was added in an amount of 60 ml/l (370 mg/l of the amino nitrogen) and the yeast starter biomass *S. cerevisiae* in the amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and pH 5.5. The fermentation speed was 4.0 l/g*h, the ethanol concentration at the end of fermentation was 8.7% vol., the
15 isopentanol concentration 470 mg/l, isobutanol concentration 290 mg/l, and the total content of C₃-C₅ alcohols was 1.2% of the volume of ethanol.

Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). To the alcohol-free mash (distillery dreg) nitrogen
20 and phosphorus mineral salts were added, and aerobic cultivation of the yeast *Candida tropicalis* was carried out. As a result of the cultivation, a yeast suspension with a biomass concentration of 15 g/l was obtained. The yeast was separated from the culture liquid by filtration, washed with water and treated by autolysis as described in Example 6. The amino nitrogen content in the obtained autolysate was 6500 mg/l, the amount
25 of autolysate 125 mg/l of the medium. The obtained autolysate was used for preparing the source medium for fermenting the molasses substrate.

EXAMPLE 8

30 Beet molasses with a saccharose concentration of 46% was diluted with water to a saccharose concentration of 18%, acidified by sulphuric acid to pH 5.5, then the acid hydrolysate of the yeast in an amount of 120 ml/l (350 mg/l of the amino nitrogen) and the yeast starter biomass *S. cerevisiae* in the amount of 5 g/l were added. The fermentation was carried out at a temperature of 38°C and pH 5.5. The fermentation speed

was 3.4 l/g^{*h}, the ethanol concentration at the end of the fermentation was 8.7% vol., the isopentaniols concentration 460 mg/l, isobutanol concentration 290 mg/l, and the total content of C₃-C₅ alcohols was 1.2% of the volume of ethanol.

- 5 Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). To the alcohol-free mash (distillery dreg) nitrogen and phosphorus mineral salts were added, and aerobic cultivation of the yeast *Candida tropicalis* was carried out. As a result of the cultivation a yeast suspension with a bio-
mass concentration of 15 g/l was obtained. The yeast was separated from the culture
10 liquid by filtration, washed with water and a biomass suspension with a dry substance content of 6% was prepared. Hydrolysis of the suspension was carried out in the presence of 4N HCl at 100°C for 12 hours. The amino nitrogen content in the obtained hydrolysate was 3100 mg/l, the amount of hydrolysate 240 ml/l of the medium. The obtained acid hydrolysate was used for preparing the source medium for fermenting the
15 molasses substrate.

EXAMPLE 9

- Chopped spruce wood (cellulose-containing plant material) was treated by acid hydrolysis at a temperature of 180°C, a sulphuric acid concentration of 0.5%, a ratio of water to wood of 12:1, and during a time of 1.5 hours. The hydrolysate of the wood was neutralized with lime to a pH of 4.5, and separated from lignin and gypsum residues. To the carbohydrate substrate obtained, with a hexose sugar concentration of 3.2% and
20 pentose sugar concentration of 0.8%, superphosphate was added in an amount of P₂O₅ 120 mg/l, the yeast autolysate in an amount of 40 ml/l of substrate (120 mg/l of amino nitrogen), and 5 g/l of the starter yeast biomass *S. cerevisiae*. The fermentation was carried out at a temperature of 38°C and pH 5.5. The fermentation speed was 3.7 l/g^{*h}, the ethanol concentration at the end of the fermentation was 1.5% vol., concentration of isopentaniols was 170 mg/l, concentration of isobutanol was 90 mg/l, and the
25 total content of C₃-C₅ alcohols was 2.1% of the volume of ethanol.
30

Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). Nitrogen and phosphorous mineral salts were added to the alcohol-free pentose-containing distillery dreg and aerobic cultivation of

Candida tropicalis yeast was carried out. As a result of the cultivation a yeast suspension with a biomass concentration of 6 g/l was obtained. The yeast was separated from the culture liquid by filtration, washed with water, and a suspension with a dry substance concentration 12% was prepared. Autolysis of the yeast was carried out by
5 treating the suspension in the thermostat at 48°C for 36 hours. The content of amino nitrogen in the obtained autolysate was 7100 mg/l, the amount of the autolysate was 50 ml/l of the medium. The obtained autolysate was used for fermenting the wood hydrolysate.

10 EXAMPLE 10

Chopped spruce wood (cellulose containing plant material) was treated by acid hydrolysis at a temperature of 180°C, a sulphuric acid concentration of 0.5%, a ratio of water to wood of 12:1, and for a time of 1.5 hours. The wood hydrolysate was neutralized by
15 lime to a pH = 4.5, separated from lignin and gypsum residues. To the carbohydrate substrate obtained, having a concentration of hexose and pentose sugars of 3.2% and 0.8%, respectively, were added: superphosphate in an amount of P₂O₅ of 120 mg/l, yeast autolysate, purified of ammonia and asparagines by known methods of ion exchange, in the amount of 40 ml/l of substrate (120 mg/l of amino nitrogen), and starter
20 yeast biomass *S. cerevisiae* in a concentration of 5 g/l. The fermentation was carried out at 38°C and pH=6. The speed of the fermentation was 4.0 l/g*h, ethanol concentration at the end of the fermentation was 1.5% vol., the isopentanol and isobutanol concentrations were 210 mg/l and 120 mg/l, respectively. The total content of C₃-C₅ alcohols was 2.9% of the volume of ethanol.

25 Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). Nitrogen and phosphorous mineral salts were added to the alcohol-free pentose-containing distillery dreg, and aerobic cultivation of the yeast *Candida tropicalis* was carried out. As a result of the cultivation a yeast suspension having a biomass concentration of 6 g/l was obtained. The yeast was separated
30 from the culture liquid by filtration, washed with water with subsequent preparation of the biomass suspension with 12% content of dry substance. Autolysis of the yeast was accomplished by letting the suspension stand at a temperature of 48°C during 36 hours. The amino nitrogen concentration in the obtained autolysate was 8000 mg/l,

the amount of the obtained autolysate was 50 ml/l of the medium. The amino acid autolysate thus obtained was treated by ion exchange to extract ammonia nitrogen and asparagines; after that the mixture of amino acids without asparagines and ammonia nitrogen was used as nitrogen nutrition for fermentation of the wood hydrolysate.

5

EXAMPLE 11

Chopped spruce wood (cellulose-containing plant material) was used together with the yeast biomass in a ratio of 50:1 and treated by acid hydrolysis at a temperature of
10 180°C, with a sulphuric acid concentration of 0.5%, a ratio of water to wood of 12:1, and for a period of time of 1.5 hours. The hydrolysate was then neutralized by lime to a pH = 4.5, separated from lignin and gypsum residues. The obtained carbohydrate substrate having a concentration of hexose and pentose sugars of 3.2% and 0.8% respectively, was subsequently added with superphosphate in an amount of $P_2O_5=120$ mg/l.
15 The content of amino nitrogen in the substrate obtained in the yeast protein hydrolysis was 130 mg/l. Disseminating yeast biomass *S. cerevisiae* was then supplied to the hydrolysate in the amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH = 5.5. The speed of fermentation was 3.5 l/g*h, ethanol concentration at the end of the fermentation was 1.5% vol., isopentanol and isobutanol concentrations
20 were 140 mg/l and 80 mg/l, respectively. The total content of C₃-C₅ alcohols was 1.8% of the volume of ethanol.

Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). Nitrogen and phosphorous mineral salts were
25 added to the alcohol-free pentose-containing distillery dreg, and aerobic cultivation of the yeast *Candida tropicalis* was carried out. As a result of the cultivation a yeast suspension having a biomass concentration of 6 g/l was obtained. The yeast was separated from the culture liquid by filtration, washed with water and dried. The yield of the yeast biomass in terms of the consumed wood was 48 g/kg. The obtained yeast biomass was
30 used for the acid hydrolysis of the wood.

Carbon dioxide obtained in the biosynthesis of alcohols was mixed with oxygen and directed to a gas generator. Granulated lignin obtained in the hydrolysis of wood was supplied to the same gas generator simultaneously with the source gas. During the

granulation lignin was added with resin, obtained in the pyrolysis of wood, colophony, and wastes obtained in the processing of turpentine, tall oil, fusel and vegetable oils. The process of carbon oxide production was carried out at a temperature of 1000-1500°C.

5

Carbon oxide thus obtained from the biological raw material was mixed with hydrogen obtained by electrolysis of water. This gas mixture was then used for synthesis of higher alcohols based on the reaction of hydroformylation, and also for producing hydrocarbons and oxygen-containing compounds by the Fisher-Tropsch method.

10

Obtaining of hydrocarbons by the Fisher-Tropsch method was carried out as follows. Synthesis gas obtained by the inventive method with a ratio of components $\text{CO}:\text{H}_2=1:0.75$ at a temperature of 190-230°C and a pressure of 2-2.5 MPa was directed through the reactor filled with a catalyst, comprising the following: 97% Fe_3O_4 + 2.5% Al_2O_3 + 0.5% K_2O . The yield of the products per 1 m³ was the following: the liquid 140-150 g + the gas 30-40 g. The gas comprised C_1 - C_4 hydrocarbons; the liquid was boiling away in the interval 30-400°C. 40-50% of the liquid are non-oxygen-containing hydrocarbons and 50-60% of the liquid are oxygen-containing compounds, with prevailing C_6 and higher alcohols. The process can also be performed at a temperature of 180-220°C and a pressure of 2.5-3 MPa in the presence of a catalyst comprising $\text{Fe}:\text{Cu}=10:1$ promoted by oxides of aluminum, calcium, zinc, magnesium, manganese and alkali agents. These parameters of the process allow using synthesis gas obtained by the inventive method and having a ratio of the components $\text{CO}:\text{H}_2=1:1.25$. In this case the yield of the products per 1 m³ is: the liquid 160-170 g + gas 20-30 g.

25

EXAMPLE 12

Beet molasses having a saccharose concentration of 46% was diluted with water to a saccharose concentration of 18%, acidified with sulphuric acid to a pH of 5.5, and the yeast acid hydrolysate after ion-exchange was added in an amount of 120 ml/l (360 mg/l of amino nitrogen), and the yeast starter biomass *S. cerevisiae* in an amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 5.5. The speed of the fermentation was 3.6 l/g*h, the ethanol concentration at the end of the fermentation was 8.7% vol.; isopentanol and isobutanol concentrations were 1000

mg/l and 490 mg/l, respectively. The total content of C₃-C₅ alcohols was 2.2% of the volume of ethanol.

Ethanol, C₃-C₅ alcohols and other volatile components were distilled from the after-fermentation culture liquid (mash). Nitrogen and phosphorus mineral salts were added to the alcohol-free mash (distillery dreg) and aerobic cultivation of the yeast *Candida tropicalis* was carried out. As a result of the cultivation a yeast suspension having a biomass concentration of 15 g/l was obtained. The yeast was separated from the culture liquid by filtration, washed with water and treated by autolysis, and a biomass suspension with a dry substance concentration of 6% was prepared. Hydrolysis of the suspension was carried out with 4N HCl at 100°C for 12 hours. The amino nitrogen content in the obtained hydrolysate was 3100 mg/l, the ammonia nitrogen content was 420 mg/l, the amount of hydrolysate 240 ml/l of the medium. The obtained acid hydrolysate was treated by ion exchange on a cationic exchanger to extract ammonia nitrogen. The obtained mixture of amino acids free of asparagine and ammonia nitrogen was used in the preparation of the source medium for fermentation of the molasses substrate.

The wastes obtained in the acid hydrolysis of the biomass, extracted after cultivation of the yeast, are mixed with a surplus of amino acids left after preparation of the source medium for fermentation of the molasses substrate, diluted with cultural liquid to the concentration 50 g/l, and directed to the methane tank, containing methane-producing bacteria *Methanobacterium thermoautotrophicum*, for producing methane. Production of methane in the form of biogas was carried out under strict anaerobe conditions. The productivity of the methane tank was 1 l of methane per 2 l of nutritious medium per 24 hours. Biogas thus obtained was used as a base for producing synthesis-gas

EXAMPLE 13

Crushed wheat grain was mixed with water in the ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using In the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch) and In the second stage glucoamylase Glucozym L-400C (pH 5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have

been used. As a result of the enzymatic hydrolysis the carbohydrate concentration in the substrate reached 16%. To the substrate were then added superphosphate in an amount providing a P_2O_5 content of 200 mg/l, amino acid leucine in the amount of 2000 mg/l and amino acid valine in the amount 1500 mg/l (amino nitrogen content of 390 mg/l). The yeast starter biomass *S. cerevisiae* was added to the substrate in an amount of 5 g/l. The fermentation was carried out at a temperature of 38°C and pH=6.0. The speed of fermentation was 3.5 l/g*h, ethanol concentration at the end of the fermentation was 8.8% vol., isopentanol concentration 1250 mg/l, and isobutanol concentration 910 mg/l. Total content of C_4 - C_5 alcohols was 2.95% of the volume of ethanol. Ethanol, C_3 - C_5 alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash).

Carbon dioxide obtained in the biosynthesis of alcohols was mixed with methane obtained in biosynthesis and water steam, and directed to the reactor for producing synthesis gas. Conversion of the source mixture was carried out in the presence of a $NiO-Al_2O_3$ catalyst at 830-850°C. The gas mixture thus obtained had the following composition: CO_2 - 4.8% vol.; CO - 24.7% vol.; H_2 - 68.0% vol.; CH_4 - 2.5% vol. Then the converted gas was cooled down, compressed to 5 MPa and directed to methanol synthesis. Methanol synthesis was carried out at 5 MPa and a temperature of 230-260°C in the presence of $CuO-ZnO-Al_2O_3$ (Cr_2O_3) catalyst. Methanol obtained from carbon dioxide was then directed to the processes for production of higher hydrocarbons and oxygen-containing compounds.

In another process for obtaining synthesis gas we used, besides carbon dioxide obtained in biosynthesis, gases and resins obtained in pyrolysis of wood, wastes of furfural, turpentine, colophony, and fusel oil. The process for obtaining synthesis gas was carried out at a temperature of 800-1100°C and a pressure of 0.1-3 MPa in the presence of a Al_2O_3 supported NiO catalyst. A gas mixture of the following composition was thus obtained: CO_2 - 4.2-4.6% vol.; CO - 41.5-32.7% vol.; H_2 - 44.8-53.3% vol.; CH_4 - 5.5-5.7% vol.; N_2 - 3.3-4.7% vol. Then the converted gas was cooled down and directed to the production of hydrocarbons by the Fisher-Tropsch method. The process was carried out as follows. Synthesis gas obtained by the inventive method and having the ratio of the components $CO : H_2 = 1 : 1.1-1.7$ at 220-330°C and a pressure 2.3-2.5 MPa was directed through the reactor filled with ferrous alloy promoted by oxides (Al_2O_3 ,

K₂O, MgO) catalyst. The yield of the products per 1 m³ was 170-180 g. The obtained product was composed of olefins and paraffins, distillation range of the liquid was 30-400°C, the liquid contained 96% of non oxygen-containing hydrocarbons and 4% of the oxygen-containing compounds, 50% of which were C₄ and higher alcohols.

5

The process can also be carried out at a temperature of 170-200°C and a pressure of 0.1-1.0 MPa in the presence of cobalt-thorium-magnesium catalyst. These process parameters allow using synthesis gas obtained by the inventive method and having a ratio of the components CO:H₂=1:1.5. The yield of the products in the process is 170-175 g per 1 m³. The product obtained contained olefins and paraffins, the liquid was distilling in the interval 30-400°C, 99% of the liquid were non oxygen-containing hydrocarbons and 1% oxygen-containing compounds, 70% of which were C₁-C₁₀ alcohols.

10

For producing synthesis gas we used, besides carbon dioxide obtained in biosynthesis, natural gas comprising, mainly, methane. Conversion of the source mixture is carried out in the presence of NiO-Al₂O₃ catalyst at 830-850°C. Thus, a gas mixture similar in composition to the synthesis gas obtained in the conversion of the biologic raw material was obtained, that is: CO₂-4.5% vol.; CO-22.9% vol.; H₂-70.1% vol.; CH₄-2.4% vol.; SO₂+SO₃ - 0.1% vol. However, presence of sulphur oxides in the mixture requires additional purification of the synthesis gas before it is supplied to the catalyst. After sulphur oxides have been extracted from the gas mixture the converted gas was compressed by a compressor to 5 MPa and directed to methanol synthesis. The synthesis of methanol was carried out at a pressure of 5 MPa and a temperature of 230-260°C in the presence of CuO-ZnO-Al₂O₃ (Cr₂O₃) catalyst. Methanol obtained from biochemical carbon dioxide was then directed to the synthesis of higher hydrocarbons and oxygen-containing compounds, including also etherifying of unsaturated and saturated C₈-C₂₄ acids obtained in the saponification of fats and extracted from tall oil.

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EXAMPLE 14

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Crushed wheat grain was mixed with water in ratio 1:3.5. Enzymatic hydrolysis of the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg

of grain). Industrial enzymes produced by Ende Industries Inc., USA have been used. The concentration of carbohydrates in the substrate as a result of enzymatic hydrolysis was 16%. To the substrate were added: superphosphate in the amount providing a content of P_2O_5 of 200 mg/l, the amino acid leucine in an amount of 1000 mg/l, amino
5 acid isoleucine in an amount 1000 mg/l, and amino acid valine in the amount of 1500 mg/l (amino nitrogen content of 390 mg/l). Starter yeast biomass *S. cerevisiae* was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0.

10 The fermentation speed was 3.5 l/g*h, ethanol concentration at the end of fermentation was 8.8% by vol., isopentanol concentration 1290 mg/l, and isobutanol concentration 910 mg/l. Total content of C_4 - C_5 alcohols was 3% of the volume of ethanol.

Ethanol, C_3 - C_5 alcohols and other volatile components were distilled from after-
15 fermentation culture liquid (mash).

Ethanol was separated from C_3 - C_5 alcohols and other volatile components and dehydrated in the presence of Al_2O_3 at 300±100°C. Ethylene thus obtained was mixed with synthesis gas, originating from biogas and having a ratio $CO:H_2=1:1$ and directed to the
20 reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and the pressure at 2±1 MPa. Propionic aldehyde thus obtained in the reactor was directed to the reactor containing Ni catalyst and hydrogenated at 150±50°C and a pressure of 1-2 MPa into n-propyl alcohol by the hydrogen obtained from biomass. Besides that, propionic aldehyde can be condensed to isohexene aldehyde, with subse-
25 quent hydrogenation into isohexanol in the presence of Ni catalyst by hydrogen obtained from biomass.

Besides that ethylene was also telomerised with methanol at 150±20°C and a pressure 7±3 MPa in the presence of tertbutyl peroxide, which has been used to initialise the re-
30 action, to obtain a mixture of oxygen-containing compounds mainly comprising C_3 - C_{12} alcohols of normal structure.

EXAMPLE 15

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of grain). Industrial enzymes produced by Ende Industries Inc., USA have been used. The concentration of carbohydrates in the substrate as a result of enzymatic hydrolysis was 16%. To the substrate were added: superphosphate an amount providing a content of P_2O_5 of 200 mg/l, and amino acid hydrolysate obtained in enzymatic hydrolysis of the distillery dreg protein in the amount of 70 ml/l (360 mg/l of amino nitrogen). Starter yeast biomass *S. cerevisiae* was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0.

The speed of fermentation was 3.5 l/g*h, ethanol concentration at the end of fermentation was 8.8% by vol., isopentanol concentration 260 mg/l, and isobutanol concentration 140 mg/l. The total content of C_3 - C_5 alcohols was 0.8% of the volume of ethanol.

Ethanol, C_3 - C_5 alcohols and other volatile components were distilled from the after-fermentation culture liquid (mash).

Suspended substances of the distillery dreg, after extraction of alcohol, obtained in the fermentation of carbohydrates yielded in starch hydrolysis were condensed to a dry substance content of 5-10%. After that, enzymatic hydrolysis of proteins of the distillery dreg, after extraction of alcohol, using at the first stage endopeptidase Pepsin 2000 FIP-U/g, EC 3.4.23.1 (pH=2, 36°C; consumption 0.5 g per 1 kg of dry substance of the distillery dreg after extraction of alcohol) and at the second stage exopeptidase Aminopeptidase K EC 3.4.11 (pH=8, 36°C, consumption 0.1 g per 1 kg of dry substance of the distillery dreg after extraction of alcohol) was carried out. The amino acid hydrolysate thus obtained having a concentration of amino nitrogen of 2000-6000 mg/l was used as nitrogen nutrition of the yeast in fermenting carbohydrate substrates.

Propyl and isopropyl alcohols were separated from C_2 - C_5 alcohols and other volatile components and dehydrated with Al_2O_3 catalyst at $300 \pm 50^\circ C$. Propylene obtained in the dehydration was mixed with synthesis gas, produced from biogas and having a ratio

CO:H₂=1:1, and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and pressure at 2±1 MPa. Butyl and iso-butyl aldehydes obtained in the reactor were transferred to the reactor with Ni catalyst, where these were hydrogenated at a temperature of 150±50°C and a pressure of 1-2 MPa, using the hydrogen obtained from biomass, into butyl and isobutyl alcohols.

Furthermore, butyl aldehyde can be first condensed into isooctene aldehydes and hydrogenated with Ni-catalyst by hydrogen obtained from biomass into isooctanols.

Besides that propylene was mixed with carbon oxide, obtained from carbon dioxide obtained at the stage of alcohols biosynthesis, and water in the ratio of 1:3:2 in the presence of a complex catalyst comprising ferrous pentacarbonyl, water and triethylamine at 100±10°C and a pressure 1-2 MPa to obtain n-butyl alcohol.

EXAMPLE 16

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. The concentration of carbohydrates in the substrate as a result of enzymatic hydrolysis was 16%. To the substrate were added: superphosphate in the amount providing a content of P₂O₅ of 200 mg/l, and amino acid hydrolysate, obtained in the acid hydrolysis of the distillery dreg proteins, in the amount 70 ml/l (360 mg/l of amino nitrogen). Starter yeast biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and a pH of 6.0. The speed of fermentation was 3.5 l/g*h, concentration of ethanol at the end of fermentation was 8.8% by vol., isopentanol concentration 240 mg/l, and isobutanol concentration 140 mg/l. Total content of C₃-C₅ alcohols was 0.65% of the volume of ethanol.

Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash).

Suspended substances of the distillery dreg, after extractions of alcohol, obtained in the fermentation of carbohydrates yielded in starch hydrolysis, were condensed to a dry substance content of 5-10%. Sulphuric acid was added in an amount providing 0.2% concentration of H_2SO_4 . After that acid hydrolysis of proteins of the distillery dreg after
5 extraction of alcohol was carried out at 90°C. The amino acid hydrolysate thus obtained having a concentration of amino nitrogen of 2000-6000 mg/l was used as nitrogen nutrition of the yeast in fermentation of carbohydrate substrates.

A mixture of butyl alcohols was separated from C_2 - C_5 alcohols and other volatile components and dehydrated in the presence of an Al_2O_3 catalyst at 250±50°C. Isobutylene
10 obtained in the dehydration was mixed with synthesis gas obtained from biogas and having a ratio $CO:H_2=1:1$ and directed to the reactor with cobalt catalyst. Temperature in the reactor was kept at 160±20°C and pressure at 30±10 MPa. The mixture of amyl aldehydes thus obtained was directed to the reactor with Ni catalyst and hydrogenated
15 at 150±50°C and a pressure 1-2 MPa by hydrogen produced from biomass, to obtain a mixture of amyl alcohols.

Furthermore, amyl aldehydes can be first condensed into isodecene aldehydes, which are then hydrogenated into isodecanols in the presence of Ni catalyst using hydrogen
20 produced from biomass.

EXAMPLE 17

Crushed wheat grain was mixed with water in ratio of 1:3.5. Enzymatic hydrolysis of
25 the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the concentration of carbohydrates
30 in the substrate was 16%. To the substrate were added superphosphate in the amount providing a content of P_2O_5 of 200 mg/l, and aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg purified of ammonia and asparagines by known methods of ion exchange, in the amount 100 ml/l (400 mg/l of amino nitrogen). Starter yeast biomass *S. cerevisiae* was introduced to the substrate at a con-

centration of 5 g/l. The fermentation was carried out at a temperature of 38°C and a pH of 6.0. The speed of fermentation was 3.6 l/g*h, the concentration of ethanol at the end of fermentation was 8.7% by vol., isopentanol concentration 920 mg/l, and isobutanol concentration 480 mg/l. The total content of C₃-C₅ alcohols reached 2.3% of the ethanol volume.

Ethanol, C₃-C₅ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash).

10 Suspended substances of the distillery dreg, after extraction of alcohol, obtained in the fermentation of carbohydrates obtained in starch hydrolysis, were condensed to a dry substance content of 5-10%. After that enzymatic hydrolysis of the distillery dreg proteins was carried out using at the first stage endopeptidase Papain 30000USP-U/g, EC 3.4.22.2 (pH=5.5, 60°C; consumption 0.1 g per 1 kg of dry substance of the distillery
15 dreg after extraction of alcohol) and at the second stage exopeptidase Carboxypeptidase A EC 3.4.17.1 (pH=7.5, 30°C, consumption 0.25 g per 1 kg of dry substance of the distillery dreg after extraction of alcohol) was carried out; the amino acid hydrolysate thus obtained having a concentration of amino nitrogen 2000-6000 mg/l was treated by ion exchange to extract ammonia nitrogen and asparagines; after that the mixture of amino
20 acids free of asparagines and ammonia nitrogen was used as nitrogen nutrition of the yeast in fermentation of carbohydrate substrates.

The mixture of amyl alcohols was separated from C₂-C₅ alcohols and other volatile components and dehydrated at a temperature of 250±50°C in the presence of Al₂O₃
25 catalyst. The mixture of pentenes obtained in dehydration was mixed with synthesis gas obtained from biogas and having a ratio of CO:H₂=1:1 and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and the pressure at 2±1 MPa. Hexyl aldehydes thus obtained in the reactor were directed to the reactor with Ni catalyst and hydrogenated at 150±50°C and a pressure 1-2 MPa,
30 using hydrogen produced from biomass, to obtain a mixture of hexyl alcohols.

Besides that, hexyl aldehydes can be first condensed into isododecene aldehydes, with the subsequent hydrogenation into isododecanols in the presence of Ni catalyst using hydrogen produced from biomass.

EXAMPLE 18

Sugar cane molasses with a saccharose concentration of 46% was diluted with water to a saccharose concentration of 18%, acidified by sulphuric acid to pH 5.5, with subsequent addition of aminoacid hydrolysate, obtained in acid hydrolysis of protein of the distillery dreg free of alcohol, purified of ammonium and asparagines by the known methods of ion exchange, in the amount 90 ml/l (370 mg/l of amino nitrogen) and yeast starter biomass *S. cerevisiae* in the amount of 5 g/l. The fermentation was carried out at 38°C and pH 5.5. The speed of fermentation was 4.0 l/g*h, C₂-C₅ alcohols concentration at the end of fermentation was 8.95% vol., including 0.2% vol. of C₃-C₅ alcohols, which amounts to 2.2% of the volume of ethanol.

C₂-C₅ alcohols were distilled off from the after-fermentation culture liquid (mash).

Suspended substances of the distillery dreg free of alcohol, obtained in the fermentation of carbohydrates obtained in starch hydrolysis, were condensed to a dry substance content of 5-10%. Hydrochloric acid was added in an amount providing a HCl concentration of 0.5%. Acid hydrolysis of protein of the distillery dreg, after extraction of alcohol, was carried out at 40°C; the amino acid hydrolysate thus obtained having a concentration of amino nitrogen 2000-6000 mg/l was treated by ion exchange to extract ammonia nitrogen and asparagine; after that the mixture of amino acids free of asparagine and ammonia nitrogen was used as nitrogen nutrition of the yeast in fermentation of carbohydrate substrates.

The mixture of C₂-C₅ alcohols obtained in the fermentation of molasses is dehydrated in the presence of Al₂O₃ catalyst at 300±100°C.

The mixture of unsaturated C₂-C₅ hydrocarbons obtained in dehydration was mixed with synthesis gas obtained from biogas and having a ratio CO:H₂=1:1 and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and pressure at 2±1 MPa. A mixture of C₃-C₆ aldehydes was obtained in the reaction of hydroformylation. Propionic aldehyde was then extracted from the mixture of C₃-C₆ aldehydes and hydrogenated at 150±50°C and a pressure 1-2 MPa into n-propanol in the presence of Ni catalyst by the hydrogen of the renewable origin. Propa-

nol is returned to the stage of C₂-C₅ alcohols dehydration. C₄-C₆ aldehydes mixture was first condensed to the mixture of unsaturated C₈-C₁₂ aldehydes, which was then hydrogenated in the presence of Ni catalyst into the mixture of saturated C₈-C₁₂ alcohols by the hydrogen obtained from the renewable raw material. C₈ alcohols are extracted from the mixture of C₈-C₁₂ alcohols and dehydrated at 250±50°C in the presence of Al₂O₃ into isooctane, which is followed by hydrogenation into a mixture of isooctane by the hydrogen obtained from the renewable raw material.

Besides that, the total of C₃-C₆ aldehydes mixture, obtained in the reaction of hydroformylation, can be first condensed into a mixture of unsaturated C₆-C₁₂ aldehydes, which are then hydrogenated with Ni catalyst by the hydrogen of the renewable origin into the mixture of saturated C₆-C₁₂ alcohols of iso-structure.

Saturated C₆-C₁₂ alcohols can then be dehydrated with Al₂O₃ at a temperature of 250±50°C into a mixture of unsaturated C₆-C₁₂ hydrocarbons. The unsaturated C₆-C₁₂ hydrocarbons obtained in dehydration with Ni catalyst by H₂ of renewable origin are hydrogenated into a mixture of saturated C₆-C₁₂ hydrocarbons of iso-structure.

Moreover, in the presence of a catalyst (metal halogenides) at 20-100°C or at 200±50°C without catalyst saturated C₆-C₁₂ hydrocarbons can be condensed with C₁-C₃ aldehydes into a mixture of unsaturated C₇-C₁₅ alcohols, which alcohols are then hydrogenated in the presence of Ni catalyst by the renewable hydrogen into a mixture of saturated C₆-C₁₂ alcohols of iso-structure.

EXAMPLE 19

Beet molasses with a saccharose concentration of 46% was diluted with water to a saccharose concentration of 18%, acidified by sulphuric acid to pH 5.5, and then the alcohol yeast autolysate was added in an amount of 50 ml/l (350 mg/l of amino nitrogen) and the yeast starter biomass *S. cerevisiae* in the amount of 5 g/l. The fermentation was carried out at 38°C and pH 5.5. The speed of fermentation was 4.0 l/g*h, C₂-C₅ alcohols concentration at the end of fermentation was 8.85% vol., including 0.1% of C₃-C₅ alcohols, that is 1.1% of the volume of ethanol.

C₂-C₅ alcohols were distilled from the after-fermentation culture liquid (mash). C₂-C₅ alcohols mixture obtained in the molasses fermentation was dehydrated with Al₂O₃ catalyst at 300±100°C.

5 The mixture of unsaturated C₂-C₅ hydrocarbons obtained in dehydration was mixed with synthesis gas obtained from biogas and having a ratio CO:H₂=1:1 and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and the pressure at 2±1 MPa. In the reaction of hydroformylation a mixture of C₃-C₆ aldehydes was obtained. Propionic aldehyde is extracted from the mixture of C₃-
10 C₆ aldehydes and hydrogenated at 150±50°C and a pressure 1-2 MPa into propanol in the presence of Ni catalyst by H₂ of renewable origin. Propanol is returned to the stage of C₂-C₅ alcohols dehydration. N-butyl aldehyde is extracted from said aldehydes mixture and condensed to 2-ethyl hexynal, which is then hydrogenated with Ni catalyst by the hydrogen of renewable origin into 2-ethylhexanol.

15 Besides that, C₅ aldehydes of iso-structure can be extracted from the mixture of C₄-C₆ aldehydes and converted into the corresponding amylenes, which in interaction with methanol form isoamylmethyl esters. The remaining mixture of C₄-C₆ aldehydes is condensed into unsaturated C₈-C₁₂ aldehydes of iso-structure, which are then hydrogen-
20 ated in the presence of Ni catalyst by the hydrogen of renewable origin into a mixture of C₈-C₁₂ alcohols. Thus obtained C₈-C₁₂ alcohols can be dehydrated with Al₂O₃ and then hydrogenated in the presence of Ni catalyst at 250±50°C by hydrogen of renewable origin into the corresponding saturated C₈-C₁₂ hydrocarbons of iso-structure.

25 EXAMPLE 20

Crushed wheat grain was mixed in a ratio of 1:10 by weight with water heated up to 80°C and kept at this temperature for 10 minutes, after which the temperature was elevated to 100°C and the mixture was let to stand for another 30 minutes. The sub-
30 strate thus prepared was directed for sterilization in autoclave at 150°C during 60 minutes, after which the substrate is cooled down to 37°C. As a result of the overcooking of the flour the starch concentration in the substrate reached about 6%. To the substrate were added: the amino acid leucine in an amount of 750 mg/l and amino acid valine in the amount of 560 mg/l (amino nitrogen content of 150 mg/l). Starter

yeast biomass *Clostridium. acetobutylicum* was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at 37°C and a pH=5.5. The speed of fermentation was 3.5 l/g*h, concentration of alcohols at the end of fermentation was 1.85% by volume, including 0.22% vol. of ethanol, 0.01% vol. of isopropanol, 0.03% vol. of isobutanol, 1.54% vol. of n-butanol, 0.05% vol. of isopentanol, and concentration of acetone at the end of fermentation was 0.9% vol.

The mixture of C₂-C₅ alcohols and acetone obtained in the starch fermentation was, after separation of acetone, dehydrated with Al₂O₃ catalyst at 300±100°C. The mixture of unsaturated C₂-C₅ hydrocarbons obtained in dehydration was mixed with synthesis gas, originating from biogas and having a ratio of CO:H₂=1:1, and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and the pressure at 2±1 MPa.

A mixture of C₃-C₆ aldehydes is obtained in the reaction of hydroformylation. The mixture of C₃-C₆ aldehydes with added acetone is hydrogenated at 150±50°C and a pressure 5±1 MPa with Ni-catalyst by the hydrogen obtained in fermentation into the mixture of corresponding C₃-C₆ alcohols. C₃-C₄ alcohols are extracted from the said mixture and returned to the dehydration stage.

The remaining C₅-C₆ alcohols, having iso-structure, are dehydrated into the corresponding unsaturated hydrocarbons and, after interaction with methanol, are converted into isoamylmethyl and isoamylcaprylmethyl ethers. Wherein methanol used in the process is obtained from the carbon dioxide obtained at the stage OF fermentation and biogas obtained in processing of the fermentation waste.

The remaining C₅-C₆ alcohols of normal structure were dehydrated into the corresponding C₁₀-C₁₂ ethers.

EXAMPLE 21

Crushed corn grain was mixed with water warmed up to 80°C in ratio of 1:10 by weight and kept at this temperature for 10 minutes, after which the temperature was elevated to 100°C and the mixture was let to stand for 30 minutes. The substrate thus prepared

is directed for sterilization in autoclave at 150°C for 60 minutes, after which the substrate is cooled down to 38°C. As a result of the overcooking of the flour the starch concentration in the substrate reached about 6%. To the substrate were added acid hydrolysate of the yeast, after extraction of ammonia by known methods of ion exchange, in the amount 120 ml/l (360 mg/l of amino nitrogen). Starter yeast biomass *Clostridium butylicum* and *Clostridium acetobutylicum* (1:4) was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at 37°C and a pH=5.5. The speed of fermentation was 4.0 l/g*h, concentration of alcohols at the end of fermentation was 2.0% by volume, including 0.22% by volume of ethanol, 0.15% by volume of isopropanol, 0.02% by volume of isobutanol, 1.58% by volume of n-butanol, 0.03% by volume of isopentanol, and concentration of acetone at the end of fermentation was 0.95% by volume.

The mixture of C₂-C₅ alcohols and acetone obtained in the starch fermentation is, after separation of acetone, dehydrated with Al₂O₃ catalyst at 300±100°C. The mixture of unsaturated C₂-C₅ hydrocarbons obtained in dehydration is mixed with synthesis gas, originating from biogas and having a ratio of CO:H₂=1:1, and directed to the reactor with cobalt catalyst modified by the phosphorus compounds. The temperature in the reactor is kept at 175±25°C and a pressure 7.5±2.5 MPa.

In the reaction of hydroformylation a mixture of C₃-C₆ aldehydes is obtained. C₄ and C₅ aldehydes of normal structure are separated from said mixture. The remaining C₃-C₆ aldehydes with added acetone are hydrogenated at 150±50°C and a pressure of 5±1 MPa in the presence of Ni-catalyst by the hydrogen obtained in the fermentation into the mixture of the corresponding C₃-C₆ alcohols. C₅-C₆ alcohols are extracted from said mixture; these are alcohols of iso structure.

These alcohols are dehydrated into the corresponding unsaturated hydrocarbons and, after interaction with methanol, are converted into isoamylmethyl and isoamylcaprylmethyl ethers. The methanol used in the process is obtained from the carbon dioxide obtained at the stage of fermentation and biogas is obtained in processing of the fermentation waste.

C₄-C₅ aldehydes of normal structure are condensed into unsaturated C₈-C₁₀ aldehydes, which are then hydrogenated at 150±50°C and a pressure of 1-2 MPa in the presence of Ni catalyst by hydrogen obtained in the fermentation into saturated C₈-C₁₀ alcohols.

5 EXAMPLE 22

Crushed wheat grain was mixed with water in ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch), and in the
10 second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the concentration of carbohydrates in the substrate was 16%. Superphosphate was added to the substrate in an amount providing a content of P₂O₅ of 200 mg/l, the amino acid leucine in an amount of 2000
15 mg/l and amino acid valine in an amount of 1500 mg/l (amino nitrogen content of 390 mg/l). Starter yeast biomass *S. cerevisiae* was introduced to the substrate at a concentration of 5 g/l. The fermentation was carried out at 38°C and a pH of 6.0. The speed of fermentation was 3.5 l/g*h, the concentration of ethanol at the end of fermentation was 8.8% by vol., isopentanol concentration 1250 mg/l, and isobutanol concentration 910
20 mg/l, the total content of C₄-C₅ alcohols was 2.95% of the volume of ethanol.

C₂-C₅ alcohols were distilled from the after-fermentation culture liquid (mash). The mixture of C₂-C₅ alcohols, obtained in the starch fermentation, was oxidized in the presence of silver catalyst at a temperature of 450-550°C by a mixture of oxygen and carbon dioxide, obtained in the biosynthesis of C₂-C₅ alcohols, to obtain a mixture of C₂-C₅
25 aldehydes. The C₂-C₅ aldehydes obtained in the oxidation were condensed into unsaturated C₄-C₁₅ aldehydes, which were hydrogenated in the presence of copper catalyst into a mixture of saturated C₄-C₁₅ aldehydes. The C₄-C₅ aldehydes were extracted from said mixture and returned to the condensation stage, and C₆-C₁₅ aldehydes were used
30 for the extraction of individual aldehydes or hydrogenated in the presence of Ni-catalyst into a mixture of saturated C₆-C₁₅ alcohols. The latter can by means of dehydration and hydrogenation be converted into the mixture of saturated hydrocarbons. Besides that, both saturated and unsaturated C₆-C₁₅ aldehydes can be oxidized into the corresponding acids. For oxidation of aldehydes into fatty acids we used carbon dioxide from the

process of biosynthesis. Oxidation of aldehydes into fatty acids was carried out in the presence of manganese acetate catalyst in the liquid phase and at 50-150°C and a pressure 0.05 MPa or in a gas phase at 150-250°C and a pressure 0.5 MPa. In contrast to the known methods, to the oxidation has been supplied heated to 50-150°C steam-gas mixture of aldehydes and carbon dioxide. Utilisation of said mixture gives a possibility to use for the oxidation oxygen or a mixture of oxygen with carbon dioxide.

EXAMPLE 23

Chopped spruce wood (cellulose-containing plant material) was treated by acid hydrolysis at 180°C, a sulphuric acid concentration of 0.5%, a ratio of water to wood of 12:1, during 1.5 hours. The wood hydrolysate was neutralized with lime to a pH=4.5, and separated from lignin and gypsum residues. To the carbohydrate substrate thus obtained, having a hexose sugar concentration of 3.2% and pentose sugar concentration of 0.8%, superphosphate was added in an amount of P_2O_5 of 120 mg/l, the yeast autolysate, previously purified of ammonia and asparagines by known methods of ion exchange, in an amount of 45 ml/l of substrate (135 mg/l of amino nitrogen), and 5 g/l of the starter yeast biomass *S. cerevisiae*. The fermentation was carried out at 38°C and pH=6. Fermentation speed was 4.0 l/g*h, ethanol concentration at the end of the fermentation was 1.5% vol., concentration of isopentanol was 210 mg/l, concentration of isobutanol was 130 mg/l, and total content of C_3 - C_5 alcohols was 2.95% of the volume of ethanol.

C_2 - C_5 alcohols were distilled off from the after-fermentation culture liquid (mash). The mixture of C_2 - C_5 alcohols obtained in the fermentation of hexose sugars was oxidized at 450-550°C in the presence of a silver catalyst by the mixture of oxygen and carbon dioxide, obtained in the biosynthesis of C_2 - C_5 alcohols, to obtain a mixture of C_2 - C_5 aldehydes. The C_2 - C_5 aldehydes obtained in oxidation are condensed in the presence of a 0.5% solution of sodium hydroxide at 0°C with furfural. The obtained mixture of unsaturated aldehydes is then hydrogenated in the presence of copper chrome catalyst at 100±50°C and a pressure of 0.1-5 MPa into a mixture of furyl-containing alcohols. The latter are subsequently hydrogenated at a temperature of 100±50° and a pressure of 5-10 MPa in the presence of nickel catalyst into a mixture of saturated alcohols containing tetrahydrofurane cycles.

EXAMPLE 24

Chopped potatoes were mixed with water in a ratio of 1:1. Enzymatic hydrolysis of the potatoe starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH 6.5, 90°C, consumption 0.25 ml per 1 kg of the potatoes starch), and in the second stage glycoamylase Glucozym L-400C (pH 5.0, 60°C, consumption 0.8 ml per 1 kg of the potatoes starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the concentration of carbohydrates in the substrate reached 8.0%. To the substrate were added: superphosphate in the amount providing a content of $P_2O_5=200$ mg/l, the amino acid leucine in the amount of 1000 mg/l, and amino acid valine in the amount of 750 mg/l (amino nitrogen content of 195 mg/l). Starter yeast biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 4.0 l/g*h, ethanol concentration at the end of fermentation was 4.3% by vol., isopenthanols concentration 630 mg/l, and isobutanol concentration 460 mg/l. Total content of C_4 - C_5 alcohols was 3.0% of the volume of ethanol.

C_2 - C_5 alcohols were distilled off from the after-fermentation culture liquid (mash). The mixture of C_2 - C_5 alcohols obtained in the fermentation was dehydrated at $300\pm 100^\circ\text{C}$ in the presence of Al_2O_3 catalyst. The mixture of unsaturated C_2 - C_5 hydrocarbons obtained in the dehydration is mixed with synthesis gas, originating from biogas and having a ratio $CO:H_2=1:1$, and then directed to the reactor containing cobalt catalyst modified by phosphorous compounds. Temperature in the reactor is $175\pm 25^\circ\text{C}$ and a pressure of 7.5 ± 2.5 MPa. As a result of the reaction of hydroformylation a mixture of C_3 - C_6 aldehydes is obtained. The mixture of C_3 - C_6 aldehydes is hydrogenated in the presence of Ni catalyst by the hydrogen produced from the renewable raw material into the mixture of C_3 - C_6 alcohols, which are then returned back to the stage of dehydration.

The process is repeated until C_8 aldehydes appear in the mixture of aldehydes. After C_8 aldehydes appear in the mixture of aldehydes the process can be carried out in two routes. In the first route C_8 aldehydes are extracted and condensed into unsaturated C_{16} aldehydes and then hydrogenated to saturated C_{16} alcohols, which, if it is needed,

are further processed into saturated C_{16} hydrocarbons. In the second route the extracted C_8 aldehydes can be directly hydrogenated in the presence of Ni catalyst by renewable hydrogen into a mixture of C_8 alcohols, which are then converted into the mixture of C_8 hydrocarbons.

5

EXAMPLE 25

Chopped potatoes were mixed with water in a ratio of 1:1. Enzymatic hydrolysis of the potatoe starch was accomplished using in the first stage thermostable amylase Zymajunt-340C (pH=6.5, 90°C, consumption 0.25 ml per 1 kg of the potatoes starch), and in
10 the second stage glycoamylase Glucozym L-400C (pH=5.0, 60°C, consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis the concentration of carbohydrates in the substrate reached 8.0%. To the substrate were added: superphosphate in an amount providing a content of P_2O_5 =200 mg/l, and acid hydrolysate of the
15 yeast, treated by ion exchange for removal of asparagine and ammonium salts, in the amount 130 ml/l (390 mg/l of amino nitrogen). Starter yeast biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and a pH=6.0. The speed of fermentation was 4.0 l/g*h, ethanol concentration at
20 the end of fermentation was 4.4% by vol., isopentanol concentration 560 mg/l, and isobutanol concentration 340 mg/l. The total content of C_3 - C_5 alcohols reached 2.65% of the volume of ethanol.

C_2 - C_5 alcohols were distilled off from the after-fermentation culture liquid (mash). The
25 mixture of C_2 - C_5 alcohols obtained in the fermentation was dehydrated at $300\pm 100^\circ\text{C}$ in the presence of Al_2O_3 catalyst. The mixture of unsaturated C_2 - C_5 hydrocarbons obtained in the dehydration was mixed with synthesis gas, originating from biogas and having a ratio $CO:H_2=1:1$, and directed to the reactor containing cobalt catalyst modified by phosphorous compounds. The temperature in the reactor was $175\pm 25^\circ\text{C}$ and
30 the pressure 7.5 ± 2.5 MPa. As a result of the reaction of hydroformylation a mixture of C_3 - C_6 aldehydes was obtained. The mixture of C_3 - C_6 aldehydes was hydrogenated in the presence of Ni catalyst by renewable hydrogen into a mixture of C_3 - C_6 alcohols, which were then returned back to the stage of dehydration.

The process was repeated until C₈ aldehydes appear in the mixture of aldehydes. After that C₈ aldehydes were condensed into unsaturated C₁₆ aldehydes and then hydrogenated into saturated C₁₆ alcohols. The latter were oxidized at 200-300°C in the presence of silver catalyst by the mixture of oxygen and carbon dioxide, obtained in biosynthesis of C₂-C₅ alcohols, to obtain a mixture of unsaturated C₁₆ acids. The obtained mixture of unsaturated C₁₆ acids was etherified by methanol in the presence of acid catalyst into a mixture of methyl esters of unsaturated C₁₆ acids. The methyl esters of unsaturated C₁₆ acids were subsequently hydrogenated at a temperature of 125-200°C by renewable hydrogen in the presence of Ni or Cu catalyst into a mixture of methyl esters of saturated C₁₆ acids.

EXAMPLE 26

Beet molasses with a saccharose concentration of 46% was diluted by water to a saccharose concentration of 18% and acidified by sulphuric acid to pH=5.5. Then, the following were added: the acid yeast hydrolysate, which had been freed from asparagine and ammonium salts by ion exchange, in the amount 120 ml/l (360 mg/l of amino nitrogen), and yeast starter biomass *S. cerevisiae* in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=5.5. The speed of fermentation was 3.6 l/g*h, the concentration of ethanol at the end of fermentation was 8.7% vol., concentration of isopentanol 1000 mg/l, isobutanol 490 mg/l, and total content of C₃-C₅ alcohols reached 2.2% of the volume of ethanol.

C₂-C₅ alcohols were distilled off from the after-fermentation culture liquid (mash). The C₂-C₅ alcohols mixture obtained in the molasses fermentation was dehydrated with Al₂O₃ catalyst at 300±100°C.

The mixture of unsaturated C₂-C₅ hydrocarbons obtained on dehydration was mixed with synthesis gas obtained from biogas and having a ratio CO:H₂=1:1 and directed to the reactor with cobalt-rhodium catalyst. The temperature in the reactor was kept at 90±10°C and the pressure at 2±1 MPa. As a result of the reaction of hydroformylation a mixture of C₃-C₆ aldehydes was obtained. Propionic aldehyde was extracted from the mixture of C₃-C₆ aldehydes and hydrogenated into propanol in the presence of Ni catalyst by hydrogen of renewable origin. Propanol is then returned to the stage of C₂-C₅

alcohols dehydration. The mixture of C₄-C₆ aldehydes is first condensed into a mixture of unsaturated C₈-C₁₂ aldehydes, which is then hydrogenated by renewable hydrogen in the presence of Ni catalyst into a mixture of saturated C₈-C₁₂ alcohols. C₈ alcohols are extracted from the mixture of C₈-C₁₂ alcohols and then dehydrated in the presence of Al₂O₃ at a temperature of 200±25° into isooctanes, which are then hydrogenated by renewable hydrogen in the presence of Ni catalyst into a mixture of isooctanes.

Moreover, the whole mixture of C₃-C₆ aldehydes obtained in the reaction of hydroformylation is first condensed into a mixture of unsaturated C₆-C₁₂ aldehydes, which are then hydrogenated by renewable hydrogen in the presence of Ni catalyst into a mixture of saturated C₆-C₁₂ alcohols of iso-structure. Saturated C₆-C₁₂ alcohols are then dehydrated in the presence of Al₂O₃ at 250±50°C into a mixture of unsaturated C₆-C₁₂ hydrocarbons. Unsaturated C₆-C₁₂ hydrocarbons, obtained in dehydration, are mixed with methanol, obtained from carbon dioxide obtained in biosynthesis of C₂-C₅ alcohols, and processed at 200±100°C and a pressure of 0.1±10 kPa by carbon oxide, obtained from carbon dioxide obtained in biosynthesis of C₂-C₅ alcohols, in the presence of ferrous, nickel, cobalt, or rhodium carbonyls promoted by halogen derivatives. Thus, C₆-C₁₂ methyl esters of saturated acids are obtained.

EXAMPLE 27

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5, 90°C, consumption 0.25 ml per 1 kg of the grain starch) and in the second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the concentration of carbohydrates in the substrate reached 16%. To the substrate were added sodium hydrogensulphite in an amount providing 3-4% content of NaHSO₃, superphosphate in an amount providing a P₂O₅ content of 200 mg/l, amino acid leucine in an amount of 2000 mg/l, and amino acid valine in the amount of 1500 mg/l (amino nitrogen content of 390 mg/l). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 3.5 l/g*h, glycerine concentration at the end of fermentation was 3.0% vol.,

ethanol concentration 4.4% vol., acetaldehyde concentration 2.2% vol., isopentanol concentration 0.15% vol., and isobutanol concentration 0.11% vol.

5 C₂-C₅ alcohols were distilled off from the after-fermentation culture liquid (mash). These alcohols can be processed into higher hydrocarbons as described in the foregoing examples. Glycerine and acetaldehyde were subsequently extracted from the after-fermentation culture liquid (mash) and acetalised at 0-50°C and a pressure 0.1-0.5MPa in the presence of hydrochloric acid or zinc chloride as a catalyst, to obtain 1,2-glycerineacetal acetaldehyde (2-methyl-4-oxymethyl-1,3-dioxane). 1,2-glycerineacetal
10 acetaldehyde can be used as a component for motor fuels.

EXAMPLE 28

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of
15 the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C; consumption 0.25 ml per 1 kg of the grain starch) and in the second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in
20 the substrate reached 16%. To the substrate were added sodium hydrogensulphite in an amount providing 3-4% content of NaHSO₃, superphosphate in an amount providing a P₂O₅ content of 200 mg/l, and aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg free of alcohol, which had previously been purified of ammonia and asparagines by known methods of ion exchange, in an amount of
25 100 ml/l (400 mg/l of amino nitrogen). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 3.5 l/g*h, glycerine concentration at the end of fermentation was 3.1% vol., the ethanol concentration 4.5% vol., acetaldehyde concentration 2.4% vol., isopentanol concentration 0.12% vol., and the isobu-
30 tanol concentration 0.06% vol.

C₂-C₅ alcohols were distilled off and acetaldehyde was extracted from the after-fermentation culture liquid (mash). After that glycerine was extracted from the after-fermentation culture liquid (mash) and mixed with vegetable and/or animal fats. This

mixture was hydrogenated in the presence of copper-chrome, zinc-chrome, nickel-chrome catalysts at $300\pm 100^{\circ}\text{C}$ and a pressure of 10-30 MPa into a mixture of n-propyl alcohol, higher $\text{C}_6\text{-C}_{20}$ alcohols and C_6 and higher hydrocarbons. The hydrogenation was carried out using hydrogen obtained from biomass and/or by biochemical method in the fermentation of carbohydrate substrates and/or from the water obtained in the processing of alcohols yielded in biosynthesis. Conversion of the water was carried out by the known methods. The mixture of glycerine and vegetable and/or animal fats can be also hydrogenated in the presence of catalysts containing precious metals, for example Pt, Pd, Re, Ru, Rh at $200\pm 50^{\circ}\text{C}$ and a pressure of 5-20 MPa.

EXAMPLE 29

Crushed wheat grain was mixed with water in a ratio of 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C ; consumption 0.25 ml per 1 kg of the grain starch) and in the second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C ; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in the substrate reached 16%. To the substrate were added sodium hydrogensulphite in the amount providing 3-4% content of NaHSO_3 , superphosphate in the amount providing P_2O_5 content of 200 mg/l, and aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg free of alcohol, and purified of ammonia and asparagines by known methods of ion exchange, in the amount of 90 ml/l (370 mg/l of amino nitrogen). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was $3.5 \text{ l/g}\cdot\text{h}$, the glycerine concentration at the end of fermentation was 3.2% vol., ethanol concentration 4.3% vol., acetaldehyde concentration 2.4% vol., and concentration of $\text{C}_3\text{-C}_5$ alcohols 0.2% vol.

$\text{C}_2\text{-C}_5$ alcohols were distilled off and acetaldehyde was extracted from the after-fermentation culture liquid (mash). After that glycerine was extracted from the after-fermentation culture liquid (mash) and mixed with glycerine obtained in the saponification of fats; the mixture obtained was dehydrated in the presence of Al_2O_3 catalyst at $350\pm 50^{\circ}\text{C}$. Acrolein obtained in dehydration of glycerine was directed to a reactor con-

taining Ni catalyst and hydrogenated at $100\pm 10^{\circ}\text{C}$ and a pressure of 1-2 MPa into n-propyl alcohol using hydrogen obtained from biomass and/or obtained in the fermentation of carbohydrate substrates and/or obtained from the water, obtained in the processing of alcohols obtained in biosynthesis. Conversion of the water was carried out by known methods.

N-propyl alcohol thus obtained was brought together with $\text{C}_2\text{-C}_5$ alcohols obtained in biosynthesis; the mixture of lower $\text{C}_2\text{-C}_5$ alcohols thus obtained was condensed to obtain a mixture of $\text{C}_4\text{-C}_{15}$ alcohols, $\text{C}_2\text{-C}_5$ fatty acids, and $\text{C}_4\text{-C}_{10}$ esters. The process of condensation of the lower $\text{C}_2\text{-C}_5$ alcohols was carried out at $150\pm 50^{\circ}\text{C}$ and a pressure of 0.1-0.5 MPa in the presence of sodium alcoholates and $\text{Ni-Cr}_2\text{O}_3$ as a catalyst. Sodium alcoholates for this reaction were prepared from sodium hydroxide directly in the process of condensation. To increase the yield of the products of condensation the water obtained in the reaction was extracted in the form of an azeotrope mixture with non-condensed alcohols. $\text{C}_2\text{-C}_5$ fatty acids were separated from $\text{C}_4\text{-C}_{15}$ alcohols and $\text{C}_4\text{-C}_{10}$ esters and etherified in the presence of acid catalyst by the mixture of terpenes into a mixture of terpene esters of fatty $\text{C}_2\text{-C}_5$ acids. Non-condensed $\text{C}_2\text{-C}_5$ alcohols were dehydrated in the presence of Al_2O_3 catalyst at $300\pm 50^{\circ}\text{C}$ and mixed with terpenes, which terpenes previously had been heated to $200\pm 50^{\circ}\text{C}$ in the presence of platinum. As a result of alkylation, which was carried out at a temperature of $0\text{-}10^{\circ}\text{C}$ and a pressure of 0.5-1 MPa using as a catalyst 90-100% sulphuric acid, a mixture of $\text{C}_{12}\text{-C}_{15}$ hydrocarbons is obtained. The process of alkylation can also be carried out in the presence of AlCl_3 catalyst at $50\text{-}60^{\circ}\text{C}$ and a pressure of 1-2 MPa. Terpene esters and higher hydrocarbons obtained from terpenes, lower $\text{C}_2\text{-C}_5$ alcohols and $\text{C}_2\text{-C}_5$ fatty acids were then used as components for motor fuels.

EXAMPLE 30

Crushed wheat grain was mixed with water in the ratio 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C ; consumption 0.25 ml per 1 kg of the grain starch) and in the second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C ; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in

the substrate reached 16%. To the substrate were added sodium hydroorthophosphate in an amount providing a 4% content of Na_2HPO_4 , amino acid leucine in an amount of 2000 mg/l, and amino acid valine in an amount of 1500 mg/l. The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 3.5 l/g*h, the glycerine concentration at the end of fermentation was 4.5% vol., ethanol concentration 4.1% vol., acetic acid concentration 4.0% vol., isopenthanols concentration 0.15% vol., and isobutanol concentration 0.11% vol..

From the after-fermentation culture liquid (mash) $\text{C}_2\text{-C}_5$ alcohols were first distilled off and acetic acid extracted, which can be further processed into higher hydrocarbons as described in the foregoing examples. After that, glycerine was extracted from the after-fermentation culture liquid (mash) and dehydrated in the presence of Al_2O_3 catalyst at 350±50°C.

Acrolein obtained in the dehydration of glycerine was directed to the reactor containing $\text{CuO-Cr}_2\text{O}_3$ catalyst and hydrogenated at 175±25°C and a pressure of 1-5 MPa into a mixture of propionic aldehyde and n-propyl alcohol by hydrogen obtained from biomass and/or obtained from the water, obtained in dehydration of glycerine. Conversion of the water was carried out using known methods. Propionic aldehyde was extracted from the mixture obtained and can be further processed in two routes. The first route provides further condensing of propionic aldehyde into isohexene aldehyde with the subsequent hydrogenation in the presence of Ni catalyst at 150±10°C and a pressure of 1-5 MPa into isohexanol by hydrogen obtained from biomass and/or obtained from the water obtained in dehydration of glycerine. Conversion of the water is carried out by known methods.

The second possibility is to condense propionic aldehyde with $\text{C}_2\text{-C}_5$ alcohols, obtained in biosynthesis, into the corresponding propanals; or to condensate propionic aldehyde with n-propyl alcohol, obtained in hydrogenation of acroleine, wherein the ratio acrolein : propionic aldehyde by mole is 2:1, into dipropyl propanal. The latter is a good component for fuels for diesel and gas-turbine engines.

EXAMPLE 31

Crushed wheat grain was mixed with water in the ratio 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C; consumption 0.25 ml per 1 kg of the grain starch) and in the
5 second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in the substrate reached 16%. To the substrate were added sodium hydroorthophosphate in an amount providing 4% content of Na_2HPO_4 , and aminoacid hydrolysate, obtained
10 in acid hydrolysis of protein of the distillery dreg free of alcohol, which had been purified of ammonia and asparagine by known methods of ion exchange, in the amount of 90 ml/l (370 mg/l of amino nitrogen). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 4.0 l/g*h, the glycerine concentration
15 at the end of fermentation was 4.7% vol., ethanol concentration 4.0% vol., acetic acid concentration 4.2% vol., and the concentration of $\text{C}_3\text{-C}_5$ alcohols 0.2%.

From the after-fermentation culture liquid (mash) $\text{C}_2\text{-C}_5$ alcohols were first distilled off and acetic acid was extracted, which can be further processed into higher hydrocarbons as described in the foregoing examples. After that, glycerine was extracted from
20 the after-fermentation culture liquid (mash) and mixed with glycerine obtained in the saponification of fats. This mixture was dehydrated in the presence of Al_2O_3 catalyst at $350\pm 50^\circ\text{C}$. Acroleine obtained in dehydration of glycerine was mixed with benzene and directed to the dimerization reactor, where, at $170\pm 10^\circ\text{C}$ and a pressure 1-2 MPa, in
25 the presence of hydroquinone, the dimer of acroleine (2-formyl-3,4-dihydro-2H-pyran) was obtained. The dimer of acrolein (2-formyl-3,4-dihydro-2H-pyran) was separated from benzene and hydroquinone and hydrogenated in the presence of Ni catalyst at $150\pm 10^\circ\text{C}$ and a pressure of 5-10 MPa into tetrahydropyran-2-methanol by hydrogen
30 obtained from biomass and/or by hydrogen obtained from the water obtained in dehydration of glycerine. Conversion of the water is carried out by known methods. Tetrahydropyran-2-methanol thus obtained is a good component for motor fuels for diesel and gas-turbine engines.

EXAMPLE 32

Crushed wheat grain was mixed with water in the ratio 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C; consumption 0.25 ml per 1 kg of the grain starch) and in the
5 second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in the substrate reached 16%.

10 To the substrate were added: superphosphate in an amount providing a P_2O_5 content of 200 mg/l, and aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg free of alcohol, which had previously been purified from ammonia and asparagine by known methods of ion exchange, in the amount of 100 ml/l (400
15 mg/l of amino nitrogen). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 3.6 l/g*h, ethanol concentration at the end of fermentation was 8.7% vol., isopentanol concentration 920 mg/l, isobutanol concentration 480 mg/l, and the total content of C_3 - C_5 alcohols was 2.3% of the volume of ethanol.

20 Ethanol, C_3 - C_5 alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). C_3 - C_5 alcohols and other volatile components can be further processed into higher hydrocarbons as described in the foregoing examples. Carbon dioxide obtained in the biosynthesis of alcohols was mixed with biogas, con-
25 taining mainly methane, and with water steam and directed to the reactor for synthesis gas production. Conversion of the source mixture is carried out in the presence of NiO- Al_2O_3 catalyst at a temperature of 830-850°C. Thus, a gas mixture of the following composition is obtained: CO_2 -4.8% vol; CO-24.7% vol.; H_2 -68.0% vol.; CH_4 -2.3% vol. Converted gas is then cooled down and compressed by the compressor to 5 MPa and
30 directed to methanol synthesis. Methanol synthesis is carried out at 5 MPa and a temperature of 230-260°C in the presence of CuO-ZnO- Al_2O_3 (Cr_2O_3). Methanol obtained from carbon dioxide was mixed with ethanol obtained in biosynthesis and the thus obtained mixture was oxidized at 450-550°C in the presence of silver catalyst by the mixture of oxygen and carbon dioxide, obtained in the biosynthesis of C_2 - C_5 alcohols, to

obtain a mixture of acetaldehyde and formaldehyde. The mixture of acetaldehyde and formaldehyde was subsequently converted at 300-400°C in the presence of Al_2O_3 into acrolein. Acrolein was processed into higher hydrocarbons, including oxygen containing hydrocarbons, as described in the foregoing examples.

5

EXAMPLE 33

Crushed wheat grain was mixed with water in the ratio 1:3.5. Enzymatic hydrolysis of the grain starch was carried out using in the first stage thermostable amylase Zymajunt-340C (pH=6.5; 90°C; consumption 0.25 ml per 1 kg of the grain starch) and in the
10 second stage glucoamylase Glucozym L-400C (pH=5.0; 60°C; consumption 0.8 ml per 1 kg of the grain starch). Industrial enzymes produced by Ende Industries Inc., USA have been used. As a result of the enzymatic hydrolysis, the carbohydrates concentration in the substrate reached 16%.

15

To the substrate were added: superphosphate in an amount providing a P_2O_5 content of 200 mg/l, and aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg free of alcohol, previously purified of ammonia and asparagine by known methods of ion exchange, in the amount of 100 ml/l (400 mg/l of amino nitro-
20 gen). The yeast starter biomass *S. cerevisiae* was introduced to the substrate in the amount of 5 g/l. The fermentation was carried out at 38°C and pH=6.0. The speed of fermentation was 3.6 l/g*h, the ethanol concentration at the end of fermentation was 8.7% vol., isopentanol concentration 920 mg/l, isobutanol concentration 480 mg/l, and the total content of $\text{C}_3\text{-C}_5$ alcohols was 2.3% of the volume of ethanol.

25

Ethanol, $\text{C}_3\text{-C}_5$ alcohols and other volatile components were distilled off from the after-fermentation culture liquid (mash). Isobutyl and isoamyl alcohols were separated from the $\text{C}_2\text{-C}_5$ alcohols. The mixture of $\text{C}_2\text{-C}_5$ alcohols obtained after extraction of isobutyl and isoamyl alcohols was dehydrated in the presence of Al_2O_3 catalyst at 300±100°C,
30 while isobutyl and isoamyl alcohols were dehydrated in the presence of Al_2O_3 catalyst at 250±50°C. Isobutene and isopentene thus obtained were then hydrogenated in the presence of Ni catalyst at 150±50°C and a pressure of 1-2 MPa into isobutene and isopentane by hydrogen obtained from biomass and/or by hydrogen obtained from the water obtained in dehydration of alcohols. Conversion of the water is carried out by the

conventional methods. Isobutane and isopentane thus obtained were mixed with unsaturated C₂-C₅ hydrocarbons obtained in dehydration of the corresponding alcohols at 0-10°C and a pressure of 0.5-1 MPa in the reactor containing, as a catalyst, sulphuric acid. As a result of the synthesis a mixture of saturated C₆-C₁₀ hydrocarbons was obtained, which is a good component for gasoline fuels.

This alkylation process can also be carried out in the presence of AlCl₃ as a catalyst and a temperature of 50-60°C and a pressure of 1-2 MPa.

Moreover, unsaturated C₂-C₅ hydrocarbons obtained in dehydration of the corresponding C₂-C₅ alcohols were mixed with terpenes, which were in beforehand heated in the presence of platinum to 200±50°C. As a result of alkylation, which was carried out at 0-10°C and a pressure of 0.5-1 MPa using 90-100% sulphuric acid as a catalyst, a mixture of C₁₂-C₁₅ hydrocarbons was obtained. This process of alkylation can also be performed in the presence of AlCl₃ used as a catalyst at 50-60°C and a pressure 1-2 MPa. Higher C₁₂-C₁₅ hydrocarbons obtained from terpenes and lower C₂-C₅ alcohols were used as components of motor fuels.

Example 34

Crushed corn grain was mixed with water heated up to 80°C in ratio 1:10 by weight and was let to stand at this temperature for 10 minutes, after which the temperature was elevated to 100°C and the mixture was let to stand for another 30 minutes. The substrate thus prepared is directed for sterilization in an autoclave at 150°C for 60 minutes, after which the substrate is cooled down to 37°C. As a result of the overcooking of the flour the starch concentration in the substrate reached about 6%. To the substrate was added aminoacid hydrolysate, obtained in the enzymatic hydrolysis of protein of the distillery dreg free of alcohol, which hydrolysate had previously been purified from ammonia by known methods of ion exchange, in the amount 100 ml/l (400 mg/l of amino nitrogen). After that starter bacteria biomass *Clostridium butylicum* and *Clostridium acetobutylicum* (in a ratio of 1:4) was introduced to the substrate in the concentration of 5 g/l. The fermentation was carried out at 37°C and a pH=5.5. The speed of fermentation was 4.0 l/g*h, the concentration of alcohols at the end of fermentation was 2.05% vol., including 0.24% vol. of ethanol, 0.12% vol. of isopropanol, 0.03%

vol. of isobutanol, 1.61% vol. of n-butanol, 0.05% vol. of isopentanol, and concentration of acetone at the end of fermentation was 0.7% by volume.

5 The mixture of C₂-C₅ alcohols extracted from the culture liquid obtained in the fermentation of the grain starch can be processed into higher hydrocarbons as described in the foregoing examples. Acetone that has been distilled off from the culture liquid was treated by aldol and croton condensation to obtain a mixture of diacetone alcohol, mesityl oxide, phorone, and mesitylene. Mesityl oxide and isophorone were extracted from the mixture obtained and hydrogenated in the presence of Ni catalyst at 150±10°C and
10 a pressure of 1-5 MPa into the corresponding C₆ and C₉ alcohols.

C₆ and C₉ alcohols, thus obtained, were brought together with diacetone alcohol and mesitylene and the obtained mixture was used as a component for gasoline.

15 Moreover, acetone distilled off from the culture liquid was condensed with glycerine, obtained in biosynthesis or in the saponification of fats, to produce acetone 1,2-glycerineketal (2,2-dimethyl-4-oxymethyl 1,3-dioxane). The latter was also used as a component for motor fuels.

20 Of course, the possible embodiments of the present invention are not limited to the demonstrated examples. These examples demonstrate only some of the possible routes of the inventive embodiments of the process of biomass processing, including biosynthesis of lower alcohols, for producing higher hydrocarbons, including oxygen-containing hydrocarbons.

CLAIMS

1. A method of intensifying fermentation of carbohydrate substrates and increasing the yield of alcohols, and utilization of non-fermentable organic substances of the fermentation medium, comprising the steps of: preparation of an aqueous carbohydrate substrate with a carbohydrate concentration of 3-20% comprising a source of nitrogen;
5 fermenting the substrate to an overall concentration of 1.5-10% of the following products C₁-C₅ alcohols, glycerin, acetaldehyde, acetic acid and acetone; and separation of desired products from the fermentation medium, **characterized in** that, as the source
10 of nitrogen, the amino acids leucine, isoleucine, valine, or a mixture thereof is added to the aqueous carbohydrate substrate in an amount providing a content of amino nitrogen in carbohydrate substrate of from 120 to 420 mg/l.
2. Method of claim 1, **characterized in** that the process of fermentation is carried
15 out at a speed of 2.8-4.0 l/g per hour.
3. Method of claim 1 or 2, **characterized in** that the carbohydrate substrate used is beet or cane molasses, saccharized starch (acid or enzymatic starch hydrolysate) of different kinds of grains or potatoes.
20
4. Method of any of the previous claims, **characterized in** that the content of amino nitrogen in the medium is of from 320 to 400 mg/l, preferably 350 to 370 mg/l.
5. Method of any of the previous claims, **characterized in** comprising the further
25 steps of: condensing yeast obtained in the fermentation of carbohydrate substrate to a dry substance content of 5-10%; and autolysis of the yeast protein at 45-55°C for 24-48 hours for obtaining an autolysate exhibiting a content of amino nitrogen of 3000-8000 mg/l.
- 30 6. Method of any of the previous claims, **characterized in** the further steps of: condensing suspended substances contained in the fermentation medium after fermentation of carbohydrate substrate and separation of alcohol therefrom and to a dry substance content of 5-10%; and, either acid hydrolysis of the protein contained in said substances using sulphur or hydrochloric acids or enzymatic hydrolysis of the protein

contained in said substances using proteolytic enzymatic preparations, for obtaining an acid hydrolysate of proteins exhibiting a content of amino nitrogen of 2000-6000 mg/l.

7. Method of any of the previous claims, **characterized in** comprising the further steps of: aerobic cultivation of yeast using the water soluble substances contained in the fermentation medium after fermentation of carbohydrate substrate and separation of alcohol therefrom; condensing the yeast thus obtained to a dry substance content of 5-10%; and autolysis of the yeast protein at 45-55°C for 24-48 hours for obtaining an autolysate exhibiting a content of amino nitrogen of 3000-8000 mg/l.

8. Method of claim 1 or 2, **characterized in** that the carbohydrate substrate is an acid hydrolysate of cellulose-containing materials.

9. Method of claim 8, **characterized in** that the content of amino nitrogen in the medium is from 120 to 150 mg/l.

10. Method of claim 8 or 9, **characterized in** comprising the further steps of: aerobic cultivation of yeast with the pentose containing fermentation medium after fermentation of carbohydrate substrate and separation of alcohol therefrom; condensing the yeast thus obtained to a dry substance content of 5-10%; and autolysis of the yeast protein at 45-55°C for 24-48 hours for obtaining an autolysate of yeast protein exhibiting a content of amino nitrogen of 3000-8000 mg/l.

11. Method of any of the claims 5-7 and 10, **characterized in** that the autolysate of yeast, the acid or enzymatic hydrolysates of yeast obtained, or a combination thereof, is used as the source of nitrogen in fermentation of carbohydrate substrates.

12. Method of claim 11, **characterized in** the further step of removing asparagine and ammonia salts from the yeast autolysate, and acid or enzymatic yeast hydrolysates containing amino acids.

13. Method of any of the previous claims, **characterized in** that a mixture of alcohols is separated from the fermentation medium by means of distillation, exhibiting an ethanol content of 96.9-99.35 a content of C₃-C₅ alcohols of 0.65-3.1% by volume.

14. Method of any of the claims 1-12, **characterized in** that a mixture of alcohols is separated from the fermentation medium, exhibiting a content of glycerin of 30.9-31.0, ethanol of 43.4-44.4, C₃-C₅ alcohols of 1.9-2.5 and acetaldehyde of 22.7-23.2% by volume.
15. Method of any of the claims 1-12, **characterized in** that a mixture of alcohols is separated from the fermentation medium, exhibiting a content of glycerin of 35.0-35.9, ethanol of 30.5-31.0, C₃-C₅ alcohols of 1.5-2.0 and acetic acid of 31.1-32.1% by volume.
16. Method of any of the claims 1-12, **characterized in** that a product mixture is separated from the fermentation medium, exhibiting a content of acetone of 25.5-32.7, n-butanol of 56.0-58.5, ethanol of 7.3-8.7%, isopropanol of 0.4-4.4, isobutanol of 1.1-1.5, and isopentanol of 1.8-2.2% by volume.
17. Method of any of the previous claims **characterized in** comprising the further step of: using C₁-C₅ alcohols, glycerin, acetaldehyde, and acetone obtained in biosynthesis in preparing a motor fuel.
18. Method of any of the claims 5-7 and 10-17, **characterized in** comprising the further step of: drying up the excess autolysate of the yeast protein for use as an animal feed.
19. Method of claims 5-7 and 10-18, **characterized in** comprising the further step of: biosynthesis of methane using suspended substances obtained in the acid or enzymatic hydrolysis or autolysis of protein with the excess hydrolysate as a substrate.
20. Method of any of the previous claims, **characterized in** comprising the further step of: obtaining higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having four and more carbon atoms in the molecule using the product mixture of C₁-C₅ alcohols, glycerin, acetaldehyde and acetone separated from fermentation medium.

21. Method of claim 20, **characterized in** comprising the further step of: using the compounds obtained in the method of claim 20 in preparation of motor fuels.
22. Method of claim 20 or 21, **characterized in** comprising the further steps of: dehydration of the product mixture of C₁-C₅ alcohols separated after fermentation in order to obtain unsaturated C₂-C₅ hydrocarbons; reacting said unsaturated C₂-C₅ hydrocarbons with synthesis gas in a hydroformylation reaction to obtain aldehydes; hydrogenation of said aldehydes into a mixture of higher alcohols, alternatively said aldehydes are first condensed into higher unsaturated aldehydes which are then hydrogenated into the corresponding higher saturated alcohols.
23. Method of claim 22 **characterized in** comprising the further steps of: preparing synthesis gas from biomass and/or from wastes obtained in the processing of the separated product mixture into higher hydrocarbons, C₂-C₆ acids and/or methane obtained by biochemical means or carbon dioxide obtained by biochemical means.
24. Method of any of the claims 20-23, **characterized in** comprising the further steps of: oxidizing the product mixture of C₁-C₅ alcohols separated after fermentation in the presence of carbon dioxide, obtained by biochemical means, into a mixture of C₁-C₅ aldehydes; condensation of said aldehydes into a mixture of higher unsaturated aldehydes; and subsequent hydrogenation into a mixture of the corresponding higher saturated alcohols.
25. Method of any of the claims 20-24, **characterized in** comprising the further steps of: dehydration of saturated C₄ and higher alcohols into the corresponding unsaturated hydrocarbons; and hydrogenation of said unsaturated hydrocarbons into the corresponding saturated C₄ and higher hydrocarbons.
26. Method of any of the claims 20-25, **characterized in** comprising the further step of: dehydration of saturated C₃ and higher alcohols to obtain the corresponding ethers.
27. Method of any of the claims 20-26, **characterized in** comprising the further step of: reacting unsaturated C₅-C₆ hydrocarbons of iso structure with methanol to obtain the corresponding methyl ethers.

28. Method of any of the claims 20-27, **characterized in** comprising the further step of: oxidizing the product mixture of C₁-C₅ alcohols separated after fermentation in the presence of carbon dioxide, obtained by biochemical means, in order to obtain a mixture of aldehydes; condensation of said mixture into a mixture of higher unsaturated aldehydes; oxidizing said unsaturated aldehydes in the presence of carbon dioxide, obtained by biochemical means, into a mixture of higher unsaturated acids; and reacting said acids with methanol to obtain the corresponding methyl esters.
29. Method of claim 27, **characterized in** comprising the further steps of: hydrogenation of the higher unsaturated acids into higher saturated acids; and reacting said saturated acids with methanol to obtain the corresponding methyl esters.
30. Method of any of the claims 27-29, **characterized in** comprising the further steps of: preparation of methanol using carbon dioxide obtained by biochemical means, methane obtained by biochemical means, and hydrogen obtained from biomass and/or by biochemical methods in fermentation of carbohydrate substrates, and/or from water obtained in processing of alcohols obtained in biosynthesis.
31. Method of claim 30, **characterized in** comprising the further step of: reaction of the methanol with fatty C₄ and higher acids to produce the corresponding esters.
32. Method of claim 31, **characterized in** comprising the further step of: oxidizing C₄-C₅ alcohols from the product mixture separated after fermentation to obtain C₄ and higher fatty acids; and/or biosynthesis of C₄-C₆ fatty acids; and/or extraction of fatty acids from tall oil; and/or saponification of fats in order to obtain fatty acids.
33. Method of any of the claims 20-23, **characterized in** comprising the further steps of: dehydration of saturated C₄ and higher alcohols into the corresponding unsaturated C₄ and higher hydrocarbons; and reaction of said hydrocarbons with C₁ and higher fatty acids to obtain the corresponding esters.
34. Method of claim 32, **characterized in** comprising the further steps of: preparation of C₁ and higher fatty acids by oxidizing C₁-C₅ alcohols from the product mixture

separated after fermentation; and/or preparation of C₂-C₆ fatty acids via biosynthesis; and/or extraction of fatty acids from tall oil; and/or preparation of fatty acids by saponification of fats.

- 5 35. Method of any of the claims 22-24, **characterized in** comprising the further step of: reacting the unsaturated C₄ and higher hydrocarbons, obtained in the dehydration of the corresponding saturated alcohols, with C₂-C₅ alcohols obtained in biosynthesis to obtain the corresponding ethers.
- 10 36. Method of any of the claims 20-24, **characterized in** comprising the further steps of: extraction of isobutane and isopentane from the mixture of saturated hydrocarbons; reaction with unsaturated C₂ and higher hydrocarbons obtained in the dehydration of the corresponding saturated alcohols to obtain saturated C₆ and higher hydrocarbons.
- 15 37. Method of claim 20 or 21, **characterized in** comprising the further steps of: processing vegetable and/or animal fats, and/or glycerin obtained in the saponification of fats, and/or glycerin obtained in biosynthesis into n-propyl alcohol; mixing said n-propyl alcohol with C₁-C₅ alcohols separated after fermentation; preparation of higher
- 20 oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having four and more carbon atoms in the molecule using said mixture.
- 25 38. Method of claim 20 or 21, **characterized in** comprising the further steps of: extraction of glycerin extracted from a product mixture of C₃-C₅ alcohols obtained in fermentation of carbohydrate substrates; dehydration of said glycerin into acrolein; hydrogenation of acrolein into propionic aldehyde and propyl alcohol; condensation of said propionic aldehyde with the C₃-C₅ alcohols obtained in fermentation of carbohydrate substrates, and propanol obtained in hydrogenation of acrolein, into the corresponding propanals; alternatively propionic aldehyde is first condensed into unsaturated isohexene aldehyde, which is then hydrogenated into the saturated alcohol isohexanol.
- 30 39. Method of claim 20 or 21, **characterized in** comprising the further steps of: extracting glycerin extracted from a product mixture of C₃-C₅ alcohols obtained in fer-

mentation of carbohydrate substrates; dehydration of said glycerin into acrolein; condensation of acrolein into the acrolein dimer (2-formyl-3,4-dihydro-2H-pyran); hydrogenation of the acrolein dimer into tetrahydropyran-2-methanol; while using the remaining mixture of C₃-C₅ alcohols obtained in fermentation of carbohydrate substrates
5 for obtaining higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having in the molecule four and more carbon atoms.

40. Method of claim 20 or 21, **characterized in** comprising the further steps of: extraction of methanol and ethanol from the mixture of C₁-C₅ alcohols obtained in fermentation of carbohydrate substrates; adding methanol, produced from carbon dioxide
10 obtained in fermentation of carbohydrate substrates, and hydrogen, derived from biomass; oxidation of said methanol and ethanol into formaldehyde and acetaldehyde, respectively; condensation of the obtained mixture of formaldehyde and acetaldehyde into acrolein; condensation of acrolein into acrolein dimer (2-formyl-4,4-dihydro-2H-pyran);
15 hydrogenation of acrolein dimer into tetrahydro-pyran-2-methanol, while the remaining mixture of C₃-C₅ alcohols obtained in fermentation of carbohydrate substrates is used for obtaining higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having four and more carbon atoms in the molecule.

20 41. Method of any of the claims 20, 21, and 37, **characterized in** comprising the further steps of: condensation of the mixture of C₁-C₅ alcohols separated after fermentation, and/or n-propyl alcohol, obtained from glycerin, to produce saturated C₆ and higher alcohols, saturated C₅ and higher esters, and C₂ and higher fatty acids; while
25 using any remaining lower alcohols, that did not condense, and gaseous products, obtained in the condensation, for producing higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having in the molecule four and more carbon atoms.

30 42. Method of claim 41, **characterized in** comprising the further steps of: dehydration of the saturated C₆ and higher alcohols, obtained in condensation of C₁-C₅ alcohols, to obtain unsaturated C₆ and higher hydrocarbons; and hydrogenation of said unsaturated C₆ and higher hydrocarbons into saturated C₆ and higher hydrocarbons.

43. Method of claim 42, **characterized in** comprising the further steps of: reacting unsaturated C₆ and higher hydrocarbons, obtained in dehydration of the corresponding saturated alcohols, with non-condensed C₁-C₅ alcohols to obtain the corresponding C₇ and higher ethers.

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44. Method of claim 41, **characterized in** comprising the further steps of: dehydration of non-condensed lower alcohols C₂-C₅ to obtain unsaturated C₂-C₅ hydrocarbons; alkylation of terpenes by unsaturated C₂-C₅ hydrocarbons to obtain C₁₂ and higher hydrocarbons.

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45. Method of claim 41 or 42, **characterized in** comprising the further step of: reacting the C₂ and higher fatty acids, obtained in condensation of C₁-C₅ alcohols, with unsaturated C₆ and higher hydrocarbons, obtained in dehydration of the corresponding saturated alcohols, to obtain the corresponding C₈ and higher esters.

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46. Method of claim 41, **characterized in** comprising the further step of: reacting the C₂ and higher fatty acids, obtained in the process of C₁-C₅ alcohols condensation, with terpenes to obtain the corresponding C₁₂ and higher esters.

20 47. Method of any of the previous claims, **characterized in** comprising the further steps of: separation of acetone from the mixture of C₂-C₅ alcohols obtained in fermentation of carbohydrate substrates; treatment of the acetone by aldol and croton condensation to obtain a mixture of diacetone alcohol, mesityl oxide, phorone, and mesitylene; while using the mixture of the remaining C₂-C₅ alcohols for obtaining higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those
25 having four and more carbon atoms in the molecule.

48. Method of claim 47, **characterized in** comprising the further steps of: extracting the mesityl oxide and phorone from the mixture of hydrocarbons obtained in the result
30 of aldol and croton condensation of acetone, and subsequent hydrogenation of mesityl oxide and phorone to obtain saturated isohexyl and isononyl alcohols.

49. Method of claims 20, 21, 22, 24, 28, 37 and 38, **characterized in** comprising the further steps of: condensation of the unsaturated C₂ and higher hydrocarbons with

C₂ and higher aldehydes into unsaturated C₄ and higher alcohols; and hydrogenation of the unsaturated C₄ and higher alcohols into the corresponding saturated C₄ and higher alcohols.

- 5 50. Method of claims 22-49, **characterized in** comprising the further step of: obtaining the hydrogen used for hydrogenation from biomass, and/or by biochemical methods, and/or from the water obtained in processing of alcohols obtained by biosynthesis.
- 10 51. Method of claims 20 or 21, **characterized in** comprising the further steps of: separation of glycerin from the mixture of C₃-C₅ alcohols obtained in fermentation of carbohydrate substrates; condensation of glycerin either with acetaldehyde, obtained by biochemical method, to obtain glycerinacetal, or with acetone, obtained by biochemical method, to obtain glycerinketal; while the mixture of the remaining C₂-C₅ alcohols is used for obtaining higher oxygen-containing compounds and/or non oxygen-containing hydrocarbons, including those having in the molecule fore and more carbon atoms.
- 15 52. Method of any of the previous claims, **characterized in** comprising the further steps of: preparation of synthesis gas from biomass and/or from wastes obtained in the processing of any of the products obtained in fermentation of carbohydrate substrate, into higher hydrocarbons, and/or methane produced by biochemical methods and from carbon dioxide, obtained by biochemical method; and using said synthesis gas obtained from biochemical raw material for producing non oxygen-containing hydrocarbons by Fisher-Tropsch method.
- 20 25 53. Method of any of the previous claims, **characterized in** comprising the further steps of: preparation of synthesis gas from biomass and/or from wastes obtained in the processing of any of the products obtained in fermentation of carbohydrate substrate, into higher hydrocarbons, and/or methane produced by biochemical methods and from carbon dioxide, obtained by biochemical method; and using said synthesis gas obtained from biochemical raw material for producing oxygen-containing hydrocarbons by Fisher-Tropsch method.
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54. Method of any of the claims 20, 21 and 22, **characterized in** comprising the further step of: reacting unsaturated C₂ and higher hydrocarbons, obtained in the dehydration of the corresponding saturated alcohols obtained in biosynthesis, with carbon oxide obtained from biochemical raw material, and water to yield the corresponding saturated C₃ and higher alcohols.
55. Method of claims 20, 21 or 22, **characterized in** comprising the further steps of: mixing of ethylene obtained in dehydration of ethanol with methanol and butylene peroxides; and treatment of the resulting mixture by telomerisation to yield a mixture of C₃-C₁₂ alcohols.