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# Biorefinery Systems as an Element of Sustainable Development

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Krzysztof Biernat and Paulina Luiza Grzelak

Additional information is available at the end of the chapter

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## 1. Introduction

As a result of the review of implementation and research work carried out in the EU countries, aiming to intensify the use of renewable energy processes, it turned out that these works are scattered and do not bring the desired effect, both in terms of environmental and savings of energy conversion. Because of that, it created a vision of the industry based on raw materials of biological origin, which also qualified waste substances from the primary and secondary processes of exploitation and processing of biomass as defined in Directive 28 [1]. The realization of this vision should lead to a transition toward the so-called “post-oil” society through a clear decoupling economic growth from resource depletion and environmental impact.

After consultation carried out in the member states set out the need for separation of a new branch of industry defined as an industry based on raw materials of biological origin (“Bio-based Industries”), which should seek to optimize the use of land and food security through sustainable, efficient (effective), raw and largely limiting the amount of waste, industrial processing of European renewable raw materials in a wide range of products of biological origin, such as:

- Advanced transport fuels
- Chemicals
- Materials
- Food and feed ingredients
- Energy [2]

Thanks to that, “the bio-industry,” which is the main component of the EU economy referred to as “bio-economy” (“bioeconomy”), will play an important role in stimulating sustainable growth and increasing Europe’s competitiveness by reindustrialization and the revitalization of rural areas, providing tens of thousands of jobs in the field of research, development, and production over the next decade [3].

The Bioeconomy Program for Europe is going to be an evolutionary program. Expected to develop so-called value chains, the implementation of which will ultimately lead to the creation of so-called biorefinery that a comprehensive and zero-waste will be recycled biomass. The most important technological challenges, political and market, therefore will be prior to commercialization of innovative solutions to full scale. These challenges cannot be overcome by an individual company or dispersed industry, so it is necessary to approach the whole system of management system biomass [4].

This is important because of the need to reverse the current trend of significant bioeconomic investments in non-European regions, where conditions seem to be more attractive. The long-term research and innovation jointly financed by public and private entities can help solve this problem. This process will be implemented through the creation and implementation of appropriate and developed value chains, which will lead to reducing the risk of investment in demonstration projects on the implementation of innovative processes.

As part of the preparatory work for the start-up of the scope of the European bio-economy, there was a plan developed for Strategic Innovation and Research Agenda (SIRA). This document proposes a coherent set of actions that should be implemented through established “Biobased Industry Consortium” (BIC), namely:

- Implementation of projects aimed toward the integration and implementation of technology and scientific results and the introduction of technology on a commercial scale by implementing demonstration and flagship projects
- Implementation of development projects aimed at filling the gaps in research and technological innovation
- Supporting projects taking challenges cross-sectors [5]

Schematically, the areas covered by value chains are shown in Fig.1.

As it can be seen from the schematic products, semi-finished and all residues of the process as a result of the implementation of the objectives set in the value chains should be directed to biorefinery systems, in order to complete the transformation into energy carriers and biochemicals for various purposes.

## 2. The exchange of mass and energy in waste management

Circulation of matter and energy flow are the two main environmental laws describing the basic rules for the functioning of ecosystems on Earth. Life on our planet is possible, thanks to

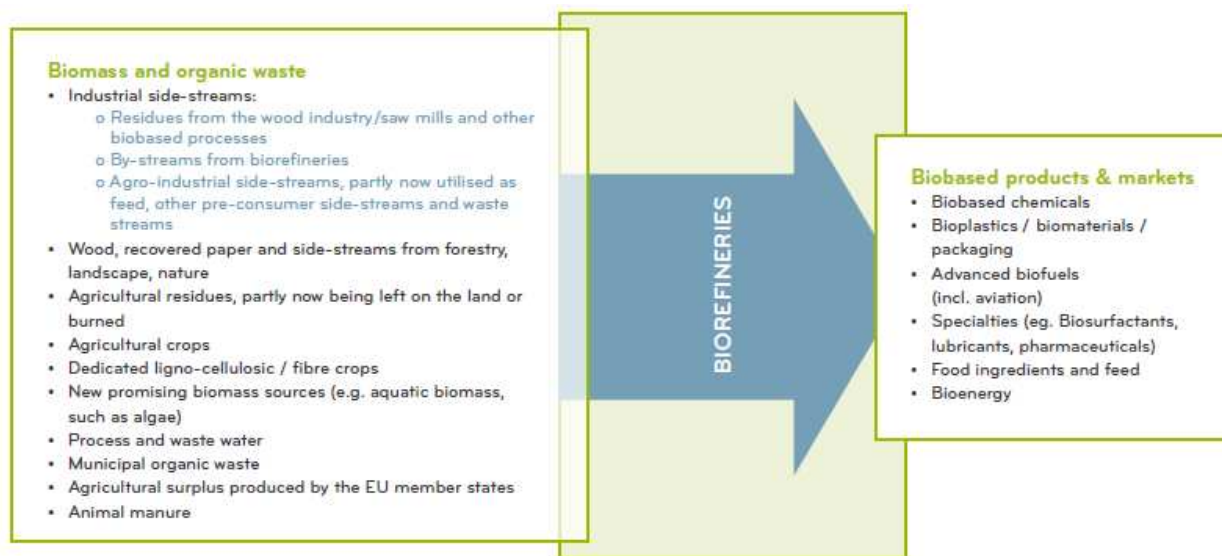


Figure 1. Value chains in bioeconomy [5]

the constant influx of solar energy. This energy flows through the ecosystem and partly returns to space in the form of thermal energy emitted by the Earth. Only a small portion of solar energy is accumulated in living organisms, and they even lose most of it forever. However, despite the exchange of energy, the Earth does not mention the matter with the environment. Earth is thus a closed system. The amount of matter on Earth is constant and circulates in the ecosystem. Under the influence of solar radiation, simple ingredients such as water and carbon dioxide are synthesized biomass, which forms a complex structure such as plants and other biological life forms, which in turn ensure the survival of other more complex forms of biological life and after their death through the action of decomposers and the way the carbon cycle and the nitrogen return to its original state [6].

Behavior of matter and energy is the subject of thermodynamics. The first law of thermodynamics states that energy can neither be created nor destroyed. It can only change its form. This means that everything which is delivered for processing must be accumulated in products in the technosphere<sup>1</sup> or leave them as waste in solid, liquid, or gas form. In addition, the system cannot get more energy than it was put into the system. Every economic activity of man is connected inextricably with the generation of waste, and it should be noted that all industrial products become waste sooner or later. The increasing amount of waste causes obvious environmental problems [7, 8].

All processes in the environment are irreversible processes, in other words, the real processes. In nature, the reversible processes are unique. This is because the reverse process cannot undergo energy dissipation that occurs in the actual process, even, for example, in effect of friction. Similarly, the industrial installations are open systems that interact with the environment together with its products. The energy introduced into the system is transformed from

<sup>1</sup> Sphere of human intervention in nature, spreading in the environment

a less useful form, which is more organized, in a more useful form, which is less organized. This interaction can be described by the change in entropy<sup>2</sup>, that is state function, which is postulated by the second law of thermodynamics [9].

Entropy is a measure of the degree of disorder of the system, a measure of the “quality” of the energy stored in the system. One version of the second law of thermodynamics states that “the arrangement is reduced (the degree of disorder increases) in any spontaneous process.” Energy and matter cannot be destroyed, but their quality is changed. Together they seek a greater mess, so their entropy increases [6, 10, 11].

According to the second law of thermodynamics for a longer period of time, entropy always increases. Each physical system, which is capable of free energy dissipation, does so in such a way that the entropy increases and the amount of used energy decreases [12, 13].

The first law of thermodynamics is a universal law of nature, from which there are no exceptions. The second law of thermodynamics is based on the concept of probability, due to the fact that it is possible when the entropy decreases. There are unlikely but possible situations. The second law of thermodynamics indicates the most likely direction of the incident and does not exclude the other less probable incidents.

Fossil natural resources used by man naturally are ordered matter of a certain structure. The products of human consumption are waste, in which the degree of order of matter is much lower, despite the fact that the elements present in the waste as well as natural resources are the same.

Entropy changes can occur either within the system or may be discharged to the environment. Export of entropy outside of the system is caused precisely by the fact that the processes are irreversible that causes irreversible increase in entropy which is the reduction in the degree of ordering. Reduction of changes in the form of entropy, for example, in the course of the technological process reduces the energy expenditure in obtaining the same effect as a final product, resulting in minimizing the losses in the process and consequently a reduction in the degree of impact on the environment. This can be done, e.g., on the way to limit the number of unit processes in technology, keeping in mind that the total entropy of unit processes will always be higher than the sum process entropy [6, 11].

The concept of entropy resulting in the way of irreversible processes occurring in the natural environment is due to spontaneity of overlapping of these processes. Spontaneous processes are irreversible processes, extending with a predetermined rate in such direction to achieve a state of balance. So it is not possible to restore the state before the occurrence of irreversible process while maintaining all the parameters of both the system and the environment. For example, if the process is reversed and the parameters of the system will return to the initial values, the environment will not return to the previous state because of the entropy emission into the environment as a result of reactions in the system.

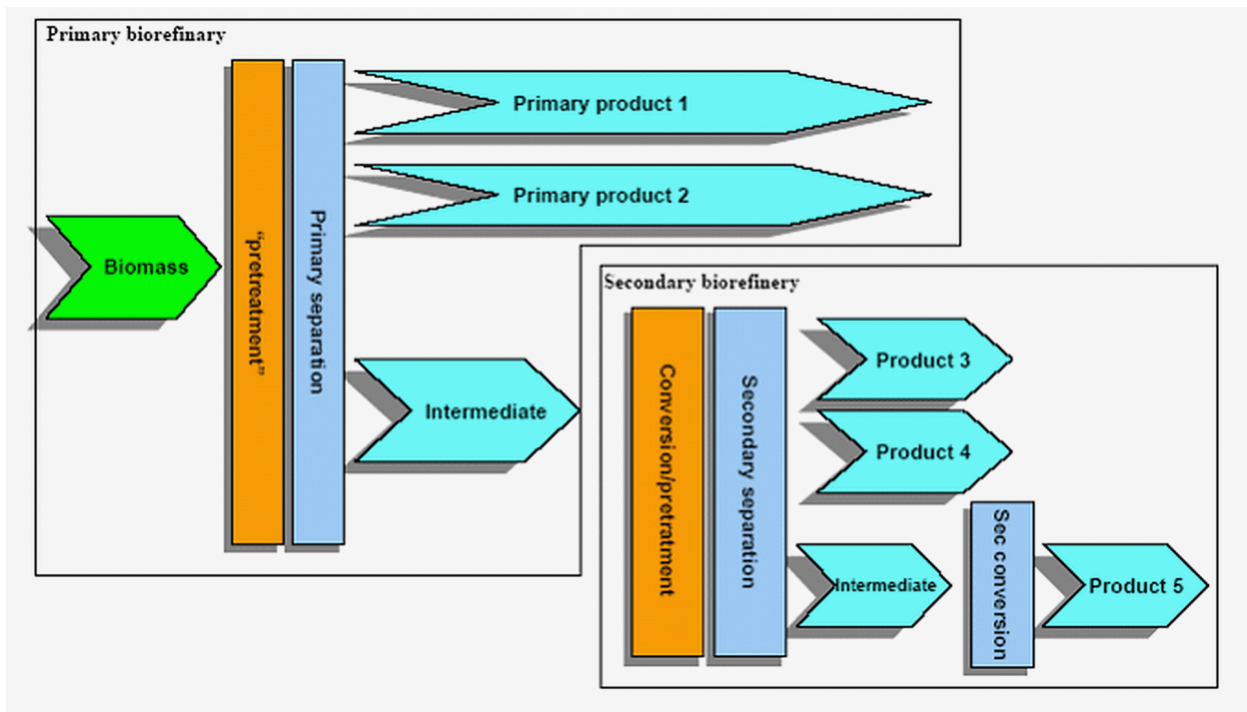
Analysis of processes for entropic changes enables optimization of technological processes used in the industry, as well as optimizing the use of raw materials and energy in order to

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<sup>2</sup> A measure of the degree of order – the higher entropy of the system, the lower the degree of order.

obtain specific products. The essence of these considerations is the production of entropy, which determines the degree of energy loss in the process, and so is the energy efficiency of the process. As it was mentioned earlier reduction of entropy production as a result of optimization technology, the substrates used and the energy introduced into the process reduce their impact on the environment. This is possible through the pursuit of the process to reversible process conditions and thus to obtain the equilibrium parameters. However, the pursuit causes inconveniences in the form of diminution of other important parameters of installation, such as enlargement of device size, which in many cases leads to the elimination of some of this type of technologies.

Therefore, the goal of reducing the impact on the environment should be carried out differently. It should be noted that the export of entropy, that is, the energy lost from the process, is carried out through the emission of unused waste heat and/or through the generation of waste. Also, the products of the process, after the step of its use, become waste. Various types of systems comprising external and internal recycles of a flow of mass and energy in the form of heat may be constructed to limit the production of all the waste from the process. This type of system, congruent with the concept of biorefinery, is shown in Fig. 2.



**Figure 2.** Scheme of biorefinery system containing recycles of mass and/or energy flow [14]

The stream of biomass (matter) and stream of energy flow into the biorefinery system, which are used and processed in the way of biorefinery processes, which results in obtaining useful products and intermediates, which at this stage are treated as process waste. However, by the internal recycle, these intermediates are used as starting materials in subsequent biorefinery processes. The same happens to the energy that is inserted into the process and allows the

incident and which may also be the product of the appropriate process. Generally, part of the energy emitted in the form of heat is waste from the process, which with properly optimized technology can be used as the feed energy flow to a subsequent process. From the example of this biorefinery system of the second row can be seen clearly that by optimizing the use of reactants and waste streams in the process, it is possible to reduce the formation of entropy, which prevents the loss of energy by providing greater energy efficiency of the system [15].

It should be noted that the internal and external recycle systems can be used not only at the level of the process but also at the level of the whole plant, as well as at the level of product user or user of energy produced and on the level of region and state. The effect of this will be reduction of the entropy of the system, reducing the consumption of energy and matter, increasing the efficiency of the process, and finally reducing the impact on the environment.

In the analysis of the energy efficiency of processes, of very help is the function of exergy. The precursors of exergy analysis were G. Gouy and A. Stodola, who formulated the law defining the loss of ability to perform work resulting from a thermodynamic irreversibility. According to the definition of the concept proposed by L. Reikerta, "exergy represents the minimum amount of work to be done, to produce from the commonly occurring components of the surrounding nature a desired substance with the required parameters, using the surrounding nature as a heat source, which is worthless in terms of thermodynamic," which in simple can be captured in the words, "exergy is the maximum capacity of the substance, which is an energy carrier, for the work in relation to the environment." Most simply speaking, the exergy is a measure of the quality of various forms of energy [16, 17].

Determination of loss of exergy is the main task of the exergy analysis, because each exergy loss causes a reduction of useful effects of the process or increases the consumption of fuels for its occurrence. Exergy losses can be divided into internal and external. Internal losses are caused by the irreversible processes extending inside the system (control cover of process). External losses result from the discharge of waste products with positive exergy into the environment, and the loss should preferably be expressed directly using the exergy of waste products. Calculation result of internal losses does not depend on the reference level adopted in the calculation of the external losses [18, 19].

However, any loss of exergy should have economic justification. Admission to the loss of exergy is necessary in order to reduce capital expenditures. For example, the flow of heat without loss of exergy would require an infinitely large surface of heat flow. So exergy analysis indicates on the possibilities of improving the thermal process. According to Jan Szargut, this analysis does not decide on the advisability of the improvements, which should be controlled by means of economic analysis. We cannot agree with this statement, because not only economic considerations will determine the attractiveness of technological solutions but also reduction of energy consumption and increase of the energy efficiency of the process will provide a means to achieving the goal of protecting the environment by reducing the impact on them through the process [20].

Analysis of entropy based on the calculation of exergy process allows for optimization of the manufacturing process and proper assessment of its impact on the environment, taking into

account all the components and stages of the production process, starting from the raw material constituting substrates in the process and ending on the disposal of waste from the process and waste resulting from the use and consumption of the final product [21, 22, 23].

Therefore, the comparison of the possible use of exergy or entropy emissions in different technological processes allows the systematization and classification of the different technologies in this field. This capability is particularly important in the case of methods of processing and disposal of waste. Among others, the studies showed that the most favorable thermal process in the waste utilization is pyrolysis. This process is ahead of the processes of gasification and combustion for energy. Also, in waste management, this classification is important. Waste actually represents the energy that is correlated with the value of primary energy resources, from which the product was formed and then the waste was produced. Using this energy should be the most efficient and should last as long as possible, and hence, its dissipation should take place as long as possible at the time. This is possible only through the repeated use of the energy contained in the products, intermediate products and wastes [24].

### 3. Sustainability in the course of processing waste

Sustainable development requires an assessment of the extent to which natural resources are in sufficient quantity and availability, to meet those needs while reducing the amount of waste (both process and also final, generated during the processing and usage of these resources).

The degree of loading of the Earth, which is the environmental capacity of the Earth, is the limited size and is determined by three interrelated factors: the size of the human population, the activity of each human being, and the impact on the environment, which is a result of this activity. The relationship of these factors and their influence on the degree of loading of the Earth is defined by the formula (1)

$$ELL = [HI_1 \cdot A_1 \cdot (\pm E_1)] + [HI_2 \cdot A_2 \cdot (\pm E_2)] + [HI_3 \cdot A_3 \cdot (\pm E_3)] + \dots + [HI_{7 \text{ mld}} \cdot A_{7 \text{ mld}} \cdot (\pm E_{7 \text{ mld}})] \quad (1)$$

where:

**EL** – loading level of the Earth

**HI** – human individual

**A** – the activity which is manifested by the human individual

**E** – the impact on the environment of the human individual through the activity

At the present time, there is a continuous and exponential growth of the human population on Earth observed and thus human activity aimed at creating wealth – as a result, omnipresent consumerism is growing globally. In results, there is greater impact on the environment through the use of its resources. To lower the burden on the environment, the value of human activity and the impact of each of the human individual through this activity should be



reduced. Human activity cannot be reduced, but this type of activity can be developed on the way of environmental education. In the same way, you can indirectly seek to reduce the environmental impact and the burden of every human activity [25, 26, 27].

There are two ways to reduce the environmental load. The first of these is to limit the use of resources, which is called dematerialization, which is gradually reducing usage of resources in technological processes. The next step should be the determined counteraction character of the life of a consumer society in developing countries and developed countries. Another way to limit the use of natural resources, including energy ones, is to replace the current raw materials for other unknown resources, by-products, or wastes from other processes, which is called transmaterialization [7, 28].

Both of the abovementioned proceedings roads are independent, but only their parallel application can provide the most tangible effect of actions to reduce the impact of human activities, including industrial environment. The Earth and its biosphere are thermodynamic systems exchanging with the environment energy only. The components of the biosphere subsystems, however, are open systems, exchanging with their environment both energy and matter. One of the subsystems, so-called man-made technosystem, collects raw materials from the environment and excretes waste. Systematic expansion of the technosystem and its impact not only contributes to an imbalance in the biosphere but also causes a real threat to its future existence [29, 30].

In the context of this situation arises question about the possibility of avoiding further destruction of the biosphere. Following Johansson, there are two possibilities for remedying this problem.

The first one is the complete separation of the technosystem of the biosphere, creating a closed technosystem. This method would involve major technological challenges for the modification of existing technologies for closing circuits of waste, which will entail a significant increase in energy consumption. Note also that technosystem separated from the biosphere would have to thus eliminate human intervention [7].

The second method proposed by Johansson is the adaptation of the technosystem to the environment in such a way that its action plays the strategy and action, which uses nature. In this solution, however, certainly limitation of many existing technological capabilities would occur, including reduction in the size and density of the local industrial activities, which, at this stage of the development of civilization, have already been exceeded in many cases. Implementation of this strategy would involve fundamental reorganization of the existing technological structure which would entail the search for new technological solutions [7].

Due to the fundamental problem of modern society as of a linear flow of matter from its source as raw materials to the waste stage and the accumulation of products of human activity in this form in order to maintain good environmental status as long as possible, our society must in its actions be inspired by nature, reducing the negative environmental impact to a minimum. A society that wishes to survive must maintain the activity causing disorder within order, possible to achieve by the energy captured from the sun. In addition, waste (degraded material

with a high degree of disorder, which comes from industries and households) should be converted back to natural resources [31].

From above it follows that the least favorable from the energy point of view is depositing waste in landfills, where primary energy accumulated in the waste is dissipated during their long storage, without its prior use. In this case, the relatively long time of the energy dissipation is ensured, but the benefit of the use of this energy and hence saving in the use of primary energy is equal to zero. Burning of waste in incinerators is a better solution for the landfill, because it allows you to recover some of the energy from waste, and this energy can be used in other processes. However, the processing of the same material by pyrolysis and gasification is even more preferred environmentally and economically in view of the minimization of oxides and heavy metal migration into the exhaust gases, as well as because of the higher efficiency of cogeneration systems. In addition, in these processes is formed synthesis gas or, in the pyrolysis process, post-pyrolysis oil, which both can be repeatedly used for the production of energy in various forms, including the ability to convert it to transport fuel. Hence, the more energy is consumed for the processing of raw materials, the more waste is created, because of the identity of mass and energy. In nature, there is a balance between the processes of formation of ordered matter, as of organic compounds in living organisms and the production of waste. Nature produces no waste and does not deplete resources, because in nature, nothing is really a waste – something that for one organism means waste is feed for another. In other words, everything is used in the life cycle [8, 32].

#### **4. Biorefinery systems**

One of the ways to mitigate the negative effects of local ecosystems is the conversion of biomass and organic waste into a different type of chemical substances or biomaterials and energy to fully exploit the value of the biomass, creating the so-called added value and minimizing the quantity of naturally produced substance or waste. This integrated approach reflects the concept of biorefineries and is gaining more and more attention in many parts of the world.

Similarly to the conventional refinery which produces energy and chemical products from petroleum, biorefineries will produce a variety of industrial products from biomass. These products are both LVHV type (low value and large volume), such as transport fuels and high-volume chemicals and other materials, and HVLV type (high value and low volume), as specialized chemicals and cosmetics, for example. In some types of plant, there also can be produced food and animal feed.

Energy sources are the main driving force behind the development of this type of installation, but sometimes when biorefineries will become more advanced and complex systems, the development of other products such as installations also occurs.

Biorefinery systems are nothing more than a kind of open systems, where part of the input streams is biomass, waste, and energy flow. Within the system there is a series of processes resulting in, for example, the energy exchange with the environment in the form of heat and

work. An output streams of biorefinery systems constitute a number of products such as fuels, chemicals (both highly valuable, which are obtained in small quantities, and of low value, obtained in large quantities), feed and food products, polymers, and other materials, as well as the energy produced in cogeneration or trigeneration (heat, electricity, and cooling) and processed waste. Please note that these wastes are waste only for the specific biorefining process. For another manufacturing process, these can be a substrate.

Biorefinery systems, imitating in its actions a living organism as open systems, in contrast to conventional petroleum refinery, may therefore constitute one of the elements of sustainable development [33].

#### 4.1. The concept of biorefinery

Repeatedly attempting to define the concept of biorefineries, and as a consequence, a number of incomplete or differing definitions have been established. After attempts to deduce from them the most important elements and characteristics of this new branch of industry, a comprehensive definition of the biorefinery has been established, according to which, it is an integrated "bio-industry," which uses a variety of technologies in order to obtain products such as chemicals, biofuels, food, feed ingredients, biomaterials (including fibers), and heat and energy, focusing on maximizing the added value, taking into account the three pillars of sustainability: environment, economy, and society. According to the definition of the International Energy Agency (IEA), biorefinery is a way for sustainable biomass processing in a wide range of bio-products of food, feed, chemicals, and biomaterials and bioenergy products such as biofuels, electricity, and heat [34].

By definition, biorefinery is a complex technological system that combines biomass conversion processes and the further processing of products of this conversion to fuels and chemicals – final or intended for further processing. Therefore, biorefinery is equivalent to crude oil processing plants (Figs. 3 and 4), where the substrate is crude oil, natural gas, or other fossil energy resources. These resources are processed in petrorefinery processes on a variety of products, mainly fuel, electricity, heat, chemicals, and various kinds of materials. The substrated in biorefineries are organic materials such as wood, energy crops, grass, and organic waste, which are processed in biorefinery processes – which are similar to the refinery processes – used in conventional petroleum refineries. Products from biorefinery are also the fuels and cogeneration or trigeneration energy, chemicals, and materials as well as food and animal feed. The basic petrorefinery scheme is shown in Fig. 3; Fig. 4 shows a general schematic diagram of a biorefinery.

As can be seen from a comparison of those two patterns, petrorefinery and biorefinery are related systems, processing a substrate or a plurality of substrates into a product or series of products by means of one or more technological processes which, as mentioned earlier, can be used both in a single and the second type of installation.

As mentioned, it should be noted that both the raw materials and also products of the biorefinery should be a much smaller threat to the environment, mainly emission of greenhouse gases. Hence, industrial biorefineries should constitute the most important element of



Figure 3. The basic scheme of the classic oil refinery



Figure 4. Ideological scheme of biorefinery

new industrial sectors, based on renewable energy sources (raw materials), offsetting at least part of the progressive deficiency of existing media such as oil, coal, and natural gas [35].

Biorefinery can be considered as a tool for the implementation of sustainable development in the processes of energy use and waste of natural resources. According to the concept of sustainable development, this type of installation procuring energy is the most optimal solution that simultaneously takes into account the continuous technological development, production of so-called “clean” energy and other products while reducing greenhouse gases and harmful compounds. This technology is almost “waste-free,” which uses the existing potential of biomass waste, which currently is not used at all or is used in an irrational way [35].

#### 4.2. Biorefinery processes

Depending on the raw material and the desired product, biorefineries use a variety of conversion technologies of raw biomass to commercial sources. These processes frequently include fermentation, gasification, and transesterification. New and less traditional methods are still in the research area, especially in the development of synthetic biofuels, such as liquid biofuels from biomass (BtL – biomass to liquid). Other substances, except fuels, produced in biorefinery processes, such as chemicals or other materials, are not as popular as energy biorefinery products and are at a much lower level of development in terms of trade with respect to fuels derived from these plants.

The fundamental biorefinery processes used after pretreatment of the biomass material include enzymatic hydrolysis, fermentation, fast pyrolysis, and hydrothermal processing (HTU – *hydrothermal upgrading*), called hydrothermal liquefaction or hydrothermal pyrolysis, with possible further hydrodeoxydation process (HDO – hydrodeoxydation) [36].

Regardless of the complexity of the biorefinery processes, the general scheme of the biorefinery can be presented as it is shown in Fig. 5.



Figure 5. General biorefinery diagram [37]

#### 4.2.1. Biomass pretreatment

Pretreatment is required in order to break the crystalline structure of cellulosic biomass, to make it accessible to the enzymes, which may be combined with the cellulose and hydrolyze the carbohydrate polymers into fermentable sugars. The purpose of the pretreatment is a pre-extraction of hemicellulose, lignin degradation, and release of the cellulose from the plant cell walls. Pretreatment is considered as one of the most costly stages of cellulosic bioethanol production but also has a large potential for its improvement and reduction of costs through continuous research and development.

Many pretreatment technologies have been developed and evaluated for different biomass materials. However, each of these pretreatment methods has its advantages and disadvantages, and one method is not suitable for all types of raw materials.

The most commonly used methods of pretreatment of biomass in order to apply it in biorefinery processes are alkaline pretreatment, pretreatment with hot water, and pretreatment with the dilute acid. Alkaline pretreatment process is carried out using dilute sodium hydroxide (NaOH), ammonia, or lime. This process aims to improve the capacity of the fermentation of cellulose. Pretreatment with hot water is a process called autohydrolysis. This process is intended to hydrate the cellulose before the actual processing. The last type of biomass pretreatment process is a dilute acid pretreatment. This process takes place with the participation of sulfuric acid of 0.5–1.0 % concentration, and it is designed to effectively remove and recover most of the hemicellulose from the processed biomass.

#### 4.2.2. Enzymatic hydrolysis

The enzymatic hydrolysis is based on conversion of carbohydrate polymers to monosaccharides. Although various processes for the conversion of biomass to ethanol were studied, the enzymatic hydrolysis of cellulose provides the ability to improve the technology, so that the ethanol from biomass could be competitive in relation to other fuels in terms of both quality and economically.

Pre-prepared lignocellulosic material is subjected to enzymatic hydrolysis. This process involves the reaction for converting complex sugars to simple compounds – cellulose to glucose and hemicellulose into pentoses (xylose and arabinose) and hexoses (glucose, galac-

tose, and mannose). Conversion processes of cellulose and hemicellulose are catalyzed by cellulase and hemicellulase. Cellulases play a significant role, because they catalyze the decomposition of cellulose into fermentable sugars. The enzymes involved in the hydrolysis of cellulose include endoglucanases, exoglucanases, and  $\beta$ -glucosidase. Endoglucanase randomly catalyze the decomposition of the internal bonds of the cellulose chain, whereas exoglucanases attack chain ends, releasing cellobiose molecules (disaccharide, which is not present in plants alone, transient degradation product of cellulose).

Enzymatic hydrolysis is a process often before fermentation, so it has to decompose cellulose and hemicellulose into fermentable monosaccharides. A solution of simple sugars can be fermented with microbes. However, some plant sugars, such as sugar beet or sugar cane, can be directly used in the fermentation process, without necessity to undergo the process of enzymatic hydrolysis [38].

#### 4.2.3. Fermentation

Lignocellulosic biomass subjected to fermentation process requires separation of hemicellulose and cellulose material from the non-fermentable lignin, which is linked by strong covalent cross bonds. This is done using a pretreatment with an acid, alkali, or steam. Lignin, as waste from the bioethanol production, can be used as fuel and subjected to further processes of combustion or co-firing, in order to obtain energy.

Fermentation of C<sub>6</sub> sugars, such as starch or sucrose, requires the use of organisms such as baker's yeast. In contrast, fermentation of C<sub>5</sub> sugars – decomposed hemicellulose – requires special organisms, which are capable of fermenting xyloses. Currently, there is a need for more efficient and robust microorganisms that are resistant to higher temperatures and pressures. For example, recent studies carried out to improve the properties of the yeast strain showed that they may contribute to the production of more biofuels from cellulosic plant material by fermentation of all five types of plant sugars: galactose, mannose, glucose, xylose, and arabinose [36].

#### 4.2.4. Fast pyrolysis

Fast pyrolysis is a process of thermal decomposition of biomass to liquid bio-oil, comprising carbohydrates and oxygen content of approx 35–40 %. Through successive hydrogenation and hydrodeoxygenation processes or gasification, bio-oil can be converted to a specific hydrocarbon.

The use of fast pyrolysis process, as well as the properties of the thus produced biodiesel, is currently under investigation. However, there is the view that this process can significantly reduce the cost of the gasification process with respect to the direct use of solid biomass in a gas generator.

Fast pyrolysis process requires only one reactor, which involves relatively low costs. The relatively high temperature, - approx. 450–500 °C, the short residence time (approx. one second) of the load at this temperature at atmospheric pressure and resulting high yield of oil, also represents a clear advantage of this process. However, this process is also characterized

by a considerable degree of non-selectivity and the formation of many products, including a large amount of soot. The feed used in the fast pyrolysis process must be drained initially, which generates costs and energy consumption and quality of the obtained fuels by the relatively poor [39].

#### 4.2.5. Hydrothermal conversion

Another process of converting biomass in biorefineries is hydrothermal conversion process HTU (*hydrothermal upgrading*), which its diagram is shown in Fig. 6. Originally, this process was used for the conversion of coal to liquid fuels in conventional refining plant. Hydrothermal conversion is the process of biomass depolymerization carried out at high temperature, after which may optionally take place a catalytic hydrodeoxygenation process HDO (hydrodeoxygenation). The temperature of this process is lower than in the fast pyrolysis process (300–400 °C), but the residence time of the feedstock in this temperature is approx. 0.5–1 h while ensuring relatively high operating pressure of approx. 5–20 MPa.

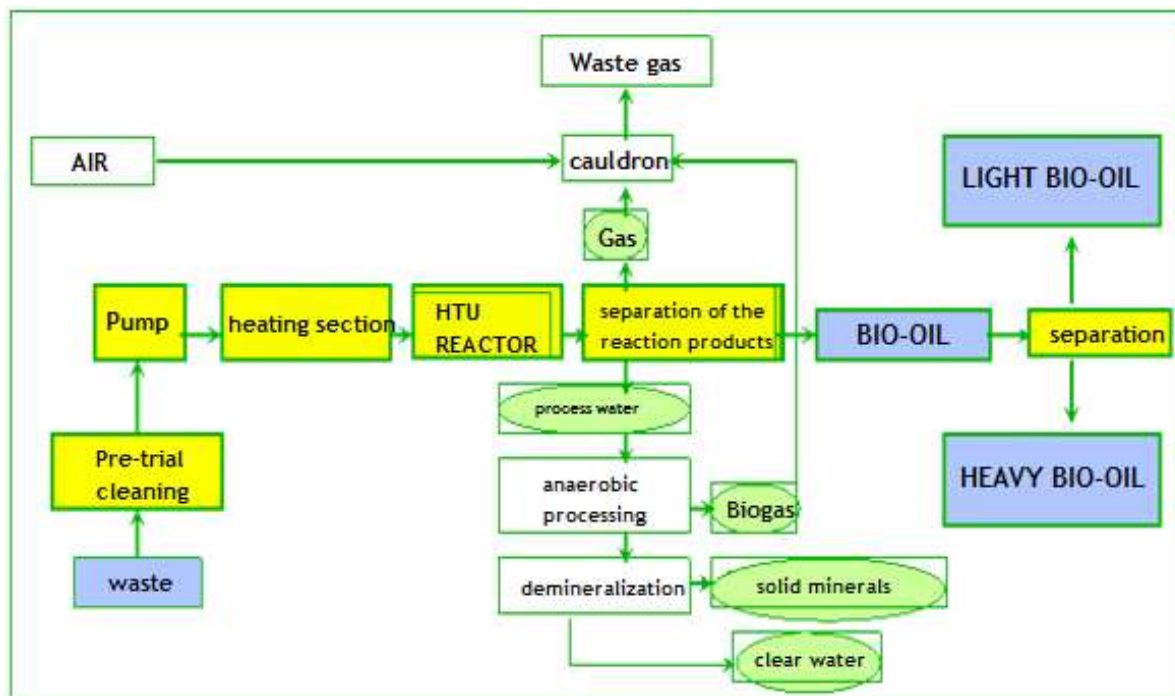


Figure 6. Diagram of HTU process [40]

In contrast to the pyrolysis in the HTU process, it is not necessary to pre-dry the biomass, so the process is particularly suitable for processing natural wet biomass.

HTU process takes place in an aqueous environment, where there are complex reaction sequences. The process involved reducing gas and a catalyst, in order to maximize the extraction of oil and its quality. HTU process is characterized by the high quality of the resultant fuel with low water content.

HTU process has a relatively low yield of oil, approx. 20–60 % dry weight of the stock. Also, the need for high pressure works against the financial side of undertaking due to the increasing demand for energy as a feed and the need for appropriate instrumentation [41, 42].

### 4.3. Division of biorefinery installations

Biorefineries can be divided into three types, based on technological advancement. The first type is analogous installation to existing installations of conventional oil refinery (petrorefineries). Then in the whole process, one type of raw material which is processed by a single technology is used, thereby providing one primary and main product. Figure 7 shows a schematic diagram of the first type of biorefinery [43].

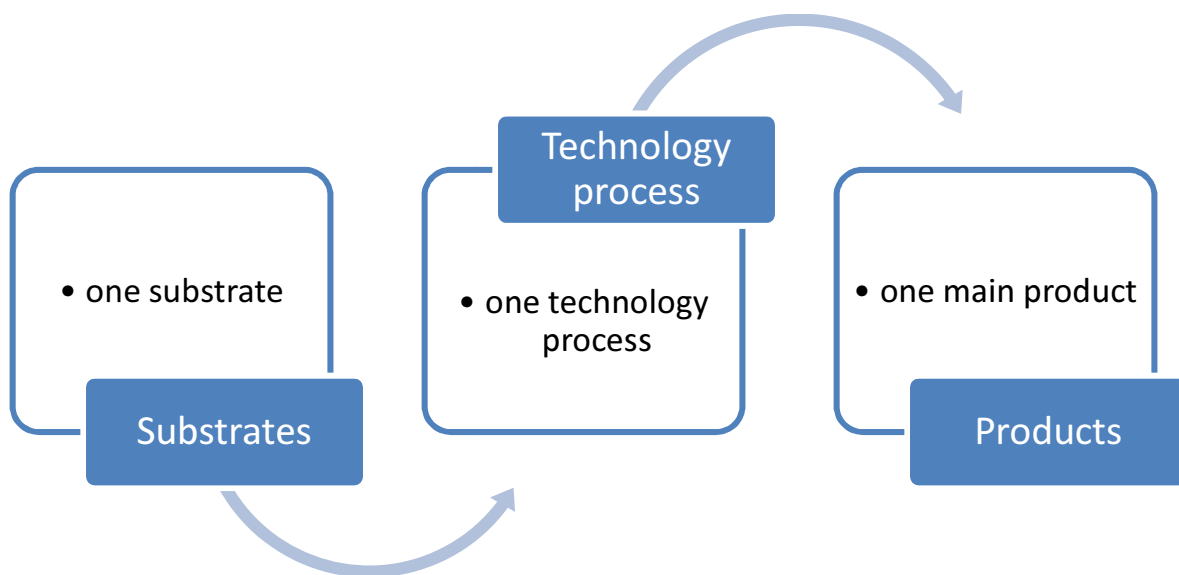


Figure 7. A schematic diagram of the first type of biorefinery (type I)

In another type of biorefinery one substrate is processed through a number of processes to many “major” products, that are equally important from the point of view of investment. A schematic diagram of this type of installation is shown in Fig. 8.

The last type of biorefinery installation is the most advanced system, which uses multiple substrates as input, processed through multiple technologies to a number of main products that are equivalent from the point of view of the investment. A schematic diagram of this type of installation is shown in Fig. 9 [43].

A very important role in the concept of biorefinery installation plays is the possibility of multiple processing of organic waste and more. Biorefinery systems – the first, second, and third type – may use various types of technologies and thus can process various types of biomass. Hence, input substances, regardless of their type, can be processed in the selection of the appropriate installation using appropriate processing technologies. Biomass processed in the so-called “primary” biorefinery systems is often transformed in an incomplete way,



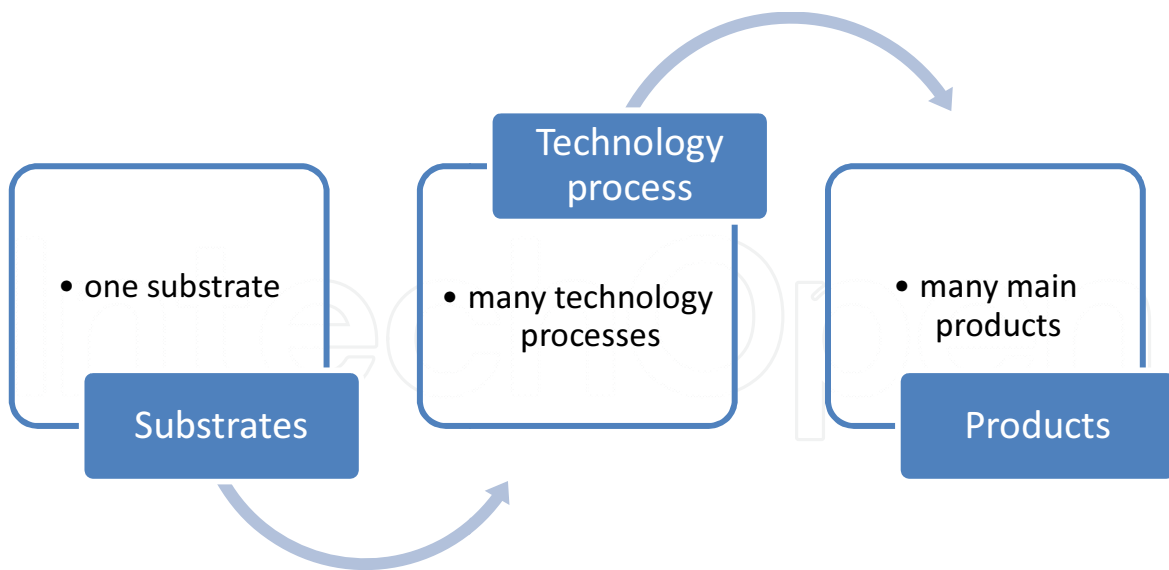


Figure 8. A schematic diagram of the second type of biorefinery (type II)

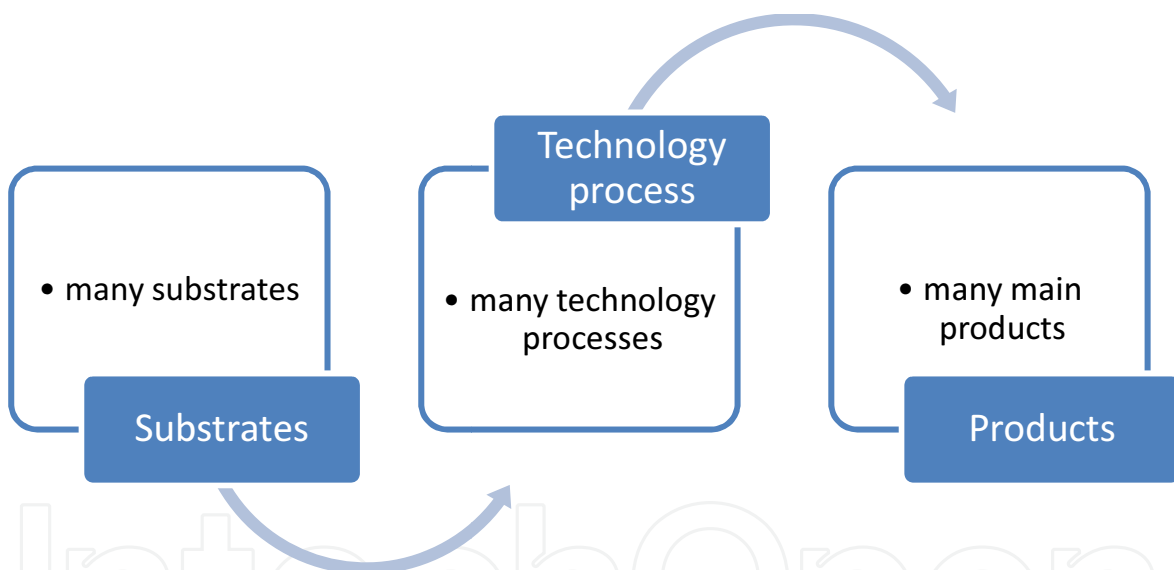


Figure 9. A schematic diagram of the third type of biorefinery (type III)

which should be understood that there are obtained some parts of the products and also are formed intermediates suitable for further processing. In this case, used are so-called secondary biorefinery installations, in which intermediates are processed by the same or other biorefinery processes. The flow of raw material through a series of biorefinery installations is applied until the total conversion of biomass and waste formation, which is not suitable for further processing [44].

Figure 10 shows the environmental biorefinery cycle, taking into account the carbon cycle in nature.

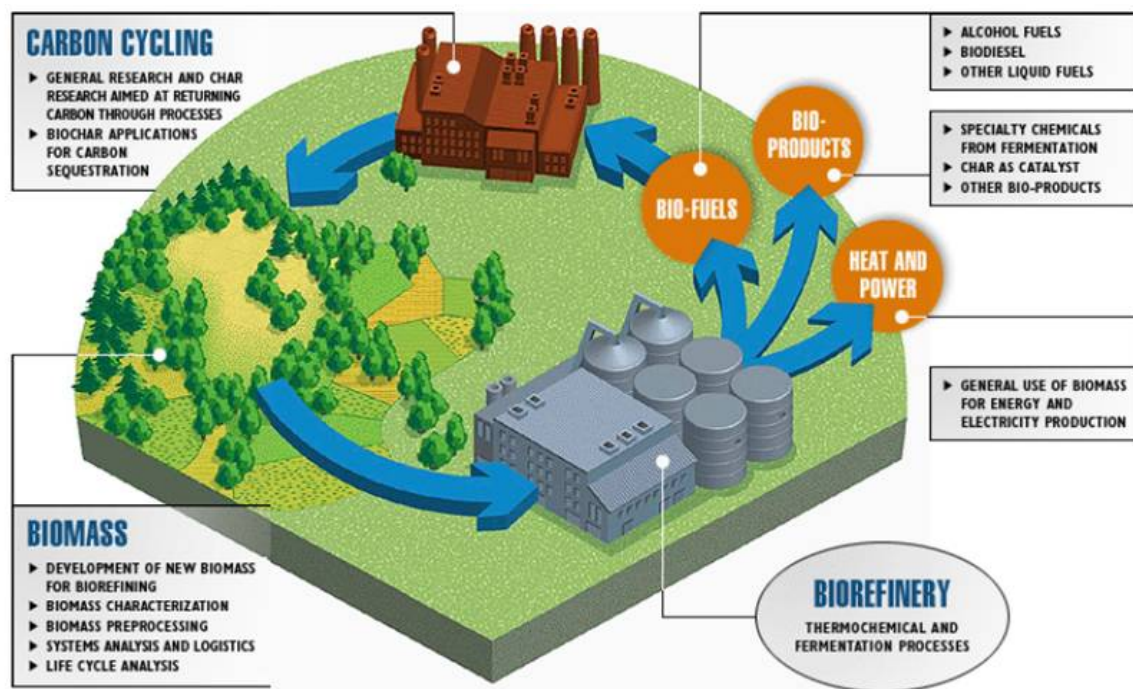


Figure 10. Biorefinery cycle – natural carbon cycle [45]

Biomass in the form of waste, energy crops, etc., shall be prepared and processed (decomposed) to simple compounds (sugars, proteins, carbohydrates, and fats) for the subsequent processes in the biorefinery. To the biorefinery plant gets adequately prepared feedstock from biomass, which is subjected to thermochemical and fermentation biorefinery processes. As a result of biorefinery processes, there are many products created: heat and electricity in co-generation; bio-products such as specialty chemicals, bio-carbon, and others; and also biofuels such as alcohol fuels, bio-oil (biodiesel), and other liquid fuels.

Considering the emissions from vehicles in the WtW cycle, meaning from the source to the wheels (well to wheel), there is the question of the carbon cycle in nature. According to this, there are undertaken research aimed at maximum reduction of carbon dioxide emissions into the atmosphere and return of carbon to nature through various processes, also the use of the resultant bio-carbon in sequestration processes.

Part of the emitted carbon dioxide throughout the lifecycle is absorbed by plants through photosynthesis process, which enables the development and creation of new plants and, consequently, new biomass for biorefinery processes.

The raw materials used in biorefineries are very diverse renewable raw materials, starting from agricultural products such as corn, wheat, and barley grains, agricultural crops such as oilseeds, waste from the agro-food and forestry industry as agro waste, wood chips and deforestation forest products, as well as special energy crops such as switchgrass or willow. Recently biorefinery raw materials also include organic waste, mainly municipal waste and any waste biomass.

As can be seen in Fig. 10, biorefinery raw materials can be a plant specifically designed for that purpose, by-products of processing of other substances, and products from different industries. Biorefinery processes also require power, assuming that the processes need to be exothermic – the energy emitting to the environment. So as biorefinery products is obtained the desired products of all kinds, as well as the energy. A side effect may also be the residual substances (waste). These substances are residues, which in the present state of knowledge cannot be further processed reasonably. It is assumed that the optimal biorefinery should be completely waste-free, because these substances should be used even as internal energy carriers. Therefore, research efforts have led to a comprehensive concept of biorefineries; the diagram is shown in Fig. 11.

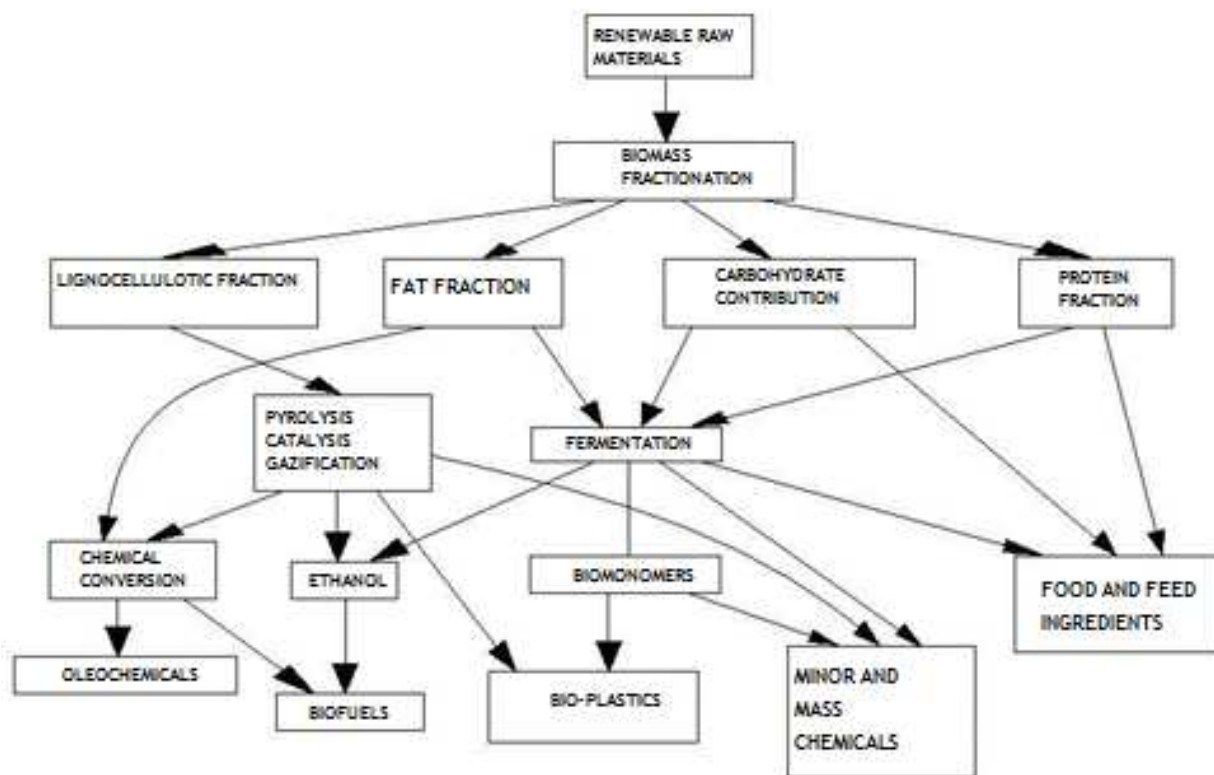


Figure 11. Comprehensive concept of biorefinery (developed on the basis of [46])

As is apparent from the diagram, the first step of biorefinery processes is biomass fractionation. The result of this process is a fraction of the cellulose, fats, protein, and carbohydrates. For each of the fractions, there are different ways of processing and hence various types of possible products, such as oleochemicals, biofuels, “bio”-plastics, chemicals, and food and feed ingredients.

The biomass can be converted into many useful forms of energy by several processes. There are two basic platforms of biorefining processes: “sugar” and “thermochemical.” Both systems can produce chemicals and fuels, including methanol, ethanol, and polymers.

“Sugar” platform is based on the breakdown of biomass to an aqueous sugar solution with the use of chemical and biological agents. Fermenting sugars can be further processed in ethanol (produced by fermentation), aromatic hydrocarbons (through a process of dehydration), or liquid paraffins (by processing the aqueous phase). The residues – mainly lignin – can be used to produce electricity (through co-firing) or can be dedicated to the production of other products (e.g., etherified gasoline).

In the “thermochemical” platform, biomass is converted to synthesis gas via the gasification process to bio-oils by the pyrolysis and hydrothermal conversion (HTC). Bio-oils can be further refined to receive a liquid fuel such as methanol, gasoline and diesel fuel, and other chemical compounds.

The comprehensive biorefinery concept, shown in Fig. 11, assumes the universality and thus the energy cost-effectiveness (economic) of multiple processes. Unfortunately, in today’s state of knowledge, those processes are mostly in the research phase (laboratory). Hence, due to the technological possibilities and availability of raw materials, there are four basic biorefinery systems in pre-industrial research phase:

- Biorefinery with the feed of the whole plant
- Biorefinery with the feed of non-edible parts of plants
- Biorefinery with lignocellulosic feedstock
- A so-called “two-platform” biorefinery

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“Sugar” platform is based on the breakdown of biomass to an aqueous sugar solution by using of chemical and biological agents [33].

#### *4.3.1. Biorefineries based on feed of the whole plant*

Biorefineries, where crops are feed material are entirely termed “agrorefineries.” Common crops so far, mainly their grain, were intended as a basic raw materials for agro-food industry, which is the basis of food security needs of humanity. While in industrialized countries, there is a surplus of food, in third-world countries there is a permanent lack of food. Thus, the earmarking of raw materials for energy purposes (nonfood) is seen as inhumane. For these reasons, the EU began to develop technologies for biofuels and bioliquids from nonfood raw materials, specifying these fuels as second-generation biofuels. Regardless, it was found that first-generation biofuels, which are made from food raw material (ethanol distillers, FAME from rapeseed, sunflower, etc.), do not change the balance of greenhouse gases and in some cases even worsen it.

In turn, further processing of nonfood use plants, and therefore useless in the agri-food industry is very beneficial for social reasons, because of the possibilities of degraded area development for food crops.

The technology assumes the breakdown of the entire crop plants into edible parts and straw. From the edible parts by biotechnology and chemical and also physicochemical methods can be obtained starch derivatives and flour, which can be considered as final products or continue to process them into fuels, chemicals, polymers, and other materials, which are the final products in this process. This process generates heat and power in cogeneration and waste. Straw, which constitutes a second portion of the raw material, is treated by biotechnology and chemical methods into the lignocellulosic material, which is further processed to the final products of the biorefinery process with production of energy in cogeneration and waste.

Figure 12 shows a general illustrative flowchart of biorefinery, where the raw material feed is whole plants.

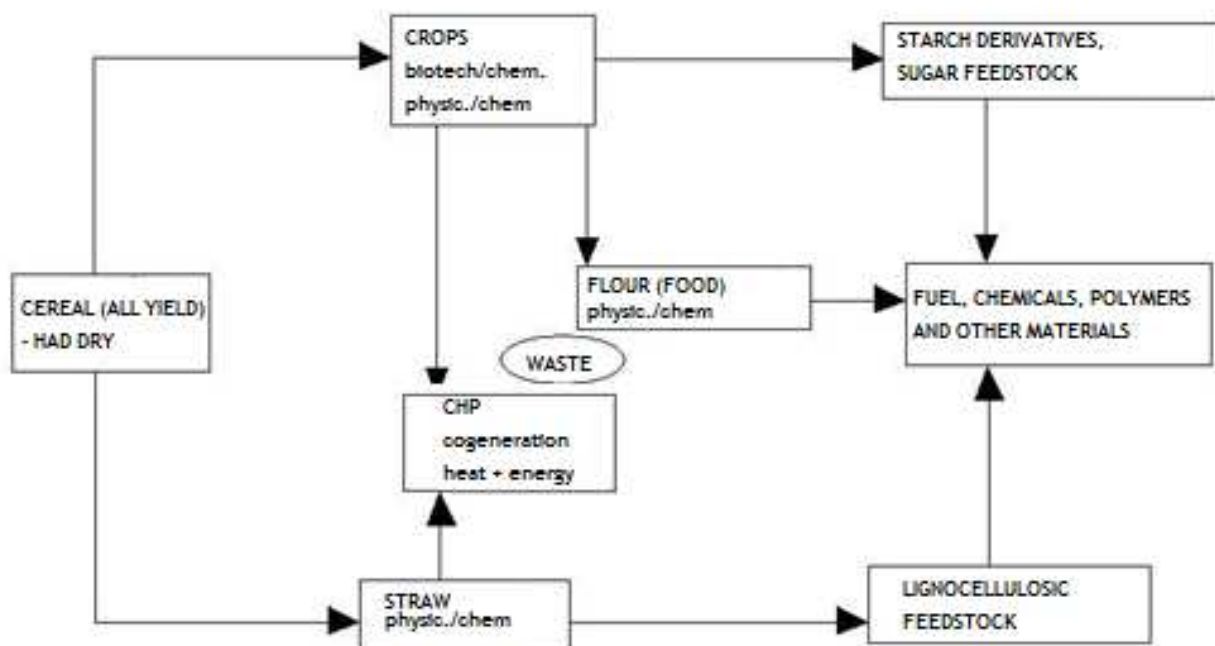


Figure 12. Biorefineries based on the full-load plant (developed on the basis of [46])

#### 4.3.2. Biorefineries with the feed of non-edible parts of plants or entire energy plants

Another type is “green” biorefinery and therefore that which conventionally uses only the “green” part of the plant as substrates.

The feed is naturally wet biomass, green grass, alfalfa, clover, immature corn. etc. Within the scope of the raw materials also includes redundant or useless for breeding and food industry plants or their parts (silage).

Green biomass (the green parts of the plant) by means of extrusion is converted into liquid and solid substances. Fluids are subjected to biotechnological processes, physical and biochemical, which leads to the formation of proteins and soluble sugars. By contrast, the solids

by the hydrothermal, enzymatic, and thermal methods are converted into cellulose and lignocellulose. The products of these two paths are processed for animal feed, fuels, polymers, chemicals, and other materials. These processes generate energy in cogeneration and waste.

Figure 13 shows a general diagram of a biorefinery platform, where the feed is the green parts of plants.

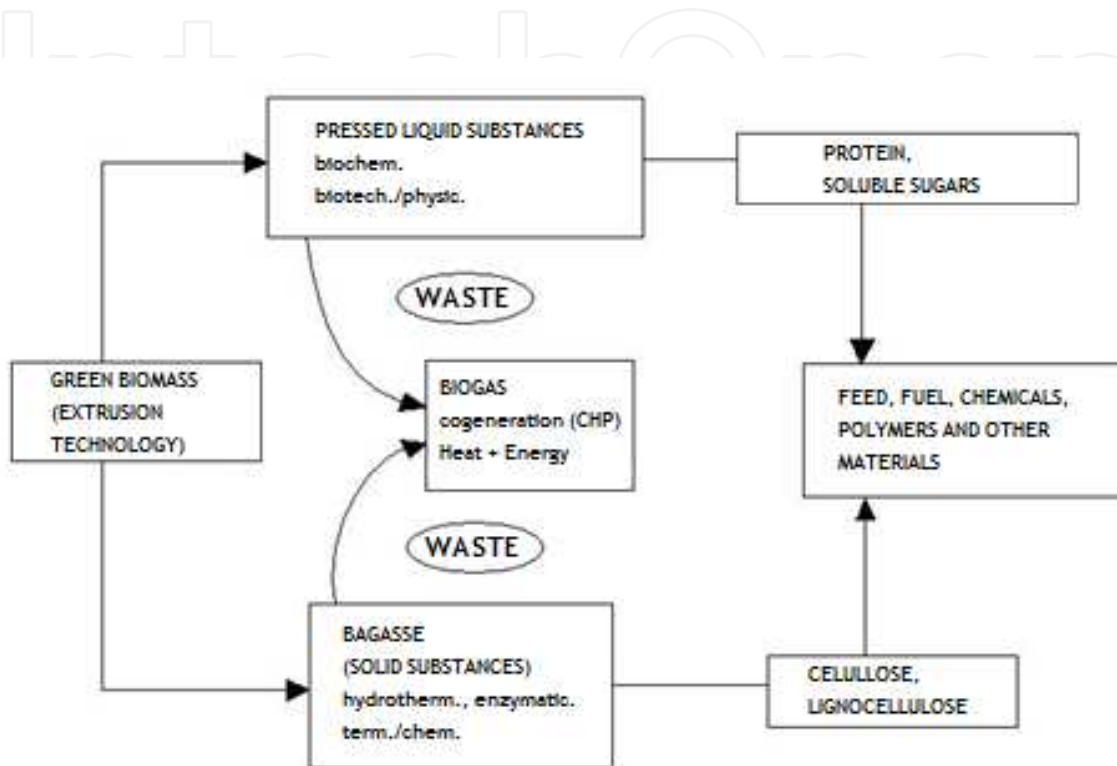


Figure 13. Biorefinery with a load of green plant parts (developed on the basis of [46])

#### 4.3.3. Biorefinery with lignocellulosic feedstock (lignorefineries)

Lignorefinery is a plant, which substrates are rich in organic substances of lignocellulose. This type of materials are, for example, naturally dry biomass, wood, straw, redundant or useless fodder maize, and cellulose-containing biomass.

Excellent raw material including this type biorefinery is waste from many industries, such as the forest industry, wood, paper, furniture, etc.

Firstly, lignocellulosic feed is separated into lignin, hemicellulose, and cellulose. In the biorefinery processes in the case of lignorefinery apply various types of auxiliary substances such as enzymes or yeast. Lignin in a chemical way is processed to obtain lignin raw material, and cellulose is converted into sugar raw material by biotechnology and chemical processes. From the products of these two processes and hemicellulose can be obtained fuel, chemicals, polymers, and other materials with energy in cogeneration and waste [47].

A diagram of lignorefinery is shown in Fig. 14.

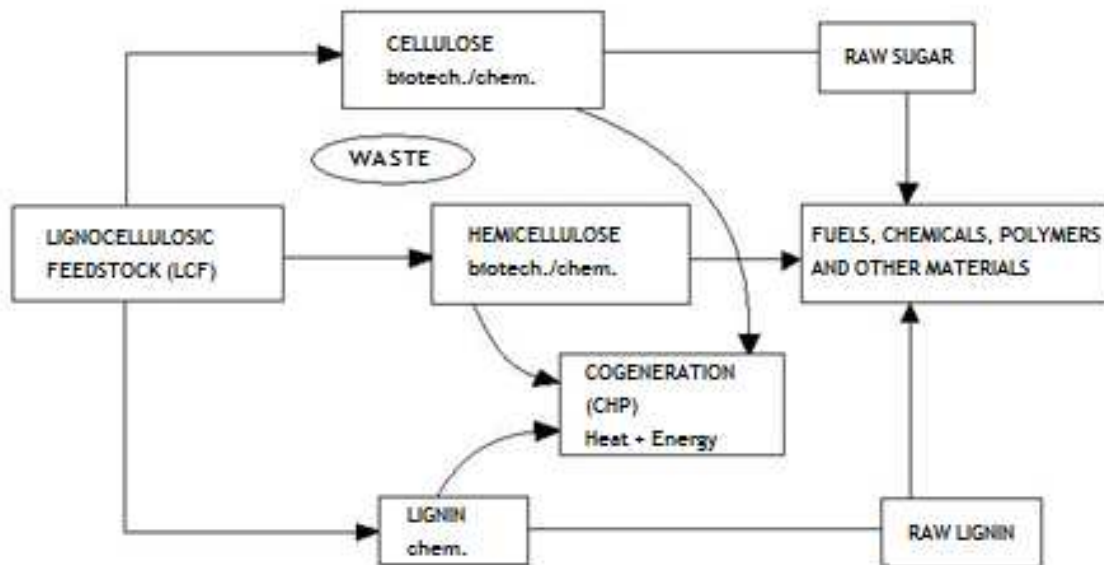


Figure 14. Lignocellulosic biorefinery – lignorefinery (developed on the basis of [46])

#### 4.3.4. “Two-platform” biorefineries

The idea of “two-platform” biorefinery is to obtain a synthesis of gas and sugars and so the parallel production of fuels based on renewable raw materials and other products, in terms of production in two technology platforms.

Raw materials used in this type of biorefinery is widely understood biomass consisting of any substances, mostly waste from various industries, such as agriculture, forestry, marine, food industry, public utilities, etc.

Biomass is divided into two contractual “platforms” – sugar and syngas platform. Sugar raw materials are converted through chemical reactions with the separation of waste, while the synthesis gas is conditioned by thermal and chemical methods. The end products of these processes are fuels, chemicals, polymers, and other materials. In these processes, the energy produced in cogeneration is produced.

Figure 15 shows a flowchart of a “two-platform” biorefinery.

#### 4.3.5. Oleorefinery concept

There is also a variety of agrefinery called oleorefinery. As the name suggests, it uses oilseeds as raw material such as canola, sunflower, olive trees, and soybeans. Typically, these seeds are used for food production. Therefore, at present, when the first-generation biofuels go into oblivion, oleorefinery may have only use these crops from degraded areas, which cannot be used in food industry. Besides oilseeds as a substrate can also be used animal fats and waste. Oleorefinery products may be biodiesel and oleochemical products such as phytosterols or

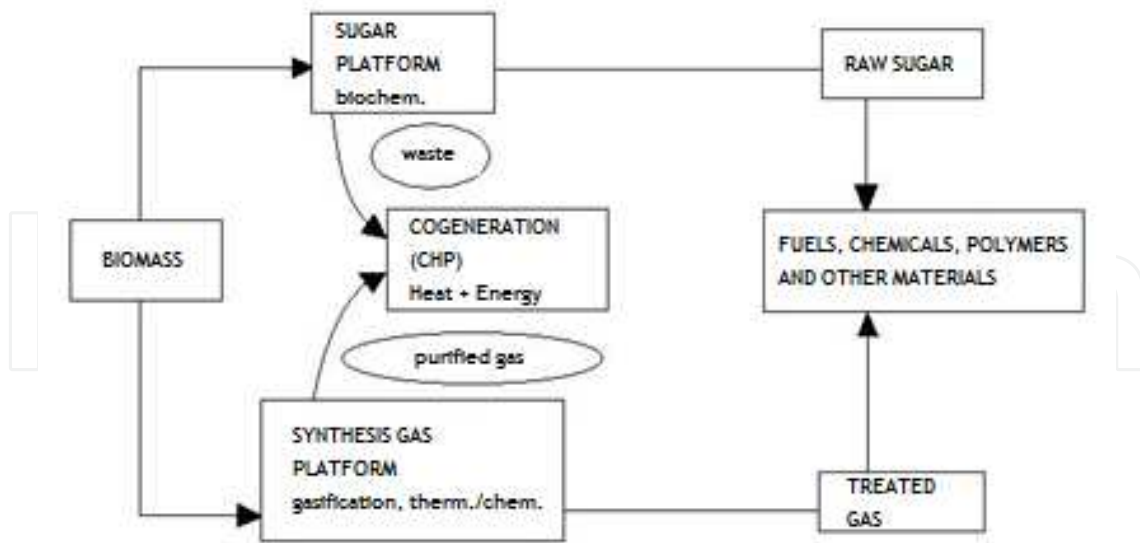


Figure 15. "Two-platform" biorefinery (developed on the basis of [46])

sphingomyelin. This process also generates energy, which in part can be used as the energy delivered to a subsequent process.

Figure 16 shows a general flowchart of oleorefinery.

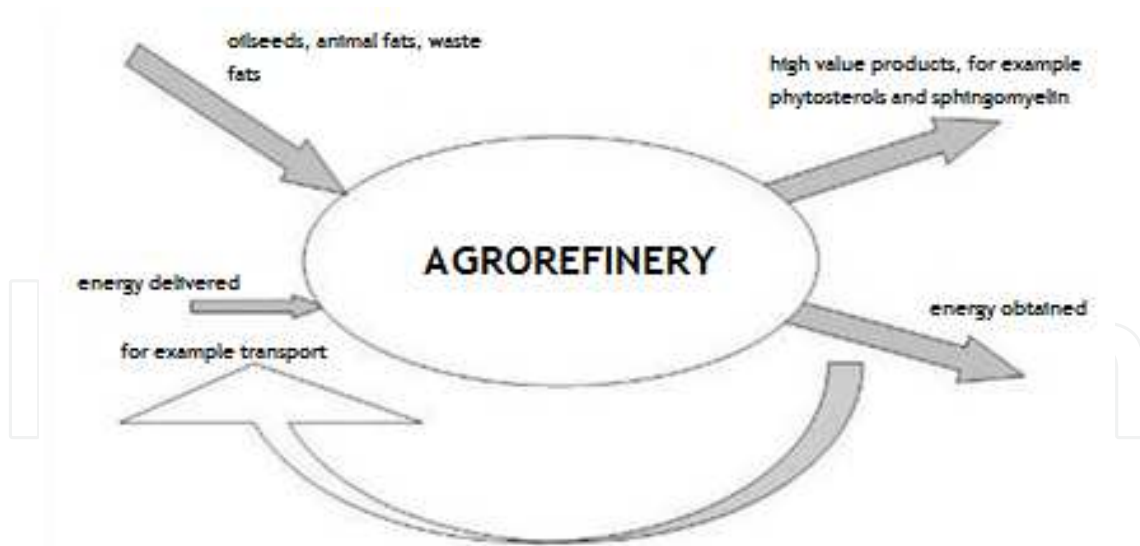


Figure 16. The general scheme of oleorefinery [37]

#### 4.3.6. Prospective biorefinery concept

There was developed a future-oriented concept of biorefinery based on the raw waste, which the diagram is shown in Fig. 17. That biorefinery practically implements processes in the field



of WtL (“wastes to liquid”). Feed for this type of installation can provide all kinds of waste oils: waste used frying oils, animal fats, grease, animal waste, etc. Oil fractions by lipid extraction and refining are converted into crude oil and waste.

The crude oil is converted by transesterification to the methyl ester or glycerol, by hydrogenation into the liquid hydrocarbon (biodiesel), or by chemical and enzymatic modification in all kinds of oleochemical products, such as fatty acids, alcohols, fatty esters, fatty ketones, dimer acids, glycerine, etc. Wastes are converted by gasification into synthesis gas, resulting in a yield of energy and heat in cogeneration. Syngas may be further converted into transport fuels or chemicals by catalytic processes [48].

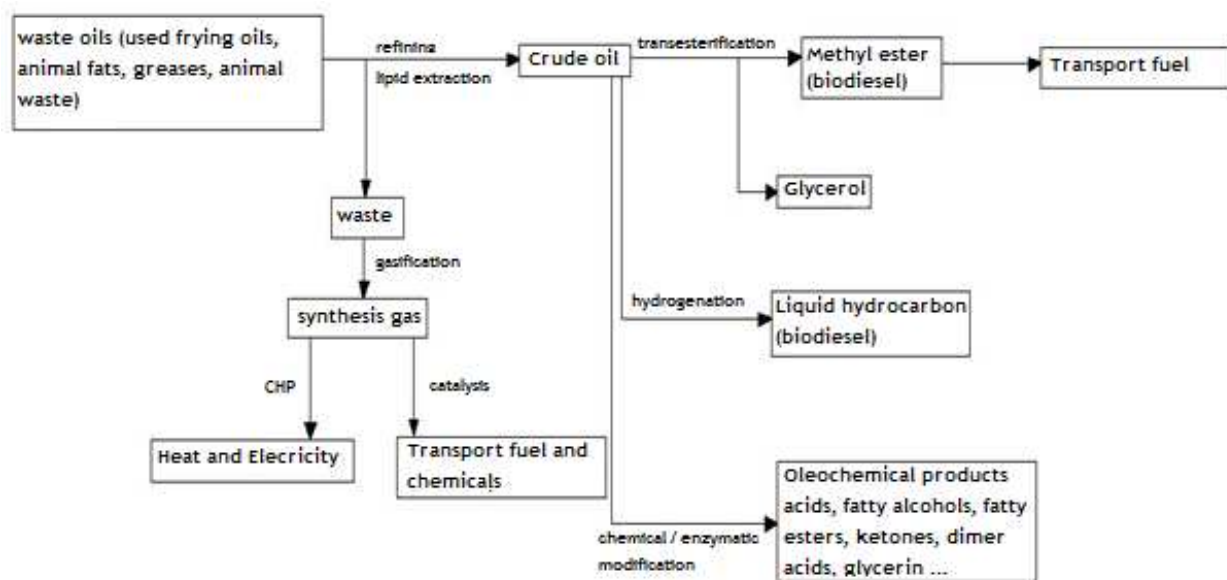


Figure 17. Biorefinery perspective based on the raw waste (developed on the basis of [46])

## 5. The existing biorefinery systems in the world

Progress in research on new, more efficient complex biomass processing methods in technological and environmental way led to the development of new technologies to enable the construction of biorefinery systems. Detailed information in this field are presented in the International Energy Agency (IEA) report, “IEA Bioenergy Task 42, Biorefining: Sustainable and synergetic processing of biomass into marketable food & feed ingredient, chemical, materials and energy (fuels, power, heat).” IEA report defines biorefinery systems, which include systems that meet the basic functions, that is, the number and the name of the technology platforms, materials, processes, and expected products. Examples of applicable platforms in biorefinery systems are placed in Fig. 18.

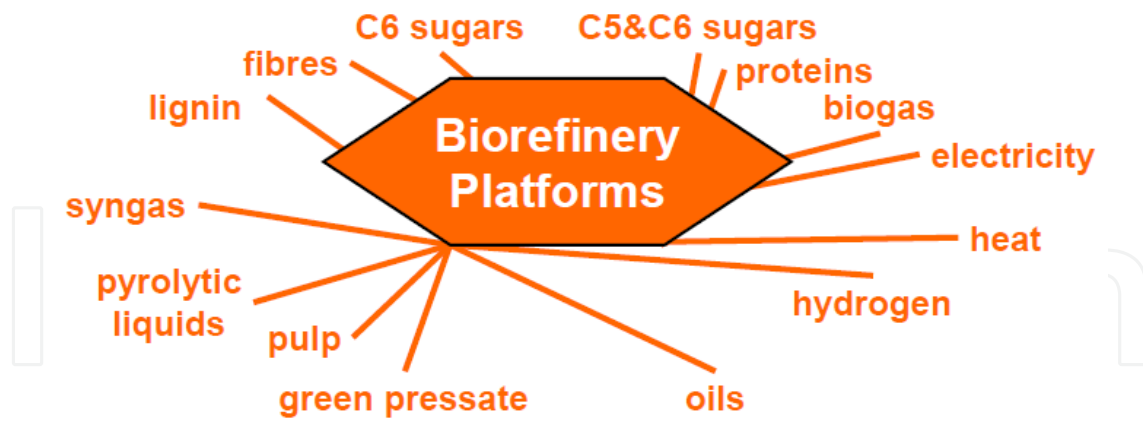


Figure 18. Examples of possible platforms in a biorefinery systems (according to IEA Bioenergy Task 42) [49]

The research in the field of the possibility of obtaining different kinds of products or chemical intermediates from biomass, so-called biochemicals, estimates the broad spectrum of these compounds, as shown in Fig. 19.



Figure 19. Portfolio of chemicals potentially to be produced from biomass (according to IEA Bioenergy Task 42) [49]

The result from the IEA report is that currently in the world, mainly in the pilot or demonstration version, there are 80 plants which can be classified as more or less complex components of biorefinery systems. In terms of some paths proposed in these technology systems, fuller research will be necessary, especially in terms of quality of products planned to be obtained and their reproducibility. In particular, reproducibility and efficiency of individual development paths can be difficult to obtain, and the difficulty is due to the heterogeneity and diversity

of biorefinery raw materials. Hence, most of the operating systems in the world are the one-platform systems and two- or three-platform systems. Production processes planned or implemented in these systems are mainly for the obtaining of bioethanol, biomethanol, and less biomethane and a few types of biochemicals, including biodegradable monomers. One of the most interesting biorefinery plants is a pilot plant LanzaTech, New Zealand, in which the fermentation process of compressed syngas obtained by the gasification of waste wood and solid urban municipal waste (MSW) is conducted. Synthesis gas fermentation process is carried out to obtain bioethanol, and regardless of this process, in a separate technology path, from the recovery of CO, CO<sub>2</sub>, and H<sub>2</sub> from syngas fermentation process, it is planned to receive a hydrocarbons from C<sub>2</sub> to C<sub>5</sub>, as a potential biofuel components and/or biochemicals, including again the ethanol and acetic acid (ethanoic), C<sub>2</sub>; isopropanol and acetone (dimethylketone), C<sub>3</sub>; and 2,3-butanediol (2,3-BDO), butane, isobutane, and succinic acid (1,4-butanedioic), C<sub>4</sub>, and isoprene, C<sub>5</sub>. A block diagram of this plant is shown in Fig. 20.

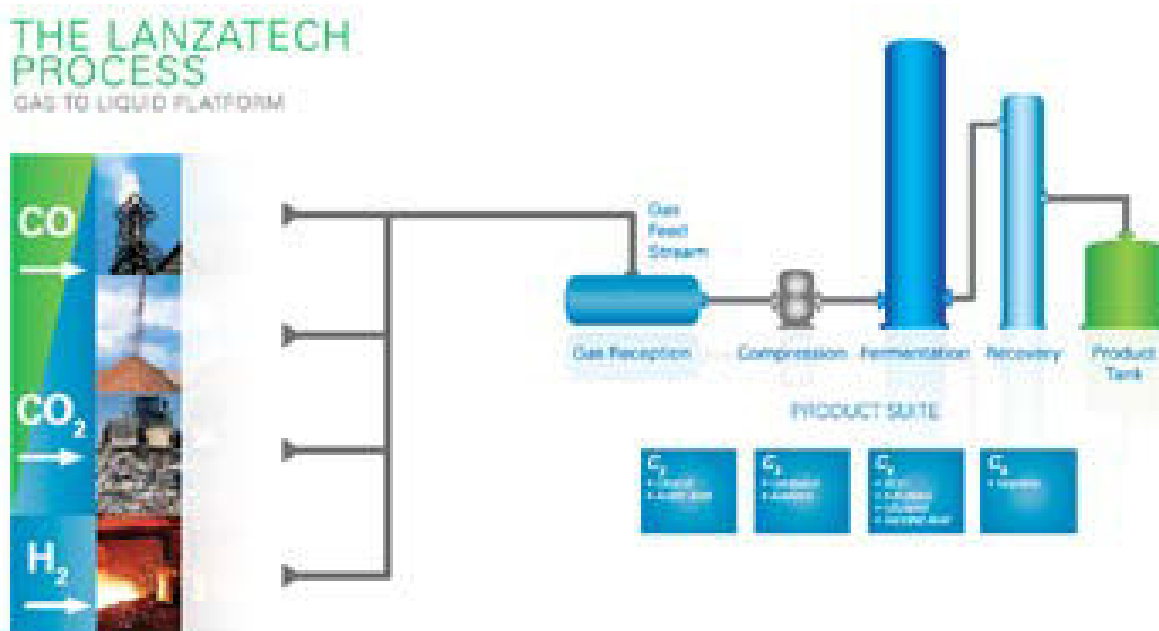


Figure 20. Block diagram of the installation LanzaTech in New Zealand (according to IEA Bioenergy Task 42) [49]

The diagram also shows the power unit which is used to supply heat and power to the plant in the biorefinery system. This block is supplied by different types of raw materials than technological resources, but also coming from renewable sources or waste substances.

Interesting system is proposed by the company Avantium Chemicals B.V. from the Netherlands. In this three-platform system (C<sub>5</sub> and C<sub>6</sub> sugars and lignin) is proposed to receive a perspective and very interesting furan fuels, polymers and monomers (furan dicarboxylic acid, furan diamine), fine and specialty chemicals (organic acids, solvents, flavors and fragrances), and solid fuels (humans and lignin residues). The raw material for the installation proposed by Avantium is generally defined lignocellulosic material (cellulose, hemicellulose, starch, and sucrose), contained in the various sources. The essence of the proposed process is to develop

the technology for obtaining derivatives of furan with catalytic processes of dehydration/etherification of carbohydrates. These derivatives can be compiled as a replacement for the relevant petroleum production of biofuels, plastics, and biochemicals. At the same time, it is possible to use emerging process residues, with the possible addition of biomass (and also coal) to produce heat and electricity, while technological processes used the resulting excess of steam and heat. As already mentioned, there are a number of streams of raw materials, possible to use in the proposed process. It may be waste from the food industry; corn stover (possibly other straw); grass, including the grass from the city greenery; as well as bagasse and municipal waste (from the households). An important and perspective solution is possible conversion of C6 sugars (glucose, mannose, galactose, and fructose) and C5 sugars (xylose and arabinose) to the derivatives of very promising chemical intermediate which is hydroxymethylfurfural (HMF), which is *inter alia* an intermediate for the preparation of DMF (2,5-dimethylfuran), the perspective biofuel, and 2,5-furandicarboxylic acid (FDCA), which can be used as a replacement to terephthalic acid (TA) [49].

## 6. Conclusion

The essence of the biorefinery processes is renewable raw materials, by-product, and waste processing for biofuels and high-value chemical products. Those processes should be led with possibly high effectiveness and in closed circulation of CO<sub>2</sub>. Process of biorefinery system creation requires high capital expenditures of technology and installation and needs assurance of appropriate raw material, personnel, and logistic background.

As can be seen from the foregoing considerations, there are a number of concepts of biorefinery development. These concepts are substantially different from each other by type of raw material used in the planned manufacturing processes to yield energy carriers like fuel and a certain group of derivatives which may be used in further chemical processes.

Generally, the biorefinery process should consist of transforming raw materials of organic origin and various origins, so to obtain a mixture of liquid components (mainly hydrocarbons), so-called bio-oil in transformation process.

The next step in the process should constitute processes similar in principle to the oil preparation processes, leading to a distillation treatment (degassing, demulsibility, dewatering, cleaning, etc.).

In the final part of the biorefining system undistilling, refining, and hydrogenation processes of bio-oil in principle are no different from the nonconservative processes realized for crude oil converting. Therefore, biorefinery complexes can be built at the beginning based on the modification of existing oil refineries by expansion of complex installation of feed transformation into mixtures of liquid fractions.

For example, in Poland, there is a few low-efficient oil refineries, which untapped technological, installation, and human potential could be used with biorefinery complex building. The potential can be used with further processing and refine processed biomass to the liquid form.

Planned undertaking widely reduces capital costs and enables obtaining chemical substances and biofuel production, which fulfill modern engines and heat devices qualitative requirements. That is why it was assumed to build an experimental biorefinery using technology potential of little oil refinery in Poland. Figure 21 shows the technological schema of planned biorefinery system.

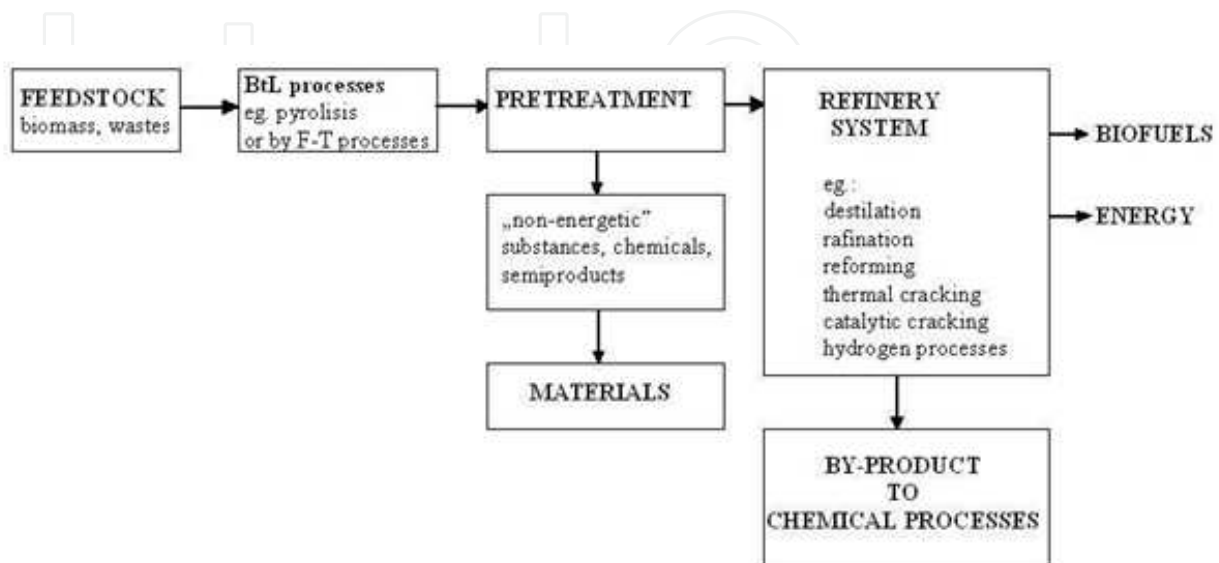


Figure 21. Diagram of biorefinery based on conventional oil refinery [50]

The essence of planned undertaking is elaboration or selection of suitable technologies of biomass liquefaction by pyrolytic process to “bio-oil” phase. It is also possible to use of gasification processes and then selective liquefaction. In this process, there is expected a technology elaboration, where from the liquid fraction will be selected “non-energetic” substances. Those substances can’t be used in further processing like biocomponents, but they could become biorefinery products or industry semiproducts for further synthesis. Refined bio-oil will become resource for obtaining and refining process using existing refinery installations like atmospheric and vacuum distillation, rectification, refinement, thermal and catalytic cracking, alternately reforming, and hydrogen process. After processing remains could become raw material for further synthesis.

Development of technology for biomass conversion in the biorefinery system based on the technology processes and systems of conventional oil refinery will require the realization of research processes in the following main areas:

- Optimization of biomass and residues pyrolysis processes or new biomass conversion processes
- Technology of production value-added co-products
- Adaptation of existing production technologies for converting bio-oil into biofuels, also second-generation biofuels

- Technology of converting co-products into marketable products

## Author details

Krzysztof Biernat<sup>1,3\*</sup> and Paulina Luiza Grzelak<sup>2,3</sup>

\*Address all correspondence to: [k.biernat@pimot.org.pl](mailto:k.biernat@pimot.org.pl)

1 Automotive Industry Institute, Warsaw, Poland

2 Motor Transport Institute, Warsaw, Poland

3 Institute for Ecology and Bioethics of Cardinal Stefan Wyszyński University, Warsaw, Poland

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