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Chapter

Biogas as a Source of Energy and Chemicals

Sonia Damyanova and Venko Beschkov

Abstract

The global economic development in the twentieth century has led to extensive use of fossils, such as oil, natural gas, and coal as fuels and chemical feedstocks. This extensive use of fossil fuels has led to enormous emissions of carbon dioxide as final product of combustion. The high absorption rate of infra-red rays by carbon dioxide has led to the so-called "greenhouse" effect. Nowadays, the renewable energy sources based on biomass have become very important with a trend to replace oil consumption at least partially and hence to remediate the emissions of greenhouse gases in atmosphere. Biofuels could be used as alternative raw material for chemical production. One of these biofuels is biogas released at anaerobic digestion of different natural organic waste. Another feature of biogas applications is its utilization as feedstock for the production of synthetic fuels and chemicals being now produced from oil and coal. A new approach is to use biogas as a fuel in fuel cells as a very promising option for energy production from renewable sources. The present review summarizes the applications of biogas for chemicals, starting with dry reforming and Fischer-Tropsch syntheses and as a source of energy, as heat and electricity production by co-generation and fuel cells.

Keywords: biogas, renewable energy, fuels, fuel cells, chemicals

1. Introduction

The mankind has relied on different sources of energy during its economic development throughout the centuries. Whereas coal has been the main energy source in the nineteenth century, oil was in twentieth one. The possible scenarios for remediation of greenhouse effect due to carbon dioxide released by energy production and industry are rendered to minimization of emissions and its recycling. The latter is accomplished by the production of energy sources and chemicals of practical importance from carbon dioxide.

The emission minimization consists in two approaches: replacement of the fossil fuels by renewable ones (solar, wind energies, biomass, etc.) or improvement of energy efficiency in all human activities in different ways. The distribution of energy sources for the European Union for the year 2016 is shown in **Figure 1**. One can see that the share of renewables is bigger than the powerful nuclear energy with a leading role in energy production. The biggest part (more than 60%) of the renewable energy sources is assigned to the biomass and waste utilization.

One of the ways to cope with the problem of carbon dioxide emissions is to close the carbon cycle using renewable fuels from presently grown biomass, by recycling

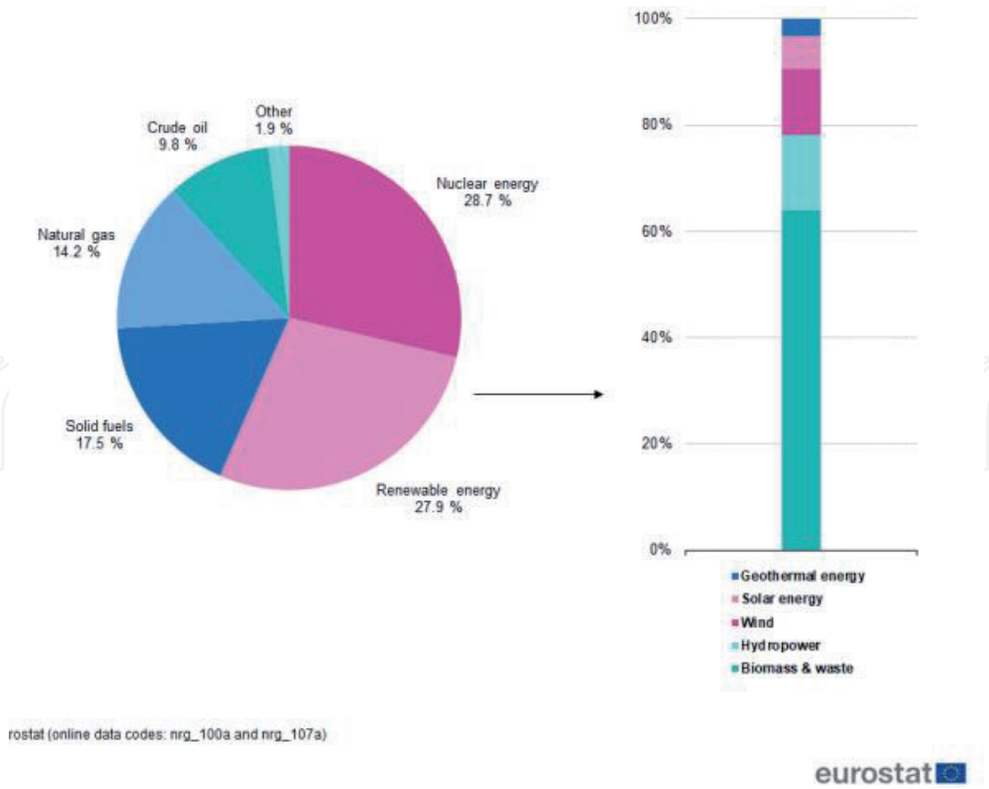


Figure 1.
Production of primary energy, EU-28, 2016 (% of total, based on tons of oil equivalent). Source: Eurostat (nrg_100a) and (nrg_107a) [1].

the released carbon dioxide by the present vegetation by photosynthesis. This is the philosophy of biomass utilization as energy source. The most spread biofuels in the present period are biogas, produced by anaerobic digestion of organic waste, bioethanol, produced from cereals and/or lignocellulosic residues and biodiesel, produced by trans-esterification of lipids with methanol or ethanol.

In this review, we shall concentrate ourselves to the application of biogas as renewable energy source and also as a feedstock for the production of chemicals and other fuels.

2. Biogas production

Biogas is produced by anaerobic digestion of organic matter of natural origin [2–4]. The main advantage of this process consists in the combined environmental and energy effect.

Biogas consists mainly of methane, carbon dioxide, and traces of hydrogen sulfide and mercaptanes, as well as residual amounts of oxygen and nitrogen. Small amounts of ethane and hydrogen are possible too. Biogas is obtained by anaerobic digestion of organic waste of biologic origin. The most exploited ones are of agricultural origin (manure, poultry litter, hay, and straw) [5], from food industry, stillage from ethanol production [6], landfill gas, activated sludge from wastewater treatment plants, etc. One of the simplest and the mostly spread flow sheets for biogas production and utilization is shown in **Figure 2** [7].

The main fuel in the scheme, shown in **Figure 2**, is biogas, utilized for energy (thermal one and electricity) or fuel for transport. The carbon dioxide released after combustion is absorbed by the vegetation by photosynthesis, thus closing the carbon cycle. The residual sludge from the digester is rich of organic nitrogen, and therefore, it is suitable for fertilizing the soil.

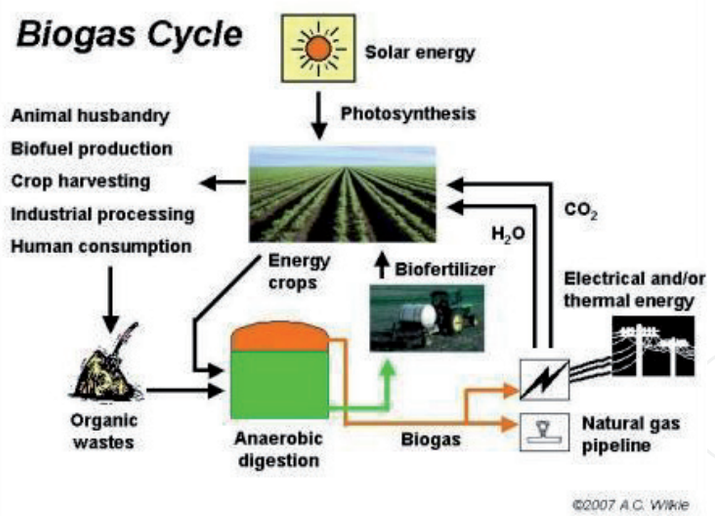


Figure 2.
Illustration of biogas cycle, formation, and applications. Scheme taken from [7].

In the past, biogas has been widely spread as an energy source in the households in the countries of Africa and Asia. Although quite primitive as design, the anaerobic digesters have solved the problems with autonomous energy supply for many households in India, Pakistan, Indo-China, etc.

Later, biogas became very important and essential share as energy source for the countries in Western Europe and Northern America. Besides heating, biogas is now more frequently used for the production of electricity and transport fuel in many municipalities. It is already added to the pipelines for natural gas distribution of household purposes.

A new trend in biogas production and utilization is the so-called biorefinery concept. This concept not only presumes the use of renewable biomass as energy source but also combines it with the production of chemicals, such as plastics, solvents, and synthetic fuels [8]. An example for this is the *Danish Bioethanol Concept* presented by Zafar [9]. It comprises the ethanol production from lignocellulosic biomass with biogas production of the stillage and cellulose waste. The residual cellulose waste is additionally recycled after wet-oxidation for additional conversion into biogas. A detailed review on biogas applications is published recently by Sawyerr et al. [10].

2.1 Some constructions of anaerobic digesters

The variety of anaerobic digesters for biogas production is very broad: from the very primitive pits to most sophisticated bioreactors, such as the floating drum reactor, the upflow anaerobic sludge blanket (UASB) reactor [11–13], and multistage bioreactor with separated compartments [14, 15]. The choice for anaerobic digester depends on the origin of substrate, and the intermediates are converted during the consecutive steps of hydrolysis, acidification, acetogenesis, and final methanation. In case an accumulation of fatty acids takes place, the reactor with separated compartments is preferable. The most exploited digester for biogas production from domestic waste, activated sludge, and manure is the UASB reactor.

2.2 Substrates for biogas

The mostly used substrates for biogas production are the manure from cattle, pigs, and poultry litter. This application competes with the traditional use of manure for soil fertilization. When the amounts of manure prevail the demand for fertilization, biogas production is welcome because double problem is solved: on the

one hand, the waste is destroyed and removed, and on the other hand, renewable energy is produced saving money and contributing for carbon cycle closing. That is why attention is paid to the utilization of cattle dung, lignocellulose waste, waste from food and beverage processing, activated sludge from wastewater treatment plants, and household solid waste with landfill gas use. The waste treatment is associated with energy production and reduction of the energy demand of the main enterprise.

2.2.1 Biogas from glycerol

Crude glycerol is the main residue from biodiesel production. The amount of this waste product is about 10% from the produced fuel. The poor quality of this glycerol, containing water, potassium hydroxide, and some methanol makes it non-suitable for market purposes even after purification. One alternative utilization of this residual glycerol is in its direct conversion into biogas, thus supplying the biodiesel plant with energy simultaneously. However, as a very simple and digestible substrate, glycerol yields large amounts of organic acids as intermediates, leading to strong inhibition of methanogenic bacteria [16–18]. That is why glycerol must be used as substrate for biogas production very cautiously with the addition of small amounts, thus making this process with little practical use. It is reported, however, that small additions of glycerol to other basic substrates, i.e. manure, can boost biogas production, as reported by Robra et al. [19] and Astals et al. [20].

Food industry is also a good source for biogas production.

3. Biogas applications

3.1 Biogas for heating

Traditional biogas contains approximately 60% (vol.) methane, almost 40% carbon dioxide, small amounts of ethane and hydrogen (less than 0.5% together), hydrogen sulfide and mercaptanes (some ppm), humidity, and traces of oxygen. Its net energy capacity is ca. 24 MJ/nm^3 at methane content of 60% (vol.). The first and most direct use of biogas is for heating purposes for maintenance of the equipment and the farm, where the animal dung is treated. The same applies for its use for domestic purposes, besides heating, e.g., cooking and lighting, as firstly used in Asian and African countries.

Another more sophisticated use of the biogas heating capacity is its utilization as heat energy in beverage and ethanol production. There the stillage remaining after distillation is recycled for biogas production. The resulting biogas is combusted for boiler heating and for energy for operation of distillation columns. Thus, the problems with the treatment of the residual stillage are solved by conversion into biogas, thus mitigating the problems with energy supply and spending. Calculations show that in some cases, stillage utilization as biogas can cover almost the whole energy demand for heating the distillation process. Besides these straightforward applications, biogas is also injected into the grid for natural gas supply for domestic use [21, 22]. For this purpose, a preliminary scrubbing of the carbon dioxide and sulfur compounds is necessary.

3.2 Biogas for electricity

Biogas is suitable for generation of electric power in combination with heat recovery. Usually the gas is combusted in engines with internal combustion coupled

to turbine. The released heat (being around 60% of the utilized energy) is used for heating purposes for maintenance of the anaerobic digester or for household needs. This method is widely applied for the treatment of activated sludge, a residue from municipal wastewater treatment plants [23, 24].

Electricity production by gas turbines can be applied by biogas as a fuel, thus replacing the natural gas for small-scale applications (or power within 25–100 kW).

3.3 Biogas for transport

The use of biogas as a fuel for civil transport and road vehicles instead of natural gas is already spread in Western Europe and the United States [25]. There are many vehicles in Sweden operating on biogas in the urban public transport [26].

3.4 Biogas in fuel cells

Another very attractive application of biogas for electricity production is its use in fuel cells. The specialized cells for these purposes are described briefly by O'Hayre et al. [27]. Prior to biogas feed, carbon dioxide and sulfur compounds must be removed by scrubbing to avoid corrosion and catalyst poisoning and to rise the gas energy capacity. A sketch of such a fuel cell is shown in **Figure 3**, cf. [28].

The classic process for methane-driven fuel cells is to convert catalytically by steam reforming methane into a mixture of carbon monoxide and hydrogen and to use the latter in a traditional hydrogen/oxygen fuel cell to generate electricity. The advantages of fuel cell applications with methane as a fuel compared to the traditional heat power stations consist in their higher efficiency, clean waste gases (containing almost only carbon dioxide), and higher efficiency at low loads than the gas turbine equipment [29]. Moreover, the released heat can be utilized for different purposes; the main one is to maintain the temperature regime in the fuel cell. There are many practical applications of these methods. It is already widely commercialized. A disadvantage of this method is the necessity of consequent reactions of steam reforming and carbon monoxide removal as well as the operation at high temperatures (about 750°C), being harmful for the metal parts of the equipment [30, 31]. Higher temperatures are preferred to avoid coke deposition on the catalyst [31].

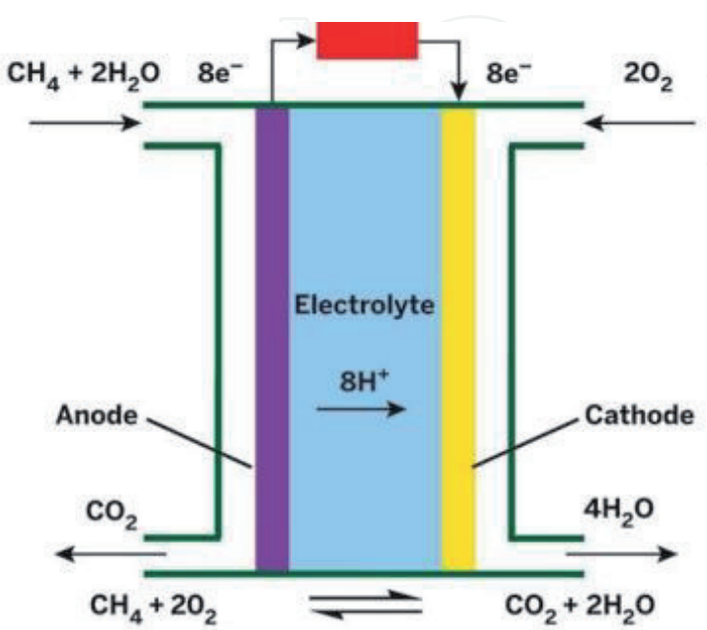


Figure 3.
Principal sketch of methane-driven fuel cell, from [28].

There are new efforts to lower the operation temperature to 500°C in order to keep the equipment durability [32, 33]. Another improvement of the technology is to use the mixture of carbon monoxide and hydrogen as a fuel simultaneously, thus simplifying the whole process, but applying new catalytic process.

The most attractive option is to convert methane (biogas, respectively) into electricity in one step, thus avoiding the steam reforming and carbon dioxide removal. There are some new studies showing direct catalytic oxidation of methane in the anodic space of solid oxide fuel cells (SOFCs), with direct activation of the C-H bonds in the methane molecule [28, 34–36]. A platinum catalyst was used for this purpose at low temperatures, e.g., 80°C. However, the catalyst deactivates, and the process is limited by methane diffusion in the anodic space. As a result, the power density is still low for practical use.

3.5 Biogas for chemicals

Besides as a fuel, biogas could be used as a feedstock for synthetic organic fuel production. There are studies claiming for biogas recovery as fuels applying catalytic auto-reforming. Another approach is the dry reforming consisting in converting the equimolar mixture of methane and carbon dioxide into synthesis gas (an equimolar mixture of carbon monoxide and hydrogen).

Afterward, this synthesis gas is converted into a mixture of light hydrocarbons by the catalytic Fischer-Tropsch process. The resulting Fischer-Tropsch process yields liquid hydrocarbon fuels (methanol and dimethyl ether). The intrinsically high-energy density of these fuels and their transportability make them highly desirable. Such synthetic fuels do not contain any sulfur. In addition, methanol (arguably the "simplest" synthetic carbonaceous fuel) is a candidate both as a hydrogen source for a fuel cell vehicle and indeed as a transport fuel, and dimethyl ether is viewed as a "superclean" diesel fuel [36]. It is well known that methanol is a starting material in chemical industry. It is a liquid at room temperature and has much easier storage and transport capabilities than alternatives such as methane and hydrogen. Methanol is used as solvent, gasoline additive, and a chemical feedstock for production of biodiesel and other chemicals of high value. Therefore, the wide application of methanol motivates its large-scale production, which is ever increasing.

However, presently, the dominant technology of methanol is a two-step catalytic process, which is too expensive. A large number of industrial-scale chemical manufacturing processes are currently operated worldwide on the basis of strongly endothermic chemical reactions. The steam reforming of hydrocarbons to yield syngas and hydrogen is a classic example:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298K} = +206.3 \text{ kJ/mol} \qquad (1)$$

The above, highly endothermic reaction is used worldwide for the high-volume production of "merchant hydrogen" in the gas, food, and fertilizer industries, i.e., other portions of energy have to be spent with the consequent air pollution by carbon dioxide.

At present, a relevant technology for methanol production resides in the transformation of CO_2 and CH_4 to molecules having industrial added values. Among such technologies, a great attention is focused on the production of synthesis gas (gaseous mixture of CO and H_2) that constitutes a versatile building block for subsequent production of methanol or chemical intermediates in petrochemical industries. Methanol is still produced on a world scale from synthesis gas, which is combination of varying amounts of H_2, CO, and CO_2 (at 200–300°C, 50–100 bar), which is itself product of steam reforming of methane (SRM; at ca. 800°C over Ni-based catalyst), followed by further conversion processes such as

Fischer-Tropsch (FT) synthesis. This two-step process incurs high energy and capital demands. Additionally, this process gives many other light and heavy weight co-products along with the methanol product. Therefore, additional energy and cost in the conventional methanol plants are directed to the separation of these coproducts from methanol prior to the final deposition of product.

The direct synthesis of methanol from syngas requires a H_2/CO ratio of about 2 [37, 38]. Since the syngas produced by dry reforming of methane (DRM) is too poor of H_2 ($H_2/CO \leq 1$) to be fed to a FT synthesis unit, the bi-reforming of methane (BRM), combining DRM with steam reforming of methane (SRM) ($H_2/CO = 3$) and the utilization of the most important two greenhouse gases CH_4 and CO_2 with water, may yield a syngas with ratio close to 2, the so-called "metgas":

$$3CH_4 + CO_2 + H_2O \Leftrightarrow 4CO + 8H_2 \quad (2)$$

To date, only one plant with the combination of steam and dry reforming has been recently demonstrated by the Japan Oil, Gas, and Metals National Cooperation. No other industrial technology for DRM has been developed because the selection and design of suitable reforming catalyst remain an important challenge. Ni-based catalysts are the most attractive candidates for large-scale industrial applications due to their high activity in DRM and SRM [39–43], low cost, and wide availability compared to noble metals. However, they are sensitive to deactivation caused by the metal particles sintering and carbon formation at high reaction temperature of reforming processes. Development of selective and coke-resistance modified Ni-based reforming catalysts is a key challenge for successful application of bi-reforming for methanol production. Modifying Ni catalysts with suitable promoters and supported on reducible metal oxide carriers will give the opportunity to develop active and stable catalysts for bi-reforming of methane.

A "super-dry" CH_4 reforming reaction for enhanced CO production from CH_4 and CO_2 was developed [44]. $Ni/MgAl_2O_4$ was used as a CH_4 reforming catalyst, $Fe_2O_3/MgAl_2O_4$ was used as a solid oxygen carrier, and CaO/Al_2O_3 was used as a CO_2 sorbent. The isothermal coupling of these three different processes resulted in a higher CO production than conventional dry reforming by avoiding back reactions with water. Equation (3) shows the global reaction of this two-step process, in which CO and H_2O are inherently separated because of the two-step process configuration:

$$CH_4\,(g) + 3CO_2\,(g) \rightarrow 4CO\,(g) + 2H_2O\,(g)\ \Delta H°_{298K} = 330\ kJ/mol_{CH4} \quad (3)$$

It is important to note that despite the apparently higher endothermic effect of the super-dry reforming process than conventional DRM (Eq. 1), the required heat input per mole CO_2 converted is much lower (110 kJ/mol CO_2 compared to 247 kJ/mol CO_2). Finally, given the availability of a renewable source of H_2, applications are possible where CO and H_2 can be combined in different ratios for the formation of chemicals or fuels [45, 46]. Indeed, an efficient and separate production of high purity CO and H_2 would further establish the role of syngas as a versatile and flexible platform mixture.

All these methods and techniques are applicable when biogas is available. Some other applications are described briefly below.

3.5.1 Biogas as a feedstock for value-added chemicals

First of all, biogas must be purified for sulfur compounds prior to its use [47]. Afterward, methane and carbon dioxide have to be separated by membrane processes using gas-liquid systems [48] or swing pressure adsorption [49]. Once methane and

carbon dioxide are separated, each of them has its own route for further application. Besides the already mentioned applications as a fuel for transport and energy purposes, dry reforming and steam reforming to obtain synthesis gas, the purified methane can be converted into light hydrocarbons, e.g., ethane and ethylene by advanced methods, like the so-called VYJ process [50–53]. By this method, methane is converted in one step into ethylene by catalytic or electrocatalytic reaction [54–56].

High yields up to 88% in total are attained [50]. The rest of nonreacted methane is trapped in molecular sieves and recycled to the reactor [50, 53, 54]. In this way, the use of methane reaches 97% with an ethylene yield of 85% [50].

As ethylene is a basic feedstock for the mostly spread polymerizations and many value-added chemicals, it is clear that this way of biogas utilization is quite promising one.

4. Methodologies for energy demand evaluation in biogas production

The usual criteria for the feasibility of an anaerobic digestion technology are the type of digester, the operation temperature, the necessary retention time of the substrate in the reactor, the substrate acidity (the initial pH value), and the presence of certain chemicals in the inlet slurry.

However, the most important one is energy demand for the biogas formation and the energy potential of the produced biogas.

There are two typical temperature ranges for biogas production: mesophilic one (at 30–35°C) and thermophilic one (at 55–60°C). Different genera of methanogenic microorganisms are capable to accomplish the processes in those two cases. The advantages of the thermophilic regime are in the higher production rate and the lack of pathogens in the outlet slurry. However, the energy input for maintenance of this regime is higher than for the mesophilic one.

The question of the energy demand for any industrial process is of crucial importance for its economic reliability. The same applies to biogas production.

There are some methodologies for the estimation of the feasibility of biogas production [57, 58]. They all involve the demand of heat for temperature maintenance and electricity for mechanical operations (stirring, pumping, and transport) and comparison to the energy yield after anaerobic digestion.

Generally, the operations for a certain flowsheet are separated into production processes and support ones. The production processes in the considered case are the reception of the substrate and its storage, pre-treatment of feed (dilution, pH adjustment, acid hydrolysis, etc.), and anaerobic digestion with biogas production. The removal of the digestate and its storage and processing are also included. This set of processes is called as Level 1 [57].

Once biogas is produced, it could be used for direct heat and/or electricity production and supplied to customers or for own use (Level 2). More sophisticated operations, such as gas cleaning, upgrading (i.e., removal of carbon dioxide), and compressing the upgraded gas, are required if the gas will be distributed by the gas distribution grid or for some chemical applications.

The methodologies for energy demand evaluation consist in the inventory of all such processes and auxiliary ones with their energy demand per unit production (i.e., amount of produced biogas with certain energy potential). Then, the overall energy demand is compared to the biogas yield with its energy potential, and the percentage of the energy input to the overall yield is a measure for feasibility of the studied technology.

The structures of the energy demand for different flow sheets and the weight of different subprocesses depend on the substrate properties (particles size, chemical

structure and content, moisture, and total solid content) and the amount to be treated, the digester construction and design.

Berglund and Borjesson [58] proposed a methodology based on the life-cycle perspective including the energy required for the production of the substrates (including crop growth, harvesting, transport, etc.). The energy efficiency is defined by the ratio of the energy input to the energy yield of the produced biogas. It was found that the energy input corresponds mainly to 15–40% of the energy content of the produced biogas. The subprocesses of extensive handling of raw materials may lead to considerably increase the energy input and thus to undermine the feasibility of the entire technology.

In case the gas will be used as a feedstock for other chemical applications (e.g., dry reforming and steam reforming), the operational costs of the processes at Levels 1 and 2 have to be compared to the operational costs for the chemical processes and the prices of the produced chemicals or other final products.

5. Residual carbon dioxide

The main disadvantage of biomass produced fuels is the inevitable release of CO_2 in the atmosphere after combustion. Therefore, big efforts are made in the recent years for remediation of this adverse effect of greenhouse gas. The best way to cope with this problem is the natural assimilation by the vegetation by photosynthesis, but it is not sufficient due to the very large emissions from industrial sources, energy production, transport, and household. That is why many other methods are proposed and studied in the recent years.

One of them is the direct use of pure carbon dioxide as a solvent in supercritical extraction in the pharmaceutical industry. However, this application is limited and cannot be a substantial solution of the problem. There are many efforts to recycle carbon dioxide to produce different organic chemicals: formic acid, methanol, dimethyl-ether, poly-carbonates, acrylic acid, etc. [59, 60]. All of these methods are applicable for the residual carbon dioxide after separation from biogas. Therefore, not only methane but also carbon dioxide in biogas is valuable source of energy and value-added product.

6. Conclusions

The data presented here illustrate one of the very important biorefinery approaches to produce simultaneous energy and value-added chemicals from biomass, thus reducing the demand of fossil fuels and resulting in overloading of atmosphere by greenhouse gases. The same applies to the water and soil pollution, since those resulting from biomass processing are nature compatible and facilitate the formation of close energy and material cycle. One of the ways to do it is biogas production from such waste.

At the end, we can say that biogas extends its area of application leading simultaneously to protect the environment by waste treatment, natural gas, and fossil fuel saving, as well as to replace, at least partially, the oil as a feedstock for organic value-added products.

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Conflict of interest

The authors declare no conflict of interest.

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