CONSIDERATION ON BIOMASS VALORIZATION

C. MÂRZA\textsuperscript{1}  G. CORSIUC\textsuperscript{1}  D. ILUŢIU-VARVARA\textsuperscript{1}

Abstract: With the development of technologies the energy consumption is constantly increasing, including in rural areas. The use of renewable sources in order to cover the energy demand would be, at the same time, a solution for reducing CO\textsubscript{2} and methane emissions. One of the renewable sources which we can consider is biomass, which can be found in the highest proportion in rural areas, in the form of residues and waste from agriculture, livestock or wood processing. Currently is most commonly used in households for heating and domestic hot water. Through mechanical, biological or thermal processes biomass can produce thermal energy but also electricity and other fuels. Each process differs depending on the type of biomass available and the desired final product.

Key words: biomass, energy, renewable, gazification, anaerobic digestion.

1. Introduction

The biomass energy potential of Romania is up most important, representing approximately 65\% of the total renewable energy resources [6].

The biomass includes the following components: cellulose, hemicelluloses, lignin, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash etc. The concentrations of each compound vary one species to another. Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals. Generally, biomass is composed of cellulose, hemicelluloses and lignin.

Celluloses consist of many sugar molecules linked together in long chains or polymers. The lignin fraction consists of non-sugar type molecules that act as a glue holding together the cellulose fibers, and contributes to structural rigidity of plant tissues. It has very high energy content structure and difficult to decompose. These are present in the complex macroscopic polymeric forms as [10,13]:

- cellulose (C\textsubscript{x}H\textsubscript{y}O\textsubscript{z})\textsubscript{x},
- hemicellulose (C\textsubscript{y}H\textsubscript{z}O\textsubscript{t}), and
- lignin (C\textsubscript{z}H\textsubscript{t}O\textsubscript{y}(CH\textsubscript{3}O)\textsubscript{x}\textsubscript{y}),

where x, y and z represent parameters of large magnitudes which define the composition of a given biomass material. The relative proportions of cellulose and lignin is one of the determining factors in identifying the suitability of plant species for subsequent processing as energy crops.
Biomass is used for facility heating, electric power generation, and combined heat and power. The term biomass encompasses a wide range of materials, including [3, 6]:
- wood from forestry, arboricultural activities or from wood processing;
- agricultural residues, from agriculture harvesting or processing;
- energy crops (high yield crops grown specifically for energy applications);
- food waste, from food and drink manufacture, preparation and processing, and post-consumer waste;
- industrial waste and co-products from manufacturing and industrial processes.
- animal and human waste.

Biomass production is not only a renewable energy resource but also a significant opportunity for sustainable rural development.

The paper presents two different ways of exploiting biomass for energy generation in rural area and describes some installations that produce heat and electricity from biomass, based on gasification respectively anaerobic digestion processes.

2. Conversion technologies and plants

Briefly are presented the main processes of biomass conversion into energy:

→ Thermochemical processes
  - Direct combustion with heat generation; the oldest method is the heat produced from biomass obtained from the burning of wood or forest residues (heat required for heating homes and cooking, especially in rural areas, is the result of consumption of vegetal waste);
  - Advanced thermal conversion; this category includes gasification with air or oxygen - producing a poor gas, syngas or ethanol, respectively pyrolysis which produces a medium gas and tar.

Pyrolysis yields bio-oil by rapidly heating the biomass in the absence of oxygen.

There are several ways to convert biomass into synthetic fuels. Thermal pyrolysis and a series of catalytic reactions can convert the hydrocarbons in wood and municipal waste into a synthetic gasoline.

→ Biological conversion, which mainly produces biogas (having variable methane content, depending on the raw material used) through anaerobic digestion;
→ Chemical conversion - such as acid hydrolysis that produces ethanol;
→ Biochemical conversion - alcoholic fermentation respectively aerobic and anaerobic fermentation of organic materials into hydrogen, methanol, ethanol or diesel fuel.

There is a wide range of conversion technologies to make optimum use of biomass. Depending on the type [15] of biomass, the technologies are different for dry (Figure 1) or wet (Figure 2) biomass.

2.1 Gasification

Combustion technologies, including raw materials and the resulting products are summarized in Figure 3.

Gasification is a process about 200 years old, which has its origins in the so-called dry distillation of materials containing carbon and had first engineering applications in 1812 at Gas Company in London. The first commercial plant was built in 1839, after which the production from coal and biomass was used on an industrial scale. In 1881 the process was used on internal combustion engines and then, in 1920, was implemented to operate of trucks and tractors. In the Second World War, due to the lack of oil, gasification of biomass for energy production has been extended so that more than a million of gasifier-powered vehicles were in operation during that time in Europe.
Finally, with the trigger of the energy crisis of the 1970s, the gasification method, as well as all technologies that do not rely on fossil fuels, returned to the attention of technicians. Their goal was to obtain as high as possible efficiency processes.

The gasification process may be regarded as a burning conversion, but involving less oxygen than combustion.
Depending on the ratio between the amount of oxygen in the reaction and that necessary to the complete combustion (the equivalent ratio) can be calculated the composition of the resulting gas.

For a ratio less than 0.1, the process is known as pyrolysis and only a small portion of the chemical energy of biomass is found in the resulting gas, the rest being found in the carbon and in the produced bio-oil. If the ratio is between 0.2 and 0.4, the process is called gasification. Here occurs the maximum power transfer from biomass to the produced gas [8].

Gasification may be applied to the biomass that has the moisture content less than 35%.

The process usually takes place at about 850°C. Because the injected air prevents the ash from melting, steam injection is not always required. A biomass gasifier can operate under atmospheric pressure or elevated pressure.

An important feature of gasification is that the system is autothermic. It creates sensible heat necessary to complete gasification from its own internal resources.

In following, prevailing chemical reactions are presented, respectively the main three gasification stages are described [7]:

- in the first stage the oxidation and other exothermic reactions take place:
  - partial oxidation: \( C + \frac{1}{2} O_2 \rightarrow CO \) (1)
  - CO oxidation: \( CO + \frac{1}{2} O_2 \rightarrow CO_2 \) (2)
  - total oxidation:
    - \( C_6H_{10}O_5 \rightarrow xCO_2 + yH_2O \) (3)
  - hydrogen oxidation:
    - \( H_2 + \frac{1}{2} O_2 \rightarrow H_2O \) (4)
  - water-gas shift:
    - \( CO + H_2O \rightarrow CO_2 + H_2 \) (5)
  - methanation:
    - \( CO + 3H_2 \rightarrow CH_4 + H_2O \) (6)
- in the second stage the combustion gases are pyrolyzed by being passed through a bed of fuel at high temperature, producing tar and char:
  - \( C_6H_{10}O_5 \rightarrow CxH_z + CO \) (7)
  - \( C_6H_{10}O_5 \rightarrow C_yH_mO_y \) (8)
- in the third stage the initial products of combustion are reconverted by reduction reaction to carbon monoxide, hydrogen and methane, which are the main combustible components of syngas:
  - steam gasification:
    - \( C + H_2O \rightarrow CO + H_2 \) (9)
  - boudouard reaction:
    - \( C + CO_2 \rightarrow 2CO \) (10)
  - reverse water shift:
    - \( CO_2 + H_2 \rightarrow CO + H_2O \) (11)
  - hydrogenation:
    - \( C + 2H_2 \rightarrow CH_4 \) (12)

Depending on the origin and quality of biomasses as well as the way in which it is brought into contact with the oxidant gasification products may have applications that can be grouped into two categories:

- heat production - used for fuelling external burners in boilers or dryers;
- electricity production;
- coupled to gas turbine or internal combustion engine for power generation.

Further in Figure 4 is presented the schematic diagram of the catalytic gasification process, having as a result the syngas [11].

2.2 Anaerobic digestion

Anaerobic digestion produces a renewable natural gas when organic matter is decomposed by bacteria in the absence of oxygen. In the Figure 5 are shown schematically the stages of biomass conversion in various energy forms.

Fermentation is a process that uses microorganisms to convert fresh biological material into simple hydrocarbons or hydrogen. We illustrate fermentation processes by describing the anaerobic digestion process, a process that is well
suited for producing methane from biomass [3, 5, 14].

The anaerobic digestion process proceeds in three stages:
- in the first stage, the complex biomass is decomposed by the first set of microorganisms. The decomposition of cellulosic material \((C_{n}H_{10}O_{5})_n\) into sugar glucose \((C_{6}H_{12}O_{6})\) occurs in the presence of enzymes provided by the microorganisms. The reaction is:
  \[
  (C_{6}H_{10}O_{5})_n + nH_2O \rightarrow nC_{6}H_{12}O_{6}
  \] (13)
- in the second stage, hydrogen atoms are removed in a dehydrogenation process that
requires acidophilic (acid-forming) bacteria. The net reaction is:
\[ nC_6H_{12}O_6 \rightarrow 3nCH_3COOH \]  \hspace{1cm} (14)

- in the third stage, a mixture of carbon dioxide and methane called biogas is produced from the acetic acid produced in stage two. The third stage requires the presence of anaerobic bacteria known as methanogenic bacteria in an oxygen-free environment. The reaction is:
\[ 3nCH_3COOH \rightarrow 3nCO_2 + 3nCH_4 \]  \hspace{1cm} (15)

In this case, biomass appears to be a source of methane.

The valorisation potential for renewable energy in rural areas, will have the following consequences:

- improving the quality of life through: creating optimal living conditions, increase of attractiveness for the area, increase the birth rate, reduce the depopulation, reduced unemployment by attracting further investors etc.;
- realising of independent autonomous applications of electrification for isolated villages, for tourist locations;
- depreciation, in the relatively small, of investment for equipment producing green energy because the produced energy is free;
- increasing the number of homes from sustainable building materials [1] etc.

Biogas production is very well suited in rural areas, to ensure the needs of households (individual or farms) and also of a community through the centralization of various forms of biomass specific to the region. It also can be used in close proximity to urban areas, like annexes to the wastewater treatment plants.

2.2.1. Biogas production for individual households

In rural areas or in remote areas, these types of installations are used in a relatively large scale. The biogas obtained in digesters is used for household needs, mainly for heating and lighting. The most common types are the underground reactors, namely:

- the chinese type (Fig. 6.a) [12]; in which new substrates are added once a day and with the same frequency an equal amount of the decanted liquid mixture is being evacuated. This type of reactor is without stirring, so that the sedimentated suspended solids should be removed 2-3 times per year, during which most of the substrate is removed and only a small portion (about one-fifth of the reactor contents) is left for the recirculation.

- the indian type (Fig. 6.b) [12]; are similar to the chinese type except that the effluent is collected at the bottom of the reactor, and a floating gas bell also functions as a biogas tank.

There is also mobile unit version, which consists of a horizontal cylindrical reactor fueled with wet biomass at one end, while the digestate is collected at the opposite end. The substrate moves through the reactor as a plug flow, a part of the outlet is re-circulated to dilute the new input, achieving in this way the inoculation.

2.2.2. Centralized biogas production

This method is also known as the centralized co-digestion and consists in collecting wet biomass from a community consumers and its centralized processing in order to reduce costs, time and labor.

This method is specific to countries having a developed zootechnical sector, such as Germany, Denmark etc.

The digestion process takes place either mesophilic (about 35 °C) or thermophilic (around 50 °C to accelerate the decomposition process). The two processes involve the participation of various types of microorganisms. The time assigned to decomposition is between 12 and 25 days.
3. Conclusions

On our planet are produced annually large amounts of dry and wet biomass. Biomass is the only renewable form of energy, which if is not properly used, produces a negative effect on the environment. As a result of microbial activities the biomass is subjected to natural anaerobic degradation and generates different gases, primarily methane. Thus, emitted directly into the atmosphere, methane is a major greenhouse gas, but recovered and used is a renewable source of energy.

The gasification plants present a series of advantages, such as:

- can be adapted to any type of organic solid fuel;
- a high energy efficiency; high electrical performance compared to other processes (for gasification efficiency is 32% compared to 22% for direct combustion using Rankine cycle);
- reduce emissions of greenhouse gases, namely up to 40% CO₂ and 100% CH₄;
- the values of emission that affect human health, such as dioxins and furans, are much lower than in combustion;
- allow the construction of smaller plants (from 0.5 MW);
- waste resulting from gasification can be eliminated or recycled;
- resulting synthesis gas are clean and usable as such;
- possibility for energy supply in remote areas.

Anaerobic digestion is an integrated system of renewable energy production, organic waste treatment and recycling of nutrients. It creates benefits to the agricultural, environmental and economic level for farmers, biogas plant operator personnel and also for society as a whole, ensuring:

- recycling cheap and safe environment animal manure and organic waste;
- production of renewable energy;
- decrease of greenhouse gas emissions;
- an enhanced animal safety by sterilizing digestate;
- an improved fertilization efficiency;
- less inconvenience caused by odors and insects;
- economic benefits for farmers.

The price of biomass itself is low (ie fuel), but power plants based on such fuel are expensive. Among the disadvantages of energy production plants using the so-
called green energy, is mentioned: low conversion efficiency, the need of land, seasonal variations in productions (of crops), high volume in fresh form - raising questions of transport, storage and usage according to the needs.

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References