(RESEARCH ARTICLE)

Thermal energy of plant biomass, its components, and secondary biofuels

Michael Ioelovich *

Designer Energy Ltd, 2 Bergman Str., Rehovot 7670504, Israel.

Abstract

The main purpose of this article was to study the content of thermal energy (Q)and energy density (ED) in various biomass types, in the biomass components such as cellulose, hemicelluloses, lignin, and some other substances, as well as, in biomass-based secondary biofuels, solid (bio-char), liquid (bio-alcohols, bio-gasoline, biodiesel fuels), and gaseous (bio-hydrogen, bio-methane, syngas). For this purpose, methods of chemical thermodynamics were used. It was found that the increased content of lignin, lipids, resins, and waxes in the biomass contributes to its high Q value, while moisture and ash reduce the Q value of the biomass. A method of additive contributions of thermal energies of main biomass components is proposed to calculate the Q value of the biomass sample. Considerable attention is also paid to studying thermal energy content in cellulose derivatives, and secondary solid, liquid, and gaseous biofuels. The Q and ED values of biochar obtained from biomass are significantly higher than those of the initial biomass. Of the various liquid fuels, bio-gasoline synthesized from synthesis gas by the Fischer-Tropsch method has the largest amount values of Q and ED. Among the various biogases, bio-hydrogen has no competitors because of its enormous thermal energy content. However, if the value of energy density is calculated, then bio-methane comes out on top.

Keywords: Biofuels; Biomass; Cellulose; Chemistry; Hemicelluloses; Lignin; Thermal Energy Content; Thermodynamics

1. Introduction

The existence and further development of the present civilization require expanded consumption of energy, chemicals, and materials. Nowadays, the main energy sources are still fossil fuels, namely coal, petroleum, and natural gas [1]. However, the increased use of fossil fuels is causing acute environmental problems, since the combustion of such fuels is accompanied by the emission of carbon dioxide triggering the greenhouse effect and global warming.

An additional problem is that fossil resources are not reproduced in nature. Therefore, their reserves are exhausted and run down in an essentially permanent manner [2]. To eliminate the imbalance in the fossil sources, an increased utilization of alternative sources of energy and raw materials is required. Considerable attention in recent years has been given to plant biomass, which in contrast to fossil sources is continuously renewed in nature [3].

The plant biomass is formed in nature from carbon dioxide and water by photosynthesis absorbing solar energy. When the plant biomass is burned, it releases the accumulated solar energy in the form of heat, along with the release of used water and carbon dioxide stored in the biomass. Therefore, plant biomass is considered a CO_2-neutral source of renewable energy [4, 5].

The total resources of plant biomass reach 1.5 trillion tons [6]. The potential resources of biomass among alternative and renewable energy sources are above 70% [7], while the biomass share in the production of alternative energy exceeds 50% [4]. Despite advances in solar and wind energy, in many countries plant biomass still accounts for a

---

* Corresponding author: Michael Ioelovich

significant share of energy production [4]. So in Africa, up to 60% of energy is generated from biomass. East Asia countries and China receive up to 25% of energy from biomass, while in Latin America, the share of biomass energy is 18%. Only in the USA, the European Union, and other developed regions and countries, the share of biomass in energy production is small and does not exceed 3%.

Currently implemented technologies for the production of liquid biofuels are based on the transformation of carbohydrates into bioethanol and vegetable oils into biodiesel fuel. The main sources of these carbohydrates are juices of sugarcane, sugar beet, and sweet sorghum, as well as starches of corn, wheat, potatoes, and some other agricultural plants. Since these carbohydrates and vegetable oils are required in the food industry, their use for the production of biofuels is limited. Moreover, further expansion of the production to a higher volume of bioethanol and/or biodiesel will cause a shortage of land areas, exhaustion of the soil, excessive consumption of water and energy, deficits of food and feed products, and increase their prices [8].

An alternative way to obtain biofuels without competing with the food and feed industry is the use of inedible biomass, which is an abundant, renewable, and inexpensive plant material. This biomass type involves energy crops (e.g., miscanthus, switchgrass, Bermuda grass, *etc*.), forest residues (e.g., sawdust, twigs, shrubs, *etc*.), residues of agricultural plants (*e.g*. stalks, husks, cobs, *etc*.), residues of textile, pulp, and paper, municipal paper waste, etc. Moreover, huge amounts of algae can be used as appropriate feedstock for the production of bioenergy or chemicals. The total resources of inedible biomass accumulated annually are estimated at 10 billion tons, the combustion of which could potentially generate about 150 EJ of bio-energy [9].

The main components of plant biomass are cellulose, hemicelluloses, lignin, and some other substances introducing their share of thermal energy to the total energy of biomass. Plant biomass is also a feedstock for producing secondary biofuels, solid fuels (biochar), liquid fuels (bio-alcohols, bio-diesel fuels, etc.), and gaseous fuels (bio-hydrogen, bio-methane, syngas).

Despite the large number of publications, data on the amount and density of thermal energy of various types of biomasses and their main components, as well as secondary biofuels, are not sufficiently reliable and are the subject of discussion. The main goal of this study is to fill the gap in this knowledge.

2. Results and Discussion

2.1. Content of thermal energy in plant biomass

Plant biomass and any its based natural organic substance is a chemical accumulator of part of the energy that was received by the plant from solar radiation and used for biosynthesis. This part of the chemical energy of the organic substance is its energy potential, which can be calculated or measured after the transformation of chemical energy into thermal energy.

To calculate the energy content of natural organic matter (e.g., biomass), methods of chemical thermodynamics are used. For this purpose, the combustion reaction of biomass sample with the general chemical formula $C_xH_yO_z$ is considered [10, 11]:

$$C_xH_yO_z + (x + 0.25y - 0.5z)\, O_2 \rightarrow x\, CO_2 + 0.5y\, H_2O \; .... (1)$$
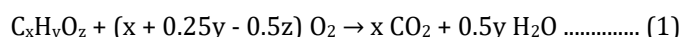
The combustion process is accompanied by an exothermic thermal effect called the enthalpy of combustion, Δ_cH. Suppose that the thermal effect of combustion is calculated for standard conditions, where a temperature is 25°C (298.15 K) and pressure is 1 atm (0.1 MPa). In that case, we obtain the standard enthalpy of combustion, which is designated as Δ_cH^o. The value of Δ_cH^o can be calculated using the Hess equation:

$$\Delta_cH^o = x\, \Delta_fH^o(CO_2) + 0.5y\, \Delta_fH^o(H_2O) - \Delta_fH^o(C_xH_yO_z) \; .... (2)$$

where $\Delta_fH^o(CO_2, g)$, $\Delta_fH^o(H_2O, l)$, and $\Delta_fH^o(C_xH_yO_z)$ are standard enthalpies of the formation of carbon dioxide, liquid water, and studied organic sample, the numerical values of which are given in handbooks and publications on chemical thermodynamics.

Let's calculate, for example, the combustion enthalpy of such sample as wood cellulose, a repeating unit of which has the chemical formula $C_6H_{10}O_5$. From eq. (1) it follows, that in this case, x=6, y=10, and x=5. Then, the combustion process of cellulose can be expressed, as follows:

$$C_6H_{10}O_5 + 6 O_2 \rightarrow 6 CO_2 + 5 H_2O \text{ .... (3)}$$
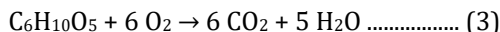
In handbooks on chemical thermodynamics, one can find that $\Delta_fH^o(CO_2, g)$ = -393.51 kJ/mol and $\Delta_fH^o(H_2O, l)$= -285.83 kJ/mol. The standard formation enthalpy of wood cellulose is evaluated at $\Delta_fH^o(C_6H_{10}O_6)$ = −969.8 kJ/mol [10]. Then, the standard enthalpy of combustion of the cellulose sample will be: $\Delta_cH^o = 6\Delta_fH^o(CO_2) + 5 \Delta_fH^o(H_2O) - \Delta_fH^o(C_6H_{10}O_5)$ = -2820.4 kJ/mol that corresponds to the content of thermal energy $Q(C_6H_{10}O_5)$ = 17.4 MJ/kg.

If the enthalpy of the formation of a sample is unknown, its energy potential can be measured experimentally in a precision oxygen bomb calorimeter [12]. This device typically consists of a strong stainless-steel bomb placed in a water calorimeter. The value of the energy equivalent of the calorimetric system was determined by the combustion of standard benzoic acid. A small sample is put in a crucible inside the bomb. Oxygen is pumped into the bomb to provide a pressure of 2 to 3 MPa. After temperature equilibrium is established, the sample is ignited. The temperature rise is measured with an accuracy of ±0.001 K, after which the change in internal energy is determined. The corrections for ignition and forming of acid traces should be made. To calculate the enthalpy of combustion at standard conditions (T=298.15 K, P=0.1 MPa) the Washburn correction, as well as the correction for the change in the number of moles of gases before and after combustion are introduced. For each sample, several experiments are performed to obtain a reliable value of the combustion enthalpy and standard deviation.

For example, after the combustion of a cellulose sample, the measured value of standard combustion enthalpy was Δ_cH^o = -2815.6 kJ/mol. Then, the content of the thermal energy of this sample will be Q = $-\Delta_cH^o$/M= 17.4 MJ/kg, where M=162 is the molecular mass of the repeating cellulose unit.

Similarly, it is possible to calculate or determine experimentally the energy potential of the biomass itself, its various components, or biomass-based secondary biofuels. If the standard combustion enthalpy, Δ_cH^o, of the biomass sample, $C_xH_yO_z$ is known, then its standard formation enthalpy can be calculated, as follows [11]:

$$\Delta_fH^o(C_xH_yO_z) = x \Delta_fH^o(CO_2) + 0.5y \Delta_fH^o(H_2O) – \Delta_cH^o(C_xH_yO_z) \text{ .... (4)}$$

Considering that some processes are carried out at elevated temperatures, instead of the standard enthalpy at temperature T_o =298.15 K it is necessary to find the enthalpy at temperature T. For this case, the formation enthalpy at temperature T for each substance participating in the process should be calculated:

$$\Delta_fH(T) = \Delta_fH^o + \int_{T_o}^{T} Cp(T)dT \text{ .... (5)}$$

where $C_p (T)$ is the specific heat capacity of the substance, which is dependent on temperature.

The experimental studies with the use of bomb calorimeter have shown that the thermal energy potential of some biomass types can vary in the range from 15 to 26 MJ/kg [11, 13-17] (Table 1).

Table 1 The content of thermal energy (Q) in dry plant biomass

Biomass type	Q, MJ/kg
Rice straw	15.7
Wheat straw	17.1
Corn stover	17.2
Switchgrass	18.3
Miscanthus	18.6
Forest residues	18.8
Hardwood	19.7

Softwood	20.5
Olive pomace	22.3
Fallen olives	26.0

The chemical composition directly affects the calorific value of biomass. Increased content of lignin, lipids, resins, and waxes contributes to achieving a high calorific value of biomass [11, 13. This is due to the increased content of combustion energy of lignin (25-27 MJ/kg) [18] compared with polysaccharides, (17.4-17.6 MJ/kg) [10,11]. In addition, extractive substances of biomass, lipids, waxes, and resins have a content of combustion energy from 36 to 38 MJ/kg [10, 11, 19-21], which is much higher than that of those of polymeric components of the biomass, lignin, and polysaccharides.

To calculate the content of the thermal energy for the biomass sample, the additive contribution of thermal energies of the biomass components is used [10, 11]:

$$Q = 0.01 \sum C_i Q_i \ \text{....................} \ (6)$$

where C_i is the percentage content of the component in the biomass; and Q_i is the content of thermal energy of the biomass component.

However, the direct use of biomass as a solid fuel raises several problems. The initial biomass is a non-dense and heterogeneous material consisting of pieces of various sizes [5]. Moreover, it can contain moisture and inorganic substances. These features of the initial biomass worsen its fuel properties, since moisture and inorganic admixtures decrease the calorific value, and the low bulk density of the initial biomass declines the density of thermal energy, which significantly reduces the productivity of furnaces.

To improve the fuel performance, the initial biomass should be demineralized, dried, and densified into pellets [5, 17, 22, 23]. For example, the initial unpressed Switchgrass biomass has unsatisfactory characteristics: bulk density, BD = 98 kg/m^3, and thermal energy density, ED = 1.8 GJ/m^3, while after pelletization these features increased 5 times [24]. When plastic waste is used as a binder, the ED of the pelletized solid biofuel increases by 8 times, which is also accompanied by a rise in the thermal energy content of the pellets.

2.2. The thermal energy content in biomass components

The main components of biomass are cellulose, hemicellulose, and lignin. Cellulose is a linear, stereoregular, semicrystalline polysaccharide consisting of repeating anhydroglucose units (AGUs) linked with chemical β-1,4-glycosidic bonds in a head-to-tail manner [7, 10, 13]. The content of thermal energy of dry cellulose is evaluated at 17.4 MJ/kg [10, 11]. Hydroxyl groups of adjacent cellulose chains are linked by strong hydrogen bonds, which leads to the formation of thread-like elementary nanofibrils and their bundles, called microfibrils, which contain crystallites and non-crystalline domains. In addition, hydroxyl groups of cellulose can be replaced by various substituents, resulting in the formation of cellulose derivatives, such as ethers, esters, etc. [25].

A study of cellulose ethers showed that the substitution of cellulose hydroxyl groups by two oxy-methyl radicals increases thermal energy from 17.4 to 21.8 MJ/kg [26]. If two oxy-ethyl radicals are used instead of oxy-methyl radicals, then the content of thermal energy can be increased to 24.9 MJ/kg.

The content of thermal energy in cellulose esters depends on the substituent type and degree of substitution [27, 28].

$$\text{Mono-esters: } Q \ (\text{MJ/kg}) = 1.464 \ N_c + 15.75 \ \text{..................} \ (7)$$

$$\text{Di-esters: } Q \ (\text{MJ/kg}) = 1.015 \ N_c + 15.49 \ \text{........................} \ (8)$$

$$\text{Tri-esters: } Q \ (\text{MJ/kg}) = 0.774 \ N_c + 15.55 \ \text{.......................} \ (9)$$

where N_c is the number of carbon atoms in a substituent.

Plant biomass contains also hemicelluloses which are highly amorphous hetero-polysaccharides [7, 29]. In the cell walls of plant fibers, hemicelluloses fulfill the function of binder between cellulose fibrils and lignin. The chemical structure

of hemicelluloses consists of chains of a variety of pentose or hexose units. The content of thermal energy of hexosans is about 17.5 MJ/kg, while that of pentosans is 17.7 MJ/kg [10, 11].

Lignin is an aromatic, amorphous, and hydrophobic polymer [7, 30, 31]. It is a complex biopolymer of phenylpropane units, which are linked to each other with a variety of different chemical bonds with the formation three-dimensional network. This biopolymer consists of three main phenylpropane units such as guaiacyl (G), syringyl (S), and hydroxyphenyl (H). Due to its aromatic nature, lignin has an increased content of thermal energy. Lignins of hardwood, herbaceous plants, and agricultural residues have a content of thermal energy of about 25 MJ/kg [10, 18]. Lignins of softwood have a higher thermal energy content, of 26.5-26.8 MJ/kg [10, 11].

The average values of thermal energy content for different components of plant biomass are shown in Table 2 [10, 11]:

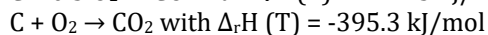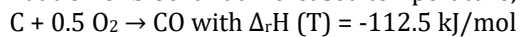**Table 2** The average content of thermal energy (Q) in components of biomass

Components	Q, MJ/kg
Cellulose	17.4
Hemicellulose	17.6
Lignin	26.0
Extractives	37.0
Ash	0

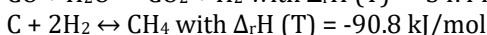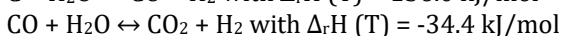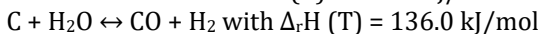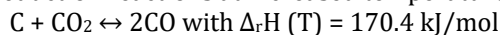## 2.3. The thermal energy content in secondary biofuels

Plant biomass is also a feedstock for producing secondary biofuels, such as biochar, bio-oil, and biogas. For this purpose, the initial biomass is pyrolyzed, i.e. subjected to heat treatment in the absence or lack of oxygen. Slow pyrolysis of biomass is carried out with a heating rate below 60 degrees/min at temperatures of about 500°C and residence time of 10-20 min with the formation of biochar, bio-oil, and biogas [7, 13]. If slow pyrolysis is processed at high temperatures, from 600 to 1000°C, then strong gasification of biomass with a predominant hydrogen fraction occurs [32, 33]. Hydrothermal gasification of biomass, especially in the presence of a catalyst, significantly increases the hydrogen content in biogas.

The yield of biochar after slow pyrolysis of woody biomass is 30-35%, and its thermal energy is 27-30 MJ/kg depending on the carbon content. The bio-oil is a dark and thick liquid containing a complex mixture of water and various organic substances (tar, hydrocarbons, furan derivatives, aldehydes, ketones, phenols, organic acids, methanol, etc.) with a thermal energy from 10 to 16 MJ/kg. The biogas can contain H_2, CO, CH_4, CO_2, water vapor, and also N_2 if gasification is performed in the nitrogen or air atmosphere. This gas is formed as a result of the following processes [7]:
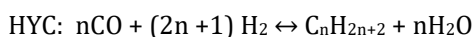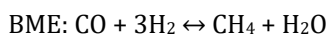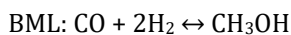
Oxidation of biochar at increased temperature, 800°C:
$C + 0.5\ O_2 \rightarrow CO$ with $\Delta_r H$ (T) = -112.5 kJ/mol
$C + O_2 \rightarrow CO_2$ with $\Delta_r H$ (T) = -395.3 kJ/mol

Reduction reactions at increased temperature, 800°C:
$C + CO_2 \leftrightarrow 2CO$ with $\Delta_r H$ (T) = 170.4 kJ/mol
$C + H_2O \leftrightarrow CO + H_2$ with $\Delta_r H$ (T) = 136.0 kJ/mol
$CO + H_2O \leftrightarrow CO_2 + H_2$ with $\Delta_r H$ (T) = -34.4 kJ/mol
$C + 2H_2 \leftrightarrow CH_4$ with $\Delta_r H$ (T) = -90.8 kJ/mol

The value of reaction enthalpy $\Delta_r H$ (T) at temperature 800°C is shown near the equation of the corresponding reaction. Depending on the ratio between combustible and non-combustible components, biogas can have a content of thermal energy from 5 to 10 MJ/m^3. To isolate bio-hydrogen, it is necessary to remove CO and/or CO_2 from biogas.

If all non-combustible gases are removed, the calorific value of biogas can increase to 12.6 MJ/m^3. The pyrolytic syngas containing mainly CO and H_2 can be used for the synthesis of various valuable products such as artificial hydrocarbon (HYC) by Fischer-Tropsch reaction, and other fuels such as bio-methanol (BML) and bio-methane (BME):

HYC: $nCO + (2n+1)\ H_2 \leftrightarrow C_nH_{2n+2} + nH_2O$

BML: $CO + 2H_2 \leftrightarrow CH_3OH$

BME: $CO + 3H_2 \leftrightarrow CH_4 + H_2O$

Fischer-Tropsch process occurs in the presence of metal catalysts (Fe, Co, Ru, Ru/TiO$_2$, etc.), typically at temperatures of 150-300 °C and pressures of one to several tens atm [34]. Higher temperatures lead to higher conversion rates but tend to favor methane production. For this reason, the temperature is usually maintained at the low or middle range, 150-200°C. Increasing the pressure leads to the formation of long-chained alkanes, However, higher pressures can lead to coke formation and catalyst deactivation. The Fischer-Tropsch process is exothermic. If the hydrocarbon (HYC) is octane, then the standard reaction enthalpy is $\Delta_r H^o$ = -1259.2 kJ/mol of HYC, while the content of its thermal energy is 47 MJ/kg.

The reaction of bio-methanol synthesis has a value of standard enthalpy of $\Delta_r H^o$ = -91 kJ/mol. Under normal conditions, this reaction does not occur due to kinetic limitations. However, at high temperatures, the reaction shifts to the left. But an increase in pressure promotes this process. Thus, bio-methanol can be produced under middle temperatures of 200–250°C and high pressure of 40–50 atm in the presence of a copper-zinc oxide catalyst [35]. The bio-methanol is a light-flying combustible liquid with a content of thermal energy of 22.7 MJ/kg.

The production of biomethane requires high temperatures (300-500°C) and pressures (20-30 atm), as well as the presence of a catalyst (Ni, or Ru on alumina, etc.) [36]. The standard enthalpy of this reaction is $\Delta_r H^o$ = -206 kJ/mol CH$_4$. However, under real conditions, T=400°C and pressure of 25 atm, the exothermic value of the reaction enthalpy ΔrH (T, P) increases to -220 kJ/mol CH$_4$. The produced biomethane has a thermal energy of 39.6 MJ/m^3.

Thus, different final products can be obtained from the biomass-based synthesis gas by changing the reaction conditions. Hydrocarbons (HC) are formed from synthesis gas at middle temperatures and low pressures in the presence of a metal catalyst. However, if the temperature is middle, but the pressure is increased to 40-50 atm, then in the presence of a copper-zinc oxide catalyst bio-methanol can be obtained. When the process is performed under high temperatures (300-500°C) and elevated pressures (25-30 atm) in the presence of Ni or Ru catalyst then the final product will be bio-methane.

The well-known liquid biofuel in bio-ethanol. It can be produced by enzymatic hydrolysis of pretreated biomass to produce glucose followed by fermentation of this sugar into ethanol [37]. The fermentation process of a sugar solution is performed usually with *S. Cerevisiae* yeast at normal or moderate temperatures. This process is the following:

$$0.5 \ (C_6H_{12}O_6 \ x \ n \ H_2O) \rightarrow CO_2 + C_2H_5OH \ x \ 0.5 \ n \ H_2O$$
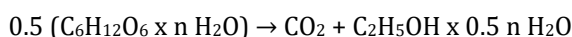
The fermentation process is exothermic with the standard enthalpy value $\Delta_r H^o$ = -41 kJ/mol [11], and therefore it does not require additional heating. The produced ethanol solution is distilled and dehydrated. The absolute bioethanol has a thermal energy of 29.7 MJ/kg or 23.2 GJ/m^3. Currently, gasoline with bio-ethanol additive is widely used in Brazil, the USA, and European countries. Some flexible-fuel vehicles in Brazil use up to 100% bio-ethanol.

3. Discussion

The results on the thermal energy content and energy density in the studied solid, liquid, and gaseous biofuels are summarized in Table 3.

Table 3 The content of thermal energy (Q) and energy density (ED) in studied biofuels

Biofuels	Q, MJ/kg	ED, MJ/m^3
*Solid biofuels**		
Rice straw	15.7	9420
Corn stover	17.2	10320
Switchgrass	18.3	10980
Miscanthus	18.6	11160
Hardwood	19.7	11820

Softwood	20.5	12300
Olive pomace	22.3	13380
Fallen olives	26.0	15600
Cellulose	17.4	10440
Hemicelluloses	17.6	10560
Lignin	26.0	15600
Bio-char (85% C)	27.0	16200
Bio-char (91% C)	30.0	18000
Liquid biofuels		
Bio-methanol	22.7	17978
Bio-ethanol	29.7	23433
Bio-diesel fuel	41.0	35000
Bio-gasoline	47.0	35000
Gaseous biofuels		
Bio-methane	55.5	39.6
Syngas: H_2 & CO 1:3 (wt.)	54.0	12.6
Syngas: H_2 & CO 1:1 (wt.)	76.0	12.6
Syngas: H_2 & CO (2:1) (wt.)	97.9	12.7
Bio-hydrogen	141.8	12.7

Among the various biomass samples, olive samples have the highest amount and density of thermal energy due to their higher content of lignin and lipids. However, the energy features of biochar obtained from biomass by slow pyrolysis are significantly higher than those of the original biomass.

Of the various liquid fuels, bio-gasoline synthesized from synthesis gas by the Fischer-Tropsch method has the largest amount of thermal energy, Q=47 MJ/kg, and energy density, ED= 35000 MJ/m^3. Nevertheless, bio-methanol has great practical significance despite its relatively low energy properties. This simple alcohol is the main feedstock for the production of a large variety of chemicals, e.g., acetic acid, methyl tert-butyl ether, etc. Methanol is also a promising energy source because it is easier to store in liquid form than hydrogen and natural gas. Moreover, it is much cheaper than gasoline or kerosene, and this alcohol is much less harmful to the environment. Fuel cells using methanol are also known. In addition, methanol is used for the transesterification of lipids to produce biodiesel fuel having a thermal energy of 40-42 MJ/kg [38].

Among the various biogases, bio-hydrogen has no competitors with its enormous calorific value of Q = 141.8 MJ/kg. However, if energy density (ED) is calculated, then bio-hydrogen and syngas become practically equal ED values, namely, 12.6-12.7 MJ/m^3. In this case, the champion is biomethane with a value of ED = 39.6 MJ/m^3

4. Conclusions

This article shows the possibility of applying chemical thermodynamics to the study of plant biomass, its main components. and secondary biofuels. It was shown that the content of thermal energy (Q) in dry biomass is in the range of 15 to 26 MJ/kg. The increased content of lignin, lipids, and other organic extractives enhances the Q value of biomass, while moisture and ash reduce its Q value. However, the initial biomass has a low density of thermal energy. To improve fuel properties, especially energy density, the plant biomass should be densified into pellets, better with the addition of binders. To calculate the combustion enthalpy of biomass, a method of additive contributions of thermal energies of main components is proposed. In addition, biomass can also be used as a raw material for the production of secondary biofuels such as biochar, biomethanol, bioethanol, biodiesel fuel, and biogases, the content of thermal energy of which was determined. The energy features of biochar obtained from biomass by slow pyrolysis are significantly higher than

those of the initial biomass. Of the various liquid fuels, bio-gasoline synthesized from synthesis gas by the Fischer-Tropsch method has the largest amount of thermal energy, Q=47 MJ/kg, and energy density, ED= 35000 MJ/m^3. Among the various biogases, bio-hydrogen has no competitors with its enormous thermal energy amount of Q = 141.8 MJ/kg. However, if the energy density is calculated, then the bio-hydrogen and syngas become practically equal values, with ED= 12.6-12.7 MJ/m^3. In this case, biomethane with a value of ED = 39.6 MJ/m^3 comes out on top.

References

[1] Ang T-Z, Salem M, Kamarol M, et al., A comprehensive study of renewable energy sources: Classifications, challenges and suggestions. Energy Strategy Reviews 2022; 43: 1-27.

[2] Lee S, Speight JG, Loyalka SK. Handbook of Alternative Fuel Technologies. 1-st ed. CRC Press: Boca Raton, USA, 2007; 568 p.

[3] Rashmi R, Tripti TT, Pandey S, Kumar, S. Transforming lignocellulosic biomass into biofuels: recent innovations in pretreatment and bioconversion techniques. IJRASET 2024; 12: 1079-1089.

[4] Saidur R, Abdelaziz EA, Demirbas A, et al. A review on biomass as a fuel for boilers. *Renewable* Sustain. Energy Rev. 2011; 15: 2262-2289.

[5] Ioelovich M. High-energy fuel pellets. Sci. Environ. 2020; 3: 147–152.

[6] Klemm D, Heublein B, Fink H-P, Bohn A. Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. 2005; 44: 2-37.

[7] Tursi A. A review on biomass: importance, chemistry, classification, and conversion. Biofuel Res. J. 2019; 22: 962-979

[8] Čuček L, Martin M, Grossmann IE, Kravanja Z. Energy, water and process technologies integration for the simultaneous production of ethanol and food from the entire corn plant. Comp. Chem. Eng. 2011; 35: 1547-1557.

[9] Ioelovich M. Chemical thermodynamics of biomass, cellulose, and cellulose derivatives. World J. Adv. Res. Reviews 2024; 24: 1295–1338.

[10] Ioelovich M. Chemical thermodynamics of biomass, cellulose, and cellulose derivatives. World J. Adv. Res. Rev. 2024; 24: 1295–1338.

[11] Ioelovich M. Application of thermodynamic methods to the study of plant biomass and its components—a review. Appl. Biosciences 2024; 3: 577–616.

[12] Francis W, Peters MC. Fuels and Fuel Technology: Summarized Manual. 2nd Ed. Pergamon Press: Oxford, etc., 2013; 732 p.

[13] Ioelovich M. Recent findings and the energetic potential of plant biomass as a renewable source of biofuels – a review. Bioresources 2015; 10: 1879-1914.

[14] Makimuk YV, Ponomarev DA, Kursevich VN, Fesko VV. Combustion heat of wood fuel. Forestry J. 2017; 4: 116-129.

[15] Nurek T, Gendek A, Roman K. Forest residues as a renewable source of energy: elemental composition and physical properties. Bioresources 2019; 14: 6-20.

[16] Shojaeiarani J, Baiwa DS, Baiwa SG. Properties of densified solid fuels in relation to chemical composition, moisture content and bulk density. Bioresources 2019; 14: 4996-5015.

[17] Tumuluru JS. Pelleting of pine and switchgrass blends: Effect of process variables and blend ratio on the pellet quality and energy consumption. Energies 2019; 12: 1-26.

[18] Demibras A. Higher heating values of lignin types from wood and non-wood lignocellulosic biomasses. Energy Sources, Part A. 2017; 39: 592–598.

[19] Abed SM, Ali AH, Noman A, et al. Structured lipids: enzymatic synthesis, health benefits and nutraceutical characteristics - a review. Int. J. Res. in Agricultural Sci. 2016; 3: 2348 – 3997.

[20] Gravalos I, Gialamas, T, Koutsofitis Z, et al. Energetic study of animal fats and vegetable oils using combustion bomb calorimeter. J. Agricult. Machin. Sci. 2008; 4: 69-74.

[21] Suharto S, Ahyati AE. The properties of vegetable cooking oil as a fuel and its utilization in a modified pressurized cooking stove. IOP Conference Series: Earth Env. Sci. 2018; 105: 1-10.

[22] Jagtap A, Kalbande S. Pelletization process for the production of fuel pellets from various surplus biomass: a review. Int. J. Env. & Climate Change 2023; 13: 200-207.

[23] Wu J. How to make wood pellets—Small pellet mill and pellet plant. G. Energy 2024; 2: 1–5.

[24] Ioelovich M. Analysis of energy potential of switchgrass biomass. Biomass 2024; 4: 1-11.

[25] Aziz T, Farid A, Haq F, et al. A review on the modification of cellulose and its applications. Polymers 2022; 14: 1-34.

[26] Ioelovich M. Thermochemistry of alkalization and etherification of cellulose. World J. Adv. Res. Rev. 2023; 20: 1166–1174.

[27] Ioelovich M. Application of thermochemical methods for the study of cellulose and cellulose esters. World J. Adv. Res. Rev. 2023; 18: 1477–1488.

[28] Ioelovich, M. Study of heat effects of topochemical esterification of cellulose. World J. Adv. Res. Rev. 2024; 23: 1232–1241.

[29] Rao J, Lv Z, Chen G, Peng F. Hemicellulose: structure, chemical modification, and application. Prog. Polym. Sci., 2023; 140: 1-15.

[30] Zhang Y, Naebe M. Lignin: a review on structure, properties, and applications as a light-colored UV absorber. ACS Sustain. Chem. Eng. 2021; 9: 1427–1442.

[31] Shorey R, Salaghi A, Fatehi P. Valorization of lignin for advanced material applications: a review. RSC Sustain. 2024; 2: 804–831.

[32] Alvarado-Flores JJ, Alcaraz-Vera JV, Ávalos-Rodríguez ML, et al. Thermochemical production of hydrogen from biomass: pyrolysis and gasification. Energies 2024; 17: 1-21.

[33] Song H, Yang G, Xue P, et al. Recent development of biomass gasification for H_2-rich gas production. Appl. Energy Combust. Sci. 2022; 10: 1-16.

[34] Zhang Y, Yang X, Yang, X, *et al.* Tuning reactivity of Fischer–Tropsch synthesis by regulating TiO_x overlayer over Ru/TiO_2 nanocatalysts. Nat. Commun. 2020; 11: 1-8.

[35] Bozzano G, Manenti F. Efficient methanol synthesis: perspectives, technologies and optimization strategies. Progress in Energy and Combust. Sci. 2016; 56: 71-105.

[36] Schmider D, Maier L, Deutschmann O. Reaction kinetics of CO and CO_2 methanation over nickel. Ind. Eng. Chem. Res. 2021; 60: 5792–5805.

[37] Ioelovich M. Specific features of enzymatic hydrolysis of cellulose. World J. Adv. Res. Rev. 2024; 22: 381–392.

[38] Sivaramakrishnan K. Determination of higher heating values of biodiesels. Int. J. Eng. Sci. Technol. 2011; 3: 7981-7987.