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THERMODYNAMIC ANALYSIS OF BIOCHAR GASIFICATION

© **M.Ya. Ioelovich**

Designer Energy Ltd., Bergman St., 2, Rehovot, 76100, Israel, ioelovichm@gmail.com

In this research, a thermodynamic analysis of the gasification process of biochar obtained by pyrolysis of wood biomass was carried out. Thermodynamic functions, such as enthalpies and entropies of the formation of biochar, water vapor, carbon oxide, and hydrogen at various temperatures and pressures were determined. The thermodynamic (TD) studies showed that the gasification process is endothermic, while the entropy of this process is positive. From TD calculations, it follows that the gasification process of biochar cannot be carried out at normal pressure if the temperature of this process is below boundary T_b=895 K because the thermodynamic Gibbs potential under these conditions has a positive value. Thus, the gasification process of the biochar can be implemented only at quite high temperatures. It has been established that increasing the gasification temperature above T_b increases the equilibrium constant, which should enhance the yield of biogas. On the other hand, pressure is a negatory factor for the gasification process, since its increase leads to a decrease in the equilibrium constant. However, the negative impact of pressure can be compensated by the rise in gasification temperature.

Keywords: biomass, pyrolysis, biochar, gasification, thermodynamic functions, thermodynamic analysis.

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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, coal, petroleum, and natural gas [1]. These sources provide about 80% of annual energy consumption or ca 500 EJ. However, fossil resources are not reproduced in nature. Therefore, their reserves are gradually but permanently depleted [2]. In addition, the increased use of fossil fuels is causing acute environmental problems, since their combustion is accompanied by the emission of carbon dioxide triggering the greenhouse effect and global warming. For example, the burning of 1 t coal produces 1780 m^3 of CO_2, the burning of 1 t gasoline gives 1570 m^3 of CO_2, and after burning 1000 m^3 of natural gas about 1300 m^3 of CO_2 is formed.

To eliminate the imbalance of fossil fuels and reduce their harmful impact on the environment, it is necessary to wider use of renewable alternative energy sources. Unfortunately, the share of these sources in global energy consumption is still small and amounts to about 15–20% [3]. Only in some countries such as Finland and Sweden the share of alternative energy amounts to 40–50% [4].

Among various sources of renewable energy considerable attention in recent years has been given to plant biomass [5]. As is known, plant biomass is formed from carbon dioxide and water by photosynthesis absorbing solar energy. When the 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 [6].

Biomass is an abundant, renewable, and inexpensive plant material. It 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. The total resources of plant biomass reach 1.5 trillion tons [7]. The resource of inedible biomass accumulated annually is estimated at 10 billion tons, the energy potential of which is estimated at 150 EJ [8].

The potential biomass resources among other renewable energy sources are above 70% [9], while its share in the production of alternative energy exceeds 50% [10]. Despite advances in solar and wind energy, in many countries plant biomass still accounts for a significant share of energy production [10]. 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%.

However, the direct combustion of biomass as a solid fuel is not efficient enough since energy generation by turbines in modern thermal power plants requires a continuous fuel supply. For this purpose, gaseous fuel is best suited. Gas engines and fuel cells also require the use of gaseous fuel. The best alternative to the currently used fossil natural gas could be biogas produced by gasification of renewable biomass. Since biomass permanently reproduces in nature, it can be a promising feedstock for the production of unlimited amounts of biogas. In addition, biogas is considered CO_2-neutral because when burned, it releases the same amount of this greenhouse gas that was accumulated by the biomass from the atmosphere during photosynthesis.

As is known, the slow pyrolysis of biomass in the absence or lack of oxygen at a temperature of 300 to 600 °C leads to biochar production with a yield of 30–35% [9, 11, 12]. A further increase in temperature to 800–1200 °C in the presence of steam causes the conversion of biochar into biogas consisting of hydrogen, carbon monoxide, carbon dioxide, and some other gases [9, 13, 14]. This biogas has a calorific value of 4 to 10 MJ/m^3 depending on the ratio between combustible and non-combustible gases [9, 11]. To increase the yield of biogas and its calorific value, and decrease the amount of tar, the initial biomass must be preliminarily dried, demineralized, and comminuted, while the gasification process should be carried out at a high temperature [9, 15–17]. The produced biogas can find application as a fuel in furnaces, boilers, gas engines, gas turbines, and fuel cells [15, 16].

The scientific literature describes the gasification process of fossil coal [9, 17, 18], as follows:

Main reaction:

$$C + H_2O \rightleftharpoons H_2 + C$$

Side reactions:

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

$$C + CO_2 \rightleftharpoons 2CO$$

$$C + H_2 \rightleftharpoons CH_4$$

Unfortunately, the biochar gasification process and its thermodynamics have not been studied either, which makes it difficult to find the optimal process conditions. The values of standard enthalpy for processes of coal oxidation and its interaction with water steam presented in some publications [17, 18] do not correspond to the real conditions of processes occurring at high temperatures and often at high pressures. Moreover, to study the thermodynamics of any reaction or process, it is necessary to know not only the enthalpy, but also the entropy, to calculate the Gibbs potential, which determines whether it is possible to carry out a reaction or not, whether it will be reversible or irreversible, and what the changes in reaction conditions, temperature, pressure, and concentration of reagents influence on it [19, 20]. To fill such a gap, a complete thermodynamic analysis of biochar gasification was carried out in this study.

Materials and Methods

Material. The starting biomass was mixed coniferous wood chips. This material was ground into sawdust and screened through a 5 mm sieve. The sawdust was then purified using extraction with an ethanol-benzene mixture according to the TAPPI T-204 standard method and dried at 105 °C up to constant weight.

Methods.

Determination of the chemical composition of biomass. The chemical composition of the biomass sample was determined according to standard NREL methods [21]. Briefly, the dry wood sample was placed in a sealed vessel and hydrolyzed with 72% sulfuric acid at 30 °C, and after its dilution, with 4% acid in an autoclave at 120 °C. The hydrolyzate containing monosaccharides (glucose, mannose, xylose, etc.) was neuralized and analyzed using HPLC to determine the content of cellulose and hemicelluloses in the wood sample. Insoluble lignin was separated from the hydrolyzate, washed to a neutral pH value, dried, and weighed to determine its content in the sample.

Pyrolysis of biomass. The pyrolysis of the starting material was performed in a muffle furnace. About 20 g of biomass was placed in the porcelain crucible inside the furnace, after which nitrogen gas was introduced into it. The furnace was heated at a rate of 20 °C/min to a temperature of 500 °C and maintained at this temperature for 20 min in an inert atmosphere. The yield of produced biochar was 33%.

Determination of standard enthalpies of combustion and formation. Combustion of the dry sample was carried out in a Parr-6200 stainless-steel bomb placed in a water calorimeter. A small sample (0.5–1.0 g) was put in a crucible inside the bomb, after which the bomb was hermetically sealed. Oxygen is pumped into the closed bomb to provide a pressure of 3 MPa. After temperature equilibrium is established, the sample is ignited. The temperature rise was measured with an accuracy of ±0.001 K, after which the change in internal energy was determined. The corrections for ignition and forming of acid traces should be made. To adjust the enthalpy of combustion to standard conditions (T_o=298.15 K, P_o=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 were introduced. Finally, the value of the standard combustion enthalpy ($\Delta_c H^o$) of the sample with the accuracy ±0.01 J/g was obtained.

The standard enthalpy of formation ($\Delta_f H^o$) of the sample having formula CH_xO_y was calculated by the equation:

$$\Delta_f H^o = \Delta_f H^o(CO_2) + 0.5x\ \Delta_f H^o(H_2O) - \Delta_c H^o \qquad (1)$$

where $\Delta_f H^o(CO_2)$ and $\Delta_f H^o(H_2O)$ are standard enthalpies of the formation of carbon dioxide and water, the values of which are presented in reference books.

The gases formed after the combustion of the samples were analyzed using a “Gasboard-3500” gas analyzer of Cubic Instruments.

Determination of thermodynamic functions of a reaction

The change in the reaction enthalpy can be calculated using the Hess law according to which the enthalpy change of a chemical reaction is equal to the difference between the sums of the formation enthalpies ($\Delta_f H_p$) of the reaction products and the formation enthalpies ($\Delta_f H_r$) of the starting reagents, taking into account their stoichiometric coefficients [19, 20]:

$$\Delta_r H = \sum n_p\ \Delta_f H_p - \sum n_r\ \Delta_f H_r \qquad (2)$$

The change in the entropy of a chemical reaction can be found using an equation similar to the Hess equation [19, 20]:

$$\Delta_r S = \sum n_p\ S_p - \sum n_r\ S_r, \qquad (3)$$

where S_p and S_r are entropy values for obtaining products and starting reagents, respectively.

Finally, the Gibbs potential of a reaction at temperature T can be calculated, as follows [8]:

$$\Delta_r G = \Delta_r H - T\ \Delta_r S \qquad (4)$$

If the process is carried out at temperature T but elevated pressure P, the Gibbs potential of the reaction is calculated using the equation:

$$\Delta_r G\ (T, P) = \Delta_r G\ (T, P_o) + \Delta n\ RT\ln(P/P_o) \qquad (5)$$

where P_o = 0.1 MPa is the standard pressure and Δn is the difference between moles of gaseous products of the reaction and starting gaseous reagents.

The Gibbs potential characterizes the degree of non-equilibrium of the reaction system. The more negative its value is, the greater the deviation of the reaction system from equilibrium and the greater the probability of the reaction being feasible. The feasibility of a reaction is facilitated by a decrease in the enthalpy and an increase in the entropy factor. On the other hand, if $\Delta_r G > 0$ then the reaction cannot be carried out.

Knowing the $\Delta_r G$ value, the equilibrium constant (K_{eq}) of the reaction can be calculated:

$$\ln K_{eq} = -\Delta_r G/RT \qquad (6)$$

Results and Discussion

Study of the chemical composition of wood biomass and biochar. The chemical analysis showed that the used wood sample contained around 49% cellulose, 23% hemicelluloses, and 28% lignin. After calculating the molar content of these components, the number of carbon, hydrogen, and oxygen atoms in the structural fragment of wood was evaluated as $C_7H_{10}O_{4.5}$. This fragment has molecular mass M=166 and the following elemental composition: C=50.6%, H=6.0% O=43.4%, which is typical for softwood.

After biochar combustion in the bomb calorimeter, the volumes of formed CO_2 and H_2O were analyzed. The analysis showed that the biochar sample contained 91.3% of carbon, 3.8% of hydrogen, and about 4.9% of oxygen. Thus, the formula of this sample is $CH_{0.5}O_{0.04}$.

Determination of standard thermodynamic functions of biochar. As a result of combustion experiments, the value of standard enthalpy of combustion of the biochar sample was determined with $\Delta_cH^o = - 420.51 \pm 1.31$, kJ/mol. On the other hand, the value of the standard enthalpy of formation of this sample, calculated by eq. (1) was $\Delta_fH^o = -33.46 \pm 1.31$, kJ/mol. The standard entropy of char is evaluated at 10 J/mol K [22].

Thermodynamics of biochar gasification at standard conditions. The main process of biochar gasification can be expressed, as follows:

$$CH_{0.5}O_{0.04} + 0.96\ H_2O \rightleftharpoons 1.21\ H_2 + CO$$

Using standard thermodynamic functions (TDFs) of the starting reagents (Chair and H_2O) and products (H_2 and CO) presented in Table 1, the thermodynamic characteristics of the biochar gasification process were found.

The calculated standard enthalpy of the gasification reaction $\Delta_rH^o = 155.13$ kJ/mol, standard reaction entropy $\Delta_rS^o = 164.24$ J/mol, and standard Gibbs potential $\Delta_rG^o = 106.19$ kJ/mol. Since the value of $\Delta_rG^o > 0$, it means that the gasification process of biochar cannot be carried out at normal temperature and pressure.

Effect of temperature and pressure on the thermodynamics of gasification reaction. To study the effect of temperature on the gasification process, the TDFs of the substances participating in this process were determined at various temperatures. The temperature dependence of enthalpy and entropy of a substance formation was calculated using the equations:

$$\Delta_f H_i(T) = \Delta_f H_i^o + \int_{T_0}^{T} Cp dT \tag{7}$$

$$S_i(T) = S_i^o + \int_{T_0}^{T} \frac{Cp}{T} dT \tag{8}$$

where C_p is the specific heat capacity of the substance (i) depending on the temperature:

$$C_p = a + bT + c/T^2.$$

The coefficients a, b, and c for each substance (i) are given in reference books.

The found values of $\Delta_fH_i(T)$ and $S_i(T)$ are shown in Tables 2 and 3.

After that TDFs of the biochar gasification reaction were calculated at temperatures from 298 to 1473 K using eq. (2), (3) and (4). These TDFs are shown in Table 4.

The obtained results showed that the gasification process of biochar is endothermic, and the entropy of this process is positive (Table 4). With an increase in temperature, the enthalpy of the gasification changes slightly, while the entropy factor ($T\Delta_rS$) increases greatly (Fig. 1). This leads to a decrease in the Gibbs potential, which becomes negative at temperatures above 895 K. Thus, the gasification process of the biochar can be carried out only at high temperatures.

Table 1. Standard TDFs of substances

Substance	Δ_fH^o, kJ/mol	S^o, J/mol K
Char	-33.46	10.0
H_2O	-241.84	188.74
H_2	0	130.6
CO	-110.5	197.4

Table 2. Enthalpies of formation for substances at various temperatures

Substance	$\Delta_f H$, kJ/mol		
	at 1073 K	at 1273 K	at 1473 K
Char	-21.20	-15.70	-11.19
H_2O	-215.77	-204.31	-195.55
H_2	22.10	29.22	35.31
CO	-87.54	-79.78	-72.98

Table 3. Entropies of formation for substances at various temperatures

Substance	S, J/mol K		
	at 1073 K	at 1273 K	at 1473 K
Char	30.73	34.42	37.71
H_2O	235.63	242.91	249.43
H_2	168.33	173.65	178.3
CO	236.73	242.4	247.37

Table 4. TDFs of gasification reaction at various temperatures and normal pressure

T, K	$\Delta_r H$, kJ/mol	T $\Delta_r S$, kJ/mol	$\Delta_r G$, kJ/mol
298	155.13	48.94	106.19
1073	167.54	196.86	-29.32
1273	167.41	235.38	-67.97
1473	168.66	273.90	-105.24

In addition, TD calculations predict that an increase in gasification temperature should enhance the equilibrium constant (Fig. 2) and yield of biogas, which is supported by literature data [17].

In addition to temperature, the gasification process can also depend on the pressure in a gasifier. The calculations showed that at the same gasification temperature, e.g., 1273 K, an increase in pressure leads to a decrease in the negative value of the Gibbs potential. As a result, the equilibrium constant (K_{eq}) of the gasification process declines (Fig. 3).

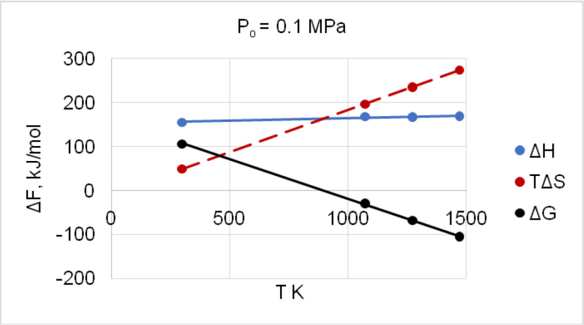

Fig. 1. Dependences of TDFs of biochar gasification process on the temperature at normal pressure P_o

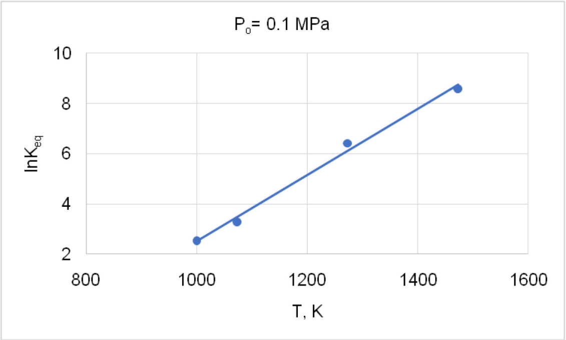

Fig. 2. Dependence of equilibrium constant of gasification process on temperature at normal pressure P_o

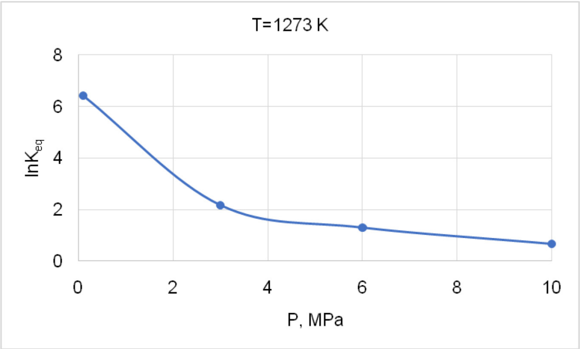

Fig. 3. Dependence of equilibrium constant of gasification process on pressure at T=1273 K

Thus, when at the constant gasification temperature the pressure in the gasifier increases the yield of biogas should decrease. This result is consistent with the Le Chatelier-Brown principle and confirmed by literature data [23]. However, the negative impact of pressure can be compensated by an increase in temperature. For example, at T=1273 K and P=3 MPa, the equilibrium constant is $K_{ev} = 8.76$, and by raising the gasification temperature to 1473 K at the same pressure, the equilibrium constant can be increased to 8.8 times.

Conclusions

A thermodynamic analysis of the gasification process of biochar obtained by pyrolysis of wood biomass was carried out. From thermodynamic calculations, it follows that the gasification process of biochar is endothermic, and the entropy of this process is positive. With an increase in temperature, the enthalpy of the gasification changes slightly, while the entropy factor increases greatly. This leads to a decrease in the Gibbs potential, which becomes negative at temperatures above boundary T_b=895 K. Therefore, the gasification of biochar should be carried out at high temperatures, above T_b. The further increase in gasification temperature enhances the equilibrium constant that should increase the yield of biogas. On the other hand, pressure is a negatory factor for the gasification process, since its increase leads to a decrease in the negative value of Gibbs potential and the equilibrium constant. However, the negatory impact of pressure can be compensated by an increase in gasification temperature. Thus, thermodynamic methods allow the prediction of optimal conditions for various reactions and processes without the need to conduct numerous experiments. In particular, according to thermodynamic calculations, the process of biochar gasification with steam is recommended to be carried out under normal pressure at a temperature of about 1273 K (1000 °C).

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Conflict of Interest

The author of this work declares that he has no conflicts of interest.

References

1. Ang T-Z., Salem M., Kamarol M. et al. *Energy Strategy Reviews*, 2022, vol. 43, 100939. https://doi.org/10.1016/j.esr.2022.100939.
2. Lee S., Speight J.G., Loyalka S.K. *Handbook of Alternative Fuel Technologies. 1-st ed.* CRC Press: Boca Raton, 2007, 568 p.
3. Energy consumption from fossil fuels and renewables in the United States from 2000 to 2023. URL: https://www.statista.com/statistics/184024/us-energy-consumption-from-fossil-fuels-and-renewables-since-1999/.
4. *Energy statistics – an overview. Eurostat, 2024.* URL: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Energy_statistics_-_an_overview#:~:text=Renewable%20energies%20accounted%20for%20the,renewable%20waste%20(2.4%20%25).
5. Rashmi R., Tripathi T., Pandey S., Kumar S. *IJRASET*, 2024, vol. 12, pp. 1079–1089. https://doi.org/10.22214/ijraset.2024.64808.
6. Ioelovich M. *Sci. Environ.*, 2020, vol. 3, pp. 147–152.
7. Klemm D., Heublein B., Fink H.-P., Bohn A. *Angew. Chem.*, 2005, vol. 44, pp. 2–37. https://doi.org/10.1002/anie.200460587
8. Ioelovich M. *World J. Adv. Res. Reviews*, 2024, vol. 24, pp. 1295–1338. https://doi.org/10.30574/wjarr.2024.24.1.3145.
9. Tursi A. *Biofuel Res. Journal*, 2019, vol. 22, pp. 962–979. https://doi.org/10.18331/BRJ2019.6.2.3.
10. Saidur R., Abdelaziz E.A., Demirbas A. et al. *Renew. Sustain. Energy Reviews*, 2011, vol. 15, pp. 2262–2289. https://doi.org/10.1016/j.rser.2011.02.015.
11. Ioelovich M. *Bioresources*, 2015, vol. 10, pp. 1879–1914. https://doi.org/10.15376/biores.10.1.1879-1914.
12. Damartzis T., Zabaniotou A. *Renew. Sustain. Energy Reviews*, 2011, vol. 15, pp. 366-378. https://doi.org/10.1016/j.rser.2010.08.003.
13. Song H., Yang G., Xue P. et al. *Appl. Energy Combust. Sci.*, 2022, vol. 10, 100059. https://doi.org/10.1016/j.jaecs.2022.100059.
14. Alvarado-Flores J.J., Alcaraz-Vera J.V., Ávalos-Rodríguez M.L. et al. *Energies*, 2024, vol. 17, pp. 1–21.

15. Bounaceur A., Gautherot L.P., Tschamber V. et al. *Solid Fuel Chemistry*, 2020, vol. 54, pp. 239–250. https://doi.org/10.3103/S0361521920040035.
16. Al-Rahbi A.S., Williams P.T. *Waste Disposal & Sustainable Energy*, 2022, vol. 4, pp. 75–89. https://doi.org/10.1007/s42768-022-00103-5.
17. Schildhauer T.J., Biollaz S.M.A. *Synthetic Natural Gas: From Coal, Dry Biomass, and Power-to-Gas Applications*. John Wiley & Sons: Hoboken, 2016, 328 p.
18. Zhang J., Weng X., Han Y. et al. *J. Energy Chemistry*, 2013, vol. 22, pp. 459–467. https://doi.org/10.1016/S2095-4956(13)60060-1.
19. Koper G.J.M. *An Introduction to Chemical Thermodynamics. 2nd ed*. VSSD: Leiden, 2008, 212 p.
20. Klotz I.M., Rosenberg R.M. *Chemical Thermodynamics. Basic Concepts and Methods. 7th ed*. John Wiley & Sons Inc.: Hoboken, 2008, 588 p.
21. Sluiter J.B., Ruiz R.O., Scarlata C.J., Sluiter A.D., Templeton D.W. *J Agric. Food Chem*., 2010, vol. 58, pp. 9043–9053. https://doi.org/10.1021/jf1008023.
22. Eisermann W., Johnson P., Conger W.L. *Fuel Proces. Technol*., 1980, vol. 3, pp. 39–53. https://doi.org/10.1016/0378-3820(80)90022-3.
23. Żogała A. *J. Sustain. Mining*, 2014, vol. 13, pp. 30–38. https://doi.org/10.7424/jsm140205.

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Information about author
Ioelovich Michael Yacob – Chief Chemist, Head of Chemical Dep., ioelovichm@gmail.com