Hydrogen production from wood waste by mean of dark fermentation

Gaweł Sołowski [1,2]

[1]*Polish Academy of Sciences Gdansk, Poland*
e-mail: gawelsolowski@gmail.com
[2] *Gdansk University of Technology, Gdansk, Poland*

Abstract

The utilization of wood wastes in clean and green chemistry method like by mean of dark fermentation, is a highly desired solution of waste management. In the article model for the estimation hydrogen potential of wood waste is given. The model has been used to calculate the potential theoretical hydrogen mass that can be produced from wood wastes in Pomerania and Silesia: pine, spruce, fir, beech and oak. In the introduction, there describes the process and background of the model and the parameters are explained. In model description the formulas of a model are given with reaction schemes and variables description. In the results and discussion there are calculations of hydrogen potential mass from wood waste in Pomerania and Silesia. The potential hydrogen production from wood waste of these two regions fulfil near 8 times the recent demand of Poland.

Key words: dark fermentation, beech, pine, oak, spruce, fir

1. Introduction

Proper management of forests needs to overcome the problem of wood waste utilization - it can be used directly as a source of heat of some household but it pollutes environment shifting greenhouse effect and some dioxins. Therefore, there is necessary to project a new way of wood waste management, more friendly to the environment. On the other hand, the best strategy of utilization of waste is to transfer it for renewable source of energy or efficient raw material of green chemistry. One of the potential methods of such an utilization considers to be dark fermentation. Dark fermentation is a microbial anaerobic conversion of simple carbohydrates to hydrogen, carbon dioxide, butyric acid or acetic acid. The most desired substrate is hydrogen ‘fuel of the future’. Therefore, in the article there has presented a model of potential hydrogen production from wood waste. Lignocelluloses wastes like wood waste can be considered as the raw material. Thus the model for hydrogen production estimation from different lignocelluloses wastes has been developed. In the models two of biopolymers of lignocelluloses are taken into account: cellulose and hemicellulose. The model gives possibility to estimate potentiality of the selected kind of wood to be hydrogen source. The presented equation can calculate potential hydrogen volume production from selected parts of the plant, all plants and group of plants. Let assumes that the model follows: that plant waste in the range of kind are from the same part of the plant and the origin of the same growth area. Other assumptions of the model follows Bartacek et al [1] and Pradhan et al [2] - maximal yield calculations for hexoses is 0.33 and for pentoses 0.32. The model estimations include parameters: yield of reactions Y_{tg} (dark fermentation of hexoses) or Y_{th} (dark fermentation of pentoses) mass of waste, fraction of biopolymer in the plant (f_c – of cellulose) and (f_h - of hemicelluloses) The hydrolysis of polysaccharides are considered as perfect. The model was used for calculation theoretical hydrogen volumes of selected lignocelluloses wastes taken of selected wood waste data from the report 2015[3], Ropińska[4], Jasiulewicz [5] for pine wood (Pinus sylvestris), spruce (Picea abies), fir (Abies alba), beech (Fagus sylvatica) and oak (Quercus robur).

2. Model description

Let’s assume that model follow: plant waste in the range of kind are in the same age and origin from the same cultivation area. The model estimations include parameters: yield of reactions Y_{tg} (dark fermentation of hexoses) or Y_{th} (dark fermentation of pentoses) mass of waste, fraction of biopolymer in the plant (f_c of cellulose) and (f_h of hemicelluloses). In the model, perfect hydrolysis of polysaccharides into simple carbohydrates (glucose, rhamnose fructose xylose, maltose and lactose) are assumed, and dark fermentation undergoes only in acetic way. The process undergoes in two reactions (1 or 2) with a maximal theoretical yield of hydrogen 0.32 – 0.33 [1,2]. Dark fermentation of carbohydrates can undergo in 2 reactions:

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{2.1}$$

$$C_5H_{10}O_5 + 2.67H_2O \rightarrow 1.67CH_3COOH + 1.67CO_2 + 3.33H_2 \tag{2.2}$$

Equation 3 has been developed to calculate optimal potential hydrogen production availability M_{Hij} (mass of hydrogen produced) of the same random waste part of age ‘j’ of plant ‘i’ of mass m_{ji}:

$$M_{Hij} = \left(\frac{Y_{tg}\, f_{cji}\, m_{ji}\, M_{GluH2}}{M_{GLU}} + Q_{hji}\, m_{ji}\right) \approx \frac{Y_{tg}\, f_{cji}\, m_{ji}\, M_{GluH2}}{M_{GLU}} + \left(\frac{Y_{th} f_{h6ji}\, M_{hekH_2}}{M_{hek}} + \frac{Y_{tp} f_{h5ji}\, M_{penH2}}{M_{pen}}\right) m_{ji} \tag{2.3}$$

where:
M_{Hij} - theoretical hydrogen mass from random part of age ‘j’ of plant ‘i’ [kg];
Y_{tg} - theoretical optimal hydrogen yield from glucose 0.33 according to reaction 1 [1];
m_{ji} - mass of random part of age ‘j’ of plant ‘i’;
f_{cii} - fraction of cellulose in part ‘j’ of plant ‘i’;
Y_{th} - theoretical optimal hydrogen yield from hexoses in hemicelluloses: (glucose, fructose, lactose,) via reactions (1 and 2) - 0.33 [2];
Y_{tp} - theoretical optimal hydrogen yield from pentoses: glucose, fructose, lactose, xylose, rhamnose) via reactions (1 and 2) - 0.32 [2];
M_{GluH2} - molar mass of hydrogen in glucose – 12 g/mol;
M_{Glu} - molar mass of glucose – 180 g/mol;
M_{hekH2} - molar mass of hydrogen in hexose – 12 g/mol;
M_{Glu} - molar mass of hexose – 180 g/mol;
M_{penH2} - molar mass of hydrogen in pentose – 10 g/mol;
M_{pen} - molar mass of pentose – 150 g/mol;
Q_{hji} - polymerization and fraction of hemicellulose factor in random age ‘j’ of the plant ‘i’ via equation (2.4)

$$Q_{hji} = \frac{Y_{th} f_{h6ji}\, M_{hekH_2}}{M_{hek}} + \frac{Y_{tp} f_{h5ji}\, M_{penH2}}{M_{pen}} \tag{2.4}$$

where:
f_{h6ji} - fraction of hexoses in fraction of hemicelluloses;
Y_{th} - theoretical optimal hydrogen yield from hexoses in hemicelluloses: glucose, fructose, lactose via reaction (1 and 2) - 0.33[2];
Y_{tp} - theoretical optimal hydrogen yield from pentoses in hemicelluloses: glucose, fructose, lactose, xylose, rhamnose via reaction (1 and 2) - 0.32 [2];
f_{h5ji} - fraction of pentoses in fraction of hemicelluloses.

In case of calculation of theoretical maximal hydrogen production from the bark of different random ‘j’ age of plant ‘i’ (for example, fir wood of different age group) equations (5) and (6) have been designed. Overall mass M_i of ‘j’ parts of the plant ‘i’ equals equation (5):

MOST WIEDZY Downloaded from mostwiedzy.pl

$$M_i = \sum_j m_{ij} \quad (2.5)$$

where: m_{ij} - mass of ‘j’ age of plant ‘i’ (for example age 21-40 and age 41-60 give j=2).

If the plant ‘i’ belongs to spermatophytes group then ‘j’ age includes (1-20 years, 21-40 years, 41-60, 61-80 and 81-100, thus j=5). Optimal potential hydrogen production availability of plant ‘i’ from all parts ‘j’ was shown in equation (2.6):

$$M_{Hi} = \sum_j m_{ij} \left(\frac{Y_{tg} f_{cij} M_{GluH2}}{M_{GLU}} + Q_{hij}\right) \quad (2.6)$$

For analysis wood of 5 different group age ‘j’ of pine are chosen: 1-20 years, 21-40 years, 41-60 years, 61-80 and 80-100. The parameters for optimal theoretical hydrogen volume are given in Table 1.

Tab 1. Values of parameters of wood waste.

Kind of wood	**Age years**	**f_{c}, %**	**f_{h}, %**	**f_{h5}, %**	**f_{h6}**	**ref**
Pine wood	1-20	47	16.8	44%f_h=7.5%	58%f_h=18.5%	[6–9]
	21-40	48.9	16.8	43%f_h=7.2%	57%f_h=16.1%	
	4160	40.8	25.9	40%f_h=10.4%	60%f_h=14.5%	
	60-81	42	25	38%f_h=9.5%	62%f_h=15.5%	
	81-100	42.5	24.8	37% f_h=9.3%	63% f_h=15.5%	
Spruce wood	41-60	40.4	32.3	42%f_h=14%	58%f_h=18,3%	[10]
Fir wood	1-20	40.7	35.2	38%f_h=13.5%	62%f_h=21.7%	[11]
	21-40	41	35.1	38.3%f_h=13.4%	61.7%f_h=21.7%	
	41-60	42.1	34	39.2%f_h=13.4%	60.8%f_h=20.6%	
	60-81	42.9	33.5	39.3%f_h=13.2%	60.7%f_h=19.7%	
	81-100	43.5	33.1	39.7%f_h=13.1%	60.3%f_h=20%	
Beech wood	41-60	46.4	22.4	47% f_h=10.5%	53%f_h=21.9%	[9]
Oak wood	21-40		39 20	43% f_h=9%	57%f_h=11%	[12]
	41-60	39.4	21	40% f_h=8%	60% f_h=13%	
	60-81	41.3	23	38%f_h=9%	62% f_h=14%	
	81-100	42	22.4	36%f_h=8%	64% f_h=14.3%	

3. Results and discussion

The model presented in the article equations (3-10) is used for estimation of potential hydrogen production by dark fermentation in Pomerania region and Silesia region. The results are given in tables (Tables 2 and 3).

Table 2. Potential mass of hydrogen produced by dark fermentation from pine, spruce, fir, beech and oak wood waste at Pomerania Region according to [3,4].

Material	**Age**	**Annual mass of wastes at Pomerania Region, 10^3 tonnes**	**Estimated hydrogen mass at Pomerania Region,·tonnes**
Pine wood	1-20	43,684	577,714
	21-40	10,593	144,264
	41-60	27,521	365,933
	60-81	25,009	337,653
	81-100	40,954	555,985
Sum Pine wood	1-100	109,210	1981,549
Spruce wood	41-60	5,379	17,645
Fir wood	1-20	652	7,696
	21-40	158	1,878
	41-60	411	4,931
	60-81	373	4,532

MOST WIEDZY Downloaded from mostwiedzy.pl

	81-100	611	7,984
Sum fir wood	1-100	1,630	18,826
Beech wood	41-60	15,974	63,914
Oak wood	1-20	1,304	4,638
	21-40	316	4,681
	41-60	821	12,792
	60-81	747	11,661
	81-100	1,223	19,339
Sum oak wood	1-100	3,260	33,771
Total waste wood		133,823	2115,526

Table 3. Potential mass of hydrogen produced by dark fermentation from pine, spruce, fir, beech and oak wood waste at Silesian Region according to [3,4].

Material	Age	Annual mass of wastes at Silesian Region, 10^3 tonnes	Estimated hydrogen mass at Silesian Region ·tonnes
Pine wood	1-20	18,200	307, 497
	21-40	4,414	76,576
	41-60	11,466	182,039
	60-81	10,420	167,283
	81-100	17,063	225,697
Sum Pine wood	1-100	45,500	733,395
Spruce wood	41-60	11,375	43,317
Fir wood	1-20	728	8,593
	21-40	177	2,097
	41-60	459	5,506
	60-81	417	5,067
	81-100	683	8,358
Sum fir wood	1-100	1,820	21,021
Beech wood	41-60	10,010	40,051
Oak wood	1-20	2,912	32,921
	21-40	706	10,451
	41-60	1,835	25,959
	60-81	1,667	42,910
	81-100	2,730	43,298
Sum oak wood	1-100	7,280	153,149
Total waste wood		74,165	567,429

The model presented in equations (3-10) assesses profitability of hydrogen production by dark fermentation. They show an upper limit of hydrogen masses that can be obtained from selected part, kind, and set of different plant wastes. The model collects parameters and data taken from literature [3,7,12]. Shown potential volumes of hydrogen are obtained under the assumption of perfect hydrolysis (all parts of the biopolymers are converted into simple sugars). From the 1 kg of selected wood wastes can be obtained maximally: from: pine wood 1-20 years 16.9g of hydrogen, pine wood 21-40 years 17.4 g of hydrogen, from pine wood 41-60 years 15.9g of hydrogen, pine wood 61-80 years 16.1g of hydrogen, pine wood 81-100 years 13.2 g of hydrogen; spruce wood 41-60 years 16.6 g of hydrogen; fir wood 1-20 years 11.8g of hydrogen, fir wood 21-40 years 11.9g of hydrogen, fir wood 41-60 years 12 g of hydrogen, fir wood 61-80 years 12.1g of hydrogen, 81-100 years 12.2 g of hydrogen, beech wood 41-60 years 17.5 g of hydrogen, oak wood 1-20 years 14.7 g of hydrogen, oak wood 21-40 years 14.8g of hydrogen, oak wood 41-60 years 15.6 g of hydrogen, oak wood 61-80 years 15.7 g of hydrogen, 81-100 years oak wood 16 g of hydrogen. The amount of hydrogen obtained from wood is smaller than from textile wastes cotton or linen. From 1 kg of cotton wastes 21g of hydrogen, from 1 kg of linen wastes 19 g of hydrogen[16]. The highest mass of hydrogen can be obtained by dark fermentation of wood wastes from beech wood of 41-60 years, pine wood and spruce wood. Dark fermentation can optimally produce hydrogen from the above mentioned annual wood waste in masses: 2 115,526 tonnes of hydrogen from Pomerania region and 567,426 tonnes of hydrogen from Silesia region. The Lotos, the greatest consumer of hydrogen in Pomerania Region in 2014 used $45.9 \cdot 10^3$ tonnes of hydrogen per year [17,18]. Recent consumption of hydrogen in Poland that is

MOST WIEDZY Downloaded from mostwiedzy.pl

$290.6 \cdot 10^3$ tonnes. Therefore, potential masses of hydrogen from Pomerania wood waste are 46 times more than Lotos demand and Silesian 12 times more than Lotos demand. Pomerania potential hydrogen mass is 7 times more than Poland demand and Silesian potential hydrogen mass is 1.95 of Poland demands of hydrogen. Therefore, however wood wastes are less efficient raw material for the hydrogen source than textile waste due to widespread of waste they can fulfill better Polish demand for this element [1,19]. The world recent demand for hydrogen is $356 \cdot 10^7$ tonnes and Pomerania potential hydrogen from wood waste fulfill it in 0.06% and Silesia in 0.02%. Pomerania and Silesia wood waste could fulfill world demand in 0.08%. The difficulty in recent technique is efficiency up to 15% and low hydrolysis level from softwood [20,21].

4. Conclusions

The article is an analysis of potential of source of hydrogen other than beet or corn waste –wood waste [22,23]. The model presented in the article allow to assess availability of hydrogen source without empirical works. The model allows to design process with high efficiency and is a useful device in scale-up of dark fermentation from lab scale into industrial wastes. The wood wastes from Pomerania and Silesia are enough to fulfil Lotos demand for hydrogen and overall recent consumption of Poland for hydrogen. The best sources of hydrogen from pine wood, spruce wood, fir wood, oak wood and beech wood are beech wood and pine wood. The potential production of hydrogen from wood waste are lower than production for textile waste, but higher than from corn waste [24]. However, textile wastes mass is lower 288,593 tonnes are smaller than wood wastes of $207{,}988 \cdot 10^3$ tonnes, therefore wood waste are more widespread material and enough high hydrogen potentiality[16,25,26]. Assessing hydrogen production from different plant waste is an important step for efficient selection of proper source for hydrogen production. The data are hints for designing industrial process, where hydrogen is used, how many renewable sources can be applied for replacing of conventional processes.

References

[1] Bartacek, J; Zabranska, J; Lens PNL. *Developments and constraints in fermentative hydrogen production*. Biofuels, Bioprod Biorefining 2007;1:201–14.

[2] Pradhan N, Dipasquale L, d'Ippolito G, Fontana A, Panico A, Lens PNL, et al. *Kinetic modeling of fermentative hydrogen production by Thermotoga neapolitana*. Int J Hydrogen Energy 2016;41:4931–40. doi:10.1016/j.ijhydene.2016.01.107.

[3] Zajączkowski, Grzegorz; Jabłoński, Marek; Jabłoński, Tomasz; Kowalska, Anna; Małachowska, Jadwiga;Piwnicki J. O STANIE LASÓW. Warsaw: 2015.

[4] Ropińska B. *Potential sources and possibilities of biomass energy utilisation for production of agricultural biogas in West Pomeranian Province*. In: Jasiulewicz M, editor. Reg. Local Biomass Potential. Polish Eco, Koszalin: Wydawnictwo Politechniki Koszalińskiej; 2011.

[5] Jasiulewicz M. Potencjał biomasy w Polsce. 2010.

[6] Sariyildiz T. *Litter Decomposition of Picea orientalis , Pinus sylvestris and Castanea sativa Trees Grown in Artvin in Relation to Their Initial Litter* Quality Variables 2003;27:237–43.

[7] Mahishi MR, Goswami DY. *An experimental study of hydrogen production by gasification of biomass in the presence of a* CO_2 *sorbent*. Int J Hydrogen Energy 2007;32:2803–8. doi:10.1016/j.ijhydene.2007.03.030.

[8] Ivanova G, Rákhely G, Kovács KL. *Thermophilic biohydrogen production from energy plants by Caldicellulosiruptor saccharolyticus and comparison with related studies*. Int J Hydrogen Energy 2009;34:3659–70. doi:10.1016/j.ijhydene.2009.02.082.

[9] Sharypov VI, Marin N, Beregovtsova NG. *Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I : influence of experimental conditions on the evolution of solids* , liquids and gases 2002;64:15–28.

[10] Xu C, Leppänen A-S, Eklund P, Holmlund P, Sjöholm R, Sundberg K, et al. Acetylation and characterization of spruce (Picea abies) galactoglucomannans. Carbohydr Res 2010;345:810–6. doi:10.1016/j.carres.2010.01.007.

[11] Kacik, Frantisek; Smira, Pavel; Reinprecht, Ladislav; Nasswettrová A. C*HEMICAL CHANGES IN FIR WOOD FROM OLD BUILDINGS DUE TO AGEING*. Cellul Chem Technol 2014;48:79–88.

[12] Wagenfuhr, R; Schreiber C. *Holzatlas*. Leibzig: V.E.B. Fachbuchverlag; 1974.

MOST WIEDZY Downloaded from mostwiedzy.pl

[13] Agencja Rynku Rolnego. Rynek zbóż w Polsce. Warsaw: 2013.

[14] Taherzadeh MJ, Karimi K. P*retreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas Production: A Review*. vol. 9. 2008. doi:10.3390/ijms9091621.

[15] Karimi K, Taherzadeh MJ. *A critical review on analysis in pretreatment of lignocelluloses: Degree of polymerization, adsorption/desorption, and accessibility.* Bioresour Technol 2016;203:348–56. doi:10.1016/j.biortech.2015.12.035.

[16] Sołowski G. *Theoretical potential of hydrogen production from textiles wastes in pomeranian region by means of dark fermentation.* Glob a Reg Ochr Sr 2016;1:313–7.

[17] Biedron J. krwioobieg nowoczesnej rafinerii, a może paliwo przyszłości? Gdańsk: 2015.

[18] Gardziński W., Molenda J. *Źródła i wykorzystanie wodoru w rafineriach ropy naftowej.* Przem Chem 2005;84:825–8.

[19] Hawkes FR, Dinsdale R, Hawkes DL, Hussy I. *Sustainable fermentative hydrogen production: Challenges for process optimisation.* Int J Hydrogen Energy 2002;27:1339–47. doi:10.1016/S0360-3199(02)00090-3.

[20] Hendriks ATWM, Zeeman G. *Pretreatments to enhance the digestibility of lignocellulosic biomass.* Bioresour Technol 2009;100:10–8. doi:10.1016/j.biortech.2008.05.027.

[21] Singh S, Jain S, PS V, Tiwari AK, Nouni MR, Pandey JK, et al. *Hydrogen: A sustainable fuel for future of the transport sector.* Renew Sustain Energy Rev 2015;51:623–33. doi:10.1016/j.rser.2015.06.040.

[22] Urbaniec K, Grabarczyk R. *Raw materials for fermentative hydrogen production.* J Clean Prod 2009;17:959–62. doi:10.1016/j.jclepro.2009.02.008.

[23] Panagiotopoulos JA, Bakker RR, Vrije T De, Urbaniec K, Koukios EG, Claassen PAM. *Prospects of utilization of sugar beet carbohydrates for biological hydrogen production in the EU.* J Clean Prod 2010;18:S9–14. doi:10.1016/j.jclepro.2010.02.025.

[24] Panagiotopoulos IA, Bakker RR, Budde MAW, de Vrije T, Claassen PAM, Koukios EG. *Fermentative hydrogen production from pretreated biomass: a comparative study.* Bioresour Technol 2009;100:6331–8. doi:10.1016/j.biortech.2009.07.011.

[25] Sołowski G. *„Obróbka Lignocelulozy- Pierwszy Etap Zielonej Energii, Chemii Wraz Z Wodorem”.* In: Szala, M., Kropiwniec K, editor. Wybrane zagadnienia z Zakr. Ochr. środowiska i energii odnawialnej. 1st ed., Lublin: Fundacja Tygiel; 2016, p. 56–75.

[26] Hawkes FR, Hussy I, Kyazze G, Dinsdale R, Hawkes DL. *Continuous dark fermentative hydrogen production by mesophilic microflora: Principles and progress.* Int J Hydrogen Energy 2007;32:172–84. doi:10.1016/j.ijhydene.2006.08.014.

MOST WIEDZY Downloaded from mostwiedzy.pl