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## PERSPECTIVES OF HYDROGEN PRODUCTION FROM CORN WASTES IN POLAND BY MEANS OF DARK FERMENTATION

### PERSPEKTYWY PRODUKCJI WODORU W POLSCE OTRZYMANEGO W WYNIKU CIEMNEJ FERMENTACJI ODPADÓW ZBOŻOWYCH

**Abstract:** A model for calculating the maximal theoretical production of hydrogen from corn wastes is proposed. The model has been used to estimate the potential for hydrogen production from cereals wastes such as wheat, barley, and corn which are cultivated in Poland. The potentials for Pomorze and other regions of Poland are compared. The hydrogen produced from cereal wastes in Poland could potentially meet 47 % of national hydrogen demand.

**Keywords:** dark fermentation, theoretical hydrogen potential, Pomorze, wheat, barley, corn

## Introduction

Dark fermentation is an anaerobic conversion of carbohydrates or glycerol into carbon dioxide, carboxylic acid and hydrogen. The process is a promising source of biohydrogen. Lignocellulose wastes can be considered as raw materials.

Urbaniec et al. [1, 2] and Grabarczyk et al. [1, 3, 4] analyzed sugar beet, wheat and potato as potential raw substrates for hydrogen production. Besides, paper-mill wastes [5] and sewage sludge [6] were analyzed. However, analysis gives results as a sum of photofermentation and fermentation of 1 kg of substrates used in Hyvolution programme [5, 7]. Panagotiopulos et al. [8, 9] works did not provide an exact explanation of the ratio for dark fermentation and dark fermentation in Hyvolution model. Hsu et al. [10] describe a technological pathway for hydrogen production from wastewater. Nasr et al. [11] models include hydrogen production profile over time using the Artificial Neuron Network (ANN) method. Sierra et al., Sangian et al., and Taufiq-Yap et al. [12-14] analyzed the energy potential of wood. The net energy generated by dark fermentation and microbial fuel cell is given by Perera et al. [15]. The dark fermentation process-parameters were analysed using CFD (computation fluid dynamics) codes in Trad et al. [16]. Singh et al. [17] analysed

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hydrogen production model based mainly on the empirical Gompertz Equation. There are also attempts related to kinetic modelling of process, similar to anaerobic digestion - see Chezeau et al. [18]. The dark fermentation experiments are based on corn, barley and wheat as the common substrates [19-23]. Li et al. [24] obtained empirically 9.4 g of hydrogen from 1 kg of corn straw. Nasirian et al. [25] found yield of 13.8 g of hydrogen from 1 kg of wheat waste, while Wu et al. [23] 8.3 g of hydrogen from kg of barley straw.

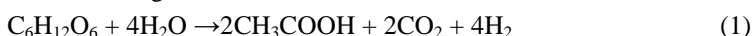
The aim of the investigation is to calculate the potential for production of hydrogen from cereal (wheat, barley and corn) wastes in all regions of Poland to determine availability of hydrogen substrates for dark fermentation. Therefore a model for estimation of hydrogen production from different lignocelluloses wastes has been proposed.

## Model description

In the model, cellulose and hemicelluloses, the two biopolymers contained in lignocelluloses, are taken into account. The model presented allows for the calculation of potential hydrogen production from selected parts of plants.

The first assumption is that wastes coming from the same plants are in the same development stage and from the same cultivation area. Besides, a perfect hydrolysis of polysaccharides is assumed and that maximal hydrogen yield for hexoses is 0.33 and for pentoses is 0.32 - see Bartacek et al. [26] and Pradhan et al. [27]. The model includes such parameters as yield of reactions  $Y_{th}$  (for dark fermentation of hexoses) or  $Y_{tp}$  (for dark fermentation of pentoses), mass of waste and fraction of biopolymers in the plant ( $f_c$  - for cellulose,  $f_h$  - for hemicelluloses). The model was used to calculate the theoretical hydrogen production from selected lignocellulose wastes (wheat, barley, corn) based on the data for Pomorze and 15 other regions of Poland from the Agricultural Market Agency (ARR) [28]. The article uses a modified version of a model used by Solowski [29, 30].

It was assumed that wastes constitute 70 % for wheat (63 % straw and 7 % bran), 55 % for barley and 48 % for corn. The model assumes perfect hydrolysis of polysaccharides into simple carbohydrates (glucose, rhamnose, fructose, xylose, maltose and lactose) and acetic acid pathway of dark fermentation. The process of dark fermentation of simple carbohydrates can proceed according to two channels:



with maximal theoretical yield of hydrogen 0.32-0.33 [26, 27] .

The theoretical hydrogen production  $M_{Hij}$  from the same waste part  $j$  of plant  $i$ :

$$M_{Hij} = \left[ f_{cji} \frac{Y_{th} M_{hekH2}}{M_{hek}} + \left( \frac{Y_{th} f_{h6ji} M_{hekH2}}{M_{hek}} + \frac{Y_{tp} f_{h5ji} M_{penH2}}{M_{pen}} \right) \right] m_{ji} \quad (3)$$

where the first term describes the hydrogen production from cellulose (biopolymer of glucose), the second and the third part describe the hydrogen production from hemicellulose (from hexoses and pentoses, respectively);  $M_{Hij}$  - theoretical hydrogen production from waste part  $j$  of plant  $i$ ;  $m_{ji}$  - mass of waste part  $j$  of plant  $i$ ;  $f_{cji}$  - fraction of cellulose in waste part  $j$  of plant  $i$ ;  $f_{hji}$  - fraction of hemicellulose in waste part  $j$  of plant  $i$ ;  $f_{h6ji}$  - fraction of hexoses in hemicellulose;  $f_{h5ji}$  - fraction of pentoses in hemicellulose;  $Y_{th}$  - theoretical hydrogen yield from hexoses: (glucose, fructose, lactose) via reaction (1) - 0.33 [26];  $Y_{tp}$  - theoretical hydrogen yield from pentoses: (xylose, rhamnose) via reaction

(2) - 0.32 [27];  $M_{hekH_2}$  - partial molar mass of hydrogen in hexose - 12 g mol<sup>-1</sup>;  $M_{hek}$  - molar mass of hexose - 180 g mol<sup>-1</sup>;  $M_{penH_2}$  - partial molar mass of hydrogen in pentose - 10 g mol<sup>-1</sup>;  $M_{pen}$  - molar mass of pentose - 150 g mol<sup>-1</sup>.

The theoretical hydrogen production from plant  $i$  can be obtained by summing over the waste parts  $j$  of plant  $i$ :

$$M_{Hi} = \sum_j M_{Hij} \quad (4)$$

If plant  $i$  belongs to spermatophytes, subset of the land plants, then  $j$  can include: leaves, straw, seeds, flowers and roots (thus  $j \in (1; 5)$ ). Here, for analysis only two  $j$  parts (wheat straw and bran) were chosen. The assumed parameters for theoretical hydrogen production are given in Table 1. In this paper wheat straws, barley straws and corn straws were analyzed.

Table 1

Values of parameters for some of cereal wastes

Material	$f_{cji}$	$f_{hji}$	$f_{h5ji}$	$f_{h6ji}$	Ref.
Wheat straw	40 %	26.6 %	0.23 $f_{hji} = 6.1$ %	0.76 $f_{hji} = 20.5$ %	[20, 31, 32]
Wheat bran	42 %	21.2 %	0.29 $f_{hji} = 6.1$ %	0.71 $f_{hji} = 15.1$ %	[33, 34]
Barley straw	31 %	20.2 %	0.31 $f_{hji} = 6.5$ %	0.69 $f_{hji} = 13.5$ %	[23, 35]
Corn straw	38 %	26 %	0.3 $f_{hji} = 7.8$ %	0.7 $f_{hji} = 18.2$ %	[36]

The theoretical hydrogen production from the wastes  $M_H$  is calculated using the equation:

$$M_H = \sum_i \sum_j M_{Hij} \quad (5)$$

## Results and discussion

### Results

The model presented above was used for the estimation of potential hydrogen-production through the process of dark fermentation in Pomorze and other regions of Poland (Tables 2-6) using cereal waste estimated by ARR [28]. Finally, the region potentials are summarized to determine the potential for hydrogen production from cereal wastes across the whole of Poland (Table 6). Parameters  $f_{cji}$  and  $f_{hji}$  were assumed using data from literature [35-37].

Table 2

The calculated potential hydrogen-production using dark fermentation from wastes of three basic cereals at Pomorze, Dolny Slask, Swietokrzyskie and Slask Voivodeships [28]

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
Pomorze	Wheat straw	400.4	5.8	651
	Wheat bran	45.7	0.6	71
	Barley straw	115.4	1.3	146
	Corn straw	7.9	0.1	12
	Sum	569.6	7.8	880
Dolny Slask	Wheat straw	764.4	10.4	1176
	Wheat bran	87.4	1.1	128
	Barley straw	233.7	1	116
	Corn straw	277.9	1.9	210

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
	Sum	569.6	14.5	1629
Świętokrzyskie	Wheat straw	144.2	2.1	234
	Wheat bran	16.5	0.2	25
	Barley straw	100.8	1.1	126
	Corn straw	12.2	0.2	19
	Sum	273.6	3.6	404
Śląsk	Wheat straw	161.8	2.4	263
	Wheat bran	18.5	0.3	29
	Barley straw	63.6	0.7	79
	Corn straw	20.6	0.4	43
	Sum	271.1	4.3	414

Table 3

The calculated potential hydrogen-production using dark fermentation from wastes of three basic cereals at Podlaskie, Lubelskie, Podkarpackie and Małopolska Voivodeship [28]

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
Podlaskie	Wheat straw	82.5	1.2	135
	Wheat bran	9.4	0.1	15
	Barley straw	39.0	0.4	50
	Corn straw	10.5	0.1	17
	Sum	153.1	1.9	216
Lubelskie	Wheat straw	662.4	9.9	1116
	Wheat bran	75.7	1.1	118
	Barley straw	225.7	2.5	286
	Corn straw	45.5	0.6	72
	Sum	1009.2	14.2	1592
Podkarpackie	Wheat straw	248.1	3.6	403
	Wheat bran	28.4	0.4	44
	Barley straw	54.2	0.6	68
	Corn straw	45.4	0.6	70
	Sum	376.1	5.3	584
Małopolska	Wheat straw	215.3	3.1	350
	Wheat bran	24.6	0.3	38
	Barley straw	94.1	1.1	117
	Corn straw	36.1	0.5	56
	Sum	276.1	5.0	561

Table 4

The calculated potential hydrogen-production using dark fermentation from wastes of three basic cereals at Mazowieckie, Warmia-Mazury, Kujawy-Pomorze, Łódź Voivodeship [28]

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
Mazowieckie	Wheat straw	284.0	4.1	461
	Wheat bran	32.5	0.5	50
	Barley straw	81.6	0.9	102
	Corn straw	41.5	0.6	65
	Sum	359.3	6.1	678
Warmia-Mazury	Wheat straw	405.5	5.9	659
	Wheat bran	46.4	0.6	72
	Barley straw	152.3	2.1	235
	Corn straw	83.0	1.2	130

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
	Sum	519.1	9.8	1094
Kujawy-Pomorze	Wheat straw	500.6	7.5	844
	Wheat bran	57.2	0.8	89
	Barley straw	275.5	3	331
	Corn straw	115.9	1.6	183
	Sum	936.0	12.9	1446
Lodz	Wheat straw	222.3	3.2	361
	Wheat bran	25.4	0.4	40
	Barley straw	122.3	1	108
	Corn straw	42.3	0.6	66
	Sum	384.7	5.1	569

Table 5  
The calculated potential hydrogen-production using dark fermentation from wastes of three basic cereals at Opole, Wielkopolska, Lubusz and Pomorze Zachodnie Voivodeship according to ARR [28]

Region	Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
Opole	Wheat straw	550.3	8	894
	Wheat bran	62.9	0.8	97
	Barley straw	192.3	2.2	240
	Corn straw	205.6	2.9	321
	Sum	1011.1	13.9	1552
Wielkopolska	Wheat straw	535.2	7.8	869
	Wheat bran	61.2	0.8	94
	Barley straw	374.0	4.2	467
	Corn straw	277.4	2.8	312
	Sum	1247.8	15.7	1742
Lubusz	Wheat straw	158.1	2.3	257
	Wheat bran	18.1	0.3	28
	Barley straw	48.3	0.5	60
	Corn straw	24.1	0.3	38
	Sum	248.5	3.4	382
Pomorze Zachodnie	Wheat straw	510.0	7.9	874
	Wheat bran	58.3	0.8	90
	Barley straw	156.0	5.6	622
	Corn straw	19.4	0.3	30
	Sum	743.7	14.5	1616

Table 6  
The potential total hydrogen production using dark fermentation from wastes of three basic cereals in Poland [28]

Material	Annual mass of wastes [Gg]	Estimated mass product [Gg]	Estimated volume product [Gm <sup>3</sup> ]
Wheat straw	5.8	90.6	10076
Wheat bran	0.7	9.2	1022
Barley straw	2.3	28.2	3142
Corn straw	1.6	14.6	1623
Sum	9	137.3	15272

## Discussion

The model presented in the paper enables the assessment of potential hydrogen production from cereal wastes by dark fermentation. It determines the upper limit of hydrogen production. The results present mass production (in Gg) and volume production

(in  $\text{Gm}^3$ ). The potential for hydrogen production in Poland is compared with recent data on world hydrogen demand [38]. The model uses parameters and data given in literature [4, 28].

The potential was obtained under assumption of perfect hydrolysis (all parts of biopolymers are converted into simple sugars) and so from 1 kg of selected crop wastes one obtains for:

- wheat straw - 14.6 g of hydrogen,
- wheat bran - 13.8 g of hydrogen,
- barley straw - 11 g of hydrogen,
- corn straw - up to 14 g of hydrogen.

This should be related to empirical results: Li et al. [24] obtained 9.4 g of hydrogen from 1 kg of corn straw; Nasirian et al. [25] 13.8 g of hydrogen from 1 kg of wheat waste, while Wu et al. [23] 8.3 g of hydrogen from kg of barley straw.

Due to high proportion of waste derived from corn and wheat, the highest production potential is in the Wielkopolska Region  $1740 \text{ Gm}^3$  (15.7 Gg) followed by Dolny Slask Region  $1629 \text{ Gm}^3$  (14.5 Gg), Pomorze Zachodnie Region  $1616 \text{ Gm}^3$  (14.5 Gg), Lublin Region  $1590 \text{ Gm}^3$  (14.2 Gg) and Opole Region  $1552 \text{ Gm}^3$  (13.9 Gg). The potential hydrogen production using dark fermentation of cereal wastes in Pomorze Region is rather medium:  $881 \text{ Gm}^3$  (7.8 Gg) of hydrogen (Table 2) half of the Wielkopolska Region  $1740 \text{ Gm}^3$  (15.7 Gg), the region with the highest hydrogen potential (Table 5). The smallest hydrogen production potentials are in Podlaskie Region  $216 \text{ Gm}^3$  (2 Gg), Lubusz Region  $382 \text{ Gm}^3$  (3.4 Gg), Swietokrzyskie Region  $400 \text{ Gm}^3$  (3.6 Gg) and Slask Region  $414 \text{ Gm}^3$  (3.7 Gg).

The total Polish potential for hydrogen production from the crop waste adds up to  $15272 \text{ Gm}^3$  (137.3 Gg) of hydrogen.

Polish potential of cereal wastes is equal 9 Pg ( $P = 10^{15}$  peta), which should be compared to 0.29 Gg of textile wastes per year. The textile wastes are potentially more efficient in hydrogen production; from 1 kg of wastes one can potentially obtain:

- 21 g of hydrogen from cotton waste,
- 19 g of hydrogen from linen waste [29].

From textile wastes can be produced in Poland up to  $6.6 \text{ Gm}^3$  (5.9 Gg) of hydrogen [29]. This can be compared with potential hydrogen production from wood wastes. From 1 kg of selected wood wastes can be potentially obtained using dark fermentation [30]:

- 16.9 g of hydrogen for pine wood 1-20 years old,
- 17.4 g of hydrogen for pine wood 21-40 years old,
- 15.9 g of hydrogen for pine wood 41-60 years old,
- 16.1 g of hydrogen for pine wood 61-80 years old,
- 13.2 g of hydrogen for pine wood 81-100 years old,
- 16.6 g of hydrogen for spruce wood 41-60 years old,
- 11.8 g of hydrogen for fir wood 1-20 years old,
- 11.9 g of hydrogen for fir wood 21-40 years old,
- 12 g of hydrogen for fir wood 41-60 years old,
- 12.1 g of hydrogen for fir wood 61-80 years old,
- 12.2 g of hydrogen for fir wood 81-100 years old,
- 17.5 g of hydrogen for beech wood 41-60 years old,
- 14.7 g of hydrogen for oak wood 1-20 years old,

- 14.8 g of hydrogen for oak wood 21-40 years old,
- 15.6 g of hydrogen for oak wood 41-60 years old,
- 15.7 g of hydrogen for oak wood 61-80 years old,
- 16 g of hydrogen for oak wood 81-100 years old.

Lotos Group, the greatest consumer of hydrogen in Pomorze Region, used 45.9 Gg of hydrogen in 2014. So, Polish potential of hydrogen production from cereal wastes (137 Gg) exceeds the Lotos consumption almost 3 times. It constitutes also 47 % of whole hydrogen consumption in Poland - 326517 Gm<sup>3</sup> (290.6 Gg) [29, 39].

Pomorze Region potential of hydrogen production from three cereals can substitute 2.7 % of recent demand of hydrogen in Poland or 17 % of Lotos demand. The Pomorze demand on hydrogen can be fulfilled by the combined hydrogen production from cereal wastes of several regions like Pomorze, Pomorze Zachodnie, and Warmia-Mazury (together 5325 Gm<sup>3</sup> - 47.9 Gg).

The recent world hydrogen demand per year is 4 Pm<sup>3</sup>; so, the Polish potential for hydrogen production from cereal wastes can fulfil only 0.3 % of this demand [40, 41].

## Conclusions

The availability of three cereals wastes as the source for hydrogen production by dark fermentation is discussed. The dark fermentation process is currently only a laboratory-scale process with no relevance for industry-scale demand. The perspectives given in this paper present upper limits of production of hydrogen by this method.

In Poland, the crop wastes of the three main cereals (wheat, corn and barley) can theoretically produce 137.3 Gg of hydrogen, less than half of the country's recent demand for hydrogen and just 0.3 % of the world demand. Pomorze can fulfill just 17 % of its own regional demand for hydrogen derived from crop waste. The hydrogen production potential from cereal wastes is much higher than that from textile wastes due to the greater quantity of cereal wastes available [26, 29]. Cereal wastes as a hydrogen source are comparable to wood waste but more easily achievable (less options and competition on the market) and more renewable (cereal grows faster than forest). Corn and wheat offer lower potential hydrogen yield per kg than pine, spruce, beech or oak wood but better than fir wood.

Wheat straw is the best hydrogen source from the three cereal wastes, slightly better than corn straw. The assessment of hydrogen production from different plant wastes is an important step in the efficient selection of substrates for hydrogen production. The data presented here can help in designing an industrial process for sustainable hydrogen production, which can contribute towards achieving a sustainable circular economy.

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