




Article

Potential of Waste Biomass from the Sugar Industry as a Source of Furfural and Its Derivatives for Use as Fuel Additives in Poland

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Abstract: Poland is one of the leading producers of sugar from sugar beet in Europe. However, the production of sugar generates large amounts of lignocellulosic waste, in the form of beet pulp and leaves. Currently, this waste is not reutilized in the chemical industry, but is only used as food for farm animals. This paper assesses the potential of using bio-waste from the sugar industry as a raw material for the production of furfurals via acid hydrolysis. Further processing of furfural into derivatives such as furfuryl alcohol (FA) or tetrahydrofurfuryl alcohol (THFA) could increase the economic profitability of the initiative. Furfuryl alcohol can be used as a fuel additive in sugar factories. Tetrahydrofurfuryl alcohol can be used as a component in agricultural fertilizers, increasing the yield of sugar beet. This approach reduces the amount of post-production waste and brings the sugar industry closer to the concept of a circular economy.

Keywords: furfural; furfuryl alcohol; tetrahydrofurfuryl alcohol; fuel additives; circular economy

1. Introduction

In response to increased social awareness, as well as to the tightening and more effective enforcement of environmental regulations, industry is switching its concept of production from that of a linear economy to one of a circular economy [1]. Environmental standards and regulations are encouraging entrepreneurs and scientists to develop such process models that allow for the use of waste in a closed cycle. One sector of the economy that generates large amounts of bio-waste is the agri-food industry. The production of finished products from agricultural crops generates large amounts of waste biomass, mainly consisting of cellulose, hemicellulose, and lignin, which has low potential for use as feed and constitutes a large-tonnage waste. Processing agro-waste into compost is one way of closing the loop. However, the disadvantage is the need to prepare an appropriate landfill and the length of time required to obtain the final product, which is neither highly valuable nor completely safe for the environment (due to the risk of introducing pathogens into the soil, for example).

Another solution is to use waste biomass as a raw material in chemical processes. Biorefineries offer the most common example. Bioethanol can be produced by the fermentation of sugars obtained by biotechnological or chemical methods from the raw materials available in the region, such as sugar cane in Brazil or sugar beet in European countries. It can then be used as a fuel additive [2,3], or in manufacturing industries, for example as a base for the production of polymers [4]. The aim is that biorefineries, like refineries working on the basis of crude oil processing, should focus on producing a limited number of chemicals (about 20), which may be used as basic raw materials in chemical syntheses. Many of these base chemicals [5,6] can be successfully obtained from biomass. One example is furfural, a platform chemical with great market potential [7–9]. New chemical products made from furfural can be used in the production cycle, e.g., as alternative fuels for power boilers or as liquid fuels in transport. They can also be used as construction materials or fertilizers, reducing the amount of waste produced and increasing the economic efficiency of the process. An example of such a solution is a biorefinery that produces ethanol, furfural, and electricity (Figure 1). In this solution, sucrose is used to produce bioethanol and the residual lignocellulosic biomass is converted into furfural and electricity. Although new biorefinery concepts based on biomass processing are being investigated [5,6], many of the proposed solutions have still not been implemented on an industrial scale.

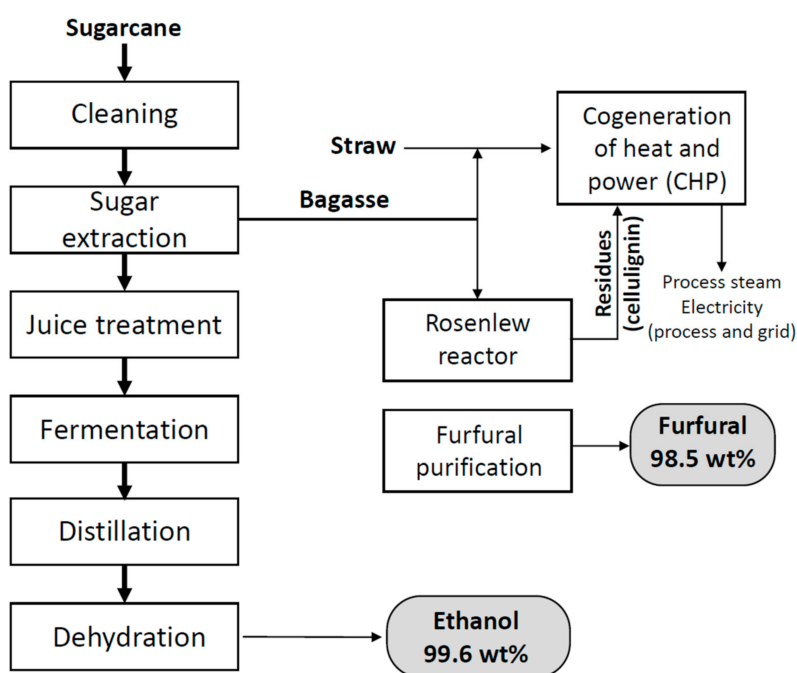


Figure 1. Block diagram of a bio-refinery producing ethanol, furfural, and electricity [7].

2. Furfural

Furfural is a golden, oily liquid with an almond-like odor. This compound has a carbonyl group and a system of conjugated double bonds in the ring, which allows it to be converted into chemical products including furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran, and alkanes [8–12]. Furfural does not mix with gasoline or diesel fuel. It is also chemically unstable and tends to polymerize. Its catalytic conversion products may be used as alternative fuels and fuel components. The octane number of furfural is 53. As a result of furfural reduction, products with a much higher octane number can be obtained, such as furfuryl alcohol (83), methylfuran (74), tetrahydrofurfuryl alcohol (83), or methyltetrahydrofuran (74) [13–15]. Fuel additives in the form of furfural derivatives work most effectively in low-octane hydrocarbon bases (hydrocracking gasoline), in amounts of 5–30 wt%. High concentrations of furfural can promote the formation of resins in fuels, which are deposited in the combustion chamber of the engine. This issue requires more research [16].

It is estimated that the size of the global furfural market will grow from USD 551 million in 2019 to USD 700 million by 2024 [17]. The estimated cumulative annual growth rate is 11.6% [18,19]. The most important raw materials for furfural production are corn cobs, which contain very large amounts of pentosans. Most furfural production plants use this raw material. The furfural market is expected to see the fastest growth of in the Asia-Pacific region. Already, this is the region with the highest production and consumption of furfural, led by China, which is expected to maintain its position in the furfural market. China produces over 80% of the world's furfural, and accounts for 72% of world consumption [13]. Other main producers of furfural include India and Thailand. Nonetheless, the furfural market is dominated by international companies, such as Transfuran Chemicals (Belgium), Central Romana Corporation (Dominican Republic), Pennakem (USA), Silvateam (Italy), Illovo Sugar (South Africa), Hongye Holding Group Corporation (China), KRBL (India), Lenzing (Austria), Tanin (Slovenia), and Shandong Crownchem Industries (China) [17].

According to statistical data published by the Central Statistical Office (GUS) in Warsaw in the Foreign Trade Base (BHZ) from 2004 to 2019 [20], the Polish furfural market is based entirely on imports. The size and value of the market for furfural and its derivatives results only from the level and structure of imports. On average, the domestic demand for furfural was 446,000 kg/year. The size of the market measured by the weight of imports for furfural over the period was 7,146,000 kg, mainly from the European Union (over 98% by weight). Among the EU countries, the main importers to Poland are Austria (3,614,000 kg, 50.6%), Slovenia (2,761,000 kg, 38.64%), and Belgium (576,000 kg, 8.01%). The furfural market in Poland is thus 97.3% dependent on imports from three countries: Austria, Slovenia, and Belgium. The analysis shows that the importance of Slovenia as an exporter to Poland of furfural is increasing. The remaining imports come from Spain, the Netherlands, Germany, Italy, and Great Britain. Another 1% by weight is imported from other developed countries (Switzerland, South Africa, and United States of America). Less than 1% of Poland's furfural by weight comes from developing countries, such as China, India, Dominica, the Dominican Republic, and Iran. The average annual value of imports in the analyzed period was 2,223,000 PLN. Over 98% of the value of these imports went to European Union countries, corresponding to the amount of imports by weight. In 2019, furfural prices were 6.65 PLN for Austria, 7.54 PLN for Slovenia, and 9.87 PLN for Belgium.

Given domestic demand, there is a clear interest in producing furfural in Poland, e.g., from agricultural waste biomass (corn cobs and straw) or waste from the food industry (spent grains, beet pulp and cereal bran). Currently, agriculture accounts for 3% of Polish GDP. Agricultural land in Poland covers 18,608,000 ha, which is 56% of Poland's territory. This places Poland in third place in Europe in terms of the share of land devoted to agriculture. The food industry is one of the few sectors of the economy that has a positive trade balance, which has steadily increased since Poland joined the European Union. This branch of industry (along with the tobacco industry) employs approximately 420,000 people on a full-time basis. This translates into around 18% of the labor force in manufacturing. In the years 2004–2018, the food industry experienced a growth rate in terms of output sold at current prices of on average 6.2% per year [21]. According to data from the Central Statistical Office of Poland, in 2009 the mass of waste generated by agriculture and the agri-food industry in Poland was estimated at 10 million Mg (Table 1). The possibility of an accurate assessment is limited by the lack of information regarding waste from households and insufficient records. Importantly, some branches of the food industry work in campaign mode. This type of production generates very large amounts of waste in a single area in a short time [22].

Table 1. Percentage of unused raw material in various branches of food production [22].

Production Process	% Weight of Raw Material Not Used in End Products
Making Yoghurt	2–6
Making Canned Fruit and Vegetables	5–30
Making Canned Fish	30–65
Making Fruit and Vegetable Juices	30–50
Poultry Slaughter and Processing of Poultry Meat	31–38
Pig Slaughter and Pork Processing	35
Cattle Slaughter and Beef Processing	40–52
Manufacture of Vegetable Oils	40–70
Manufacture of Corn Starch	41–43
Making Fish Fillets, Salted Fish	50–75
Wine Production	20–30
Manufacture of Wheat Starch	50
Manufacture of Starch from Potatoes	80
Manufacture of Cheese	85–90
Making Sugar from Sugar Beet	86

The current research suggests that bio-wastes such as bran obtained from grinding cereals (over 4 wt%) and brewing spent grain (over 8 wt% under optimal reaction conditions) have the greatest potential for furfural production [23,24]. Various types of pomace from agro-food industries, such as from the production of fruit and vegetable juices or sugar production waste (beet pulp and sugar-beet leaves) also show good potential [25]. The advantage of processing waste from the agri-food industry into furfural is the possibility of using mobile installations at the point of waste generation. Despite the fact that the content of hemicellulose in various industrial wastes differs, the technology for converting biomass into furfural remains practically the same.

Sugar beet is one of the most important agricultural crops in Poland. Each year, approximately 14 million tons of sugar beet is produced in Poland, which is the third largest producer of sugar in Europe [26,27]. The main product of processing sugar beet is sugar (saccharose) [28]. However, after the extraction of saccharose, approximately 5 million tons of wet sugar beet pulp (SBP) or 1 million tons of dried biomass is also generated [25]. This agro-waste consists of polysaccharides (22–24 wt% cellulose and 30 wt% hemicelluloses) and pectin (15–25 wt%), with small amounts of fat (1.4 wt%), protein (10.3 wt%), ash (3.7 wt%), and lignin (5.9 wt%). Sugar beet pulp is used mainly as feed for farm animals, in the form of dry pellets or silage. Sugar beet leaves are another waste product, an estimated 8.5 million tons of which is produced in Poland each year. Sugar beet leaves are composed mainly of cellulose (13–18%), hemicellulose (11–17%), and pectin (14–18%), with small amounts of lignin (5–6%), as well as protein and ash [29–31]. Due to the lower nutritional value of this waste and the presence of saponins which cause cattle indigestion, beet leaves are used much less frequently as fodder. Sugar beet pulp and sugar beet leaves are attractive raw materials for the chemical and biotechnological industries. Hydrolysis of hetero-polysaccharides leads to the formation monosaccharides: xylose, glucose, mannose, galactose, rhamnose, and arabinose [32,33]. Hydrolysis of sugar beet pectin gives glucose, arabinose, and galacturonic acid, as well as smaller amounts of galactose and rhamnose [34–36]. The products from hydrolysis can be used as chemical raw materials or subjected to biological valorization.

Acidic hydrolysis is one of the most commonly-used methods for the chemical processing of biomass [37–43]. It is performed using a mineral acidic, such as sulfuric acid [37], hydrochloric acid [38], or phosphoric acid [39], or with organic acids, mainly dicarboxylic acids [40], in concentrations of 0.5–10%. Elevated pressures and temperatures of 140–190 °C are usually required throughout the process [41–43]. As alternative to acids in aqueous phase heterogeneous catalysts may be used, which are sources of Brønsted and Lewis acid centers [44,45]. Biomass conversion over these acid centers can lead to various products, depending on the activated acid centers and the reaction conditions. One example is selective hydrothermal conversion of cellulose into lactic acid (LA), under mild reaction

conditions in the presence of ErCl_3 grafted onto mesoporous silica (MCM-41) [44]. This is also a very promising process the chemical industry, since like furfural LA is a platform molecule.

Acid hydrolysis of waste biomass from a variety of sources, including straw, bagasse, corncobs, oats, and wheat bran, can be used to produce furfural on an industrial scale. Due to their similar compositions, sugar beet leaves and pulp could also be used. Based on our previous research, we have established that furfural can be obtained from beet pulp with yields of about 4.5–5% and of 1.5–2% from sugar beet leaves (see Section 4 Results). If we assume that on average 40 kg of furfural can be obtained from 1 ton of beet pulp dry matter, the annual national demand in Poland for 448,438 kg of furfural would be covered by processing 11,211 tons of beet pulp dry matter, which is only 1.12% of the waste generated by the Polish sugar industry. Moreover, a single installation for processing dried beet pulp at one of the sugar factories in Poland would be sufficient cover domestic demand for furfural. One advantage of processing pulp biomass into furfural is the economic value added to the cost-free raw material, which can be increased by further steps leading to other chemical compounds (Figure 2) [46–48].

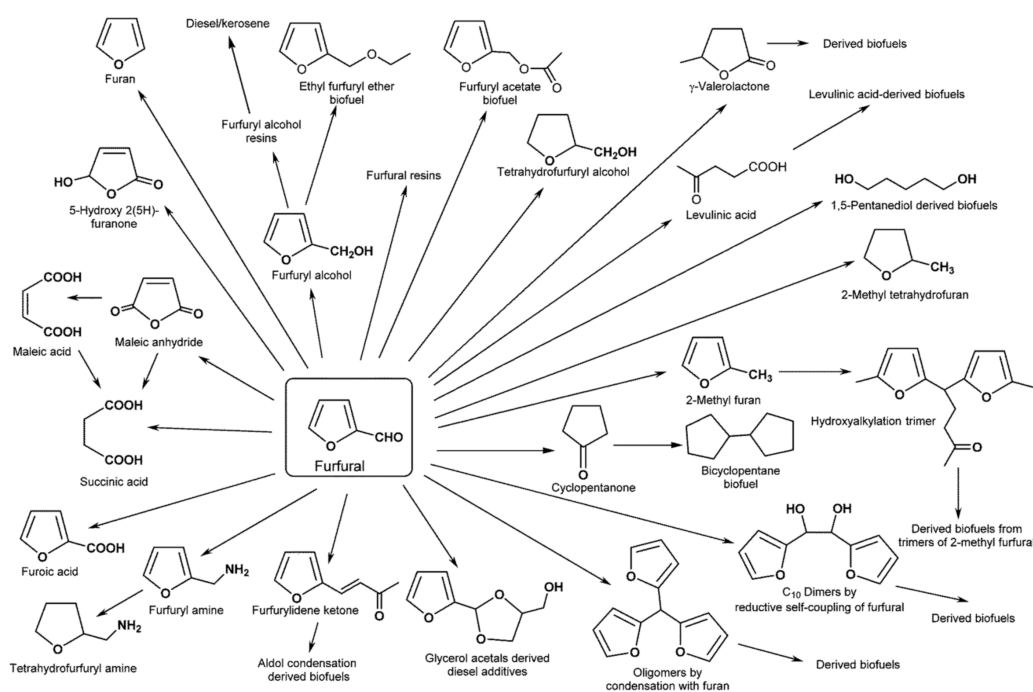


Figure 2. Furfural as a platform chemical [48].

A pilot installation for the processing of beet pulp and beet leaves into furfural on a quarter-technical scale has been built in the sugar factory in Dobrzelin (Figures 3 and 4). As part of the preparations for this installation, an initial profitability analysis was performed for the production of furfural on an industrial scale. The aim of the analysis was to determine the optimal scale of furfural production, guaranteeing a high return on the invested capital. The analysis was based on the discounted cash flow method and the following assumptions were made: (1) post-process waste from industrial plants belonging to KSC S.A. would be used for biomass hydrolysis (beet pulp from sugar factories); (2) the process would be powered mainly by waste heat and electricity from sugar factories; (3) sales revenues were estimated on the basis of the weighted average import price of furfuryl alcohol from the main import directions in 2019; (4) the weighted average cost of capital (discount rate) was 10%; and (5) 24/7 production was assumed during the sugar campaign (100 days). The subsequent scenarios examined the impact of changes in the production of furfural on the value of discounted cash flows over a 10-year period. The results of the analysis are summarized in Table 2.

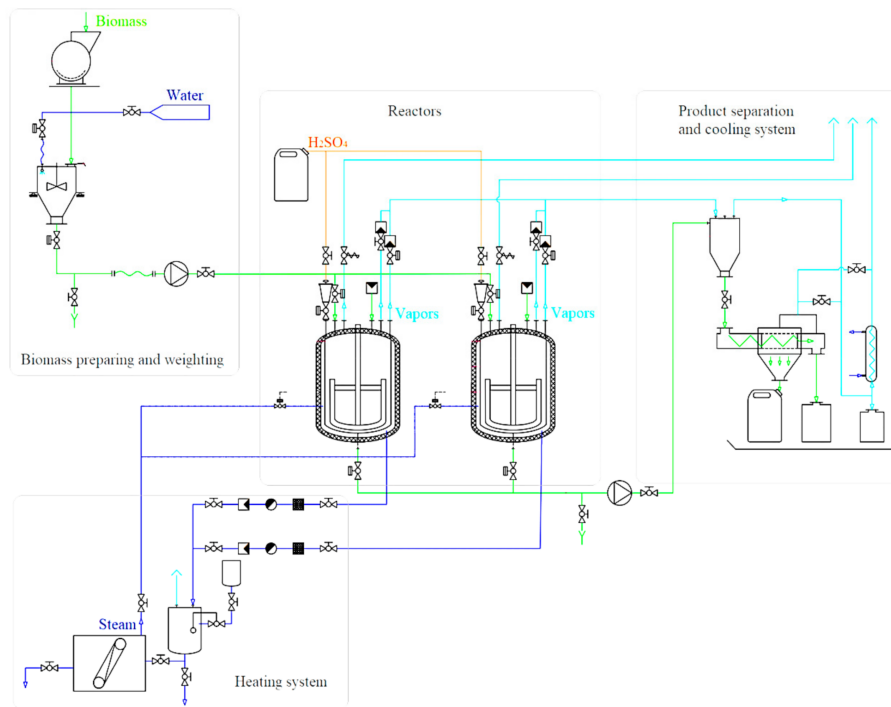


Figure 3. Diagram of an installation for the processing of beet pulp and beet leaves to furfural on a quarter-technical scale.



Figure 4. Photographs of an installation located in the sugar factory at Dobrzelin for processing beet pulp and beet leaves into furfural on a quarter-technical scale (a) right side view (b) left side view.

Table 2. Influence of changes in furfural production volume on the value of discounted cash flows over a 10-year period.

Biomass Hydrolysis				
Number of Reactors (cs)	1	2	3	4
Reactors capacity (m ³)	40	80	120	160
Productivity of furfural/year (t)	226	454	680	907
Profitability analysis (PLN)				
Estimated investment outlays	5,000,000	6,500,000	8,000,000	9,500,000
Sales revenue/year	1,587,000	3,175,000	4,763,000	6,350,000
Operating profit after tax (10 years)	420,000	4,954,000	9,480,000	14,022,000
Net present value (NPV) of discounted cash flows (DCF)	(-1,889,000)	6000	1,902,000	3,797,000

The discounted cash flow method was used to calculate investment projections, assuming a 10% rate of return. The investment period was assumed to be 10 years and the calculations were made for the entire 10-year period.

Based on the operation of the installation shown in Figure 3, a comprehensive assessment of the environmental impact of the manufactured product was performed, using the standardized life cycle assessment method (LCA). The LCA technique is based on the procedures described in ISO 14040 and 14044:

- PN-EN ISO 14040:2009 Environmental management. Life Cycle Assessment. Principles and structure. This standard covers the basic principles and structure of an LCA without describing the method in detail.
- PN-EN ISO 14044:2009 Environmental management. Life Cycle Assessment. Requirements and guidelines.

These standards describe the principles and structure of the LCA, as well as the requirements and procedures necessary for the assessment. Life Cycle Assessment traces the entire life cycle of a product, from its production to the stage of recovery or disposal, and seems to be a natural extension of both the waste management strategy and the environmental management system. The LCA showed that the greatest environmental impact was related to the heating and stirring of the pressurized reactor vessel for furfural production, accounting for almost 87% of the total impact. The impact of the electricity required for the production of furfural was calculated at 91.9% of all negative impacts. Increasing the size of the installation to the industrial scale could theoretically reduce the electricity requirement significantly, and its environmental footprint. For example, the energy used for heating and stirring the 40 m³ capacity autoclave account for 69.3% of the total negative impact. During the sugar campaign, waste heat from sugar processes could be used to heat the pressure reactors, significantly reducing the demand for electricity. This is another example of closing the energy cycle in the process.

An IPCC 2013 GWP 100a carbon footprint study was also conducted. Like the LCA analysis, it showed that the process would have a lower environmental impact on an industrial scale. Greenhouse gas emissions in equivalent CO₂ were lower by approximately 42%. Over 68% of the carbon footprint was due to the electricity use under laboratory conditions. Waste management processes accounted for 33.34% of the carbon footprint. On an industrial scale, electricity accounted for 38.83% of the carbon footprint, whereas the processing of waste accounted for 54.27%. These results show the benefit of building a larger-scale installation for the production of furfural in a sugar factory.

Overall, the process of furfural production was found to have a large environmental impact. On the pilot scale, this amounted to 24.3% of all revenues. On the industrial scale, it would increase to 44.5%. Our environmental impact study, including waste management, identified the following as the most important impact categories: climate change (from a human health and ecosystems perspective), human health toxicity, particulate formation, farmland use, and fossil fuel consumption. The greatest risk is to human health.

The following key conclusions can be drawn from the analysis: (1) given the assumed rate of return on capital and estimated investment outlays, to be profitable the capacity of the reactors for biomass hydrolysis should be at least 80 m³; (2) to increase profitability, the methods and costs of supplying the installation with renewable thermal energy beyond the period of the sugar campaign should be considered; and (3) the porous carbon material obtained by anaerobic combustion of the residues from hydrolysis can be used effectively to revitalize post-industrial areas and absorb pollutants from soil.

3. Furfuryl Alcohol (FA) and Tetrahydrofurfuryl Alcohol (THFA)

Furfural obtained as a result of acid hydrolysis of sugar waste can be further converted into more valuable chemical compounds, such as furfuryl alcohol (FA) and tetrahydrofurfuryl alcohol (THFA) (Figure 5). The most popular chemical compound obtained from furfural is furfuryl alcohol (FA), which is formed a result of hydrogenation of the furfural aldehyde group. The catalysts for the production of FA are based on copper, typically chromium-copper. The traditional method of

fuels to 10% [58]. The addition of biofuels such as levulinate esters to fuels requires an additional solvent. Tetrahydrofurfuryl alcohol can be used as this co-solvent, usually in amounts of 2–5 wt%. [59]. A number of fuel additives can also be obtained from the oxidative conversion of tetrahydrofurfuryl alcohol. Some of the most attractive derivatives for this purpose are tetrahydrofurfuryl tertbutyl ether and acetal or ditetrahydrofurfuryl polyacetal. Compounds of this type can be used in diesel engines at low concentrations, as additives in standard diesel fuels or in fuels containing other additives such as alkyl esters from vegetable oils. The concentration of oxidized compounds in fuels can range from 0.01% to 1%, with the optimal content being within the range of between 0.05% and 0.2 wt%. Oxidized tetrahydrofurfuryl alcohol derivatives can also provide a base for diesel fuel. Used in this way, their content may be up to 40 wt%, optimally 30 wt%. Most often, however, oxidized THFA derivatives are added to fuels in amounts of 10–15 wt%. Adding these derivatives to fuel does not preclude the use of other typical fuel additives and does not change their permissible content. Such fuel can power all types of diesel engines with indirect or direct fuel injection [60]. The addition of THFA also allows for the refinement of heavy crude oil, such as heavy oil, ultra-heavy oil, bitumen, heavy sour crude oil, and oil refinery heavy hydrocarbon residues. It is possible to use THFA as a cracking additive, distillation additive, and for hydrocarbon distillates obtained by the distillation of heavy crude oil in the presence of THFA [61].

Based on data provided by the Central Statistical Office [20], it can be concluded that the Polish market for FA and THFA, is currently based on imports, with no domestic production. Exports in the period 2004–2019 amounted to 133 kg, which is insignificant. Moreover, the exported alcohol was not made in Poland. The main export destinations were Belarus, Ukraine, Lithuania, and Slovakia. It can be assumed therefore that the economic value of the market corresponds to the statistical data relating to the level and structure of imports. The size of the market, measured by the weight of net imports for FA and THFA in the studied period (2004–2019), was 12,951,000 kg, while the average domestic demand for FA and THFA was 809,438,000 kg/year. The greatest recorded demand was 1,032,000 kg in 2014. In the analyzed period, the market was entirely shaped by imports from three locations:

- from developing countries—694,478,000 kg, which was 5.36% of the total mass. China was the only developing country that supplied furfuryl and tetrahydrofurfuryl alcohol.
- from other developed countries—4,827,918,000 kg, which constituted 37.28% of the total mass. The main importer in this group of countries was South Africa, supplying 97.75% by weight. The remaining imports came from countries such as Switzerland, Canada, Norway, and the United States of America.
- from the European Union—7,428,604,000 kg, which constituted 57.36% of the total weight. Among the EU countries, Belgium was the main importer, supplying 91.51% of imports from EU countries. Other imports came from countries such as Austria, the Netherlands, France, Germany, Italy, and the United Kingdom.

The list of countries that currently export to Poland includes Belgium, Italy, Great Britain, Ukraine, Tunisia, Switzerland, the United States, Slovakia, Russia, South Africa, Norway, Germany, Moldova, Lithuania, Canada, the Netherlands, Georgia, France, and China. However, in 2019 the largest exporters of FA and THFA were still Belgium, China, South Africa, and the Netherlands. The Polish market for furfuryl and tetrahydrofurfuryl alcohol thus very much depends on imports from Belgium and South Africa, and to a lesser extent from China. Since 2012, the importance of South Africa has been decreasing in favor of China.

The market value for FA and THFA in the years 2004–2019 corresponding to the volume of imports amounted to PLN 80,932,000. The average annual value of imports in the analyzed period was PLN 5,058,000. The largest value of imports was recorded for Belgium, at PLN 42,747,000 (52.8%), and for the Republic of South Africa, at PLN 27,339,000 (33.8%). The share of Chinese imports in the analyzed period amounted to PLN 5,127,000 (6.3%). Prices per kilogram in 2019 were as follows: for imports

from Belgium PLN 6.29; from South Africa PLN 5.79; from China PLN 7.38. It can be assumed that the high level of imports from Belgium results from price competition.

The research and development carried out by the authors so far under the BIOSTRATEG2/296369/5/NCBR/2016 project indicate the possibility of expanding furfural production by catalytic reduction to FA or THFA, depending on the catalyst used [16,36,37,39,42,43,46]. The direct production of THFA from furfural may be the most advantageous, from the point of view of the low toxicity of the product. The THFA could then be used as an ingredient in foliar fertilizers for sugar beet plantations, closing this material cycle in the production of sugar from sugar beet. Such closing of loops is essential to realizing the concept of a circular economy in sugar processes.

4. Results

Table 3 presents furfural yields obtained in the processes of acid hydrolysis of beet pulp and sugar beet leaves in a quarter-technical installation built in the Sugar Plant in Dobrzelin. Average yields of furfural from beet pulp are approximately 4.5% when the process is carried out at 120 °C in an environment of 0.5% H₂SO₄ under increased pressure (resulting from raising the temperature in a closed system). The yields of furfural from the sugar beet leaf hydrolysates were less than half those for beet pulp under the same conditions, at below 2%. The efficiency of furfural production was taken into account when calculating the profitability of an industrial-scale installation in a sugar factory.

Table 3. Influence of material and processing parameters on the efficiency of furfural production on a quarter-technical scale at the Dobrzelin Sugar Plant.

Raw Material	Dry Matter (%)	Raw Material Weight (kg) (Dry Matter of Raw Material (kg))	Water Weight (kg)	H ₂ SO ₄ Conc. (%)	Time (h)	Temp. (°C)	Furfural Conc. (g/kg)	Yield of Furfural (%)
Sugar Beet Pulp	19.71	10 (1.971)	50	0.5	2	140	1.596	4.86
	19.71	10 (1.971)	50	2.0	2	140	1.754	5.34
	23.34	10 (2.334)	50	5.0	2	140	2.136	5.49
	23.34	10 (2.334)	50	0.5	2	120	1.762	4.53
	19.71	20 (3.942)	40	0.5	2	140	2.286	3.48
Sugar Beet Leaves	11.75	10 (1.175)	50	0.5	2	160	0.497	2.53
	11.75	10 (1.175)	50	0.5	2	140	0.359	1.83
	11.75	10 (1.175)	50	0.5	2	120	0.298	1.52
	11.75	10 (1.175)	50	2.0	2	140	0.467	2.38
	11.75	20 (2.350)	40	0.5	2	140	0.496	1.27

Table 4. shows the results of the catalytic reduction of commercial furfural in an aqueous solution ($C_0 = 0.1 \text{ mol/dm}^3$) and of solutions with the same concentration of furfural prepared from pulp hydrolysates and sugar beet leaves. Neutralized hydrolysates initially concentrated by membrane nanofiltration (FILMTEC Membranes NF270-2540) to a concentration of approximately 0.25 mol/dm^3 were used to prepare the reaction solutions. The results of the catalytic reduction of the aqueous solutions of furfural obtained by acid hydrolysis of beet pulp and beet leaves indicate the high potential of this method for the production of furfuryl alcohol and tetrahydrofurfuryl alcohol from waste biomass. The use of 5% Pd/Al₂O₃ catalysts leads mainly to the production of tetrahydrofurfuryl alcohol, whereas use of the 5% Cu/Al₂O₃ catalyst only results in the selective reduction of the carbonyl group of furfural, preserving the double bonds in the furan ring. Our results are consistent with previously performed catalytic tests of model reactions [49].

Table 4. Reduction of furfural over 5% Cu/Al₂O₃ and 5% Pd/Al₂O₃ catalysts.

Furfural	5% Cu/Al ₂ O ₃			5% Pd/Al ₂ O ₃		
	X (%)	S _{FA} (%)	S _{THFA} (%)	X (%)	S _{FA} (%)	S _{THFA} (%)
Commercial	81	100	0	100	28	72
From sugar beet pulp hydrolysate	90	100	0	100	31	69
From sugar beet leaves hydrolysate	78	100	0	100	26	74

Activation of catalysts: drying in air at 110 °C, 6 h; oxidation in O₂ at 500 °C, 2 h; reduction in H₂ at 300 °C, 2 h.
 Reaction conditions: T = 90 °C, m_{cat} = 0.5 g, V_{furfural} = 25 mL, C_{furfural} = 0.1 M, p_{H₂} = 20 bar.

5. Materials and Methods

5.1. Lignocellulosic Plant Material

The lignocellulosic plant raw materials used for the production of furfural by acid hydrolysis were sugar beet pulp and beet leaves. These wastes were obtained from a sugar factory located in Dobrzelin, during the sugar campaigns of 2019 and 2020. We first determined the amount of dry matter in raw material, using a Radwag MA 50.r moisture analyzer with IR radiator (Radwag, Radom, Poland). The raw material was then subjected to acidic hydrolysis processes.

5.2. Acidic Hydrolysis of Biomass

Hydrolysates containing furfural were obtained by acidic hydrolysis of sugar beet pulp and sugar beet leaves in the semi-industrial installation shown in Figures 3 and 4. Biomass hydrolysis was performed in a pressure reactor with a volume of 75 dm³, at a temperature of 120–160 °C. Prior to each reaction, 10–20 kg of fragmented biomass and 40–50 kg of water (60 °C) was weighed in the homogenizer (a steel tank with a stirrer) resting on technical scales. After loading the biomass and water, the agitator was turned on to ensure even mixing of the mixture. The contents of the tank were then pumped into the 75 dm³ pressure reactor using a peristaltic pump. Concentrated H₂SO₄ (analytical grade, 95%, P.P.H. “Stanlab” sp. j., Lublin, Poland) corresponding to 0.5–5% by weight of the reaction mixture was introduced into the reactor by an automatic system and the reactor was heated with steam from a steam generator. The start of the hydrolysis process was considered to be the moment when the reaction mixture reached the desired temperature, and typically lasted for 0.5 h. After the reaction run, the reaction mixture was cooled in the reactor to 80 °C and the gaseous products were discharged from the reactor first through the cooling system. Once the pressure was equalized, the reaction mixture was pumped using a diaphragm pump into the separation system, where the hydrolysate and solid residues were separated. Samples of the hydrolysates were then neutralized by the addition of CaCO₃ (CaCO₃, analytical grade, POCh, Gliwice, Poland) to pH 6–7. After filtration on syringe filters, the hydrolysates were subjected to chromatographic analysis for furfural content (see Section 5.3) and used as a substrate in reduction processes.

5.3. Catalytic Reduction of Furfural

Hydrogenation of the aqueous furfural solution (0.1 M, 0.025 dm³, commercial: POCH, pure or prepared by acidic hydrolysis of sugar beet pulp and sugar beet leaves) was conducted in a 0.050 dm³ autoclave (Parr Instrument Company, Moline, IL, USA) at 90 °C and 20 bar hydrogen pressure. Equal amounts of home-made catalysts 5% Pd/Al₂O₃ or 5% Cu/Al₂O₃ [49] (m_{cat} = 0.5 g) were used in each reaction. The catalyst suspended in liquid reactants was mixed at 500 rpm. Further increases in mixing speed no longer resulted in changes in activity, ensuring that the reaction proceeded within the kinetic area (diffusion restrictions were eliminated). To remove the air, the autoclave was flushed with argon (Ar, Linde 5.0, 0.020 dm³·min⁻¹, at 20 °C, for 15 min). After 15 min, hydrogen was passed through the autoclave (H₂, Air Products, Premium Plus, 99.999%, at 20 °C) for about 15 min. The system was then closed. The H₂ pressure was raised to 20 bar and the temperature was increased

to 90 °C, using a linear temperature rise of 20 °C·min⁻¹. After reaching the desired temperature and pressure, the process was continued for 2 h. Reaction conditions were optimized for mono- and bimetallic palladium catalysts. The qualitative and quantitative composition of the reaction mixture was analyzed using a dual-channel gas chromatography system with FID and quadrupole MS detector and a SHIMADZU liquid sample feeder QP-2010 SE equipped with two SPL dispensers (GCMS-QP2010 SE). Separation of the analyte components was performed independently on two of the same columns (Zebron ZB-5MSplus Capillary GC Column 30 m × 0.25 mm × 0.25 µm PHX-7HG-G030-11) connected to FID and MS detectors (sample volume 1 µL; injector temperature 200 °C; furnace operation: initial temperature 50 °C for 5 min, heating with a linear increase of 5 °C/min to 150 °C and thermostating at 150 °C for 5 min). Quantitative analysis of furfural, furfuryl alcohol, and tetrahydrofurfuryl alcohol was performed on the basis of the calibration curve for a range of glucose concentrations of 0–10 g/dm³ (the curves in the analyzed range were linear for all compounds: furfural: $y = 9834.464x - 40,630.07$, $R^2 = 0.9998569$, $R = 0.9999285$; furfuryl alcohol; $y = 5759.799x - 105,940.5$, $R^2 = 0.998118$, $R = 0.9990586$; tetrahydrofurfuryl alcohol: $y = 13,478.67x - 253,621.9$, $R^2 = 0.9999688$, $R = 0.9999844$).

6. Conclusions

This paper has presented the acid hydrolysis of beet pulp and sugar beet leaves, performed on a quarter-technical scale in a sugar factory in Dobrzelin. The results indicate the great potential of this method for the production of furfural. The average yield of furfural from beet pulp was 4.5–5%, and from sugar beet leaves about 1.5–2%. Based on the initial outlay and operating costs required for the quarter-technical scale installation, the profitability of a full industrial-scale installation for furfural production from sugar waste was estimated. The discounted cash flow method was used for the projections, assuming a 10% rate of return and a 10-year investment period. Four technological variants were considered, assuming the operation of between one and four reactors with a capacity of 40 m³ each. It was found that the optimal variant is an installation consisting of three hydrolysers working on a charge of beet pulp.

Poland is the leading producer of sugar from sugar beet in Europe. As a result of the processing of sugar beet, large amounts of lignocellulosic waste in the form of beet pulp and beet leaves are generated, which can be successfully used for the production of furfural in amounts covering domestic demand. Further processing of furfural into less toxic derivatives, such as tetrahydrofurfuryl alcohol, could contribute to increase the profitability of the process and also lead to a reduction in the negative environmental impact of the manufactured product. Tetrahydrofurfuryl alcohol can be successfully used as a component in agricultural fertilizers, increasing the yield of sugar beet plants. This approach reduces the amount of post-production waste and contributes to the closing of material cycles, bringing the sugar industry closer to the concept of a circular economy.

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