Possibilities of Biorefinery by Sweet Sorghum (Sucrosorgo) on Brownfield Site

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Abstract: There are several thousand hectares of so-called brownfield sites in Europe, which are not suitable for agricultural use due to industrial pollution. Green biorefinery technologies allow economical reutilization of hydrocarbon or heavy metal contaminated sites by growing agricultural plants and herbs, which are able to tolerate pollutions and produce high amount of biomass or can be sources of valuable products. The applicability of biorefinery was tested on a heavy metal polluted soil. Complete by-product utilization of the biomass was aimed for energetic use and for the production of precursors for chemical industry from plants cultivated on brownfield site. Near hundred species and varieties were cultivated and tested for potential utilisable components. In the present study sweet sorghum was chosen for testing biorefinery, because of its high sugar content and tolerance against heavy metals. After pressing, the liquid fraction was tested as potential raw material for bioethanol production in a pilot system, and the cellulose-rich solid fraction was investigated for biogas and thermal energy production. Our results show that biorefinery is a real possibility for the utilization of brownfield sites for industrial purposes. Furthermore, we established a technology that ensures the biomass cycle and the utilization of solar energy bound in plants.

Key words: Biorefinery, brownfield, heavy metal pollution, phytoremediation.

1. Introduction

The definition of brownfield sites is not consistent in Europe; however, the CABERNET (Concerted Action on Brownfields and Economic Regeneration) generally defines them as “sites that have been affected by the former uses of the site and surrounding land; are derelict and underused; may have real or perceived contamination problems; are mainly in developed urban areas; and require intervention to bring them back to beneficial use”. Economical utilization of brownfield sites is a great problem all over the world; however, there are several thousand hectares of brownfields in Europe [1].

These underused and contaminated sites have been threatening the environment including the surface and subsurface water resources. Additionally, environmental pollution generally hampers the utilization of brownfields. In most cases, these pollutions formed anthropogenically by industrial activity. The contaminants have very diverse chemical composition: like paraffins and olefins, cyclic paraffins and olefins, polyaromatic hydrocarbons originating from crude oil, or heavy metals from mining and halogenated compounds, solvents, xenobiotics, pesticides originating from chemical industry and agriculture [2]. Heavy metals mostly originate from mining, metallurgy and traffic. The heavy metal pollution changes the microbiological composition of the soil, which has a detrimental effect on soil quality.
Heavy metal pollution is a serious environmental threat in Europe, however, the expansion and the degree of the contamination is variable. For example, in Western Europe approximately 1,400,000 sites were affected by heavy metals, of which, over 300,000 were contaminated, i.e., the total heavy metal content is higher than the environmental limit value [4].

Biorefinery is a complex technology, with the aim to utilize biomass by conversion to useful materials (e.g. fuels, solvents, plastics, cosmetic and pharmaceutical materials and food for humans) and/or energy carriers. The produced energy can cover the energy consumption of the technology partially or totally. By-products and the waste streams reducing can contribute to the sustainable development [5, 6]. During biorefinery, the first step is the separation of different plant organs and the physically and chemical fractioning of them by cracking, milling, pressing and extracting to produce primary products (carbohydrates, vegetable oils, volatile oils, enzymes, antioxidant compounds, pigments etc.). Primary products convert to secondary products chemically or biotechnologically. Secondary products can be for example solvents, lubricants, surfactants, bio-plastics, dyes, cosmetics, pharmaceutical agents, etc.. Finally, residues utilized by energetically producing biogas or pellets and briquettes can form electricity or heat energy [7, 8].

Use of agricultural lands to produce non-food plants (e.g. for the energy or chemical industry) causes social resistance currently. In contrast, the case is different with the above-mentioned brownfields, where classical agricultural output is not feasible due to the quality of soil and the high level of contaminants, such as heavy metals. In this case, plant biorefinery may be a possible method of utilization, since heavy metal tolerant plants have been described [9, 10]. Heavy metal uptake differs between and within plant species. Accumulators concentrate heavy metals in their aerial parts; indicators regulate the uptake and transport of metals to the shoot, thus internal concentration reflects the external levels, at least until toxicity occurs. Excluders can grow on heavy metal contaminated sites, however they maintain the concentration in the shoot at low levels [11].

Consequently, growing plants for biorefinery is a possibility to utilize brownfields beneficially. However, plants, which can tolerate, but do not accumulate the contaminants, have to be chosen. Since the area of the brownfield sites is usually limited, the applied plants have to yield high biomass (e.g. energy crops) or contain a high value material (e.g. medicine herbas), which enable an economically sustainable cultivation and biorefinery.

Sorghum and sunflower can take up heavy metals to their shoot. However, accumulation is limited in plants by phytotoxicity, therefore, metal content is still at safe levels for humans and animals [12]. Moreover, plants that contain high amounts of carbohydrates, such as sorghum or millet, ethanol or lactic acid can be produced [13]. Bioethanol is a valuable industrial raw material, biofuel, solvent [6]. Lactic acid is used in the food, textile, and chemical industries and it is a raw material to produce polylactate, which is a biodegradable plastic [14].

The aim of present paper is to show that biorefinery is a proper technology to profitable utilization of brownfields and sweet sorghum, which is a good plant to produce high-level biomass on heavy metal contaminated site. Furthermore, we presented a pilot-scale system to produce bioethanol from the liquid phase and we investigated the energetically utilization of the solid phase of sorghum.

2. Materials and Methods

2.1 Description of the Experimental Site

A refuse heap with extremely high-level of heavy metal content was gathered at the Mátra Metal Mines (Gyöngyös oroszi, Hungary) due to local ore enrichment processes. Biomass production capacity, heavy metal uptake and potential applicability for chemical industry and energetic utilization of sweet sorghum (Sucrosorgo) were investigated on a trial plot
of 3,000 m², which was established on a moderately heavy metal polluted soil near the Toka stream, in its catchment area. TERRASOL compost of 30 t·ha⁻¹ dose and MAP (mono-ammonium phosphate) of 200 kg·ha⁻¹ dose were applied to satisfy the nutrition demand of plants.

At the beginning of blooming, plant samples were taken from 1 m² areas of the plant standings to establish the biomass production and to investigate the possibility of biorefinery of the biomass.

2.2 Heavy Metal and Soil Parameter Analysis

The plant and soil samples were prepared by aqua regia and Lakanen-Erviö method and the heavy metal content was determined by ICP-OES according to MSZ 21470-50:2006 and MSZ EN 13657:2003 standards.

Other soil parameters, such as pH, ammonium, nitrate, phosphate, were determined by MSZ 21470-2:1981.

2.3 Arrangement of the Pilot System

Based on our previous results and conceptions [15, 16], Elgoscar-2000 Ltd. has developed a pilot-scale biorefinery manufactory in Győngyösoroszi. The design of the arrangements was visualised by CAD program (inventor) [17]. A controller and data collecting system is connected to the manufactory with the following parameters: RS232/485 data collecting net, 9600 baud 6 digital unit, 20 A/D channels (10 bit), 2 impulses-register, saving data per 10 s, 12 MB per day. The test factoring was carried out in three independent series.

2.4 Monitoring of Fermentation

Shoots of the plants were physically crushed and fractioned by a fruit press. 200 L of the liquid phases were incubated in a fermentor at 20 °C for 4 days after inoculation of Saccharomyces cerevisiae to convert the sugar content of plant extracts to ethanol. The liquid phases were not sterilized before the fermentation and the inoculum was grown in DSM-186 medium and incubated at 20 °C for 72 hours. 2,000 mL inoculum was applied in the 200 L volume.

During the fermentation 1 mL liquid phase sample was taken from the fermentor and the daily carbohydrates, organic acids and ethanol content were measured by HPLC. The samples were centrifuged at 13,000 rpm for 20 min and diluted to 20-fold in 0.01 N H₂SO₄ eluent and centrifuged again for 20 min (13,000 rpm). The supernatant was analyzed by GynkoTek HPLC with isocratic elution, on Transgenomic ICSep Coregel 87H3 column and at 30 °C, and the eluent was 0.01 N H₂SO₄ Carbohydrates (sucrose, glucose, fructose), organic acids (acetic acid, lactic acid), and ethanol were detected by refractive index detector and the organic acids and ethanol were detected by UV detector, too. Data were integrated by the Chromeleon software.

2.5 Energetical Utilization of the Biomass

2.5.1 Sample Preparation

After crushing and fractioning, the solid phase of sweet sorghum (Sucrosorgo) was tested for biogas production and analyzed of its combustion characteristics. The plants samples were dried at 105 °C for 2 hours then the dried mass were determined. Dried solid phase for biogas production and wet solid phase for combustion characteristics were investigated.

2.5.2 Biogas Production

In our experiments, the reactor volume was 1,000 mL, which contained 800 mL anaerobe sludge and 20 g dried solid. The reactors were incubated at 37 °C. The produced biogas were trapped and measured for a month. The methane content of the biogas was investigated continuously. Methane content was determined by GC-MS (Gaschromatograph with 5975 MS Detector). Parameters of the measurement were: front inlet: 250 °C; split rate: 1:50; GS-GASPRO (60m × 0.320mm) column; at 40 °C for 6 min, heating to 130 °C by 30 °C/min; at 130 °C for 2.0 min; method:
C1-C2GAS.M.; detecting in AUTO tune mode; carrier gas: He (Linde).

2.5.3 Combustion Experiments

The goals of the measurements include the determination of the combustion characteristics of the sample. The combustion characteristics include measurement of moisture, volatiles, ash, chemical composition and calorific values. During our examinations, we determined the total moisture content of the sample with a cascade drying according to MSZ (Hungarian Standards) 24000-23:1977 standard and determined the ash content according to the MSZ ISO 1171:1993 standard. We carried out the determination of the volatile content according to the regulations of the MSZ 24000-10:1983 standard. According to the MSZ, ISO, DIN, or CEN standards referring to the instrumental determination of carbon, hydrogen, nitrogen and sulfur content, we carried out our measurements with a component analyzer. Following the referring standards, we determined the caloricity/combustion heat. We carried out 3-3 parallel measurements of the sample.

3. Results and Discussion

3.1 Description of the Experimental Site

We measured the heavy metal content of the hoarded refuse at the Mátra Metal Mines (Győngyösoroszi, Hungary), which is the reservoir of contaminants of Toka stream, and its catchment area. The refuse contains high amounts of heavy metals. We found that cadmium, copper, lead, selenium and zinc concentrations are 7-17-fold of the environmental limit value (Table 1). In the experimental area, the heavy metal contents are under the environmental limit value, however, this site is continuously polluted by the Toka stream, which comes from the closed mine area. Heavy metal contents were investigated by not only the aqua regia method, but also Lakanen-Erviov method was applied, because it can characterize better the available metal contents for plants and amount of metals, which can be leached by the stream. In most cases, the heavy metal contents of the refuse approach or pass the limit values (The limit values are regarded to the aqua regia method). According to our results the bioavailable metal content is not high on the experimental site, however this is a brownfield, due to the continuous contamination and other soil features, for example slightly acidic pH (6.16 ± 0.35), low amounts of ammonium (10.90 ± 6.94 mg L⁻¹), nitrate (0.84 ± 0.86 mg L⁻¹), phosphate (0.72 ± 0.30 mg L⁻¹) ions and the history and localization of the site. The low nitrogen and phosphorous contents of the soil made the fertilization necessary for the efficient crop production, therefore we applied the TERRASOL compost and MAP.

Table 1  Heavy metal (HM) content of the experimental site and the refuse heap, which is the reservoir for contamination.

<table>
<thead>
<tr>
<th>HM</th>
<th>Experimental site at the catchment area of Toka stream near the refuse heap</th>
<th>Heavy metal content of the refuse heap</th>
<th>Limit value (mg kg⁻¹)⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heavy metal content (mg·kg⁻¹) (by Lakanen-Erviov method)</td>
<td>Total heavy metal content (mg·kg⁻¹) (by aqua regia method)</td>
<td>S.D.</td>
</tr>
<tr>
<td></td>
<td>S.D.</td>
<td>S.D.</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.17</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cd</td>
<td>0.28</td>
<td>0.19</td>
<td>0.48</td>
</tr>
<tr>
<td>Co</td>
<td>2.44</td>
<td>0.65</td>
<td>17.70</td>
</tr>
<tr>
<td>Cu</td>
<td>18.60</td>
<td>3.08</td>
<td>58.53</td>
</tr>
<tr>
<td>Fe</td>
<td>472.67</td>
<td>320.96</td>
<td>45583.33</td>
</tr>
<tr>
<td>Ni</td>
<td>1.45</td>
<td>0.16</td>
<td>18.87</td>
</tr>
<tr>
<td>Pb</td>
<td>12.07</td>
<td>4.03</td>
<td>59.40</td>
</tr>
<tr>
<td>Se</td>
<td>0.12</td>
<td>0.01</td>
<td>0.78</td>
</tr>
<tr>
<td>Zn</td>
<td>20.13</td>
<td>7.85</td>
<td>179.00</td>
</tr>
</tbody>
</table>

* Source from Ref. [18].
3.2 Biomass Yield and Heavy Metal Uptake of Sweet Sorghum (Sucrosorgo)

We measured the biomass production capacity and heavy metal uptake of sweet sorghum grown on the brownfield site. The plants were not growing uniformly, because of the extremely rainy year of 2010 in Hungary. The regular rainfall retarded both sowing and plant growth. After all, at the beginning of blooming or yield ripening plant samples were taken. We established that the biomass yield was generally 53 ± 3 t ha⁻¹. Based on the normal productivity of the applied sweet sorghum variety (80-100 t ha⁻¹), its estimated productivity would be 60-70 t ha⁻¹ in normal weather conditions. After pressing, about 40% liquid phase formed depending on the wet mass. Based on our observations, the biomass production of this plant can be increased by the improvement of the agro-ecological conditions (water regime, organic matter content, nutrient supply, etc.) of the brownfield sites.

The heavy metal contents of plants grown on the experimental site were compared to plants grown on an unpolluted agricultural site (Karcag, Hungary). The results were referred to the dry mass, which was 24.81 ± 0.04% (23.47 ± 2.45% in case of plants originating from Karcag) in the total plants and 33.95 ± 0.50% in the solid phase. The results show that cadmium, lead and zinc content of plants grown on the brownfield experimental site were high (Table 2), in spite of that the heavy metal content was not higher in the soil than the environmental limit value.

Moreover, we investigated the distribution of heavy metals between solid and liquid phases after pressing (Table 3). Results show that most part of the heavy metals were present in the solid phase, therefore heavy metals may cause problems during combustion and biogas production.

Heavy metal recovery was calculated based on biomass-yields and the measured heavy metal contents, similarly to heavy metal distribution. However, we would like to highlight that approximately 1 kg·ha⁻¹ zinc was recovered in the Sucrosorgo sweet sorghum variety. This result indicates the possibility of utilization of this variety for phytoremediation purposes to maintain the low heavy metal concentration in the soil in spite of the regular contamination by the Toka stream.

3.3 Arrangement of the Pilot System

A pilot-scale biorefinery manufactory was established in Gyöngyösoroszi, Hungary. The system has involved a Bosch Axt 2000 Rapid shredder, an modified Aquapress Garda (80 L, 6 bar), a fermentor (200 L) with an engine to ensure the mixing (0-100 rpm, 1500 W), a heating and cooling cycle with a Hajdu type water heater and a spooler (100 L), and an Agromex
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KZK60 distillatory (60 L, propane-butane gas heater) with a cooling cycle (100 L + 275 L spooler) (Fig. 1). The liquid flow in the system is moved by a Rover 20 CE type peristaltic pump. The CAD design of the planned pilot biorefinery system is shown in the Fig. 2. A controller and data collecting system monitors the following parameters: temperature of the liquid and air phase of the fermentor; the temperature, current consumption and quantity of the circulated water in the heating cycle; temperature of the liquid and the air phase in the distillatory; the temperature, current consumption and quantity of the circulated water in the cooling cycle; and the operating time of the pumps. The temperature of the liquid phase is regulated in the fermentor. It is hold between 16 and 23 °C.

In this system, we could produce ethanol; however, acidic fermentation is started spontaneously after shredding and pressing (Fig. 3). The effectiveness of the pressing was 41.41% ± 0.07.

The controlling system worked appropriately, the temperature of the liquid phase in the fermentor changed between 15-22 °C, and temperature of the distillation was 78-80 °C. However, a mixing engine was connected to the fermentor, it was not operated to maintain of anaerobic conditions for fermentation. The current consumption of the system was 48.7 ± 8.7 kWh (i.e. 175,440 ± 31,323 kJ) in a fermentation cycle (4 day). The produced ethanol, the spontaneously produced lactic and acetic acid and the sugar (sucrose, glucose, fructose) contents were monitored daily.

3.4 Monitoring of the Fermentation

In the pilot-scale biorefinery system, 200 L liquid phase of the sorghum was transferred to the fermentor. The liquid was inoculated by yeast (Saccharomyces cerevisiae) and incubated for 4 days at optimal temperature for growth (15.24-21.62 °C). During the fermentation, carbohydrates, organic acids and ethanol content were monitored daily. 3.4 Monitoring of the Fermentation

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The results show that sucrose and glucose was decreased during the ethanol production (Fig. 3). The sugar content of the liquid phase of the sorghum was low (1.84-3.55 g L⁻¹ sucrose, 4.04-11.94 g L⁻¹ glucose), it was converted to ethanol, in spite of that spontaneous acidic fermentation was observed during the shredding and pressing. The spontaneous acidic fermentation produced 0.36-2.41 g L⁻¹ acetic acid and 1.95-9.91 g L⁻¹ lactic acid, which turned the pH to 4.48-5.83. The acetic and lactic acid content did not change in the 2nd and 3rd (F2, F3) fermentation phases, however it increased in the first (F1). The reason of this phenomenon may be that oxygen was dissolved into the liquid after mixing during the sampling. Based on these results, mixing was omitted in the 2nd and 3rd (F2, F3) fermentation. On this pH and the conditions above 3.36-8.48 g L⁻¹ ethanol was produced. From this material 12.5 L purified ethanol was produced by distillation having 20.00 ± 4.08% ethanol. In a second distillation step, 6 L ethanol was produced with 40% ethanol content.

Consequently, sweet sorghum is an appropriate raw material for ethanol production. However, the shredding and pressing must be further optimized to inhibit the spontaneous acidic fermentation. Probably, cooling and increasing the pH might be appropriate
Fig. 3  Changes of the (a) sucrose, (b) glucose, (c) fructose, (d) ethanol, (e) lactic acid and (f) acetic acid content during the three independent (F1, F2, F3) fermentations.
3.5 Energetic Utilization

The solid phase of sweet sorghum (Sucrosorgo) was tested for biogas production and its combustion characteristics were analyzed. The results were referred to dry mass in case of the biogas production, and wet mass in case of combustion experiments.

3.5.1 Biogas Production

20 g dried solid phases were mixed with 700 mL anaerobic sludge. The produced biogas and methane content were measured for 30 days. Since the most heavy metal was present in the solid phase, we compared the results to solid phase of sweet sorghum (Sucrosorgo) grown on agricultural soil (Karcag). The results show that the added sorghum samples increased the biogas production significantly and the heavy metal content did not influence the produced biogas (Fig. 4). During the biogas production, the methane content reached approximately 40% after a week and about 60% after a month. The methane content of the biogas was equalized (i.e. added sorghum samples does not significant effect on methane production), however, having regard to the higher amount of biogas we could produce approximately 4-fold amount of methane in the same period.

According to our results, the solid phase of sweet sorghum grown on brownfield site is utilisable for biogas production, and the energy obtained from this biogas may supply the energy consumption of the biorefinery system. Since special equipments are necessary for biogas utilization (for example gas engine with specific settings), we also investigated the parameters of combustions of sweet sorghum.

3.5.2 Combustion Experiments

In the solid phase of sweet sorghum, significant energy is available. Therefore, combustion characteristics which include measurement of moisture, volatiles, ash, chemical composition and calorific values (Table 4) were determined to find the critical parameters of this plant (herbaceous, grown on brownfield site) during the combustion.

The results referred to the wet plants. The results show that carbon content is lower, while nitrogen and ash is higher than the same parameters of ligneous plants. Other parameters, like volatile, sulfur, hydrogen and the calorific values were consistent with ligneous plants. The calorific values (combustion heat and calorimetric value) are similar to that of ligneous plants; therefore, this herbaceous plant was as efficiently utilisable for heat (energy) production as ligneous plants [19]. Moreover, 11.7 ± 2.1 kg solid phase of
sorghum is enough to cover the energy consumption of the pilot-scale biorefinery system during an ethanol fermentation cycle and it can be cultured only on $2.2 \pm 0.4 \text{ m}^2$. The critical parameter is high ash content (1-1.2 m/m% in case of woods), therefore a special boiler is needed. However, the ash content can be decreased by producing pellets or briquettes, which compression techniques are reported to change the combustion characteristics of both ligneous and herbaceous plants [20, 21].

4. Conclusions

The present study provided evidence that sweet sorghum is able to adapt to the unfavorable ecological conditions of heavy metal contaminated soils. It could be cultivated effectively on a brownfield site after custom soil improvement procedures. The sweet sorghum grown on brownfield site was successfully integrated to biorefinery in a pilot-scale system. The total biomass was processed, namely the liquid phase to ethanol production and the solid phase to energy production (i.e. biogas production and combustion).

Additionally, we noticed that this sorghum variety (Sucrosorgo) can accumulate high levels of zinc, thus seems suitable for phytoremediation applications, too.

Based on our results sweet sorghum seems to be an applicable plant for the economic utilization of brownfield sites with complex processing by biorefinery.

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