GLOBAL CHANGE BIOLOGY
BIOENERGY

GCB Bioenergy (2017) **9**, 202–214, doi: 10.1111/gcbb.12346

Valorization of Sida (*Sida hermaphrodita*) biomass for multiple energy purposes

NICOLAI DAVID JABLONOWSKI[1], TOBIAS KOLLMANN[1,2], MORITZ NABEL[1], TATJANA DAMM[3], HOLGER KLOSE[3], MICHAEL MÜLLER[4], MARC BLÄSING[4], SÖREN SEEBOLD[4], SIMONE KRAFFT[1], ISABEL KUPERJANS[5], MARKUS DAHMEN[5] and ULRICH SCHURR[1]

[1]*Forschungszentrum Jülich GmbH, Institute of Bio- and Geosciences, IBG-2: Plant Sciences, 52428 Jülich, Germany,* [2]*Project Management Jülich, Renewable Energies – EEN, 52425 Jülich, Germany,* [3]*RWTH Aachen University, Institute of Botany and Molecular Genetics IBMG, Worringerweg 3, 52074 Aachen, Germany,* [4]*Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-2: Microstructure and Properties of Materials, 52428 Jülich, Germany,* [5]*FH Aachen, Aachen University of Applied Sciences, Institut NOWUM-Energy, Heinrich-Mussmann-Str. 1, 52428 Jülich, Germany*

Abstract

The performance and biomass yield of the perennial energy plant *Sida hermaphrodita* (hereafter referred to as Sida) as a feedstock for biogas and solid fuel was evaluated throughout one entire growing period at agricultural field conditions. A Sida plant development code was established to allow comparison of the plant growth stages and biomass composition. Four scenarios were evaluated to determine the use of Sida biomass with regard to plant development and harvest time: (i) one harvest for solid fuel only; (ii) one harvest for biogas production only; (iii) one harvest for biogas production, followed by a harvest of the regrown biomass for solid fuel; and (iv) two consecutive harvests for biogas production. To determine Sida's value as a feedstock for combustion, we assessed the caloric value, the ash quality, and melting point with regard to DIN EN ISO norms. The results showed highest total dry biomass yields of max. 25 t ha^{-1}, whereas the highest dry matter of 70% to 80% was obtained at the end of the growing period. Scenario (i) clearly indicated the highest energy recovery, accounting for 439 288 MJ ha^{-1}; the energy recovery of the four scenarios from highest to lowest followed this order: (i) ≫ (iii) ≫ (iv) > (ii). Analysis of the Sida ashes showed a high melting point of >1500 °C, associated with a net calorific value of 16.5–17.2 MJ kg^{-1}. All prerequisites for DIN EN ISO norms were achieved, indicating Sida's advantage as a solid energy carrier without any post-treatment after harvesting. Cell wall analysis of the stems showed a constant lignin content after sampling week 16 (July), whereas cellulose had already reached a plateau in sampling week 4 (April). The results highlight Sida as a promising woody, perennial plant, providing biomass for flexible and multipurpose energy applications.

Keywords: biogas feedstock, biogenic energy source, biomass, flexible biomass application, lignin source, perennial energy crop, plant development, Sida hermaphrodita, solid fuel

Received 19 November 2015; revised version received 21 January 2016 and accepted 2 February 2016

Introduction

In terms of a growing bio-based economy, a sustainable plant biomass supply is becoming a major challenge to meeting the demands. The increased share of bio-based energy carriers is challenging both society and energy supply systems. In Germany, only the share of renewable energy of total electricity production reached 25.8% in 2014 and shall further increase in the future to 40–45% until 2025 (Bundesministerium für Wirtschaft und Energie, 2015). Because biomass can be stored and is therefore ready for use on demand as a reliable supply source, energy production from biomass plays an important role in the variety of renewable energy sources, such as water, wind, and solar power (Carroll & Somerville, 2009; Graham-Rowe, 2011).

To cover the demand of plant biomass, biomass production should not compete with crop production traditionally used for food and feed (Graham-Rowe, 2011; Voigt *et al.*, 2012). The food vs. fuel controversy must be avoided by directly searching for nonfood plant species and by indirectly avoiding the use of highly valuable crop land to obviate land-use conflicts (Schröder *et al.*, 2008). Therefore, plants characterized by high-yield, low-nutrient demand, and a valuable biological composition for a variety of bioeconomic applications should be emphasized. The perennial nature of such plants could decrease the energy input for its produc-

Correspondence: Dr Nicolai David Jablonowski, tel. +49-2461-61-8682, fax +49-2461-61-2492, e-mails: n.d.jablonowski@fz-juelich.de; n.d.jablonowski@daad-alumni.de

tion because annual field preparation and plant establishment becomes unnecessary. Additionally, such a plant biomass production system may even exhibit additional benefits for ecosystem services and soil protection, following the idea of a 'low input–high output system' in terms of energy investments and additional benefits (Blanco-Canqui, 2010). However, perennial cropping systems reduce the ability of farmers to react to sudden changes on the market. To tackle these relevant aspects of biomass production for energy purposes, we investigated the perennial plant *Sida hermaphrodita* (L.) Rusby (hereafter referred to as Sida), also known as Virginia mallow or Virginia fanpetals. From 1930 until 2000, some research, mostly published in Russian or Polish language, was conducted on this plant with regard to its propagation and establishment (Spooner *et al*., 1985). The native North American species Sida was introduced to Poland during the 1950s as a fodder and fiber source, but it developed further as a promising energy crop (Spooner *et al*., 1985; Borkowska *et al*., 2009). However, in the recent past, Sida attracted attention again as a promising plant for bioenergy production (Borkowska & Wardzinska, 2003; Borkowska & Molas, 2012; Barbosa *et al*., 2014; Nabel *et al*., 2014). Along with *Miscanthus*, another perennial, high-yield energy plant, Sida recently attracted attention due to its wood-like, high-yield biomass (Borkowska & Molas, 2012, 2013). Besides its high biomass yield, Sida is also highly attractive for pollinators due to its long flowering period and therefore has high ecosystem service values. Due to the numerous shoots per plant, the biomass yield of Sida is higher compared to that of currently used energy plants like corn (Slepetys *et al*., 2012). In addition to soil fertility, precipitation, and climate conditions, the organic dry matter yield depends on the age of the plant and the time of harvest and generally varies from 9.6 to 19.7 t ha^{-1} (Slepetys *et al*., 2012; Borkowska & Molas, 2013).

While Sida is commonly used as a solid fuel for combustion, the first biogas batch tests with Sida showed a potential of 435 Ndm^3 kg^{-1} organic dry matter (oDM) from silage made from a biomass harvest in July, suggesting that Sida is also useful as a substrate for biogas production (Oleszek *et al*., 2013). Methane obtained from biogas production plays a major role as an energy carrier from biogenic resources. To date, approximately 7800–8000 operating biogas facilities in Germany are producing 27.6–29.0 billion MWh, while a total of 49.1 TWh were produced from biomasses, of which biogas and solid fuels contributed with 59.1% and 24.2%, respectively (Deutscher Bauernverband, 2015; FNR, 2015). Anaerobic batch tests on Sida biomass revealed methane concentrations of 280 to 293 Ndm^3 kg^{-1} oDM (Hartmann & Haller, 2014). However, the determined biogas potential and methane yield of Sida biomass are lower compared with major energy crops like corn (Schattenhauer & Weiland, 2006), even though this varies with the time of harvest. First attempts with chemical pretreatment have been carried out to increase the biological availability and to improve the resulting biogas yield of Sida as a biogas feedstock (Michalska *et al*., 2012).

To date, Sida has not yet been evaluated as a feedstock for flexible, demand-driven energy applications by analyzing its cell wall composition and energy yield with regard to the plant development stage and time of harvest. A flexible use of the Sida biomass would allow operators to react to market changes using the biomass either as feedstock for solid fuel and biogas production or for industrial applications.

In this study, we evaluated the overall performance, biomass, and energy yield of *Sida hermaphrodita* (L.) Rusby at weekly harvest intervals throughout an entire growing period at agricultural field conditions in the second year after field establishment. The aim of this study was to develop a plant growth and development code allowing a general determination of the best Sida harvesting time: (i) with regard to the maximum biomass yield depending on the plant development stage; (ii) to determine the energy value in terms of biogas production and solid fuel energy content with regard to its verification in accordance with the German industry standard DIN EN ISO 17225-7:2014-09 for solid biogenic fuels (DIN-EN-ISO-17225-7, 2014); and (iii) to obtain a biomass comprising the most suitable cell wall composition enabling specific utilization and upscaling for technical applications. Additionally, we determined that the ash content, composition, and melting point of Sida were important parameters when it is used as a solid fuel in accordance with the aforementioned DIN norm.

To determine the best energy use of Sida biomass and identify the highest energy output, four application scenarios were evaluated in terms of solid fuel and biogas applications. The four tested scenarios were as follows: (i) one harvest for solid fuel only; (ii) one harvest for biogas production only; (iii) one harvest for biogas production, followed by a subsequent harvest of the regrown biomass for solid fuel; and (iv) two consecutive harvests for biogas production.

Material and methods

Experimental site and setup

The experimental site was located in Mersch, Germany (100 m o. NN, 6°22′34 east and 50°57′50 north using ETRS89). The site was exposed to an annual mean temperature in 2014 of 11.5 °C, with a minimum temperature of −5.1 °C, a maximum temperature of 34.7 °C, and an annual precipitation of 801 mm

during the time of the experiment. The soil was Orthic Luvisol consisting of 5.6% sand, 79.0% silt, 15.4% clay, with pH 6.2 ($CaCl_2$), containing 2.4% C_{org}, 32 mg kg^{-1} P_2O_5, 18 mg kg^{-1} K_2O, and 9 mg kg^{-1} Mg. The experiment was established in May 2013 using seedlings of the perennial mallow plant *Sida hermaphrodita* (L.) Rusby in the BBCH-Sida plant development stage 12–13 (Table S1). Seedlings were precultivated in the greenhouse at controlled conditions from March until the beginning of the field experiment in May in 2013, using compostable pots made of peat (pot type 30023092, 8 × 8 cm square; Jiffy®, Moerdijk, The Netherlands). A total of 436 individual seedlings were planted in the arable field soil in a plant distance of 0.5 m and a row distance of 0.75 m, in a total area of 165 m^2, equaling 2.7 plants m^{-2}. The herbicide glyphosate (RoundUp, 4 L ha^{-1}) was applied prior planting and in-between the plants and rows during the plant establishment phase to control weed growth. No fertilizers were applied prior and throughout the entire experiment.

Determination of plant development stages: BBCH-Sida code

Plant physiological traits of *Sida* were monitored throughout the experiment. To allow a future estimation of desired harvest times assuming different biomass application scenarios, we analyzed and described the plant development stages for Sida in a modified BBCH code. Our numeric BBCH-Sida code was developed following previous BBCH codes for other plant species created by Hack *et al.* (Hack *et al.*, 1992). The BBCH-Sida code is provided in full length in the Supporting Information of this manuscript (Table S1). The first given number of the numeric BBCH-Sida code 0 (i.e., seed germination) to 9 (aging process, senescence) describes the macrostages of the plant. The second number 0–9 describes the microstages within the macrostages, for example, number of branches. For the assessment of a Sida stand, it must be considered that at least 50% of the plants display the respective development stage. Macrostages, such as leaf or side branch development, may emerge simultaneously. In this case, only the higher development stage is being considered. Our numeric BBCH-Sida code was developed with regard to its application on both the agricultural (stand/plant population) and detailed laboratory level (single plants). Emphasis is attributed to the timely application of pesticides particularly during the establishment phase and to potential harvest during the growing period.

Biomass harvest and preparation

The evaluation of biomass yield started in the second year (2014) after establishment when the mean plant height reached BBCH-Sida development stage BBCH 17 (approximately 38 cm height). To determine the total yield development, biomass of five individual plants was harvested weekly, following a totally randomized design, by cutting the stems approximately 7 cm above ground. All replicate plants were separated into stems and leaves including side branches. All leaves and stems for each individual plant were shredded (<2 cm, Viking AE 1180 E) and dried at 85 °C until weight constant. For further handling, the dried Sida biomass was milled (<1 mm, Retsch SM 200) and homogenized. Subsamples were additionally milled to powder using a Retsch MM 400 for subsequent elemental and calorific analysis. To determine the optimal biomass use for energy purposes, the following harvest scenarios were applied: (i) Plants were grown throughout the vegetation period and were harvested at BBCH-Sida stage 98 to determine its calorific value when used as a solid fuel only (sample F1, Table 1). (ii) Plants were harvested only once at BBCH-Sida stage 91 to determine its biogas potential only at a late plant development stage (sample B2, Table 1). (iii) To determine the biogas potential of green Sida biomass, randomly selected plants were firstly harvested at BBCH-Sida development stage BBCH 55 and a dry matter content of 16.5% (sample B1.1, Table 1). The freshly shredded biomass was compressed in 60 L PE bins for subsequent ensilaging for 12 weeks. Subsequently, the regrown biomass was harvested as dried biomass at the end of the entire vegetation period at BBCH-Sida 98 to evaluate its calorific value as a solid fuel (sample F2, Table 1). (iv) To determine the maximum biogas potential of green Sida biomass, plants were firstly processed in accordance with scenario (iii) (sample B1.2). The regrown biomass of the previously harvested plants was harvested again in BBCH-Sida development stage 71, exhibiting a dry matter content of 28.5%, to evaluate the biogas potential of the regrown fresh plant material (sample B1.2, Table 1).

Biomass harvests for solid fuel application were aimed at obtaining high dry matter content. Harvest times for scenario (iii) and (iv) were chosen to allow a potential supply of alternative biogas feedstock before fresh biomass of other feedstock sources (e.g., maize silage) would be available. Harvest in October for scenario (ii) and (iv) was chosen to obtain a high biomass yield and to avoid late shooting and frost damage of the plants during winter. The two repeated harvests in scenario (iii) and (iv) were meant to evaluate the added energy value of Sida biomass as a feedstock for additional solid fuel and biogas, respectively.

The described harvest scenarios are summarized in Table 1. In every scenario, a total of 10 plants were randomly harvested as biological replicates.

Evaluation of calorific values, ash content, composition, and behavior

Subsamples of the pulverized biomass were compressed into pellets and analyzed for their higher heating value in five biological replicates employing a Parr calorimeter Type 6200, in accordance with DIN 51900-3:2005-01 (DIN-51900-3, 2003). Simultaneously, the ash content, composition, and behavior were analyzed using subsamples of the milled biomass in triplicates. For the investigation on ash melting behavior, the samples were oxidized at 550 °C in platinum crucibles under constant air flow in a muffle furnace for 24 h at constant temperature. The heating rate of the samples was 5 K min^{-1}. The samples were weighed after ashing and ground in a mortar to ensure the homogeneity of the ash samples. X-ray powder diffraction (XRD) was used to identify crystalline compounds of the ashes using a Siemens D500 powder diffractometer. The

Table 1 Overview of the four different Sida harvest and biomass evaluation scenarios to determine the optimum energy usage of Sida biomass

Scenario	1. Harvest: purpose/sample #	BBCH-Sida development stage/Date of sampling	Dry matter content	2. Harvest: purpose/sample #	BBCH-Sida development stage/Date of sampling	Dry matter content
(i)	Solid fuel/F1	BBCH 98/15.01.2015	75.9%	–	–	–
(ii)	Biogas/B2	BBCH 91/15.10.2014	36.1%	–	–	–
(iii)	Biogas/B1.1	BBCH 55/12.06.2014	16.5%	Solid fuel/F2	BBCH 98/15.01.2015	76.3%
(iv)	Biogas/B1.1	BBCH 55/12.06.2014	16.5%	Biogas/B1.2	BBCH 71/15.10.2014	28.5%

Table 2 Comparison of Sida biomasses silages prepared for biogas tests

	B1.1	B1.2	B2
Time of harvesting	12.06.2014	15.10.2014	15.10.2014
Type of ensilage	In barrel	In barrel	In barrel
Time of ensilage	12 weeks	12 weeks	12 weeks
Dry matter after ensilage	20.2%	26.0%	30.8%
Organic dry matter after ensilage	18.0%	23.6%	28.1%

fusibility of the ashes was determined by hot-stage microscopy according to DIN 51730:2007-09 (DIN-51730, 1998).

The higher heating value of the Sida biomass was determined employing the above-mentioned calorimeter. Because the Sida biomass exhibited a residual moisture content, the net calorific value (i.e., lower heating value) was determined mathematically using the preceding equation (Equation 1: Equation for the calculation of the higher heating value of moist biomass).

$$q_{FM} = q_{TS} * \left(\frac{\mathrm{DM}}{100}\right) - 0.02443 * (1 - \mathrm{DM})$$

The higher heating value (q_{TS}) is given in MJ kg^{-1}, the dry matter (DM) in %, and the value 0.02443 is the enthalpy of water vaporization at constant pressure and a temperature of 25 °C, given in MJ kg^{-1}. At harvest, the DM content of the Sida biomass for the solid fuel scenario (samples F1 and F2) accounted for 76%; however, from the literature, DM values of 85–89% were reported (Stolarski *et al.*, 2013). Therefore, the corrected heating value was calculated with a dry matter content of 88% and a residual moisture of 12%. For the overall calculation of the energy yield per ha, the resulting heating value was multiplied with a corrected fresh biomass yield, that is, the obtained dry matter yield plus 12% residual moisture. The determination of the dry and organic dry matter was performed using a furnace (Heratherm, Thermo Scientific, USA) and a muffle furnace (N100/14, Nabertherm, Germany), according to DIN EN 12880:2001 (DIN-EN-12880, 2001).

Elemental analysis

Prior elemental analysis all Sida biomass samples were oven dried at 85 °C and subsequently milled (<1 mm, Retsch SM 200) and homogenized. Subsamples were additionally powdered employing a ball mill (Retsch MM400). Al, Ca, Cr, Fe, K, Mg, P, S, and Si were measured and quantified using ICP-OES. As, Cd, Cu, Hg, and Pb were determined using ICP-MS due to a lower detection limit. To do so, subsamples of 100 mg were diluted and decomposed in a mixture of 3 mL HNO_3 and 2 mL H_2O_2 in a microwave. Subsequently, 1 mL of HF was added. The samples were adjusted to a volume of 14 mL and were measured in a dilution of 1 : 10. For C, H, N, and O determination, triplicate samples of approximately 2.5 and 2 mg, respectively, were oxidized employing an element analyzer (Vario EL Cube, Elementar). The relative standard deviations for the abovementioned methods were for elemental contents of >1 ± 3%, and for elemental contents of <0.1 ± 20%. The total Cl content in the Sida biomass was analyzed in accordance with DIN EN 15408 (DIN-EN-15408, 2011).

Evaluation of biogas potential

The calculated biogas production of Sida was measured in eudiometer batch test systems derived from the specification of the German DIN 38 414-8:2006-03 (DIN-38414-8, 1985). Silage of Sida biomass from scenario (ii), (iii), and (iv) (harvested in June and October) was prepared from shredded and homogenously mixed Sida biomass that was highly compressed into 60-L PE bins. As inoculum, active digestate originating from a commercially operating biogas plant fed with maize silage was used. Prior analysis, the dry matter of the digestate and the Sida silage was determined at 105 °C. The inoculum and the Sida silage was homogeneously mixed in 1 L Shott Duran glass bottles, and the tests were carried out at mesophilic conditions at 37 °C in the dark using a temperature-controlled water bath. The gas volume was measured daily, and the ambient air temperature and air pressure were monitored for calculation to norm conditions. The test ended when the relative gas yield after 24 h was below 1% of the total produced gas volume. Each Sida biomass silage was tested in four replicates. The detailed information about the different silages is shown in Table 2.

Analysis of Sida lignocellulosic residues

Extraction and analysis procedures were modified according to Foster *et al.* (Foster *et al.*, 2010a). We further ground 70–73 mg dried homogenized Sida leaf, side branch, and stem material to a fine powder using a M 400 mill (Retsch, Haan, Germany) with a frequency of 30 s^{-1} for 2 min (leafy material) or 10 min (stem material). Plant cell wall residues were isolated by washing once with 70% (v/v) ethanol solution and four times with

chloroform/methanol (1 : 1; v/v) solution and once with 1 mL acetone solution collecting the pellet every time at 20 000 g (Foster *et al.*, 2010a). The pellet was dried under air flow at room temperature. Starch was removed by enzymatic digestion with α-amylase (3 U) and amyloglucosidase (1.5 U) (Megazyme, Bray, Ireland). The remaining de-starched, alcohol-insoluble residues (d-AIR) were washed four times with water, once with acetone, and then subsequently dried. All analyses were performed with approximately 2 mg d-AIR. The matrix polysaccharide composition was determined by extraction and hydrolysis with 2 M trifluoroacetic acid (Foster *et al.*, 2010a). We collected 100 μL of TFA, which was evaporated under air flow and the remaining pellet was dissolved in water. Single sugar analysis was performed according to Voiniciuc *et al.* (Voiniciuc *et al.*, 2015) using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). For the separation of monosaccharides, a CarboPac PA20 column was used with a flow rate of 0.5 mL min^{-1} and was equilibrated with 2 mM NaOH for 10 min before sample injection. Neutral sugars were separated with 2 mM NaOH over a time course of 18 min. Afterward, 550 mM NaOH was used for 10 min to separate uronic acids. The column was rinsed finally with 800 mM NaOH for 10 min. Monosaccharide amounts were normalized to an internal standard and quantified using standard calibration curves of the different monosaccharides.

The crystalline cellulose content was determined after hydrolyzing and removing the noncrystalline cellulose with acetic and nitric acid (Updegraff, 1969). The remaining crystalline cellulose residues were hydrolyzed with 72% (w/v) sulfuric acid. Carbohydrate content was determined using anthrone assay (Scott & Melvin, 1953).

Lignin content was determined according to Foster *et al.* (Foster *et al.*, 2010b) using the acetyl bromide spectrophotometric method. Different amounts (0.1–0.7 mg) of Kraft-Lignin (Sigma-Aldrich, Seelze, Germany) were used as a standard.

Results

Biomass productivity

The evaluation of the plant performance and biomass yield was conducted in the second year after the establishment of the field trail. Because the biomass yield of a perennial energy plant such as Sida is generally relatively low in the first year, the second year after plant establishment was chosen to allow the development of the BBCH-Sida code and to obtain reliable biomass yield estimations.

The established BBCH-Sida code allowed a detailed characterization of the respective plant development stage at each weekly harvest and enables future comparison of Sida plants irrespective of the climate or the geographic conditions of the experiment (Table S1). The analysis of the Sida cell wall composition at each harvest allows a further, general estimation of the plant BBCH-Sida development stages and the associated plant biomass characteristics. This enables a detailed, demand-driven application of the biomass at the ideal plant development stage and application purpose.

Sida plants started to regrow in late March 2014 of the second year and increased rapidly in biomass yield, accounting for a maximum of 25 t ha^{-1} dry matter total biomass equivalents for both stems and leaves in sampling week 22 at a BBCH-Sida development stage 71 (Fig. 1). At peak biomass production, the share accounted for approximately 15 t ha^{-1} of stem biomass only (Fig. 1). The subsequent decrease of dry matter biomass yield is attributed to the loss of the plant leaves, resulting in a final dry biomass yield of 15 t ha^{-1} of dried woody stems at the end of the experiment (Fig. 1). In return, the dry matter content increased continuously throughout the growing period (Fig. 2). The highest dry matter content was reached at the termination of the vegetation period and at the harvesting of the dead standing dried biomass in January 2015, accounting for more than 70% dry matter content. The increase of the dry matter content is associated with a loss of leaves and a relative increase of lignin and cellulose in the side branches (Fig. 4). Until the termination of the experiment, the dry matter content increased to 90% until March 2015 (data not shown).

Calorific evaluation and ash characterization

The higher heating value of the Sida biomass used as a solid fuel was equally high for both samples, irrespective of a single or double biomass harvest (sample F1 vs. F2), accounting for approximately 19.5 MJ kg^{-1} (Table 3). However, due to the much higher biomass yield after a single biomass harvest, sample F1 resulted in a 3.6 higher total energy yield compared with the sample F2 (Table 3).

To determine whether Sida biomass meets the prerequisites of a solid fuel in accordance with DIN EN ISO 17225-7:2014-09, we analyzed the heating and calorific value, water and ash content, and the content of N, S, and Cl, among other elements (DIN-EN-ISO-17225-7, 2014). Table 4 shows the elemental analysis from Sida biomass, both harvested in January 2015 at a BBCH-Sida development stage 98.

The crystalline compounds in the two resulting ashes of both samples (F1 and F2) identified by XRD are given in Table 5. The variance of the measurement is 10% (relative). The ash composition of the two Sida samples is very similar, and both are strongly enriched with alkaline earth metal and alkali metal compounds. The main phases are calcium carbonate, fairchildite, and calcium hydroxyapatite, which together count for 87% to 88% of the weight of the ash. Earth alkali silicates and oxides were found only in minor amounts. Sulfur and chlorine compounds have not been found because of the low sulfur and chlorine content of the raw material (Table 4).

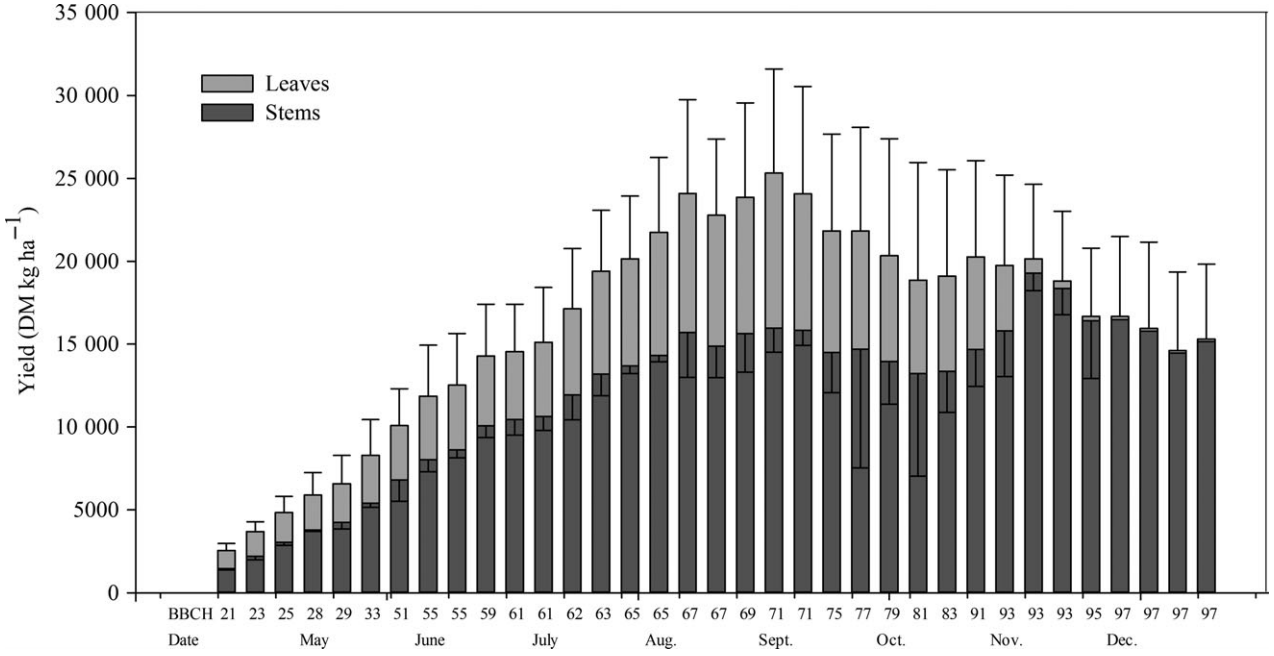


Fig. 1 Share of biomass development (dry mass basis) of stems and leaves over the entire growing period; values are presented in a 5th order moving average; bars indicate the standard error of $n = 5$ biological replicates.

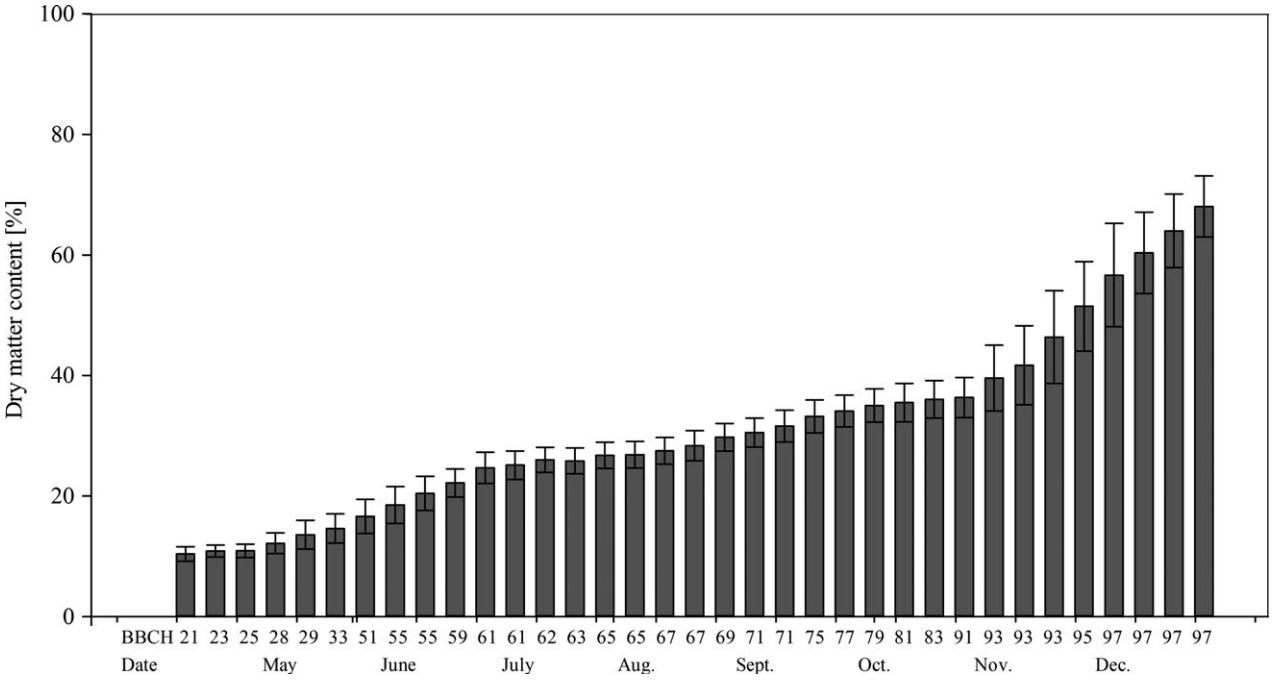


Fig. 2 Development of the total dry matter content in the Sida biomass throughout the entire growing period; values are presented in a 5th order moving average; bars indicate the standard error of $n = 5$ biological replicates.

Biogas production

The parameters of Sida after ensiling showed an increased organic dry matter (oDM) and dry matter content over time. Sample B2, the biomass resulting from a single harvest in October at BBCH-Sida development stage 98, showed the highest dry matter and organic dry matter content, accounting for 30.8% and 28.1%, respectively (Table 2).

Table 3 Calculated values for the energy yield of Sida biomass used as solid fuel

Parameter	One harvest: sample F1	Second harvest: sample F2	Unit
Corrected fresh biomass (FM_c)	26.43	7.11	t ha^{-1}
Corrected dry matter content (DM_c)	88	88	%
Higher heating value	19.21 ± 0.18	19.61 ± 0.27	MJ kg^{-1}
	5.34 ± 0.05	5.45 ± 0.08	kWh kg^{-1}
Net calorific value (q_{FM})	16.62 ± 0.16	16.96 ± 0.24	MJ kg^{-1}
	4.70 ± 0.04	4.79 ± 0.07	kWh kg^{-1}
Energy yield (EE_{ha})			
Total Higher heating value ha^{-1} (q_{TSha})	446 794 ± 4186	122 696 ± 1689	MJ ha^{-1}
Total Net calorific value ha^{-1} (q_{FMha})	439 266 ± 4229	120 586 ± 1706	MJ ha^{-1}

Table 4 Overview of the DIN EN ISO requirements of non-wood biomasses used for energy purposes as solid fuels. Elemental composition of Sida biomass harvested for solid fuel purposes in January at BBCH-Sida development stage 98. The relative standard deviations for all elements were for elemental contents of >1% ±3% and for elemental contents of <0.1% ±20%. The total Cl content in the Sida biomass was analyzed in accordance with DIN EN 15408 (DIN-EN-15408, 2011)

Characteristics	Unit	DIN EN ISO 17225-7: 2014-09	Sida-biomass samples F1	F2
Water content	m-%	12 ≤ 12	12	
Ash content	m-%	6.0 ≤ 6	2.99	2.69
Gross density	g cm^{-3}	0.9 ≥ 0.9		
Net Calorific	MJ kg^{-1}	14.5 ≥ 14.5	16.62	16.96
value	kWh kg^{-1}	4.0 ≥ 4.0	4.62	4.71
Nitrogen, N	m-%	1.5 ≤ 1.5	<0.26	<0.26
Sulfur, S	m-%	0.20 ≤ 0.20	0.028	0.024
Chlorine, Cl	m-%	0.10 ≤ 0.10	0.030	0.053
Arsen, As	mg kg^{-1}	≤1	<0.05	<0.05
Cadmium, Cd	mg kg^{-1}	≤0.5	0.44	0.38
Chrome, Cr	mg kg^{-1}	≤50	<50	<50
Copper, Cu	mg kg^{-1}	≤20	2.25	2.09
Lead, Pb	mg kg^{-1}	≤10	0.34	0.28
Mercury, Hg	mg kg^{-1}	≤0.1	<0.1	<0.1
Nickel, Ni	mg kg^{-1}	≤10	2.51	1.43
Zinc, Zn	mg kg^{-1}	≤100	<50	<50

The batch test of the biomass resulting from the three harvests of Sida showed different maximum biogas production rates and the time needed (kinetics) to reach the given maxima (Fig. 3). The first biomass harvested in June at BBCH-Sida development stage 55 (sample B1.1) reached an average specific biogas maximum of 420 L kg^{-1} oDM. The second harvested biomass (sample B1.2) and the biomass of the single harvest of B2, both collected in October at BBCH-Sida stage 91, yielded a similar specific maximum of 260 L biogas kg^{-1} oDM. Changes in the kinetic of the biogas production of the three tested samples can be observed from the fourth day (Fig. 3).

Table 5 Composition of the ash in weight-% obtained after an oxidation of the Sida biomass at 550 °C

Compound	Sample F1	Sample F2
$CaCO_3$	49	55
$K_2Ca(CO_3)_2$	21	17
$Ca_{10}(PO_4)_6(OH)_2$	17	16
MgO	4	7
$CaMgSi_2O_6$	4	2
SiO_2	2	2
$Ca(OH)_2$	2	2
CaO	1	1

The data in Table 6 show much higher organic dry matter per hectare in sample B2 collected solely in October (BBCH-Sida 91), compared with samples B1.1 and B1.2, which represents two harvests from the same plants at different times and plant development stages (June and October, BBCH-Sida 55 and BBCH-Sida 77). The biggest specific biogas yield was found for sample B1.1. The given methane concentration was calculated in accordance with literature values based on other plant biomasses using a mean value for calculation of 53.5%.

Energy yield evaluation

Allowing a comparison of the total obtained energy values for the Sida biomasses for both biogas and solid fuel feedstock scenarios, we calculated the energy yields into fuel oil equivalents per ha, assuming 36 MJ per L fuel oil (Table 7). Scenario (i), solid fuel obtained from a single harvest of the dried biomass at termination of the plant growing period (harvest in January), yielded by far the highest energy, accounting for 440 GJ, equaling 12 202 L of fuel oil. The energy yield of scenario (iii) – the first biomass harvest used for biogas production, and a subsequent second harvest of the biomass used for solid fuel – accounted for approximately 212 GJ. Scenario (iv) yielded 135 GJ when Sida biomass was harvested two consecutive times to be used as biogas feedstock, whereas scenario (ii), the one late harvest for

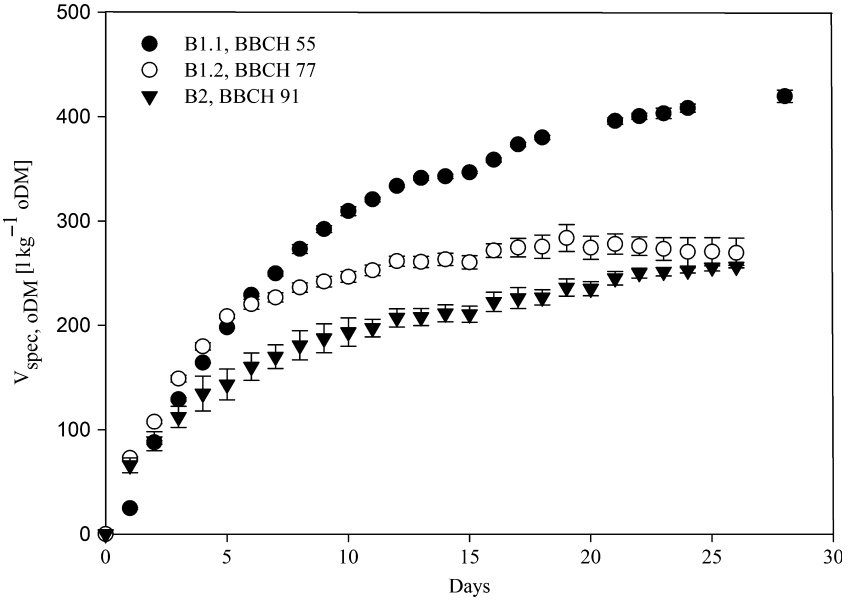


Fig. 3 Specific norm biogas yields from batch tests using biomass silage originating from different harvest dates and Sida plant development stages. B1.1 is biomass from a first harvest at BBCH-Sida development stage 55 (June); B1.2 is biomass from a second harvest of B1.1 plants at BBCH-Sida development stage 77 (October); B2 is biomass from a single harvest at BBCH-Sida development stage 91 (October).

Table 6 Characteristics of the three Sida biomasses harvested at different growth stages and times tested as a feedstock for biogas production used as a silage; EE is energy yield per hectare; oDM is organic dry matter

Parameter	B1.1	B1.2	B2
Organic dry matter (t ha^{-1})	12.5 ± 0.2	9.4 ± 0.2	19.0 ± 0.4
Ensilage loss (t ha^{-1})	1.1 ± 0.4	0.9 ± 0.3	1.7 ± 0.6
Methane content (%)	53.5 ± 1.5	53.5 ± 1.5	53.5 ± 1.5
Biogas yield (m^3_N t^{-1} oDM)	419.5 ± 26.6	269.3 ± 14.3	256.3 ± 1.3
CH_4 (m^3_N t^{-1} oDM)	204.2 ± 16.3	131.1 ± 9.5	124.8 ± 6.2
CH_4 (m^3_N ha^{-1})	2542.7 ± 202.7	1235.0 ± 89.4	2367.1 ± 117.5
EE (MJ ha^{-1})	91537.2 ± 7292.2	44460.0 ± 3218.4	85215.6 ± 4230.0

Table 7 Total energy yield from the four studied Sida biomass energy use scenarios; n = 5 biological replicates, calculated per ha

Scenario	(i)	(ii)	(iii)	(iv)
	1. Harvest solid fuel F1	1. Harvest biogas B2	1. Harvest biogas B1.1	1. Harvest biogas B1.1
EE_{ha} (MJ)	–	–	91 022 ± 7292	91 022 ± 7292
	–	–	2. Harvest solid fuel F2	2. Harvest biogas B1.2
EE_{ha} (MJ)	439 288 ± 4229	85 215 ± 4230	120 760 ± 1706	44 460 ± 3218
Total (MJ ha^{-1})	439 288 ± 4229	85 215 ± 4230	211 782 ± 8998	135 482 ± 10510
Total (l_{oil} ha^{-1})	12202.4 ± 117.5	2367.1 ± 117.5	5882.8 ± 249.9	3763.4 ± 291.9

biogas only, yielded the comparably lowest energy yield of 85 GJ.

Lignocellulose analysis

To characterize Sida lignocellulose, we monitored the crystalline cellulose content, TFA-soluble matrix polysaccharides (MPS), and AcBr soluble lignin (ABSL) during the entire growing period (Foster *et al*., 2010b). Two different tissues of the plants, that is, main stem and leaves including side branches, were analyzed. ABSL in stem tissue rose from 8% to an almost constant level of 17% from week 20 at BBCH-Sida development stage 67 onwards. The crystalline cellulose content rose

from 32% to 50% of d-AIR from the second to the eighth week, that is, BBCH-Sida development stage 17–33, respectively, and remained constant. The amount of TFA-soluble MPS varied between 12% and 20% of d-AIR within the analyzed time period. In the leaf fraction, ABSL was constant at approximately 5% until week 16, that is, BBCH-Sida 63, and was elevated subsequently up to 15% in week 32, equaling BBCH-Sida 93. Crystalline cellulose varied between 17% and 25% within the first 16 weeks and rose afterward up to 42% in week 32, describing the BBCH-Sida development stages 20–63, and 93, respectively. TFA-soluble MPS was low in weeks 2 and 4 (8% to 10%, BBCH-Sida 17 and 23) and remained constant between 17% and 20% until week 32 (BBCH-Sida 93).

Discussion

Biomass production

In our study, we evaluated the biomass growth and development of Sida throughout an entire growing period at real agricultural field conditions. Even though Borkowska & Molas (2013) reported that Sida biomass yield significantly increases in the first 4 years after plantation establishment, our values accounted for approximately 20 t ha^{-1} biomass dry weight when harvested in November at a BBCH-Sida development stage 93. Already 1 year after the plants' establishment, this value even exceeded the reported values from earlier studies by a factor of 1.5–1.6 when the plants were harvested in November as given in the referenced studies (Borkowska & Molas, 2012, Borkowska & Molas, 2013). This could be explained by the favorable field environment and conditions, but it clearly shows the high possible biomass yields of Sida even in the second year after plant establishment when grown at beneficial conditions. However, when used as a solid fuel, a high dry matter content is preferred to increase the energy yield of the biomass and to avoid costly drying processes prior to storage (Borkowska & Molas, 2013). Therefore, we recommend a biomass harvest of the dried Sida stems only in early spring, prior to the regrowth of the plants, because the dried stem material is free of leaves (Borkowska & Molas, 2013) and possesses the highest content of lignin and cellulose, as described below.

The high standard error in the biomass yield throughout the experimental growing period is attributed to the high variation in the phenotype of the Sida plants because this plant is a wild type and varies strongly in its individual biomass yield. An attempt to breed the plants may result in a more homogeneous plant growth and overall appearance with similar biomass yields. Furthermore, considering Sida as a promising lignocellulosic biomass plant for energy applications and molecular breeding activities may improve future applications as a second generation bioenergy crop (Allwright & Taylor, 2015).

Published data on Sida have not sufficiently considered the time of harvest and the respective plant development stage, which makes detailed comparison between the data rather vague. The established BBCH-Sida development code, given in detail in the Supporting Information (Table S1), allows an estimation of the biomass composition irrespective of the location and environmental influences. This will allow future comparisons between the harvested Sida biomasses and their target-oriented application as a feedstock for energy or other industrial applications, for example, fibers for the paper industry or raw material for chemical applications (Bogusz *et al.*, 2015; Grande *et al.*, 2015).

Cell wall composition

Sida lignocellulose was monitored over the whole growth period by determining a set of standard parameters, which enabled a clear discrimination of primary growing tissue (primary cell walls) and adult tissue (secondary cell walls) characterized by higher ABSL and crystalline cellulose values. Also, the change in the composition of the TFA-soluble MPS in, for example, the leaf fraction, indicates the formation of more adult tissue between the weeks 16 and 32, that is, BBCH-Sida development stage 63 and 93, respectively (Table S1, Supporting information). The overall development of secondary cell walls and therefore the increasing amounts of cellulose and lignin are in line with previous observations (Borkowska *et al.*, 2009; Borkowska & Molas, 2012). However, a direct comparison of distinct lignin values is often difficult due to differences in the determination method and unknown cultivation conditions. Within this study, ABSL determination was used to enable a high throughput measurement. Nevertheless, the observed lignin content in fully developed plants is comparable to previous studies using other methods like Klason determination (Michalska *et al.*, 2012). Determined cellulose and MPS levels are in line with previous observations (Michalska *et al.*, 2012) although measured cellulose in our study reflects only the crystalline part and not holocellulose, suggesting an overall high crystallinity in Sida cellulose fibers. The correlation of the established BBCH-Sida code with the biochemical properties of the plant material enables a targeted harvest strategy for a tailored utilization of Sida biomass.

Energy yield

Solid fuel. The analysis of the Sida biomass revealed its high potential as a solid fuel meeting all guidelines in accordance with DIN EN ISO 17225-7:2014-09 (Table 4) (DIN-EN-ISO-17225-7, 2014). As shown in our analysis, the energy content of the Sida biomass accounted for approximately 19 MJ kg^{-1} dry mass. This measured value is in accordance with the value used in a previous study for the calculation of combustion heat (Borkowska *et al*., 2009) and is further in line compared with values obtained from *Miscanthus* as another important perennial energy crop (Baxter *et al*., 2014). The overall energy yield for Sida as a solid fuel accounts for a calorific value of 446 GJ ha^{-1} (net calorific value: 440 GJ ha^{-1}) in its second year after the establishment of the field experiment. As previously reported, the Sida yield increased even during the fourth year after establishment (Borkowska & Molas, 2013). The energy value obtained in our study is even 22% higher than the values of an earlier study from the fourth to the sixth year after plant establishment (Borkowska & Molas, 2012), and even 168% higher when compared with a 4-year average energy yield of Sida cultivated in a light soil (Borkowska *et al*., 2009). Because no fertilizers were applied in our study, these higher values might be attributed to the higher silt and C_{org} content as well as a higher soil pH value among other environmental factors that were beneficial for the overall plant performance at our field trials.

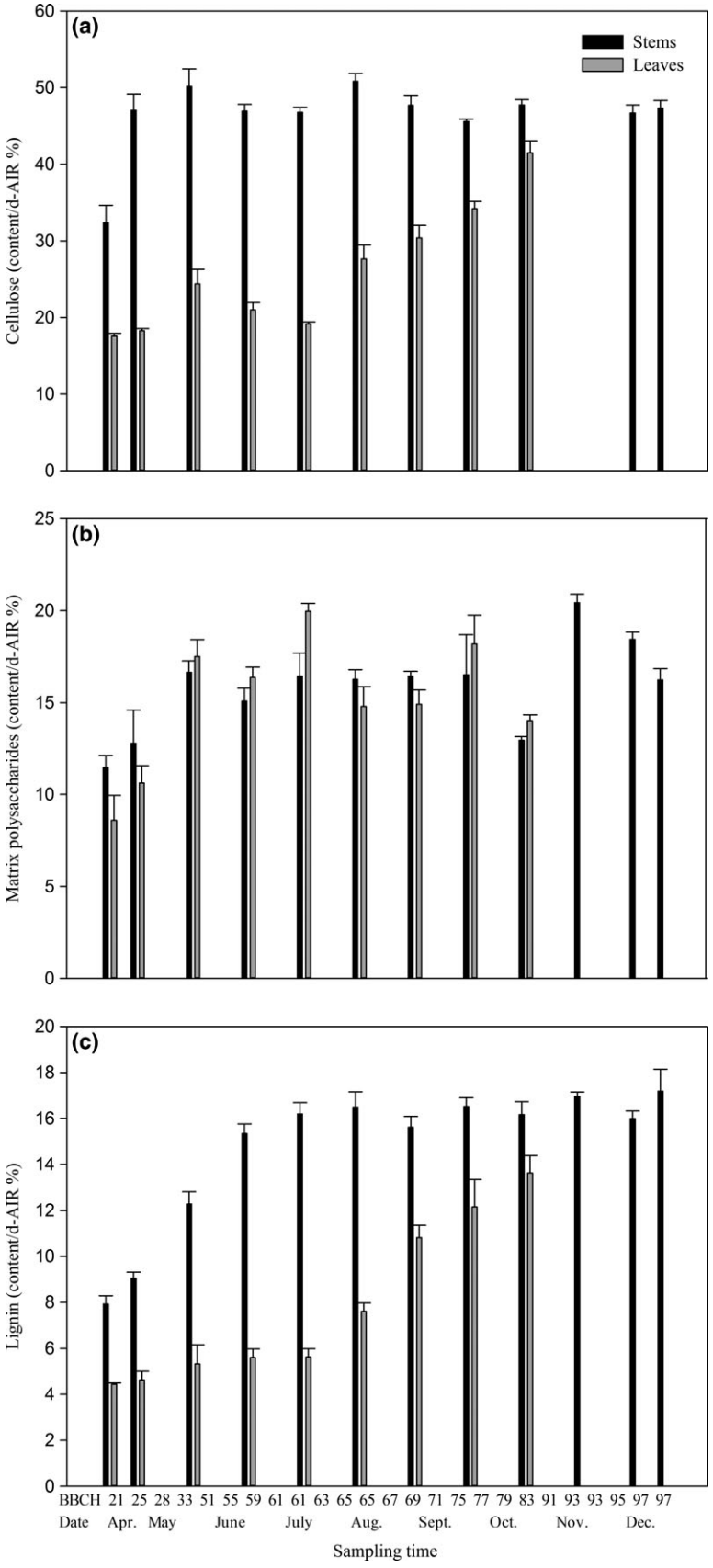
Even though samples of F1 showed slightly higher values of heavy metals such as Cd, Cu, Pb, and Ni compared with F2 samples, the determined values were still meeting the DIN guidelines. Even though Sida plants express the ability to accumulate heavy metals, the detected values are low and must be attributed to the longer growing period of F1 biomass (Borkowska & Wardzinska, 2003). However, our data were significantly lower compared with data from Sida grown on municipal sewage sludge compost and high-calcium brown coal ash (Krzywy-Gawronska, 2012), and were in accordance with the requirements of DIN EN ISO 17225-7:2014-09 to be classified as a biogenic solid fuel (DIN-EN-ISO-17225-7, 2014).

The presence of Cl and S in solid biomass used for combustion is crucial due to their high corrosion potential in the furnaces. The values of Cl and S in the analyzed Sida biomass were below the maximum values as specified in the norm DIN EN ISO 17225-7:2014-09 for solid biomass fuels, making Sida biomass a promising candidate as a sustainable energy carrier for combustion (DIN-EN-ISO-17225-7, 2014).

Ash analysis

The aim of the investigation was the characterization of the ash composition and the determination of the ash melting temperature of the promising solid fuel Sida. The amount of ash after biomass combustion accounted for 2.7% to 3.0%, which is lower than the 3.6% value reported in another study on Sida (Michalska *et al*., 2012), which might be due to a different development stage of the used plant biomass. However, the obtained ash values are in the same range as described for numerous wood and woody biomasses (Vassilev & Baxter, 2010) and for *Miscanthus*, which is also considered to be a valuable energy crop used for combustion (Baxter *et al*., 2012). The analysis of the Sida ashes revealed that both samples did not melt at 1500 °C, which is the maximum temperature achievable in the hot-stage microscope that we used. The explanation for the high melting temperature for Sida ash is in principle based on the amount of compounds with a high melting temperature (Misra *et al*., 1993; Wang & Dibdiakova, 2014). This is due to the high content of $CaCO_3$, which will decompose to CaO with a melting temperature of 2580 °C. The decomposition of the carbonate starts between 650 and 900 °C. Additionally, $K_2Ca(CO_3)_2$ will decompose, increasing the amount of the high melting compounds. Furthermore, low-melting potassium silicate compounds were not formed due to the insignificant amount of silica in the ash. As shown, the chemical composition of Sida is favorable for combustion in comparison to herbaceous biomass because the mineral content with a high melting point is much higher, leading to a comparably higher melting point of the ash. Therefore, problems related to ash melting, for example, slagging or bed agglomeration, should be less significant for Sida, as shown in this study. In general, the ash behavior of Sida is related more to the woody biomass used for combustion, assuming that a substitution of wood burning systems with Sida biomass seems to be worthwhile.

Fig. 4 Lignocellulose analysis of harvested Sida plants. AcBr soluble lignin (ABSL), TFA-soluble matrix polysaccharides (MPS), and crystalline cellulose content are depicted. The values represent the mean of 5 biological replicates. After week 32, Sida plants were defoliated; therefore, no leaves were harvested from that point. Stem tissue lignification is completed in week 20 (approximately 17% of d-AIR), whereas lignin level rose until defoliation (approximately 14% of d-AIR) in the leaf fraction. Bars indicate the standard deviation of 5 biological replicates.


(a)
Stems
Leaves
Cellulose (content/d-AIR %)
0
10
20
30
40
50
60
(b)
Matrix polysaccharides (content/d-AIR %)
0
5
10
15
20
25
(c)
Lignin (content/d-AIR %)
0
2
4
6
8
10
12
14
16
18
20
BBCH 21 25 28 33 51 55 59 61 61 63 65 65 67 69 71 75 77 79 83 91 93 93 95 97 97
Date Apr. May June July Aug. Sept. Oct. Nov. Dec.
Sampling time

Biogas production

To determine whether the energy yield of Sida biomass could be improved by numerous harvests for both solid fuels and biogas feedstock, we investigated the Sida biomasses from two different development stages of the plants in batch tests. The first cut of Sida in June at a development stage of BBCH-Sida 55 (sample B1.1) displayed a dry matter content of 20% consisting of approximately 90% organic dry matter, which is comparable with grass silage (Michalska *et al*., 2012). The second cut of the biomass at development stage 77 (sample B1.2) showed a higher organic content due to an increased lignification of the biomass. The sample B2 obtained from a single harvest for biogas production at development stage 91 showed the highest organic content. In the initial stages of the Sida plant's development, a high amount of short-molecule biomass like cellulose is developed, leading to more complex organic compounds like hemicellulose and lignin to achieve stability (Hendriks & Zeeman, 2009). Therefore, the different organic plant tissue composition can be associated with the higher biogas yield of B1.1 sampled at a much earlier plant development stage compared to the biogas yield from samples B1.2 and B2 harvested in October at a development stage of 77 and 91, respectively (Fig. 4). Lignin as a complex polymer consists of three different phenolic monomers that are difficult to hydrolyze for microorganisms and appear to be an inhibitor for the biogas production process, limiting the digestibility (Hendriks & Zeeman, 2009).

As indicated, sample B1.1 contains the least amount of lignin, cellulose, and hemicellulose and shows the highest biogas production rate after 25 days. In comparison, sample B2 showed the highest lignin, cellulose, and hemicellulose content, which resulted in an inhibited biogas production rate. As shown by Brown *et al.* (Brown *et al*., 2012) using different lignocellulosic biomasses at liquid anaerobic digestion, methane production has an inverse linear relationship with the lignin content (Pokój *et al*., 2015). As further shown by Pokój *et al*., Sida silage tested as a biogas feedstock produced from biomass harvested at the same development stage as used in our study (BBCH-Sida development stage 55, i.e., flowering phase) showed a lignin removal efficiency of approximately 45% and an overall organics removal rate of approximately 65% (Pokój *et al*., 2015). However, as concluded in the study by Pokój *et al*., lignin content is an inadequate criterion for estimating the methane production.

As further demonstrated in a study by Michalska *et al*., (2015), chemical and enzymatic pretreatment of Sida biomass resulted in an increased biogas production of 316 L kg^{-1} total solids, equaling a methane content of 200 L. Interestingly, our results revealed a biogas production from Sida silage of approximately 420 L kg^{-1} organic dry matter for sample B1.1 and approximately 269 and 256 L kg^{-1} organic dry matter for samples B1.2 and B2, respectively. These values correspond to a methane content of 204, 131, and 124 L kg^{-1} organic dry matter, respectively, within the same time of incubation. These values also correspond to a previous study using fresh Sida biomass for biogas production at mesophilic conditions (Dêbowski *et al*., 2012). Our results give evidence that a Sida biomass harvest at plant BBCH-Sida development stage 55 following a thorough homogenization and ensilaging of the biomass makes Sida biomass a promising candidate for biogas feedstock.

Combining our results of the overall measured energy yields from Sida biomass used as a solid fuel and biogas feedstock from the various developments stages, we saw that the four energy-use scenarios clearly indicated the highest energy recovery for scenario (i) (solid fuel) of 439 288 MJ ha^{-1}. The energy recovery of the four scenarios from most to least is as follows: scenario (i) >> (iii) (first biomass used for biogas, subsequent harvest used as solid fuel: 211 782 MJ ha^{-1}) >> (iv) (two times biomass harvest at development stage 55 and 77, respectively, used for biogas: 135 482 MJ ha^{-1}) > (ii) (one harvest for biogas only at plant development stage 91: 85 215 MJ ha^{-1}). Although scenario (iii) resulted in approximately half the energy yield of scenario (i), the flexible application of the Sida biomass as biogas feedstock when harvested at the BBCH-Sida stage 55 is an added value. How much the energy yields could be increased with regard to earlier or later harvests at different plant development stages needs further investigation. At this point, it remains unknown to what extent intermediate harvests of Sida biomass may result in sustainable production and continuous yield in subsequent years due to the interruption of the natural plant development. However, harvest of the dried Sida biomass at BBCH-Sida 98–99 allows both a maximum energy yield and reduced impact on the living plants, which results in a sustainable supply of Sida biomass over years (Borkowska *et al*., 2009; Borkowska & Molas, 2012). The calculated energy yields for the Sida biomass do not consider necessary energy investments for plant establishment, maintenance, and harvest of the biomass; therefore, given energy values represent the possible energy yield depending on the utilization scenario obtained from our measurements.

Acknowledgements

We gratefully acknowledge the help and assistance by Lucy Harrison and the funding of the OrCaCel project by the Bioeconomy Science Center (BioSC). The scientific activities of

the BioSC were financially supported by the Ministry of Innovation, Science, and Research within the framework of the NRW Strategieprojekt BioSC (No. 313/323-400-002 13).

References

Allwright MR, Taylor G (2015) Molecular breeding for improved second generation bioenergy crops. *Trends in Plant Science*, **21**, 43–54.

Barbosa DBP, Nabel M, Jablonowski ND (2014) Biogas-digestate as nutrient source for biomass production of *Sida Hermaphrodita*, *Zea Mays* L. and *Medicago sativa* L. *Energy Procedia*, **59**, 120–126.

Baxter XC, Darvell LI, Jones JM, Barraclough T, Yates NE, Shield I (2012) Study of *Miscanthus x giganteus* ash composition – variation with agronomy and assessment method. *Fuel*, **95**, 50–62.

Baxter XC, Darvell LI, Jones JM, Barraclough T, Yates NE, Shield I (2014) Miscanthus combustion properties and variations with Miscanthus agronomy. *Fuel*, **117**, 851–869.

Blanco-Canqui H (2010) Energy crops and their implications on soil and environment. *Agronomy Journal*, **102**, 403–419.

Bogusz A, Oleszczuk P, Dobrowolski R (2015) Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water. *Bioresource Technology*, **196**, 540–549.

Borkowska H, Molas R (2012) Two extremely different crops, Salix and Sida, as sources of renewable bioenergy. *Biomass and Bioenergy*, **36**, 234–240.

Borkowska H, Molas R (2013) Yield comparison of four lignocellulosic perennial energy crop species. *Biomass and Bioenergy*, **51**, 145–153.

Borkowska H, Wardzinska K (2003) Some effects of Sida hermaphrodita R. Cultivation on sewage sludge. *Polish Journal of Environmental Studies*, **12**, 119–122.

Borkowska H, Molas R, Kupczyk A (2009) Virginia fanpetals (sida hermaphrodita rusby) cultivated on light soil; height of yield and biomass productivity. *Polish Journal of Environmental Studies*, **18**, 563–568.

Brown D, Shi J, Li Y (2012) Comparison of solid-state to liquid anaerobic digestion of lignocellulosic feedstocks for biogas production. *Bioresource Technology*, **124**, 379–386.

Bundesministerium für Wirtschaft und Energie (2015) *Bruttostromerzeugung in Deutschland 2014*.

Carroll A, Somerville C (2009) Cellulosic biofuels. *Annual Review of Plant Biology*, **60**, 165–182.

Dębowski M, Dudek M, Zieliński M (2012) Effectiveness of methane fermentation of virginia fanpetals (*Sida hermaphrodita* Rusby) under mesophilic conditions. *Ecological Chemistry and Engineering*, **19**, 1445–1453.

Deutscher Bauernverband (2015) *Situationsbericht 2014/2015 des deutschen Bauernverbandes*.

DIN-38414-8 (1985) German standard methods for the examination of water, waste water and sludge; sludge and sediments (group S); determination of the amenability to anaerobic digestion (S 8).

DIN-51730 (1998) Prüfung fester Brennstoffe Bestimmung des Asche-Schmelzverhaltens. *DIN 51730*.

DIN-51900-3 (2003) Prüfung fester und flüssiger Brennstoffe Bestimmung des Brennwertes mit dem Bomben- Kalorimeter und Berechnung des Heizwertes Teil 3: Verfahren mit adiabatischem Mantel. *DIN 51900-3*.

DIN-EN-12880 (2001) Charakterisierung von Schlämmen - Bestimmung des Trockenrückstandes und des Wassergehalts.

DIN-EN-15408 (2011) Solid recovered fuels - Methods for the determination of sulphur (S), chlorine (Cl), fluorine (F) and bromine (Br) content.

DIN-EN-ISO-17225-7 (2014) Solid biofuels – Fuel specifications and classes – Part 7: Graded non-woody briquettes.

FNR (2015) Basisdaten Bioenergie Deutschland 2015.

Foster CE, Martin TM, Pauly M (2010a) Comprehensive compositional analysis of plant cell walls (Lignocellulosic biomass) part II: carbohydrates. *Journal of Visualized Experiments*, 10–13.

Foster CE, Martin TM, Pauly M (2010b) Comprehensive compositional analysis of plant cell walls (lignocellulosic biomass) part I: lignin. *Journal of Visualized Experiments : JoVE*, 2–5.

Graham-Rowe D (2011) Agriculture: beyond food versus fuel. *Nature*, **474**, S6–S8.

Grande PM, Viell J, Theyssen N, Marquardt W, Domínguez de María P, Leitner W (2015) Fractionation of lignocellulosic biomass using the OrganoCat process. *Green Chemistry*, **17**, 3533–3539.

Hack H, Bleiholder H, Buhr L, Meier U, Schnock-Fricke U, Weber E, Witzenberger A (1992) Einheitliche Codierung der phänologischen Entwicklungsstadien mono- und dikotyler Pflanzen-Erweiterte BBCH-Skala, Allgemein. *Nachrichtenblatt des deutschen Pflanzenschutzdienstes*, **44**, 265–270.

Hartmann A, Haller J (2014) Silphie und Co als Biogassubstrat – Erste Ergebnisse aus dem Dauerkulturanbau. *TFZ-Merkblatt: 14PHm004*, **49**.

Hendriks ATWM, Zeeman G (2009) Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology*, **100**, 10–18.

Krzywy-Gawronska E (2012) The effect of industrial wastes and municipal sewage sludge compost on the quality of virginia fanpetals (SIDA HERMAPHRODITA RUSBY) biomass Part 1. Macroelements content and their uptake dynamics. *Polish Journal of Chemical Technology*, **14**, 2.

Michalska K, Miazek K, Krzystek L, Ledakowicz S (2012) Influence of pretreatment with Fenton's reagent on biogas production and methane yield from lignocellulosic biomass. *Bioresource Technology*, **119**, 72–78.

Michalska K, Bizukojć M, Ledakowicz S (2015) Pretreatment of energy crops with sodium hydroxide and cellulolytic enzymes to increase biogas production. *Biomass and Bioenergy*, **80**, 213–221.

Misra MK, Ragland KW, Baker AJ (1993) Wood ash composition as a function of furnace temperature. *Biomass and Bioenergy*, **4**, 103–116.

Nabel M, Bueno D, Barbosa P, Horsch D, Jablonowski ND (2014) Energy crop (Sida hermaphrodita) fertilization using digestate under marginal soil conditions: a dose-response experiment. *Energy Procedia*, **16**, 14000.

Oleszek M, Matyka M, Lalak J, Tys J, Paprota E (2013) Characterization of Sida hermaphrodita as a feedstock for anaerobic digestion process. *Journal of Food, Agriculture & Environment*, **11**, 1839–1841.

Pokój T, Bułkowska K, Gusiatin ZM, Klimiuk E, Jankowski KJ (2015) Semi-continuous anaerobic digestion of different silage crops: VFAs formation, methane yield from fiber and non-fiber components and digestate composition. *Bioresource Technology*, **190**, 201–210.

Schattenhauer A, Weiland P (2006) Handreichung Biogasgewinnung und – nutzung. *Fachagentur Nachwachsende Rohstoffe e.V.*, 29–31.

Schröder P, Herzig R, Bojinov B *et al.* (2008) Bioenergy to save the world. Producing novel energy plants for growth on abandoned land. *Environmental Science and Pollution Research International*, **15**, 196–204.

Scott TA, Melvin EH (1953) Determination of dextran with anthrone. *Analytical Chemistry*, **25**, 1656–1661.

Slepetys J, Kadziuliene Z, Sarunaite L, Tilvikiene V, Kryzeviciene A (2012) Biomass potential of plants grown for bioenergy production. *International Scientific Conference: Renewable Energy and Energy Efficiency*, 66–72.

Spooner DM, Cusick AW, Hall GF, Baskin JM (1985) Observation on the distribution and ecology of *Sida hermaphrodita* (L.) Rusby (Malvacea). *Sida*, **11**, 215–225.

Stolarski MJ, Szczukowski S, Tworkowski J, Krzyzaniak M, Gulczyński P, Mleczek M (2013) Comparison of quality and production cost of briquettes made from agricultural and forest origin biomass. *Renewable Energy*, **57**, 20–26.

Updegraff DM (1969) Semimicro determination of cellulose in biological materials. *Analytical Biochemistry*, **32**, 420–424.

Vassilev SV, Baxter D, Andersen LK, Vassileva CG (2010). An overview of the chemical composition of biomass. *Fuel*, **89**, 913–933.

Voigt TB, Lee OK, Kling GJ (2012) Perennial herbaceous crops with potential for biofuel production in the temperate regions of the USA. *CAB Reviews*, **7**, 45–57.

Voiniciuc C, Schmidt MH-W, Berger A *et al.* (2015) MUCI10 produces Galactoglucomannan that maintains pectin and cellulose architecture in Arabidopsis seed mucilage. *Plant Physiology*, **169**, 403–420.

Wang L, Dibdiakova J (2014) Characterization of ashes from different wood parts of Norway spruce tree. *Chemical Engineering Transactions*, **37**, 37–42.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. BBCH-Sida code for *Sida hermaphrodita* (L.) Rusby.

Table S2. Lignocellulose composition of the Sida biomass at the different development stages at harvest given as percentage of the de-starched alcohol-insoluble residues samples.