Characterisation of biogas digestate as raw material for fibre composites

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Zusammenfassung

In der Faserverbundindustrie werden verschiedene synthetische Fasern und Naturfasern als Verstärkungsfaser eingesetzt. Aufgrund von Bestrebungen zu nachhaltigen Produkten und der Vermeidung von Flächennutzungskonkurrenz werden zunehmend Alternativen gesucht. Hierfür stellen Bioraffinerien eine mögliche Lösung dar. Biogasanlagen vergären strukturreiche pflanzenbasierte Biomasse. Die entstehenden Gärreste sind bereits teilweise abgebaut. Als Verstärkungsfasern genutzte Naturfasern werden chemisch oder biologisch aus Pflanzen extrahiert, dies legt eine Verwendung von Gärresten nahe. Die vorliegende Arbeit beschäftigt sich mit der Frage, ob Biogasgärreste als Faserrohstoff für Verbundwerkstoffe infrage kommen.

Es werden Gärreste aus vier verschiedenen kommerziell betriebenen Biogasanlagen in Deutschland betrachtet. Neben drei Anlagen mit einem durchschnittlichen Substratmix aus tierischen Exkrementen und Pflanzen, werden auch Gärreste aus einer rein pflanzlich betriebenen Anlage betrachtet. Die festen Anteile der Gärreste werden zunächst hinsichtlich der Faserqualität untersucht. Dazu werden die Faserdimensionen (Faserlänge und Schlankheitsgrad) und die Dichte der Gärreste bestimmt. Mittels einer Futtermittelanalyse nach van Soest werden die Anteile an Zellwandbestandteilen untersucht. Die Ergebnisse der Untersuchungen werden mit gängigen Fasern wie Flachs und Holz verglichen. Neben den Eigenschaften wird auch die mögliche Faserausbeute aus den verschiedenen Gärresten betrachtet. Hier wird insbesondere der Einfluss der Ausgangssubstrate betrachtet. Dazu wird zunächst die Verteilung verschiedener Größenklassen mittels Nasssiebanalyse ermittelt. Diese Ergebnisse werden mit der Trockensubstanz kombiniert.

Anschließend werden Gärreste einer Anlage, die ausschließlich pflanzliche Substrate, mit einem hohen Anteil an Hopfenreben gesondert betrachtet. Es wird betrachtet, ob das zusätzliche Waschen der Gärreste für die Faserqualität einen Vorteil bringt. Zur Überprüfung der These werden die gängigsten Fasereigenschaften untersucht und mit Holzfasern verglichen. Diese Gärreste dieser Biogasanlage werden für die nachfolgenden Untersuchungen genutzt.

Verbundwerkstoffe werden häufig mit einem Textil als Verstärkung hergestellt. Daher werden die Gärreste zunächst zu einem Vlies verarbeitet. Dazu wird die Nassvliestechnik genutzt, da diese für verschiedene Fasern geeignet ist. Als Bindematerial wird ausschließlich Zellstoff verwendet, sodass das Vlies vollständig biobasiert ist.

Zur Herstellung der Verbundwerkstoffe wird die Heißpresstechnik mit duroplastischer Matrix verwendet. Die verwendete Matrix ist ein teilweise biobasiertes Epoxidharzsystem. Mithilfe zweier Versuchsszenarien werden die am besten geeigneten Prozessparameter ermittelt. Im ersten Durchgang wird der Anteil an zugegebener Matrix bei konstantem Druck variiert. Beim zweiten Durchgang wird der Druck bei konstantem Matrixgehalt variiert. Zur Überprüfung der Werkstoffeigenschaften werden zerstörende und nicht zerstörende Werkstoffprüfungen durchgeführt. Um eine Aussage über eine geeignete Anwendung zu treffen, sind insbesondere die mechanischen Eigenschaften und die Wasseraufnahme von Bedeutung. Zusätzlich wird das Verhalten gegenüber Chemikalien untersucht, um die Beständigkeit des Werkstoffs beurteilen zu können. Dazu wird der Verbundwerkstoff mit den zuvor ermittelten Prozessparametern hergestellt und in verschiedene Chemikalien eingelegt.

Abschließend wird die Dauerhaftigkeit der Verbundwerkstoffe betrachtet. Dazu wird der Verbundwerkstoff mit den zuvor ermittelten Prozessparametern hergestellt. Als Matrix wird jedoch ein Epoxidharz mit höherem biobasiertem Anteil verwendet. Der Werkstoff wird über drei Monate hinweg UV-Strahlung und feuchter Luft ausgesetzt. Danach werden erneut die mechanischen Eigenschaften und die Wasseraufnahme untersucht.

Die wesentliche Erkenntnis der Arbeit ist, dass sich die festen Bestandteile von Gärresten zu Verbundwerkstoffen verarbeiten lassen. Die Eigenschaften der Gärreste sind ähnlich zu denen von Holzfasern. Für die Ausbeute an Gärrestefasern ist es vorteilhaft, wenn in der Biogasanlage nur ein geringer Anteil an tierischen Exkrementen als Substrat eingesetzt wird. Eine zusätzliche Aufbereitung nach der Vergärung führt zu einer Steigerung der Faserqualität. Die Heißpresstechnik hat sich als geeignetes Verfahren erwiesen, da vollständig imprägnierte Verbundwerkstoffe mit reproduzierbaren Eigenschaften hergestellt werden können. Ein Druck von mindestens 4.5 MPa und eine Matrixzugabe von 60 %, was einem Überschuss von ca. 10 % entspricht, werden als beste Prozessparameter ermittelt. Die Eigenschaften der Verbundwerkstoffe sind mit Wood Plastic Composites vergleichbar. Daher sind sie als angemessen anzusehen. Die Dauerhaftigkeit zeigt sich aufgrund der stark verminderten mechanischen Eigenschaften nach der künstlichen Bewitterung und der Chemikalienlagerung als verbesserungswürdig. Die Dauerhaftigkeit ist hauptsächlich durch die Matrix definiert. Aufgrund der beschriebenen Ergebnisse ist eine Anwendung für die Gärresteverbundwerkstoffe als Möbelwerkstoff zu empfehlen.

Summary

Various synthetic fibres and natural fibres are used as reinforcing fibres in the fibre composite industry. Efforts towards sustainable products and the avoidance of land-use competition are increasingly driving the search for alternatives. Biorefineries are one possible solution. Biogas plants process structurally rich plant-based biomass. The resulting digestates have already been partially degraded. Natural reinforcement fibres are extracted chemically or biologically from plants, the use of digestates is obvious. This paper deals with the question whether biogas digestate can be used as a fibre raw material for composite materials.

Digestates from four different commercially operated biogas plants in Germany are considered. Besides three biogas plants that utilize an average mix of animal excrement and plants one plant is operating solely plant-based. The solid portions of the fermentation residues were first examined regarding fibre quality. For this purpose, the fibre dimensions (fibre length and degree of slenderness) and the density of the fermentation residues were determined. Utilizing a feed analysis according to van Soest, the proportions of cell wall components were examined. The results of the investigations were compared with common fibres such as flax and wood. In addition to the properties, the possible fibre yield from the various fermentation residues was also considered. In this study, the influence of the starting substrates was considered in detail. For this purpose, the distribution of different size classes was first determined utilizing wet sieve analysis. These results were combined with the dry matter content.

Digestates from a plant using exclusively plants as substrates, with a high proportion of hop vines, are considered separately. It is considered whether the additional washing of the fermentation residues brings an advantage for the fibre quality. To prove this thesis, the most common fibre properties are also examined and compared with wood fibres. These digestates from this biogas plant are used for the following investigations.

Composite materials are often produced with a textile as reinforcement. Therefore, the digestate is first processed into a nonwoven. The wet laying technology is used, as it is suitable for various types of fibres. Only cellulose is used as a binding material so that the nonwoven is completely bio-based.

The hot-press technology with a thermoset matrix is used to produce the composites. The matrix used is a partially bio-based epoxy resin system. The most suitable process parameters are determined with two test scenarios. In the first run, the proportion of added matrix is varied at constant pressure. In the second run, the pressure is varied at constant matrix content. Destructive and non-destructive material tests are carried out to check the material properties. To make a statement about a suitable application, the mechanical properties and the water absorption are of particular importance. In addition, the behaviour towards chemicals is examined to be able to assess the resistance of the material. For this purpose, the composite material is produced with the previously determined process parameters and immersed in various chemicals.

Finally, the durability of the composite materials is examined. For this purpose, the composite material is also produced with the previously determined process parameters. An epoxy resin with a higher bio-based content is used as the matrix. The material is exposed to UV radiation and humid air for three months. Afterwards, the mechanical properties and water absorption are examined again.

The main finding of the presented study is that the solid components of digestate can be processed into composite materials. The properties of the digestate fibres are similar to those of wood fibres. For the yield of digestate fibres, it is advantageous if only a small proportion of animal excrements is used as substrate in the biogas plant. Additional processing after fermentation leads to an increase in fibre quality. The hot-press-technology has proven to be a suitable process, as fully impregnated composites with reproducible properties can be produced. The process parameters determined are a pressure of at least 4.5 MPa and a matrix addition of 60 %, which corresponds to an excess of about 10 %. The properties of the composites are comparable to Wood Plastic Composites. Therefore, they can be considered adequate. The durability is shown to be inadequate due to the strong reduction in mechanical properties after artificial weathering and chemical storage. The durability is mainly dependent on the matrix. Based on the results described, an application for the digestate composites as furniture material is recommended.

Acronym

ADF acid detergent fiber

ADL acid detergent lignin

BMC bulk molding compound

CHP combined heat and power plant

F1 fermenter

F2 secondary fermenter

FRP fiber reinforced plastics

GFRP glass fiber reinforced plastics

IR infrared

MDF middle density fiber board

NDF neutral detergent fiber

NFRP natural fiber reinforced plastics

SDG sustainable development goals

ST storage tank

UV ultra violet

WPC wood plastic composites

Contents

1 Introduction

Bioenergy and biobased products are being introduced in all industries. In Germany, the federal cabinet approved the National Bioeconomy Strategy on January 15, 2020. Germany is to become a leader in sustainable processes and products. To this end, economy and ecology are to be combined (BMBF, 2020).

To achieve the goal of a temperature, increase of only 2 °C, more bioenergy is needed (Hasegawa et al., 2020). Increased use of biomass for bioenergy means increased demand for agricultural land, but land is a limited resource (Niewöhner et al., 2016). If agricultural land is used for energy production instead of food production, food will have to be produced elsewhere. Converting non-agricultural land causes a negative carbon footprint, emitting 17 to 420 times more carbon dioxide than is saved by bioenergy (Mellor et al., 2021). Using waste streams to increase product value is a pathway to a more sustainable industry (Moretto et al., 2020). The biorefinery concept helps avoid waste streams by using biomass in an efficient way (Andersen et al., 2018). Typically, biorefineries add value to biomass through cascade use and coupled production of food, raw materials for industrial processing, and energy (Cherubini, 2010; Steinbach, 2020). Fibres are possible raw materials which can be obtained in a biorefinery.

Fibres in general are thin structures which can be processed into a textile (DIN, 2001). Their main characteristic is that they are longer than wide. The minimum slenderness ratio (length to width) is 3:1, but for textile production it is usually 1000:1 or higher (DIN, 2001; Kozlowski et al., 2005; Schenek, 2001). The fibres used in industry today are either produced from fossil raw materials or obtained from various natural sources. DIN 60001-1 defines natural fibres as "natural, linear structures which can be processed into textiles. They can be obtained from plant parts or from the pelage of animals, or be obtained from the cocoons of silk moths, or be of mineral, natural origin" (DIN, 2001). Plant fibres are divided into hard fibres, bast fibres, seed fibres and wood fibres (Schenek, 2001). Figure 1.1 provides an overview of the different types of fibres. Plant fibres are cells whose cell walls are composed of lignocellulose. Plant fibres can be used for various purposes such as fabrics, technical textiles, or composites. For composites, mainly bast fibres are used.

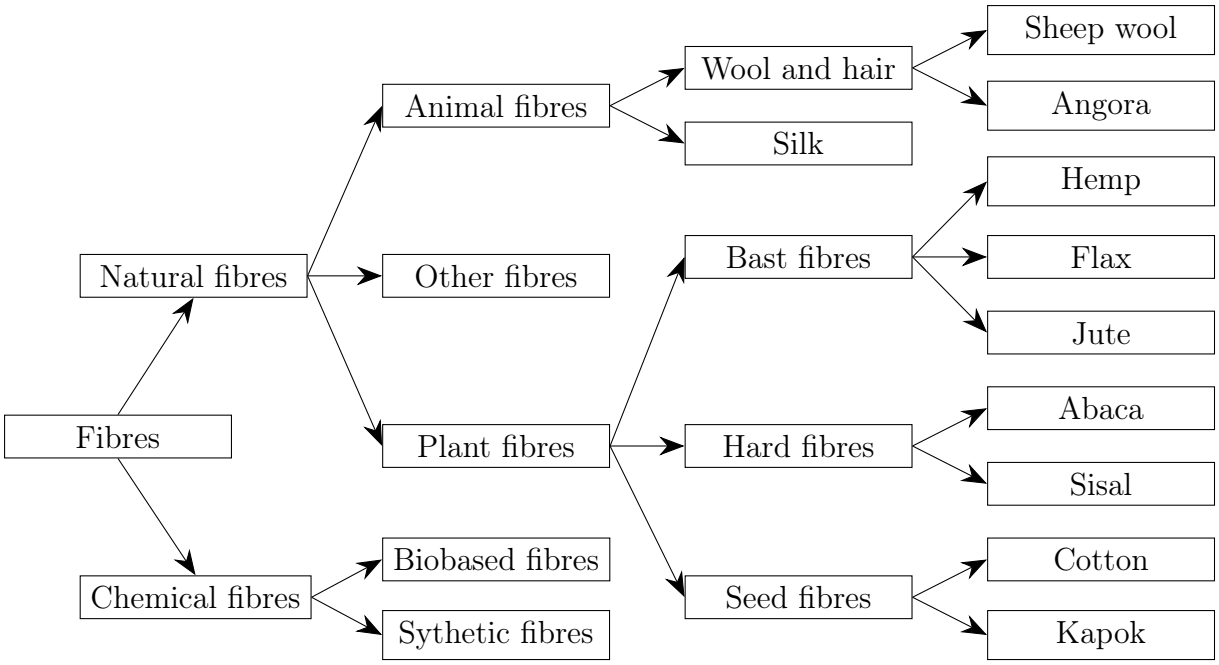

Figure 1.1: Overview of different fibre types with examples (Schenek, 2001)

Bast fibres are obtained from the stems of annual plants. The plant fibres are bundles of plant cells which are connected by pectines. The fibre bundles must be extracted from the plant stem. The different extraction methods available are compared in table 1.1.
Fibre composites are the most common representative of composites. Generally, fibre composites contain a fibre component as reinforcement embedded in a matrix component (Zweben, 2015). The matrix, often a polymer, determines the shape of the composite and protects the fibre from environmental influences. The main advantage of fibre composites is their high mechanical properties combined with low weight (Martin, 2006). High performance materials such as glass or carbon fibre reinforced plastics are common in aerospace or automotive industries (Aleksendrić and Carlone, 2015; AVK, 2013). In 2018, 1.14 Mt of glass fibre composites were produced in Europe and 229 kt in Germany. The amount of carbon fibre composites demanded in Europe in 2018 was 52.5 kt, which was about one third of the global demand (Sauer, 2019). There are various production processes for composites. Typical processes using textiles (AVK, 2013) as reinforcement and thermoset polymers are:

- Hand layup: Matrix is applied to the textile by hand
- Vacuum infusion: Matrix floats through vacuum into the textile in an open die
- Pre-impregnated textiles: Pre-impregnated textile is consolidated with composite

Compression moulding is the most commonly used process for natural fibre reinforced plastics (Paul, 2006) and accounted for 95 % of composites in (Carus et al., 2015). In 2020, the production of compression moulded parts for the automotive sector was 10

Table 1.1: Different fibre extraction methods (Sisti et al., 2017; Ahmed and Akhter, 2001; Lee et al., 2020; Naupert et al., 1967)

Extraction	Process	Method	Duration	Comment
Water retting	Storage in water (natural or tanks)	Microorganisms	Cold: 7 d to 14 d Warm: 3 d to 5 d	High quality
Dew retting	Plants remain on the field	Microorganisms	3 week	Old process, grey fibres, cheap
Mechanical extraction	Beating & combing of plants	Mechanical forces		Old process, lower quality
Chemical retting	Plants are soaked in chemicals	Chemicals	1 h to 3 h	Repeatable, stiffer

times higher than that of natural fibre injection moulded products (3N Kompetenzzentrum, 2022).The type of fibre reinforcement depends on the application and can vary widely. Fibres can be embedded as short fibres unprocessed or as textiles, for example, as woven textiles or nonwovens (Schürmann, 2007). Nonwovens are defined as fibre-based textiles. The fibres are bonded in a form-fitted way (Fuchs and Albrecht, 2012). One advantage of nonwovens is that they are processed directly from fibres without further process steps such as yarn production. Nonwoven processes are divided into dry and wet processes (Gries, 2015). The wet laying process is similar to the production of paper. A mixture of fibres and water is floated onto a sieve band. The water drains off and the fibres remain on the sieve forming a mat. After several dewatering and drying steps, a textile is produced. To strengthen the bond between the fibres, various additives such as special bonding fibres or adhesives can be added. The main advantage of this process is the wide range of processable fibres in terms of slenderness ratio. This makes the process interesting for alternative fibre materials (Russell, 2006; Fuchs and Albrecht, 2012).

The production of carbon fibres is very energy intensive, therefore the environmental impact is high (Schürmann, 2007). In many applications, natural fibres, for example flax or hemp fibres, can be a substitute. In 2012, 92 kt of natural fibre composites were produced in Europe (Sauer, 2019), which is about 8 % of the amount of glass fibre composites. They are used in non-structural parts of automobiles or for sports equipment (Sathish et al., 2021). Natural fibres are grown on agricultural land, so they cause the same land-use competition as bioenergy (Gessner, 1955). Therefore, the use of alternative fibre sources is of interest for the composites industry. The agricultural land used for fibre crops was 440000 ha in Europe in 2020 (FAO, 2021).

In line with the idea of biorefineries, the use of by-products from biomass utilisation for composite production is of great interest. In the Canary Islands, the grass Arundo donax is an environmental problem because the plant is invasive. Ortega et al. (2021) investigated that up to 20 % ground Arundo donax has no negative impact on the properties compared to unfilled polyethylene. The use of coconut fibres as reinforcement in composites is also being investigated. Every year, 64 billion coconuts are harvested (Bradley and Conroy, 2019) and about 60 % of coconut is shells, which are actually waste (Obeng et al., 2020). A powder made from coconut shells increases the tensile modulus of polyethylene by 56 % (Bradley and Conroy, 2019). The use of waste wood is already common in the production of wood-based materials such as medium-density fibreboard. wood plastic composites (WPC) can be made from thermoplastics and virgin wood flour or fibres, but the use of sawdust it is also a well-known option (Vogt, 2006).

Biogas plants are a way to produce renewable energy. The energy output is gas, which is often converted into electricity and heat in a combined heat and power plant (CHP). The biomass is degraded by microorganisms in 4 steps to biogas (methane (CH_4) and carbon dioxide (CO_2)), see Figure 1.2 (Deepanraj et al., 2014).

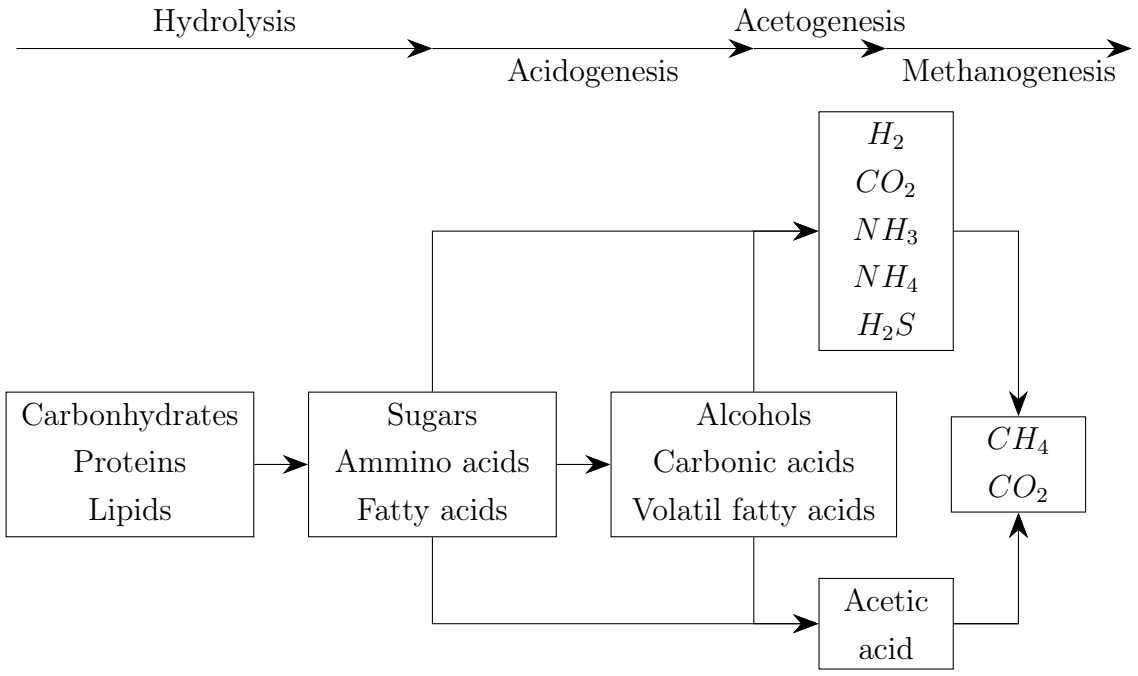

Figure 1.2: Anaerobic digestion, based on Deepanraj et al. (2014)

Mostly, energy crops, by-products of food production or manure from agricultural animal husbandry are used as substrates for biogas production. While millions of small-scale household biogas plants are still in operation in China today, most of the large-scale plants are located in the United States or Europe. In Germany, there are about 10000 biogas plants (Torrijos, 2016; Königsberger et al., 2019). Most biogas plants use a mix of

energy crops and excrement as substrate, in Germany about 12 % are fed only with energy crops and another 12 % almost only with excrement (Daniel-Gromke et al., 2020). Figure 1.3 shows the variation of biogas substrates in Germany and typical dry matter contents of substrates (Steffen et al., 1998; Daniel-Gromke et al., 2017; Scarlat et al., 2018). In Europe, biomass is used on a large-scale in biogas plants to generate energy.

In an anaerobic, microbial conversion process, the easily degradable components are converted into CH_4 and CO_2. The digestate from biogas plants is rich in nutrients and is therefore mostly used as fertilizer. Moreover, digestate as an organic material has positive effects on soil microorganisms (Schneider-Götz and Mastel, 2007; Koszel et al., 2017; Wulf and Roth, 2018). Another use of digestate is as fuel pellets. Zeng et al. (2012) investigated the thermal utilization of pellets made from 50 % wood and 50 % digestate.

Lignocellulosic compounds remain in the fermentation residues (digestate) of the plants. The digestate therefore offers interesting possibilities for obtaining alternative fibres for composite production. Taurino et al. (2016) has added ground digestate as a filler to unsaturated polyester resins; 30 % digestate increased the strength by 25 % compared to the unfilled matrix. Digestate can be blended with wood in the production of medium density fibreboard. A digestate content of 30 % was achieved (Essel et al., 2015). Digestate in fibrous form was also used by König (2005) as an additive in polymer films or insulation panels to increase the degradability of the plastic film.

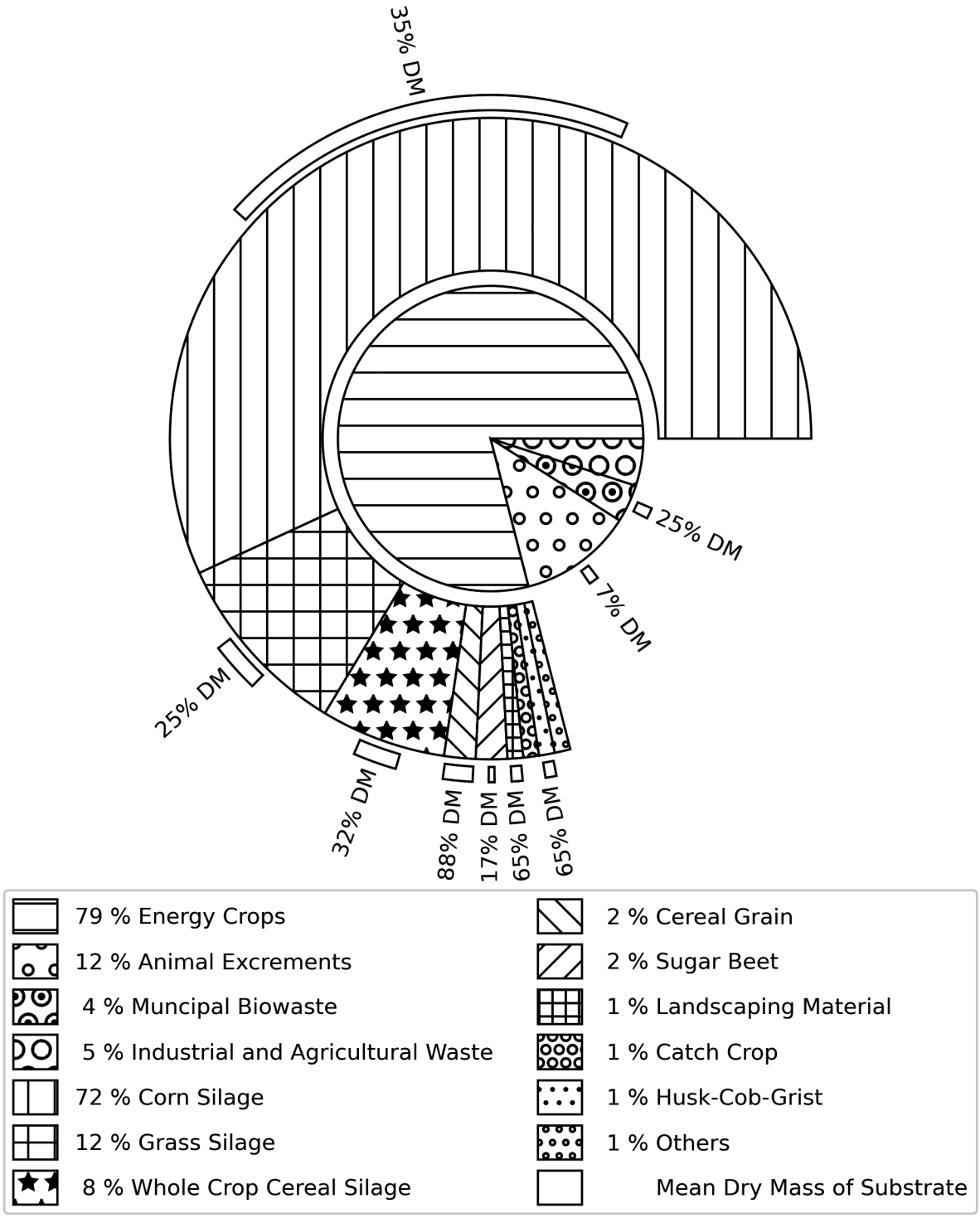

Figure 1.3: Used biogas substrates in Germany with typical dry matter contents, own figure after Daniel-Gromke et al. (2017)

1.1 Objectives

The use of agricultural waste completes the biomass value chain and is a way to produce sustainable products. In the field of composites, alternative fibres made from waste materials are of particular interest. Due to the high number of biogas plants in Europe, the availability of digestate is high and the lignocellulosic substrates suggest that digestate can be a potential source of fibres. In the process of anaerobic digestion, the part of the biomass that is not lignocellulosic is degraded by various microorganisms. This process is comparable to the usual biological rotting processes. This fact makes it interesting to investigate the use of digestate as fibres for reinforced plastics without further fibre extraction.

The aim of the presented work is to develop a sustainable composite material based on digestate from anaerobic digestion. Considering the points discussed, this goal leads to the following research objectives:

- To explore the possibility of obtaining fibres for composites from biogas digestate and evaluate the fibre quality
- To investigate a production method for fibre composites based on digestate
- To analyse the properties and durability of composites based on digestate

Finally, the results of the work are evaluated in terms of sustainability. For this purpose, the production process and the final composite material are considered.

1.2 Structure of the thesis

The presented thesis investigates wether the solid fraction of digestate is a potential raw material for fibre-reinforced plastics and wether these materials have comparable properties to other materials. The research questions described are discussed in the following chapters. Chapter 2 describes the analysis of digestates from various biogas plants. The digestates are analysed with respect to different fibre properties. Digestates from substrates with a high content of hops showed the best quality, therefore these digestate fibres are compared with conventional naturals fibres in chapter 3. This was done with different material tests for fibres. The digestate fibres have properties which allow the production of composites.

To produce the composites, a nonwoven was first made from the digestate fibres. The nonwoven production was investigated with various experiments to find the best fibre

preparation and process parameters for the wet laying machine. To remove dirt and avoid further degradation, the materials were washed with water in an ultrasonic bath, disinfected with hydrogen peroxide, dried and sieved with a 0.8 mm sieve. To obtain homogeneous and finer fibres, all digestate samples are treated with a Hollander beater prior to the production of a nonwoven. In this process step, the digestate fibres were mixed with water and floated through a roller with knives to carefully break them up. The influence of the hollander beater on fibres are shown in Figure 1.4.

(a) Washed digestate **(b)** Washed and beaten digestate

Figure 1.4: Digestate before and after beating in a Hollander beater

The change in length deviation of the beaten fibres is shown in Figure 1.5. In the past, this process was common in the paper industry.

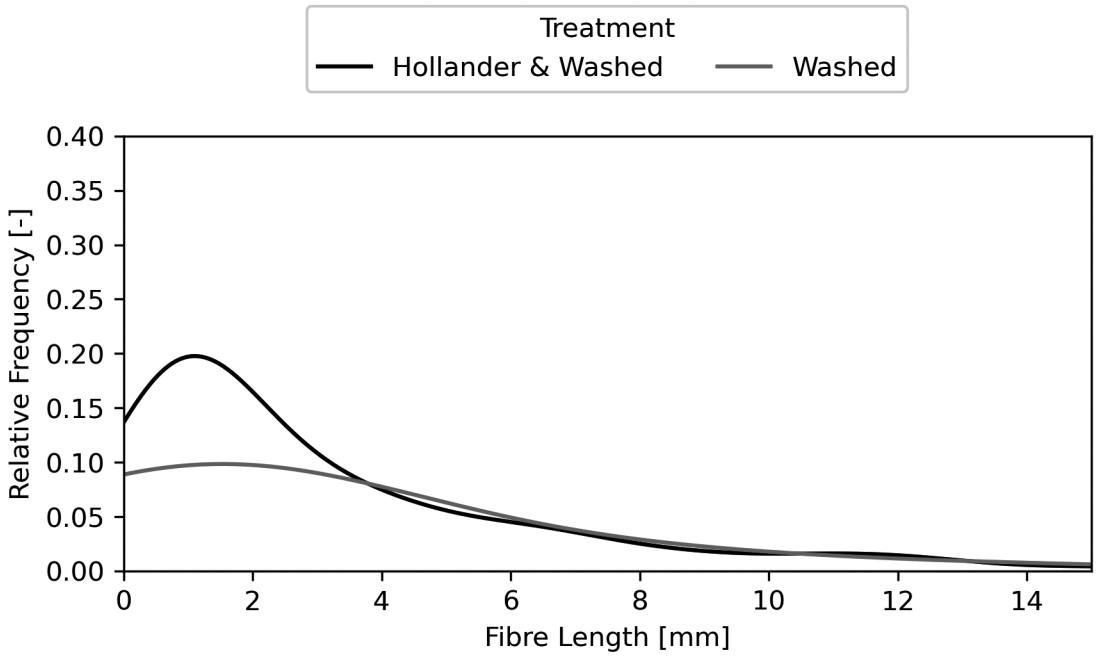

Figure 1.5: Length deviation of the digestate before and after beating in the Hollander beater

A wet layup machine was used to produce a nonwoven with the following process parameters:

- Fibre concentration of $3\,\mathrm{g\,l^{-1}}$
- Drying with infrared radiation, hot air dryer 100 °C, drying cylinder 150 °C
- Addition of abaca pulp 12 % of the fibre weight

The resulting nonwoven has a basis weight of $600\,\mathrm{g\,m^{-2}}$ and is shown in Figure 1.6.

Figure 1.6: Digestate nonwoven used for the production of composites

The production of composites using the compression moulding process is described in chapter 4. To identify the best process parameters, two experimental setups were used, a variation of the pressure and a variation of the amount of matrix. To evaluate the composite quality, destructive and non-destructive material tests were performed.

As an indicator of potential applications, the aging of the composites was analysed. For this purpose, the material was artificially weathered and then retested. This is described in chapter 5. Finally, the results are discussed in terms of fibre quality, the possibility of composite production and composite quality.

2 Investigation of Biogas Digestate as Fiber Materials for Composites

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Abstract

Fiber reinforced plastics with synthetic fibers are widely used. Plant fibers are also known to produce more sustainable composites. However, there is a great interest in finding alternatives to classical natural fibers. The digestate of biogas plants seems to be such an alternative. Biogas plants are fed with plant based substrates and during the digestion, the biomass is degraded. In this study, the fiber quality of digestates from four biogas plants with different initial substrates is investigated. Therefore, typical fiber properties, such as slenderness ratio, cell wall components and the potential fiber performance, are measured. According to the general definition, the solid part of the digestate is a fiber material. The slendernessratio is 5 or higher and the density is $1.5\,\mathrm{g\,cm^{-3}}$, which is typical for natural fibers. Fibers with similarproperties are already used in composite materials.

Keywords: Bio composites, Waste material, Natural fibers, Biorefinery

2.1 Introduction

Fiber-based composites with different reinforcing fibers are used in various industries. Fiber reinforced composites typically consist of a reinforcing fiber component, which absorbs the forces, and a matrix, which gives the shape and protects the fibers from environmental influences. In general, fibers are defined as thin filamentary structures (Crowther, 1995) that have a slenderness ratio (length/diameter) of at least 3:1 (Schenek, 2001). It is possible to mix individual short (1 mm to 10 mm), long (smaller 25 mm), or continuous fibers with the polymer matrix. Fibers are often processed into reinforcing textiles (e.g., nonwovens, woven or tailored fabrics) (Schürmann, 2007). Fibers for textile applications have a very large slenderness ratio of 1000:1 and more (Schenek, 2001). The requirements for nonwoven technology are fibers with a length of up to 5 mm to 30 mm, which must not be too slender. Very short fibers are often processed as fillers in thermoplastics, for example in WPC, where wood flour and wood fibers are common (Schürmann, 2007; Vogt, 2006). The scarcity of resources and the goal of reducing the high energy consumption in the production of many composites are forcing the industry to use alternatives. Natural fibers, especially plant fibers such as flax, are often used to produce sustainable composites. The density of plant fibers is typically about $1.5\,\mathrm{g\,cm^{-3}}$ (Schenek, 2001) and their specific (density-related) properties are comparable to those of glass fibers (Salit et al., 2015; AVK, 2013).

Plant fibers must be extracted from plants by biological, chemical, or sometimes mechanical methods. This causes additional process steps and energy consumption (Ahmed and Akhter, 2001; Gessner, 1955). Plant fibers are grown on agricultural land that cannot be used for feed or food production. Various fiber crops are grown around the world. For example, 264152 ha of flax and 82265 ha of hemp were harvested in 2019 (FAO, 2021). Fiber yield varies due to weather conditions and crop varieties (Riedel and Nickel, 2000). In 2019, the global flax fiber yield was $4.2\,\mathrm{t\,ha^{-1}}$, while yield of hemp and sisal fibers was both $2.5\,\mathrm{t\,ha^{-1}}$ (FAO, 2021). As a lignocellulosic material, plant fibers are mainly composed of the cell wall materials cellulose, lignin and hemicellulose.

To save land and energy, it is interesting to find other fiber sources. Fibrous residues are sometimes used in short-fiber reinforced plastics or filled plastics. An example of residue use is fibers from coconut production in nonwovens for composites (Obeng et al., 2020; Bradley and Conroy, 2019; Sergion. et al., 2005). Another example is fibers or wood flour from sawmill by-products of the wood industry in thermoplastic WPC and derived timber products (Vogt, 2006; Sörgel et al., 2006). Cellulose and lignin content and length of selected plant fibers and agricultural waste materials are shown in table 2.1.

Digestate from biogas plants is mostly used as fertilizer. In Germany, industry is urged to use more sustainable raw materials to achieve the goal of a bioeconomy (BMBF, 2020). Digestate can be a solution for fiber and composite production. Due to the lignocellulosic components, digestate can be an interesting raw material for industrial purposes. Essel et al. (2015) mixed small amounts of purified and treated digestate into the production process of medium-density fiberboard. An addition of 20 % digestate does not influencethe mechanical properties, a higher addition leadsto a decrease. In another study, digestate was added to various plastic products such as films to reduce weight and increase biodegradability (König, 2005).

Table 2.1: Cellulose and lignin content of different plants related to dry mass from (Fortea-Verdejo et al., 2017; Garrote et al., 1999; Ververis et al., 2003; Obeng et al., 2020; Bradley and Conroy, 2019; Tiefenthaller, 2006)

Fibrous part of the plant or waste material	Cellulose [%]	Lignin [%]	Fibre Length [mm]	Dry Mass [%]	Dry Mass after Digestion [%]
Cotton	90	NN	12-64	-	-
Flax	70	2	3-4	-	-
Softwood	42	29	4	-	-
Hardwood	41	19	1	-	-
Coconut Husk	-	41-46	-	-	-
Grass Silage	34	9	-	-	-
Corn Silage	21	7	-	32	11
Cattle Slurry	15-25	7-9	-	8	6
Pig Slurry	10-23	4-10	-	6	4
Solid Manure	13	17	-	25	15

Biogas technology is used worldwide to generate renewable energy through anaerobic microbial conversion of substrates fed to the digesters of these plants. Approximately 132000 technical-scale plants are currently in operation worldwide. In addition, the number of small-scale household biogas plants installed is estimated to be in the millions (Jain, 2019). In Europe, there are currently about 17000 biogas plants, of which 10000 are located in Germany (Königsberger et al., 2019). In Germany, the most commonly used substrates for biogas plants are manure from livestock with 12 % of the substrates (dry mass 12 %) and energy crops with 79 % (dry mass 17 % to 32 %), with corn silage accounting for the largest share (Torrijos, 2016; Scarlat et al., 2018; Foreest, 2012; Daniel-Gromke et al., 2017). The anaerobic degradability of substrates and their conversion rate into biogas is mainly influenced by the proportion of cell wall components and their water content. In contrast to the cell contents, the lignocellulose complexes of the cell walls can only be degraded to a small extent under the anaerobic conditions of the biogas process and are

found as fibrous materials in the aqueous suspension of the fermentation residues (digestate) together with the minerals (Schimpf, 2014).

Undegraded fiber materials from the digestate of biogas plants are potentially suitable for the production of composite materials. During anaerobic digestion, the biomass is partially degraded and the fibers are released, which corresponds to the typical biological extraction processes for fiber production. If the solids of the digestate are used for the production of fiber composites, the added value of biogas production can be increased. The biogas plant can be a kind of biorefinery because energy and industrial raw materials are produced. The fibers of the digestate are potentially very interesting raw materials for industrial use, as they can be produced in large quantities at low cost and with low energy input. So far, little is known about the quantity and quality of extractable fibers from digestate. The aim of this work is therefore to evaluate the influence of different initial substrates on fiber quantity and quality.

2.2 Materials and Methods

Samples are taken from four economically operating biogas plants in southern Germany (hereafter referred to as A, B, C, and D). The samples were taken from the three process steps: the fermenter (F1), the secondary fermenter (F2) and the storage tank (ST). A questionnaire was used to obtain further information about the biogas plant and the quantities of substrates processed.

For initial characterization, the extracted fibrous materials were analyzed using the van-Soest analysis (Van Soest and Robertson, 1970) based on DIN EN ISO 13906 and 16472 (DIN, 2008, 2006). Prior to analysis, the digestate was ground to powder with a cutting mill. The different cell wall components were determined in three steps. To obtain neutral detergent fiber (NDF), all components that do not belong to the cell wall were washed out with a so called neutral detergent solution. For the so-called acid detergent fiber (ADF), the cell wall components, except lignin and cellulose, were removed by boiling for 1 h in acid detergent solution. To obtain the so-called acid detergent lignin (ADL), cellulose was removed by exposure to 72 % sulfuric acid for 3 h. After all three steps, the samples were washed with hot water to remove the solutes and dried at 105 °C. After performing the dissolution steps, the remaining material was burned at 500 °C to obtain the ash content. The proportions of the solution fractions (NDF/ADF/ADL) were calculated using the mass of the dried material m_{dry}, the mass of the fresh material m_{fresh} and the mass of the ash after burning m_{ash} with equation (2.1).

$$\mathrm{NDF/ADF/ADL\%} = 100\frac{m_{\mathrm{dry}} - m_{ash}}{m_{\mathrm{fresh}}} \tag{2.1}$$

The exact content of cellulose, hemicellulose, and lignin were determined by subtracting the individual percentages (see eq. (2.2) - eq. (2.5)). The amount of each component is given as a ratio of dry mass (Schuldt and Dinse, 2010).

$$\text{soluble\%} = 100\% - \text{NDF\%} \tag{2.2}$$

$$\text{hemicellulose\%} = \text{NDF\%} - \text{ADF\%} \tag{2.3}$$

$$\text{cellulose\%} = \text{ADF\%} - \text{ADL\%} \tag{2.4}$$

$$\text{lignin\%} = \text{ADL\%} - \text{ash\%} \tag{2.5}$$

The dry mass content was determined according to DIN 12880 and DIN 12879. For the determination, a quantity of the respective fermentation residue was weighed and dried at 100 °C until no further mass loss was detected and then weighed again (Pfeiffer and Thrän, 2015). Equation (2.6) was used to calculate the dry mass content.

$$\text{DM\%} = \frac{m_{\text{dry}}}{m_{\text{fresh}}} 100 \tag{2.6}$$

To avoid errors related to cavities in the fiber material, the dried digestate was compacted and formed into flat tablets of 10 mm diameter at a pressure of about 10 bar. The density measurement was carried out according to EN ISO 1183-2. Instead of a density column, a row of density mixtures with n-heptane ($0.68\,\mathrm{g\,cm^{-3}}$), carbon tetrachloride ($1.59\,\mathrm{g\,cm^{-3}}$) and 1,3 dibromopropane ($1.99\,\mathrm{g\,cm^{-3}}$) was prepared in different beakers. The fermentation residue pills were immersed in the solvent mixtures one after the other until a floating state was reached. At this point, both materials have the same density (DIN, 2004).

Fiber length was determined for all digestates according to DIN 53808-1 (Saville, 1999). First, a sample of each of the digestates was placed in a glass dish and scanned. On the resulting image, all the individual fibers of each sample were traced and measured using an image processing program (Rueden et al., 2017). This way, approximately 1000 individual measurements were taken from each sample.

In addition to the fiber length, the slenderness ratio is also an important parameter. To determine this ratio, the fiber diameter must first be determined. The shapes of the digestate are very irregular and do not have a uniform round cross section. To obtain an approximate value for the slenderness ratio, the width of the fibers was measured directly from the scans. This determination was carried out on 100 individual fibers of each sample.

Using wet sieve analysis according to DIN 66165, the samples were allocated and classified according to their size (Fritsch, analysette3, Idar-Oberstein, Germany). In this way,

the proportion of potentially processable fibers was determined. Sieving was performed with water and vibration (amplitude 2 mm) at cycles of 10 min. The sieves had a mesh size of 2 mm, 1 mm, 0.5 mm, 0.25 mm and 0.125 mm and were stacked in descending order. Each sample was placed on the coarsest sieve and then sprinkled with water. The sample material remaining on the sieves was rinsed, filtered and dried. To determine the proportions of each size class, the filtration residues are weighed (Schmidt et al., 2003).

2.3 Results and Discussion

2.3.1 Description of the biogas plants and the used substrates

All four biogas plants investigated are located in southern Germany. In biogas plant A, the gas is purified and fed into the public gas grid. In plants B, C and D, the gas is used in a CHP to generate electricity. In all four selected biogas plants, mainly agricultural materials are used as substrates. The input substrates with the corresponding quantity shares of the investigated biogas plants are shown in table 2.2. The collected samples and data represent for only one month of the year.

Plant A uses only plant substrates, with chopped hop vines making up the largest portion. Plant B uses cereal whole-plant silage and manure as main substrate. Plant C is also fed mainly with animal excrement and the second main component is grass silage. Plant D is mainly fed with animal excrement (liquid and solid manure) and maize silage. Plants B to D are representatives of typical German biogas plants as described (see Section 2.1), because around 70 % of the biogas plants are fed with up to 50 % excrements (Daniel-Gromke et al., 2020). Plant A is an exception as it does not use animal excrement and only a small amount of energy crops.

In addition to the feedstocks, data were also collected on the average gas production in the biogas plants. Taking into account the density of the biogas produced, the average amount of digestate formed was calculated using the difference between the feedstock and biogas produced. The monthly digestate formation varied between 5709 $\mathrm{t\,m^{-3}}$ (plant A) and 240 $\mathrm{t\,m^{-3}}$ (plant C). Biogas plants A, B, and D separated the materials from the ST into a solid and a liquid fraction. The investigated material was the solid fraction.

Table 2.2: Relative shares of the input substrates, produced gas, and digestate in the month of sampling at the investigated biogas plants

			Biogas plants			
			A	B	C	D
Substrate fresh mass [t month^{-1}]			7377	499	290	805
Substrates [%]	Plant Silage	Maize Silage	23	7	0.06	48
		Grass Silage	5	19	43	4
		Whole Plant Silage	-	29	-	-
		Hope Vines Silage	60	-	-	-
	Solid Manure	Horse Manure	-	-	19	13
		Cattle Manure	-	35	0.1	10
		Liquid Manure	-	-	36	23
	Other Plant Material	Sugar Beet	-	2	-	-
		Digestate	-	3	-	-
		Corn Cob Grist	11	-	-	-
		Grain	-	5	2	-
		Grain Dust	-	-	-	0.7
Biogas [m^3 month^{-1}]			1263322	53465	37657	137962
Digestate fresh mass [t month^{-1}]			5709	381	240	623

2.3.2 Dry mass content

Figure 2.1 shows the dry mass content of the samples studied. The dry mass content is in the same range for the three separated ST-digestates (ST-S) for plants A, B, and D. As in the material from plant C (ST-L), the liquid fraction is not separated, dry mass content is lower. The digestate from the plants with a separation of liquid and solid fractions has a dry mass content of more than 15 %, while the material from plant C (without separation) has a dry mass content of 6 % only. However, similar dry mass contents were found in all four plants in the process steps F1 and F2, as substrate as well as digestate were treated in the same way in all plants. Standard deviation is highest in the samples obtained from plant A. The dry mass content of the solid fraction of the digestate is in the same range as the initial substrates. This is caused by the separation, because in general, the fermentation decreases the dry mass content (see Table 2.1) (Zethner et al., 2002). The comparison between the separated and unseparated digestate shows that the separation increases the dry mass. For the yield of potential fibers, separation is a helpful process

step. If only dry mass content is considered, fiber recovery from the initial substrate would be preferable. Under these circumstances, however, a combination of energy extraction and industrial raw material is not possible.

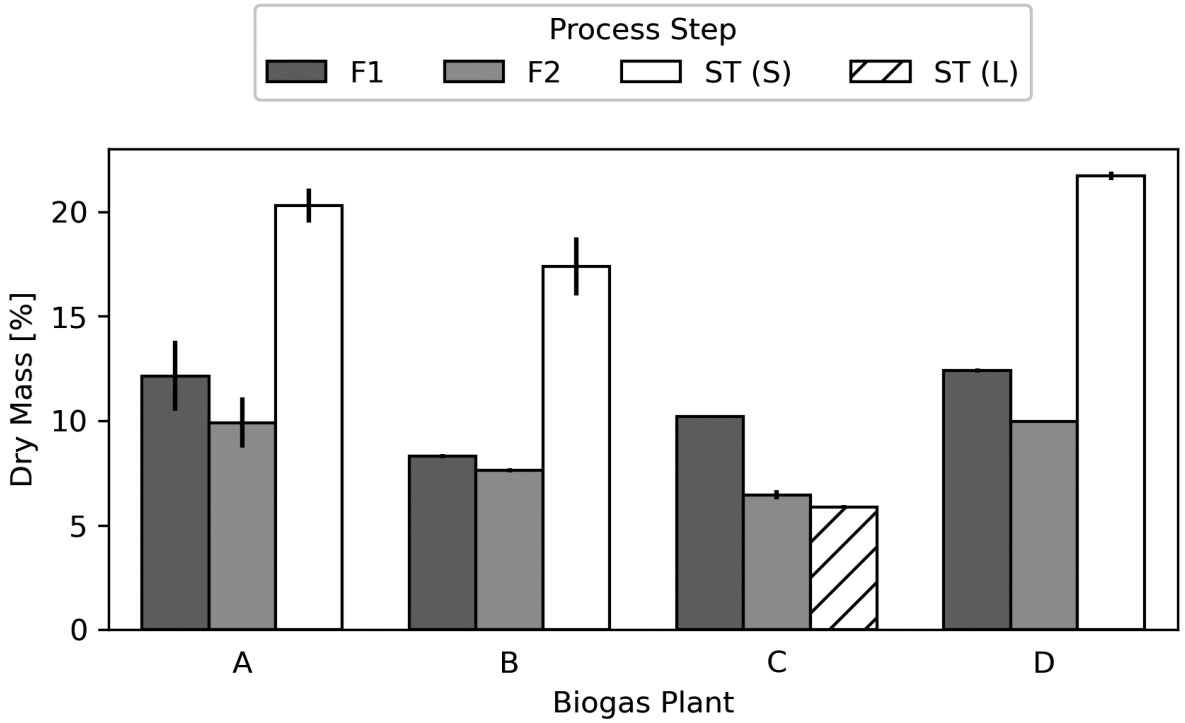

Figure 2.1: Dry mass content in % of the digestate samples from the investigated biogas plants A-D in the different process steps F1, F2, ST separated (S) and not separated (L)

2.3.3 Cell wall components

Figure 2.2 shows the content of the cell wall components cellulose and lignin, related to the dry mass content. To evaluate the fiber quality, shares of cellulose and lignin are most important. In all plants, cell wall content increased during the process, with a higher cell wall content in ST in comparison to F1 samples. The lowest cell wall content was found in D-F1 with 45 %.The cellulose content of all samples examined decreases from F1 to F2 and increases again in ST. However, the trend was less clear for the lignin content. In the material from ST, highest lignin content was found in plant B with 37 %.

Compared to the values of the initial substrates (literature data, see Table 2.1), the lignin content of the digestates is higher at all process stages and for all plants. The cellulose content of the digestates is similar compared to that of the silages, but clearly higher than that of the animal excrement. This fact is also due to the degradation in the biogas plant. The high proportion of cell wall components is related to their impeded degradation in the fermentation. The remaining biomass is degraded, therefore the proportion of cell wall substance increases. The reason is, that cell wall components are hard to degrade by the

microorganisms in the fermentation (Schimpf, 2014). Since the content of cellulose and lignin is an important characteristic for natural fibers, the use of digestate is preferable to the use of the initial substrates. The proportions of cellulose and lignin are in the range of wood fibers (see Table 2.1) in all the samples from process step ST. However, compared to wood fibers, their cellulose content is lower and their lignin content is higher. For a possible application of the digestate fibers in composites, it is positive that the digestate fibers have a similar composition to wood fibers, which are already used (Vogt, 2006).

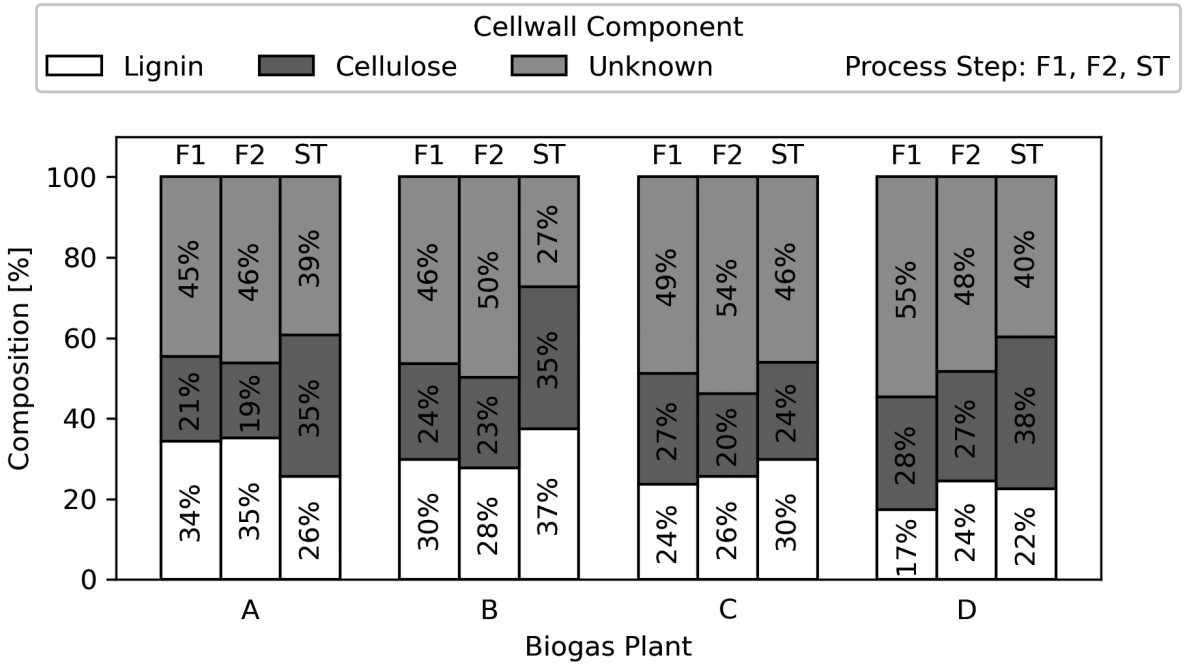

Figure 2.2: Cell wall composition of the investigated samples of the biogas plants A – D in the process steps F1, F2, and ST related to dry mass

2.3.4 Wet sieve analysis

Figure 2.3 shows the amount of material in the sieves after wet sieving. The percentage of digestate over 1 mm (1 mm and 2 mm mesh size) accounts for more than half of the total fermentation residues in the plants A, B, and D. This result was the same for all process steps and for all three plants. The materials from biogas plant C have a more uniform distribution across all sieves. Only for C-F1 the share of particles on the 2 mm-sieve is slightly higher.

The proportion of 2 mm fibers decreased from F1 to ST. While more than 80 % coarse particles were found in ST, F1, and F2 contained 70 % and 60 %, respectively. In the case of C, approximately 50 % of coarse particles were found for F1, where as for the other two process stages, only approximately 20 % were found. For B, the share of coarse particles varied between 76 % (F1) and 47 % (ST) depending on process step. D did not show such

a clear decrease, as more fibers were found in ST with 55 % than in F2 with 47 %.

The lower content of coarse particles in process step ST compared to F1 is caused by the duration of the digestion. The longer the materials remain in the digestion process, the more the plant materials are degraded. The differences between the biogas plants are caused by the substrates used. Plant B and D were fed with a high proportion of maize silage and plant A shows a high proportion of ensiled hop vines. Both are high-fiber feedstocks, as indicated by literature data in Table 2.1. Plant C contains a high proportion of manure (liquid and solid) and has fewer coarse particles.

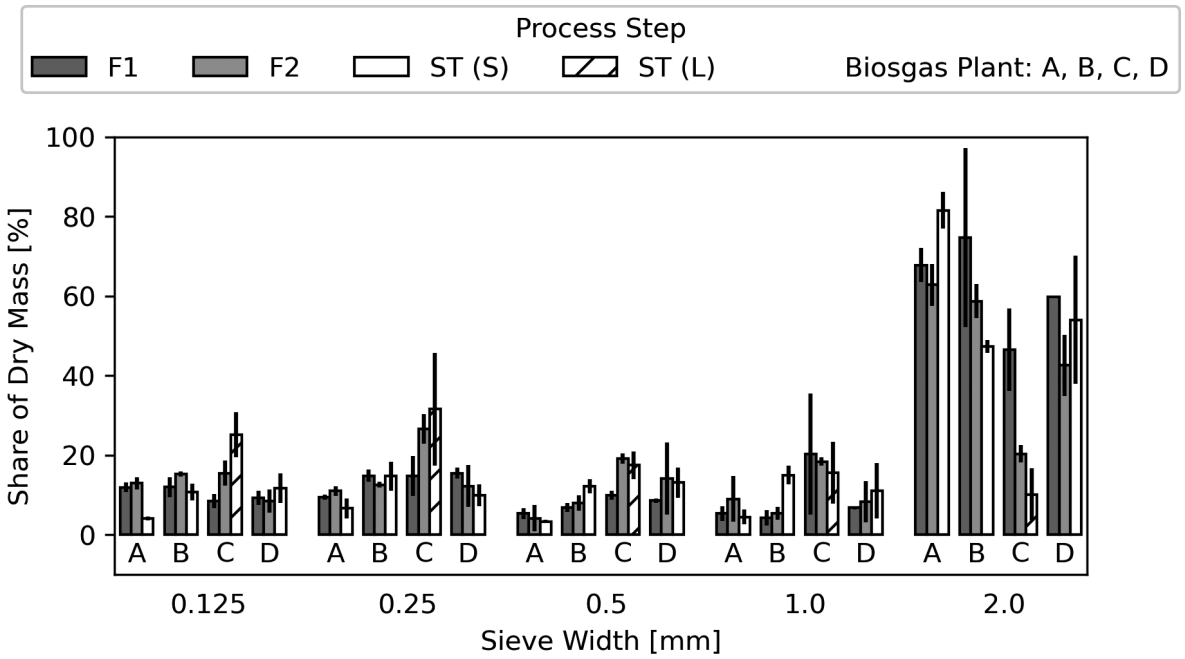

Figure 2.3: Share of the digestate samples in sieves with different sizes after wet sieving. Biogas plants A - D in the process steps F1, F2, and ST, separated (S) and not separated (L) related to dry mass.

2.3.5 Fiber Geometry

Results of the fiber measurement are presented in Figure 2.4. Classified by process stage, the fiber length distribution and the degree of slenderness are shown for all studied fermentation residues. Before data analysis, outliers were identified based on the interquartile range and excluded (Frigge et al., 1989; Shevlyakov et al., 2013). In the figures, only the density function of the length and the slenderness ratio are shown for readability. For fiber length, the functions of the samples from F2 and ST show clear peaks and a small distribution. The material from F1 has a wider fiber length distribution. For the F1 samples from all plants, no clear differences in length distribution were found. The mean fiber length of all samples is approximately 3 mm, and the upper limit is 8 mm to 9 mm.

In the F2 samples, larger differences in length distribution were found, with a mean fiber length of 4 mm for plant A and a mean fiber length of 2 mm to 3 mm for the other plants. The same applies to the upper limit. For plant C it is 6 mm and for plant A 12 mm. The ST-digestates have a similar distribution, except for A-ST. The mean value of C-ST is the lowest with 1.6 mm, while the others are in the range of 2 mm to 3 mm. In addition to the mean value, the upper limit is also striking. The lowest maximum fiber length was found for C-ST with 4.2 mm, the highest is found for A-ST with 9.5 mm.

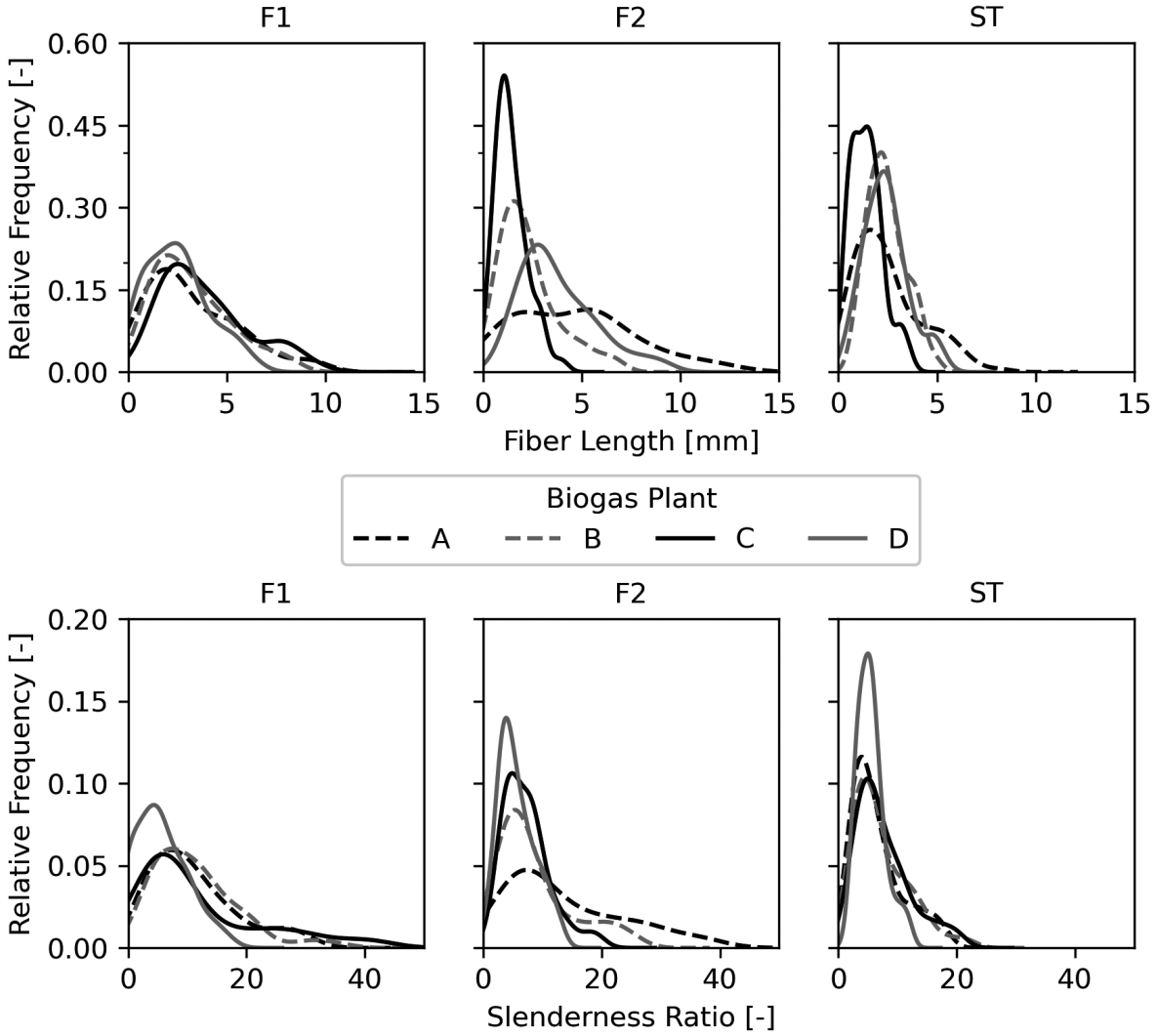

Figure 2.4: Slenderness-Slenderness and Length deviation of the samples from the four biogas plants in the process steps F1, F2, and ST. The three upper diagrams show the length deviation, and the lower diagrams show the slenderness-slenderness deviation

The mean and maximum values of the slenderness ratio of all samples increased from F1 to F2, but decreased in the last process step ST. D-F1 had the lowest mean slenderness ratio, which is 5, while the highest value of 10 was found for B-F1. The fibers of A-F1 showed a wider distribution of the slenderness ratio compared to the other samples. Unlike the others, the function has no peak at one slenderness ratio. The samples from

process step ST showed a more equal distribution compared to the previous process steps. The median of all the plants is 5 to 6, but the maximum values show larger differences. The highest slenderness ratio of the samples D-ST is 13 and not approximately 20 as compared to the other plants.

D and C are the plants with the highest proportions of liquid manure, which could potentially explain the difference in the slenderness ratio. The fact that D is the only plant using cereal dust is also an indication of this. In addition, a higher proportion of maize silage is used compared to the other plants. This is also likely a reason for the different geometry of the fibers. A is the only plant that contains ensiled hop vines, and in a comparatively very high proportion. The presence of the vines also explains the fact that the length and the slenderness ratio in the F2 differ from those of the other plants. The hop vines are the only lignified biomass among the substrates. Due to the different composition, the degradation also differs from that of the less lignified substrates. As with the slenderness ratio, the different substrate composition may cause different degradation and, thus, also affect the length distribution during the biogas process. However, compared with the common natural fibers, the fibers (see Table 2.1) are rather short and the length is more similar to the fibers of softwood.

For all four plants, most of the fibers have a mean slenderness ratio of at least 5. According to the common definitions for fibers, a large part of the fermentation residue particles therefore counts as fibers. On the other hand, they cannot be called textile fibers suitable for textile production, as their slenderness ratio is well below 1000:1. Thicker and short fibers can be used for the nonwoven production (Russell, 2006; Fuchs and Albrecht, 2012). The fermentation residues meet all the requirements of a fiber and a suitable fiber for nonwoven production. Nonwovens are a common reinforcement for composites (Schürmann, 2007). Short fibers and particles like sawmill by-products are commonly used for composites (Vogt, 2006). For these reasons the use of digestate should also be possible.

2.3.6 Density

The density of natural fibers is usually given as $1.5\,\mathrm{g\,cm^{-3}}$. Table 2.3 shows the density values of all studied digestate samples. All fermentation residues studied are close to $1.5\,\mathrm{g\,cm^{-3}}$ and are, thus, comparable to other natural fibers. The density is also in the same range independent of plant and process stage. The variations observed are caused by the substrate composition; no trend was observed with respect to the process stage.

Table 2.3: Density of the dried digestates from the four biogas plants A-D and the three process steps F1, F2, and ST

Biogas Plant		A			B	
Process Step	F1	F2	ST	F1	F2	ST
Density [g m^{-3}]	1.51	1.53	1.53	1.55	1.54	1.47
Biogas Plant		C			D	
Process Step	F1	F2	ST	F1	F2	ST
Density [g m^{-3}]	1.54	1.54	1.57	1.54	1.54	1.51

2.3.7 Output of usable fibers from the digestate

Using the information obtained from the digestate, listed in Table 2.1 and the fractions of the sieves with 1 mm and 2 mm mesh size, the number of usable fibers is estimated. The data of process step ST is used for the calculations because this material is eligible for production. The biogas plants are fed with plant-based biomass and excrements, so the influence of these substrate classes on the fiber output is of interest. Figure 2.5 shows the relationship between the amount of animal excrement and the ratio of potentially usable fibers in the dry mass of the digestate.

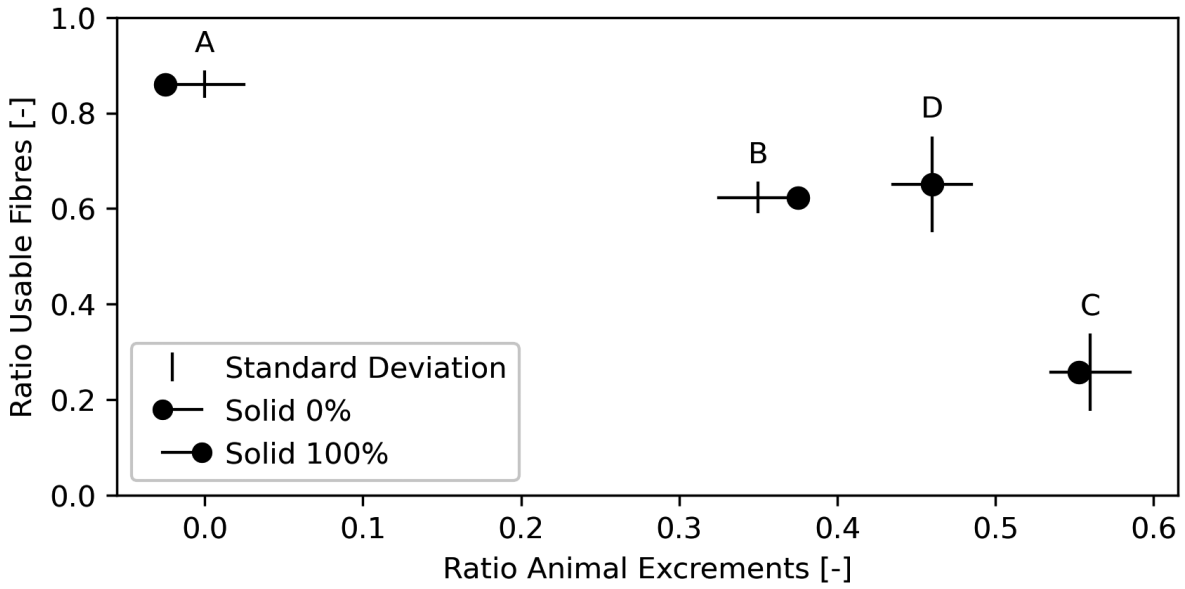

Figure 2.5: Relationships between quantity of excrements in the substrate and the potential fiber output in the dry mass for the ST samples of the four biogas plants A-D

With 86 %, plant A, the plant without animal excrements, has the highest ratio of potentially usable fibers in the dry mass. The lowest ratio of usable fibers (25 %) was found for plant C. The difference between plant B and D is small (62 % and 65 %). A higher ratio

of excrements leads to a higher deviation of the fiber output, compared with plant-based substrates. The more excrement, especially liquid excrement, is included in the substrate mix, the lower is the ratio of usable fibers. Since animal excrement is one of the main initial substrates in German biogas plants (Daniel-Gromke et al., 2017), the number of plants with a high output of fibers seems to be low.

2.4 Conclusions

The digestate, according to the general definition, is a fiber with properties similar to those of wood fibers. The initial biogas substrate does not affect the fiber quality, but the quantity of potential fibers. A high proportion of (liquid) animal excrement reduces the quantity of fibers, however, excrement is commonly used. A long time in the biogas plant results in shorter fibers, but the quality (cell wall content) increases. The degradation during the anaerobic digestion cannot fully replace fiber extraction. Because of the high output and the similarity to wood fibers, digestate is an option for composites.

References

Ahmed, Z., Akhter, F., 2001. Jute retting: an overview. Online Journal of Biological Science 7, 685–688.

AVK, 2013. Handbuch Faserverbundkunststoffe/Composites. Springer.

BMBF, 2020. National bioeconomy strategy. `https://www.bmbf.de/SharedDocs/Publikationen/de/bmbf/FS/31617_Nationale_Biooekonomiestrategie_Langfassung_en.pdf?__blob=publicationFile&v=5` visited on 23.06.2022.

Bradley, W.L., Conroy, S., 2019. Using Agricultural Waste to Create More Environmentally Friendly and Affordable Products and Help Poor Coconut Farmers. E3S Web of Conferences 130, 1–10.

Crowther, J. (Ed.), 1995. Oxford Advanced Learner's Dictionary of Current English. Oxford Universty Press.

Daniel-Gromke, J., Rensberg, N., Denysenko, V., Barchmann, T., Oehmichen, K., Beil, M., Beyrich, W., Krautkremer, B., Trommler, M., Reinholz, T., Vollprecht, J., Rühr, C., 2020. Optionen für Biogas-Bestandsanlagen bis 2030 aus ökonomischer und energiewirtschaftlicher Sicht. Umweltbundesamt.

Daniel-Gromke, J., Rensberg, N., Denysenko, V., Stinner, W., Schmalfuß, T., Scheftelowitz, M., Nelles, M., Liebetrau, J., 2017. Current developments in production and utilization of biogas and biomethane in germany. Chemie Ingenieur Technik 90, 17–35.

DIN, 2004. DIN EN ISO 1183-2 Kunststoffe- Verfahren zur Bestimmung der Dichte von nicht verschäumten Kunststoffen.

DIN, 2006. EN ISO 16472:2006 Animal feeding stuffs – Determination of amylase-treated neutral detergent fibre content (aNDF).

DIN, 2008. EN ISO 13906:2008 Animal feeding stuffs – Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents.

Essel, R., Breitmayer, E., Carus, M., Pfemeter, A., Bauermeister, U., 2015. Stoffliche Nutzung lignocellulosehaltiger Gärprodukte für Holzwerkstoffe aus Biogasanlagen. Nova-Institut.

FAO, 2021. Data - crops and livestock products - fiber plants. `https://fenixservices.fao.org/faostat/static/bulkdownloads/Production_Crops_Livestock_E_All_Data.zip` visited on 12.1.2021.

Foreest, F., 2012. Perspectives for biogas in Europe. The Oxford Institute for Energy Studies.

Fortea-Verdejo, M., Bumbaris, E., Burgstaller, C., Bismarck, A., Lee, K.Y., 2017. Plant fibre-reinforced polymers: where do we stand in terms of tensile properties? International Materials Reviews 62, 441–464.

Frigge, M., Hoaglin, D.C., Iglewicz, B., 1989. Some implementations of the boxplot. The American Statistician 43, 50–54.

Fuchs, H., Albrecht, W. (Eds.), 2012. Vliesstoffe. Wiley-VCH.

Garrote, G., Dominquez, H., Parajo, J.C., 1999. Hydrothermal processing of lignocellulosic materials. Holz als Roh- und Werkstoff 57, 191–202.

Gessner, W., 1955. Naturfasern Chemiefasern. Fachbuchverlag Leipzig.

Jain, S., 2019. Global Potantial of Biogas. The World Biogas Association.

König, Ulich; Fudel, A., 2005. Verfahren zur Herstellung von Naturfasern aus Biogasanlagen und deren Verwendung. DE 10 2005 034 586 B3.

Königsberger, S., Deorte, M., Reuland, G., 2019. EBA Statistical Report 2018. European Biogas Association.

Obeng, G.Y., Amoah, D.Y., Opoku, R., Sekyere, C.K.K., Adjei, E.A., Mensah, E., 2020. Coconut wastes as bioresource for sustainable energy: Quantifying wastes, calorific values and emissions in ghana. Energies 13.

Pfeiffer, D., Thrän, D. (Eds.), 2015. Messmethodensammlung Biogas. DBFZ.

Riedel, U., Nickel, J., 2000. Konstruktionswerkstoffe aus nachwachsenden rohstoffen (Bio-Verbunde), in: Tagungshandbuch - 3. Internationale AVK-TV Tagung für Verstärkte Kunststoffe und Duroplastische Formmassen, pp. 493–498.

Rueden, C.T., Schindelin, J., Hiner, M.C., DeZonia, B.E., Walter, A.E., Arena, E.T., Eliceiri, K.W., 2017. Imagej2: Imagej for the next generation of scientific image data. BMC Bioinformatics 18.

Russell, S.J., 2006. Handbook of Nonwovens. Woodhead.

Salit, M.S., Jawaid, M., Yusoff, N.B., Hoque, M.E. (Eds.), 2015. Manufacturing of Natural Fibre Reinforced Polymer Composites. Springer International Publishing.

Saville, B., 1999. Physical Testing of Textiles. Woodhead.

Scarlat, N., Dallemand, J.F., Fahl, F., 2018. Biogas: Developments and perspectives in europe. Renewable Energy 129, 457–472.

Schenek, A., 2001. Naturfaser-Lexikon. Deutscher Fachverlag.

Schimpf, U., 2014. Enzymatischer Abbau des Lignocellulosekomplexes in Energiepflanzen unter besonderer Berücksichtigung der Silierung und der Biogasproduktion. Ph.D. thesis. Humboldt-Universität zu Berlin.

Schmidt, P., Körber, R., Coppers, M., 2003. Sieben und Siebmaschinen. Wiley-VCH.

Schuldt, A., Dinse, R., 2010. Übungen zur Tierernährung im Rahmen des Moduls Tierernährung und Futtermittelkunde.

Schürmann, H., 2007. Konstruieren mit Faser-Kunststoff-Verbunden. Springer.

Sergion., M., Terrones, L.A.H., Lopes, F.P., d'Almeida, J.R.M., 2005. Mechanical Strength of Polyester Matrix Composites Reinforced with Coconut Fiber Wastes. Revista Matéria 10, 571–576.

Shevlyakov, G., Andrea, K., Choudur, L., Smirnov, P., Ulanov, A., Vassilieva, N., 2013. Robust versions of the tukey boxplot with their application to detection of outliers, in: International Conference on Acoustics, Speech and Signal Processing, IEEE. pp. 6506–6510.

Sörgel, C., Mantau, U., Weimar, H., 2006. Standorte der Holzwirtschaft – Aufkommen von Sägenebenprodukten und Hobelspänen.

Tiefenthaller, F., 2006. Futterwerttabelle für Wiederkäuer. Landwirtschaftskammer Oberösterreich Abteilung Tierproduktion/Referat Fütterung.

Torrijos, M., 2016. State of development of biogas production in europe. Procedia Environmental Sciences 35, 881–889.

Van Soest, P.J., Robertson, J.B., 1970. Systems of analysis for evaluating fibrous feeds, in: Pigden, W.J., Balch, C.C., Graham, M. (Eds.), Standardization of Analytical Methodology for Feeds, pp. 49–60.

Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., Santas, R., 2003. Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Industrial Crops and Products 19, 245–254.

Vogt, D., 2006. Studie wood plastic composites, Holz-Kunststoff-Verbundwerkstoffe. Landwirtschaftsverlag.

Zethner, G., Pfundtner, E., Humer, J., 2002. Qualität von Abfällen aus Biogasanlagen. Umweltbundesamt.

3 Comparison of fibers from hop rich biogas digestate with natural fibers as raw material for composites

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Abstract

Fibrous Material extracted from biogas digestate is investigated as a possible raw material for composites. Digestate is a by-product of every biogas plant and consist mostly water, undegraded plant biomass and minerals. On the other hand natural fibers and fibrous by-products are increasingly used as fiber component, especially in short-fiber reinforced plastics. the fibrous solid fraction of biogas digestate can be another alternative fiber source. The properties are decisive to determine the suitability of raw materials. Information on the length and constituents of woody and various non-woody plants can be found in the literature. In the study presented, fibrous solids obtained from digestate with a high contend of hop vines are investigated. Fiber length and cell wall matter content are analyzed to characterize the digestate. The results are compared with classical plant fibers. It turns out that the investigated fibrous solids from digestate have a very inhomogeneous length distribution. The equalization can be achieved through an additional process step. The proportion of cell wall matter is comparable to that of woody

plants and various non-woody plants. The fibers extracted from hop digestate can be regarded as an ecological and favorable alternative to wood fibers in composite materials.

Keywords: Biocomposites, Biogas digestate, Natural fibers, Waste

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3.1 Introduction

The world fibre production of synthetic and natural fibers in genaral shows an increase of 35000000 t in the last ten years (DNFI, 2018). The increasing use of composites concerns both high-performance fibers and natural fibers. The demand of carbon composites increased by 10 % from 2018 to 2019 (Sauer, 2019). The production of natural fibers has increased 4 times in 10 year, only for application in automotive interieur (Siebel, 2020). Natural fiber plant need agricultural land to grow. In 2019, 4165168 ha of fiber plants are cultivated world wide and 291742 ha of them in europe (FAO, 2021). This land can not be used for growing food. One solution to solve this problem is to use waste and byproducts instead of new material. This study deals with an alternative material for fiber composites.

In fiber composites, fibers are combined with a plastic matrix. In (Campbell, 2010) it is said that composites show beneficial properties that the individual components do not exhibit. The fibers are divided into short fibers, long fibers and continuous fibres, depending on their length. The fibers can be embedded individually into the matrix or can first be formed into a textile. The task of the fibers is to carry the load. The load is introduced into the fibers through the matrix. Besides transforming the limp fibers/textiles into a rigid material, the matrix protects the fibers from environmental influences (Campbell, 2010).

Crowther (1995) defines fibers generally as thread-like structures. The length to diameter ratio of fibers in technical application is at least 3:1; In the textile field the ratio can be more than 1000:1, see (Schenek, 2001). Natural fibers are defined in DIN 60001-1 as "natural, linear structures which can be processed into textiles. They can be obtained from plant parts or form the pelage of animals, or be obtained from the cocoons of silk moths, or be of mineral, natural origin" (DIN, 2001). Plant fibers are classified into the following groups: Hard fibers, bast fibers, seed fibers and wood fibers. Examples for the different fibre types are given in the following: Hard fibers are the fibers of the leaf sheath of the sisal plant (*Agava Sisalana*). Cotton (*Gossypium ssp.*) is a seed fiber and is processed in particular into clothing. Bast fibers are obtained from the stems of plants. Flax (*Linum Usitatissimum*) fiber is a representative of bast fibers native to

Central Europe (DIN, 2001; Kozlowski et al., 2005; Schenek, 2001). Wood fibers can be obtained from soft- and hardwood. They are used in middle density fiber board (MDF) (Essel et al., 2015). To obtain plant fibers, mechanical and chemical processes are used to extract the fibers from the plant. Plant fibers have different lengths depending on their plant of origin. Some examples of the length of single fibers from various plants are presented in table 3.1 (Berger et al., 2011; Riley, 2012). Bundles of single fibers are called technical fibers and can reach lengths of over one meter (Berger et al., 2011). The typical density of plant fibres is around $1.5\,\mathrm{g\,cm^{-3}}$, examples are flax with $1.5\,\mathrm{g\,cm^{-3}}$ and Sisal which differs between $1.3\,\mathrm{g\,cm^{-3}}$ and $1.45\,\mathrm{g\,cm^{-3}}$ (Cherif, 2011).

Table 3.1: Length of plant fibers from (Berger et al., 2011; Riley, 2012)

Plant	Botanical Name	Length [mm]
Sisal	*Agava Sisalana*	3 - 4
Flax	*Linum Usitatissimum*	3 - 4
Cotton	*Gossypium ssp.*	12 - 64
Softwood	-	3 - 4
Hardwood	-	1 - 1.5

The main component of plant fibers is cell wall. The largest proportion of the cell wall is cellulose, the other parts are lignin and hemicellulose. Table 3.2 shows the cellulose and lignin content of various plant fibers. In Fortea-Verdejo et al. (2017) it is written that cotton has an extremely high cellulose content of up to 90 %. The value for wood fibres is an average value, the exact value depends on the wood type, see (Garrote et al., 1999). One possibilty to detect the chemical composition of fibres is the fourier transform infrared spectroscopy. Lignin is typically represented by a signals of $1750\,\mathrm{cm^{-1}}$ to $1150\,\mathrm{cm^{-1}}$(Galletti et al., 2015), cellulose is represented due to signals in the range of $3660\,\mathrm{cm^{-1}}$ to $2900\,\mathrm{cm^{-1}}$ and $1630\,\mathrm{cm^{-1}}$ to $900\,\mathrm{cm^{-1}}$ (Hospodarova et al., 2018; Cichosz and Masek, 2020). To determine hemicellulose a peek around $1000\,\mathrm{cm^{-1}}$ can be used (Galletti et al., 2015).

In fiber composites, natural fibers are increasingly used as an alternative to glass fibers. The reasons for the substitution is described in different studies. On the base of there low density, natural fibers have good specific properties. Natural fibers are processed into interior components for the automotive industry. This saves energy due to the low weight and reduces the CO_2 impact (Riedel and Nickel, 2000; Cantero et al., 2003). Another example are the so-called WPC. Wood flour and wood fibers are mixed with thermoplastics and processed into injection-molded parts, which are often used outdoors as decking boards (Barbos et al., 2020; Vogt, 2006). In order to improve the utilization of natural resources, the upcycling of waste materials is a field of growing interest. Wood

and natural fibers are specially grown for fiber composites, causing reduction of land for food production (Lütz et al., 2019). In the field of composites investigations into the use of recycled fiber or plastics, waste from natural fiber production, and other agricultural wastes are intensified (Ramamoorthy et al., 2014; Macatangay et al., 2012). Some examples for alternative materials in composites are feathers (Mishra and Nayak, 2010), coconut waste (Sergion. et al., 2005; Bradley and Conroy, 2019) or hair from coffieurs (Eshwara et al., 2018). In the meantioned studies is is said, that the materials are choosen because of their high amount and beause they are regionally available. This makes the raw materials a sustainable alternative.

Table 3.2: Cellulose and lignin content of different plants from (Fortea-Verdejo et al., 2017; Garrote et al., 1999; Ververis et al., 2003)

Plant	Cellulose [%]	Lignin [%]	Hemicellulose [%]
Cotton	90	NN	NN
Cereal straw	38-45	12-20	15-31
Rice straw	36-47	10-24	19-25
Softwood (Pine)	42 29	26	
Hardwood (Birch)	41	19	36
Flax	70	2	19

Biogas technology is widespread worldwide with about 132000 plants and more than 10 % of the world's biogas plants are located in Europe (Jain, 2019; Königsberger et al., 2019). The substrates used are mainly agricultural products. Depending on used substrate for the anaerobic digestion the digestate has different structures. Besides water and minerals the digestate largely consists of nondegraded lignocellulosic plant biomass. The cell wall components cellulose and lignin are difficult to decompose, this is explained in detail in (Schimpf et al., 2013). For this reason, it is obvious to consider digestate as a fiber raw material. Currently, digestate is returned to the fields as farm fertilizer. There are already approaches to in- crease the added value by processing digestate into fibrous material, which can be mixed into wood fiberboard and achieves a maximum content of 30 % this process (Essel et al., 2015).

Digestate represents potentially fibrous biomass that is not used for any industrial processing. No investigation of digestate with respect to its usability in composites has taken place up to now. In this work, the qualification of the digestate as a fiber raw material is investigated. The necessity, as well as the influence, of processing will be considered. Digestate with lignocellulosic starting substrate is expected to have a high content of fibrous material. In the presented work, digestate from a biogas station using high amounts of hop residues with a substantial lignocellulose content has been selected. Hop belongs to the hemp family and was used to gain fibers until the 1950s. The fibers were for example

raw material for the paper industry (Ulrich, 1956; Hanausek, 2012). The aim of the utilization of the fermentation residues is to increase the value-added chain of the biogas plants. By utilizing the digestate, food, energy and materials can be produced from a single harvest. The presented study serves to gain first basic knowledge about the fibers obtained from hop-containing digestate.

3.2 Material and Methods

3.2.1 Material

The used digestate originates from a biogas plant located in Germany's largest hop-growing region, the Hallertau. The plant has a primary digester volume of 6000 m3 and operates at a temperature of 43 °C with a daily substrate feeding of 244532 kg. The hydraulic retention time is 83 days for the primary digester. The resulting biogas is upgraded to natural gas quality and the yield is 25000 cm^{-1} methane per day. The used substrate is a mixture of 75 % chopped hop vines and 25 % corn silage, grain whole plant silage and corn cob mix. The solid part of the digestate, which was taken after separation with screw press, is used for the experiments.

The digestate was treated in two different ways. In the first variant the digestate was only dried at room temperature with circulating air (called d-untreated) and in the second variant it was additionally cleaned. For the secound variant, the digestate was sanittized with 3 % hydrogen peroxide solution (H_2O_2) at a dosage of 1 L kg^{-1}.

For actual cleaning, five washing passes were performed in an ultrasonic bath (40 kHz). The cleaned digestate was then sieved with a sieve opening of 0.25 mm (called d-treated). Figure 3.1 shows a comparison of the untreated and treated digestate. The digestate has a distinct elongated, slender shape and is obtained from lignocellulosic substrate, it will be referred as fiber in the following. The influence of preparation on fiber quality will be investigated. Commercially available flax fibers are used as comparative material.

(a) Before cleaning with highlighted dirt particles

(b) After cleaning

Figure 3.1: Digestate

3.2.2 Methods

Sieving of the digestate fibers

By sieving the dried digestate, an initial rough characterization of the size fractions is made. It is determined which fraction of the digestate is suitable for further processing in the fiber composite sector. Four sieve with different opening sizes are used (3.0 mm, 2.0 mm, 1.0 mm, 0.5 mm), each is moved gently for 30 seconds, by hand at about 2.5 Hz to 3.0 Hz. The fiber content of each sieve, as well as the bottom is determines by weighting. The sieving is repeated three times for each variant.

Fiber length determination

For a reproducible production of composites from the digestate, knowledge of length range is crucial. Dust and fine particles should not be measured as they are not used as fibers. For this reason, the fibers from the sieved fractions (content of the sieves with 1.0 mm to 3.0 mm opening size) are measured. The measurement is based on DIN 53808-1:2003-01. A material sample is taken and the length of each individual fiber is determined with a ruler. A measurement must have an amount of at least 100 fibers. To ensure that enough fibres are measured, the whole sieved material was measured. In addition to the length the aspect ratio (length/diameter) is calculated from the cleaned digestate by measuring the diameter.

Determination of the density

The Density is determined in comparison to other media. To measure the materials density a ground sample of digestate is pressed into a pill. The density is approximated by comparing it to solvents with known density. The following chemicals are used: n-heptan ($0.68\,\mathrm{g\,m^{-3}}$), carbon tetrachloride ($1.59\,\mathrm{g\,m^{-3}}$) and 1,3-dibrompropane ($1.99\,\mathrm{g\,m^{-3}}$). These three solvents are mixed to get a row of densities. The digestate pill is placed into a test glass with a solvent. When the material sinks to the bottom of the test glass the density is higher compared to the solvent, when it swims the density is the same and when it stays on the surface the density is lower than the solvent density. A difference of $0.01\,\mathrm{g\,m^{-3}}$ is chosen to get a precise result.

Determination of the chemical composition - FTIR

To determine the chemical composition of the digestate material the fourier-transform infrared spectroscopy is used. Infrared (infrared (IR)) spectra were recorded on a Perkin Elmer "FT-IR/NIR Spectrometer Frontier" with a "GladiATR" from PIKE technologies in the range from $4000\,\mathrm{cm^{-1}}$ to $400\,\mathrm{cm^{-1}}$ and a with resolution of $4\,\mathrm{cm^{-1}}$. Both, background and sample were measured with each 24 scans. The spectra were baseline

corrected. A software named "Spectrum IR", provided by Perkin Elmer, was used to analyze the data. Both samples, the treated and untreated digestate was analyzed.

Determination of the ingredients - Feed analysis according to van SOEST

In order to be able to compare the fermentation residues with the previously used plant fibers and wood, the proportion of cell wall constituents is determined. For the determination, the feed analysis according to van Soest is used (Van Soest and Robertson, 1970). The digestate material is ground and washed out in three successive steps in different solvents. Flax fibers are also analyzed to verify the method. The determination is based on DIN EN ISO 13906 and 16472 (DIN, 2008, 2006). The analysis is done with the Gerhardt-FibreBag system (see Fettweis and Kühl (2010)). The analysis steps are shortly discribed in the following: In the first step, a neutral detergent solution is used to dissolve all the non-cell wall components. The remaining part is called NDF. The samples are washed out with hot water and dried at 105 °C. Subsequently, acid detergent solution is used for dissolving everything except cellulose and lignin. The remaining part is called ADF. For this purpose, the samples remain in boiling acid dertegent solution for one hour. The samples are washed out again and dried. Exposure to 72 % sulfuric acid for three hours removes the cellulose as well. The remaining part is called ADL. The samples are dried again. In one batch, five replicates each containing 1.0 g of ground fiber were added to 360 ml of the respective solution. After performing the solution steps, the remaining material is burned at 500 °C to get the ash content. The proportions of the structural component fractions (NDF / ADF / ADL) can be calculated. The equation (3.1) is used for calculating the NDF %. The calculation of ADF and ADL are following the same approach.

$$\mathrm{NDF\%} = 100\frac{m_{\mathrm{dry}} - m_{ash}}{m_{\mathrm{fresh}}} \tag{3.1}$$

The exact contents of cellulose, hemicellulose and lignin can be determined by subtracting the individual percentage (see in equation (3.2) - (3.5)).

$$\mathrm{soluble} = 100\% - \mathrm{NDF\%} \tag{3.2}$$

$$\mathrm{hemicellulose} = \mathrm{NDF\%} - \mathrm{ADF\%} \tag{3.3}$$

$$\mathrm{cellulose} = \mathrm{ADF\%} - \mathrm{ADL\%} \tag{3.4}$$

$$\mathrm{lignin} = \mathrm{ADL\%} - \mathrm{ash\%} \tag{3.5}$$

3.3 Results

3.3.1 Sieving fractions

The table 3.3 presents the percentages of the four different size categories.

Table 3.3: Sieve fractions in percentage of dry fibers

Sieve	Opening [mm]	Mean [%]	Std. Dev. [%]	Mean [%]	Std. Dev. [%]
1	≥ 3.0	43.2	13.3	57.5	4.5
2	≥ 2.0	30.5	2.2	20.4	2.6
3	≥ 1.0	20.1	7.1	16	1.4
4	≥ 0.5	4.9	3.2	4.8	0.6
floor	< 0.5	1	1	1.4	0.3

The size range > 3 mm is the largest proportion in the untreated and treated digestate. Due to the washing of the digestate the finest particles are already removed. As the result the proportion of coarser material increases by 14 %. Overall, the distribution of the various particle sizes is comparable to that of the untreated digestate. It is noticeable that the scattering of the values is reduced due to the washing. The coarse fraction (sieve 1) shows a standard deviation of 13.3 % for d-untreated and 4.5 % for d-treated. Because of the removals of the small particles due to the wahing process the scattering of the whole matieral is reduced.

3.3.2 Fibre Length

The figure 3.2 shows the fiber length of the different treated digestates. The distribution of the fibres among the different length fractions is approximately the same in both variants. The fiber length of the untreated digestate ranges from 1 mm to 42 mm. The treated digestate has a fiber length from 1 mm to 46 mm. The average fiber length of the untreated digestate is 9.75 mm compared to the washed digestate with 12 mm. This difference is explained by the low percentage of fine fibers (< 2 mm). The higher average fiber length of the treated digestate can be attributed to the washing process. The higher average fibre length of the treated digestate as well as the larger proportion of fibers over 18 mm can be attributed to washing processes. The ustrasonic bath shakes off the dust and other small particles which adhere to the longer particles. The sieving, which is included in the washing process, leads to a removal of the small particles with the washing water. Because all small particles are gone, the middle fibre length is higer for the treated material. The rather high scattering of the values is common in the field of natural fibers. Compared to common natural fibers like flax and cotton, digestate fibers are shorter (compare table 3.1). A large proportion of the digestate fibers are within a length range of 4 mm to

11 mm. They are in a similar range as the wood fibers used for WPC with a length between 3 mm and 10 mm.

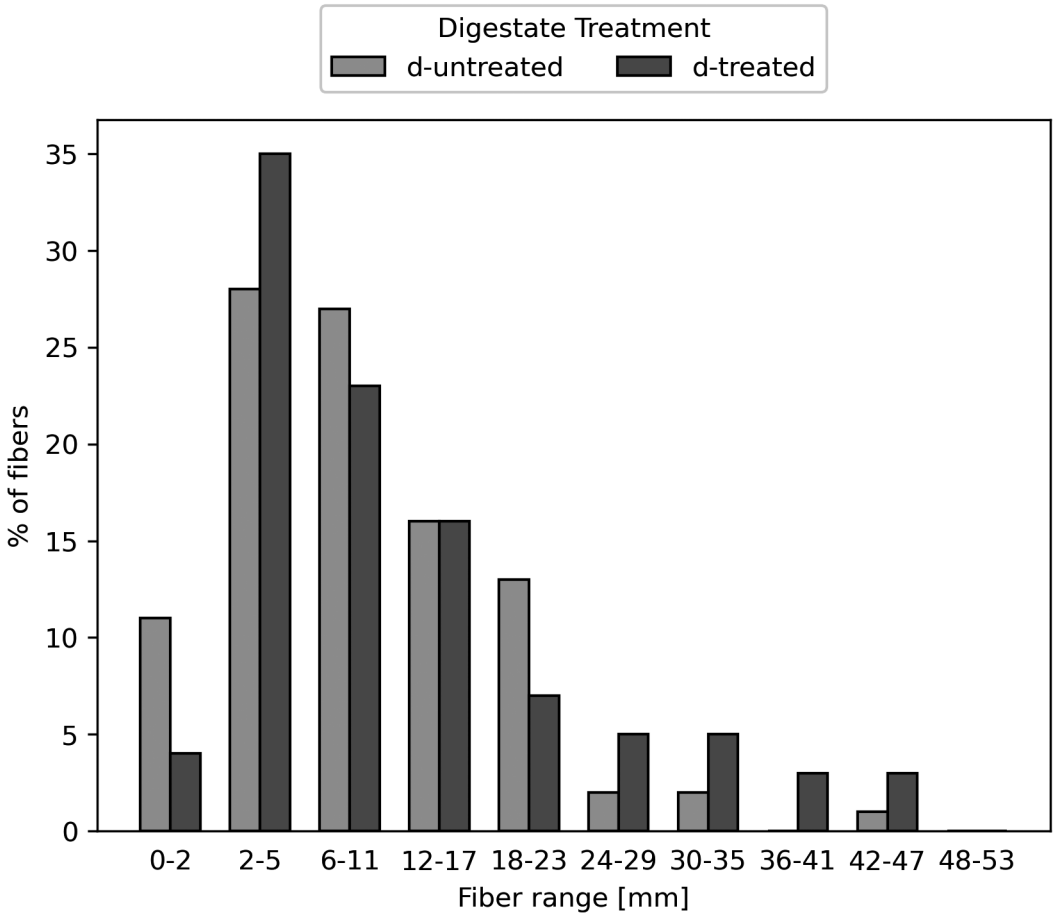

Figure 3.2: Fiber length distribution of treated and untreated digestate in percentage

The aspect ratio of the cleaned digestate ranges from 2 to 43 where as the main part (50 %) has an aspect ratio between 3 and 8. As figure 3.1 shows, the digestate is inhomogeneous and the material has no roundly diameter. The calculation of the aspect ratio is not reliable because of this fact, it can only be an estimation. Most of the digestate fiber have an aspect ratio of 3 what is the minimum ratio for a fiber.

3.3.3 Density

The density of the treated and untreated digestate sample is comparable to the density of other plant fibers. The treated digestate has a density of $1.46\,\mathrm{g\,m^{-3}}$ - $1.47\,\mathrm{g\,m^{-3}}$, the density of the untreated sample is with $1.48\,\mathrm{g\,m^{-3}}$ a little bit higher. In the washing process dust and dirt particles are removed, this can lead to the minimal lower density.

3.3.4 Chemical composition

The IR sprectrum is shown in figure 3.3. The infrared spectra are dominated by cellulose as compared to the literature. In addition, signals resulting from lignin can be found in the range from 1150 cm^{-1} - 1750 cm^{-1} and the presence of hemicellulose is underlined by an intensive peak just above 1000 cm^{-1}. The treated and the untreated samples show minor differences. The spectrum of the treated one shows a reduced signal intensity around 1000 cm^{-1} and the signal at 870 cm^{-1} almost vanished. The small differences show, that the washing process does not influence the chemical composition of the digestate.

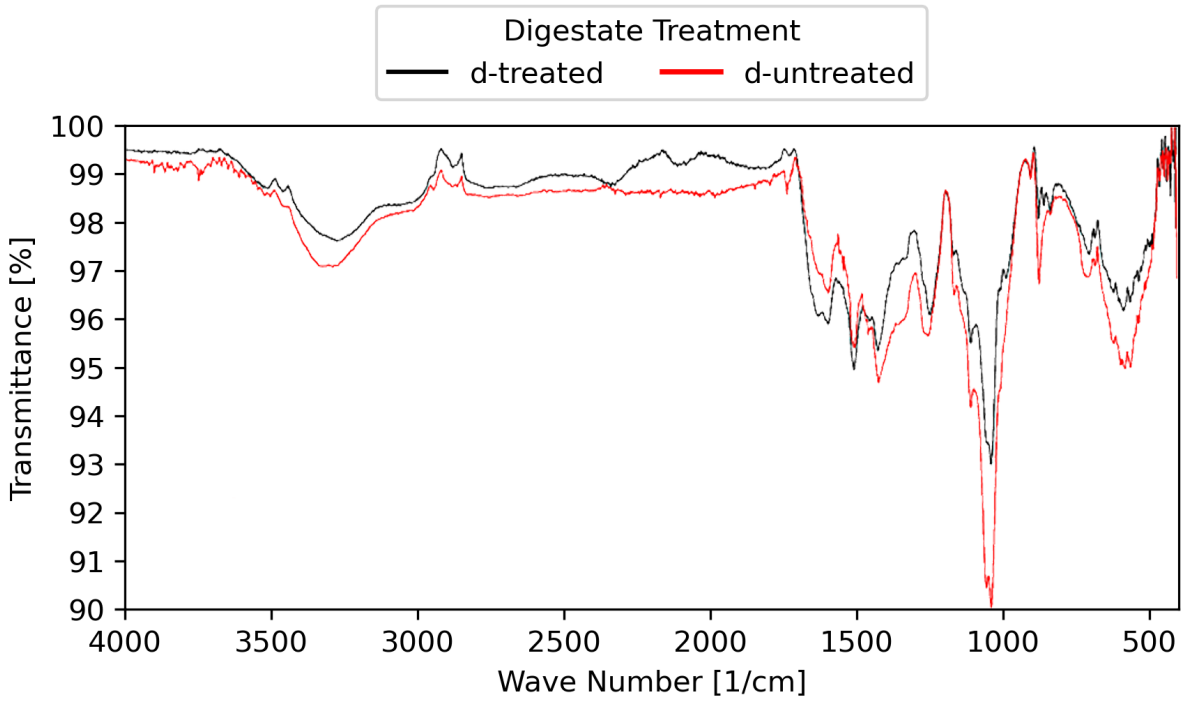

Figure 3.3: Result of the FTIR, red: untreated, black: treated

The figure 3.4 shows the percentages of soluble components, hemicellulose, cellulose, lignin and ash of digestate and comparative fibers. For a better classification the values from wood (table 3.2) are integrated in the figure.

Washing of the digestate decreases the percentage of soluble components from 37 % to 17 %. After washing, the digestate has a cellulose content of about 30 %; compared to 23 % without washing. The flax fibers have a significantly higher cellulose content of 81 % 81. The lignin content of treated digestate is about 33 %, while flax fiber contains only about 3 % lignin. The literature data for flax are a little bit lower, this can be caused by the fiber type, which is not known. The cellulose content of the washed digestate is lower than that of andceral or rice straw. The lignin content is similar to hardwood. The initial substrate of the digestate largely consists of woody hop vines. This explains the

similarity of the proportions of structural components to woody plants. Large parts of the plant biomass are degraded in the biogas process. In the residue mainly, indigestible cell wall constituents are found, even though the substrate contains grasses in addition to the vines. The ingredients are comparable to wood fibers. Washing in an ultrasonic bath removes other adhering substances, thus increasing the cell wall content in the washed material.

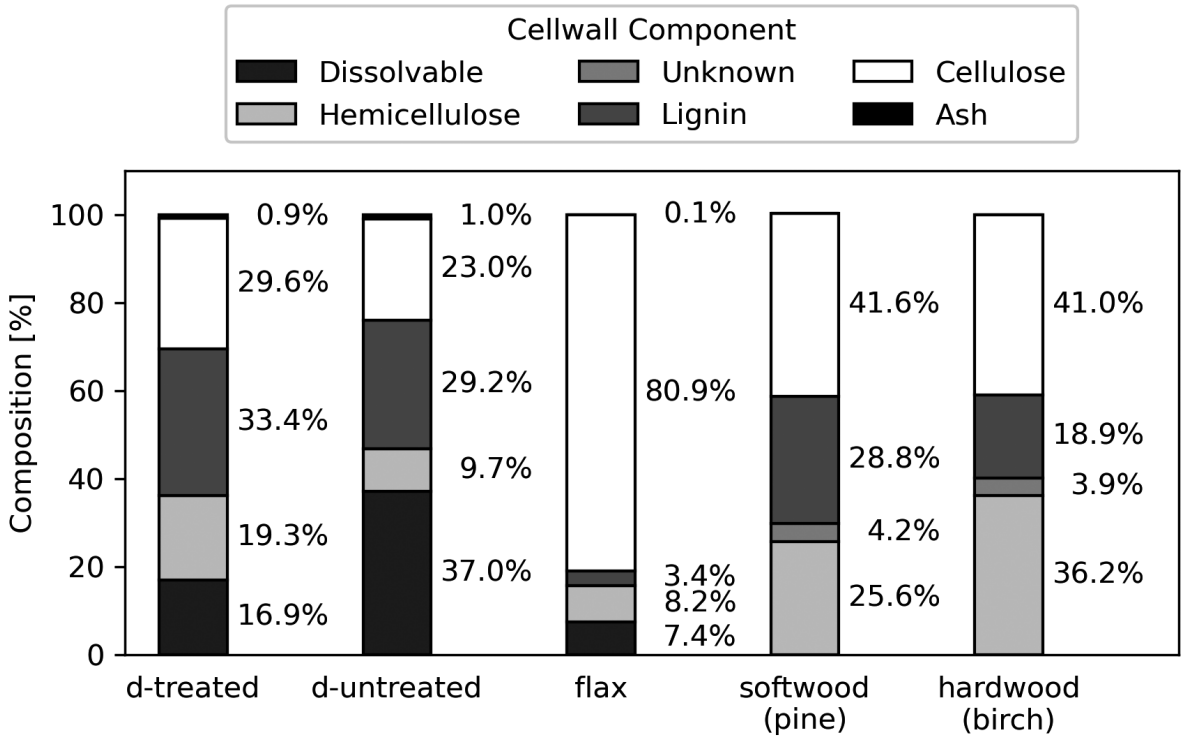

Figure 3.4: Results of feed analysis in percentages of dry mass

3.4 Conclusions

The hop-containing digestate shows comparable ingredients and properties to wood fibers. The experiments show that the washing of the digestate leads to a fiber-like material. The washing homogenizes the length distribution of the digestate fibers and increases the relative cell wall content. The composition of the digestate is similar to that of wood flour and fibers which are mixed into WPC. The use of the washed digestate in composites is conceivable. A digestate composite can be a possibly fiber for composites in automotive interrior. Like described in the literature this sector uses a lot of natural fibers, so the use of digestate can have a great effect.

References

Barbos, J.D.V., Azevedo, J.B., da Silva M. Cardoso, P., da Costa Garcia Filho, F., del Rio, T.G., 2020. Development and characterization of wpcs produced with high amount of wood residue. Journal of Materials Research and Technology 9, 9684 – 9690.

Berger, W., Faulstich, H., Fischer, P., Heger, A., Jacobasch, H.J., 2011. Textile Faserstoffe. Springer.

Bradley, W.L., Conroy, S., 2019. Using Agricultural Waste to Create More Environmentally Friendly and Affordable Products and Help Poor Coconut Farmers. E3S Web of Conferences 130, 1–10.

Campbell, F.C., 2010. Structural Composite Materials. ASM International.

Cantero, G., Arbelaiz, A., Llano-Ponte, R., Mondragon, I., 2003. Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. Composites Science and Technology 63, 1247 – 1254. Eco-Composites.

Cherif, C. (Ed.), 2011. Textile Werkstoffe für den Leichtbau. Springer.

Cichosz, S., Masek, A., 2020. IR study on cellulose with the varied moisture contents: Insight into the supramolecular structure. Materials 13, 4573.

Crowther, J. (Ed.), 1995. Oxford Advanced Learner's Dictionary of Current English. Oxford Universty Press.

DIN, 2001. DIN 60001-1:2001-05 Textile Fibres - Part 1: Natural Fibres and Letter codes.

DIN, 2006. EN ISO 16472:2006 Animal feeding stuffs – Determination of amylase-treated neutral detergent fibre content (aNDF).

DIN, 2008. EN ISO 13906:2008 Animal feeding stuffs – Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents.

DNFI, 2018. Forecast world fibre production bremen cotton report 05/06. `https://textile-network.com/en/Technical-Textiles/Fasern-Garne/Forecast-world-fibre-production` visited on 26.4.2020.

Eshwara, P.K., Divakara, R.P., Udaya, K.C., 2018. Experimental Studies on Behavior of Keratin Based Human Hair Fiber - A New Reinforcing Material for Composites. International Journal of Engineering & Technology 7, 459–463.

Essel, R., Breitmayer, E., Carus, M., Pfemeter, A., Bauermeister, U., 2015. Stoffliche Nutzung lignocellulosehaltiger Gärprodukte für Holzwerkstoffe aus Biogasanlagen. Nova-Institut.

FAO, 2021. Data - crops and livestock products - fiber plants. https://fenixservices.fao.org/faostat/static/bulkdownloads/Production_Crops_Livestock_E_All_Data.zip visited on 12.1.2021.

Fettweis, Kühl, 2010. Comparative Tests for the Purposes of a Crude Fibre Analysis using both the Official VDLUFA Method and FibreBag Technology (C. Gerhardt), in: Landschaftselement oder Rohstofflieferant - zur Multifunktionalität des Grünlandes, VDLUFA-Verlag. pp. 804–810.

Fortea-Verdejo, M., Bumbaris, E., Burgstaller, C., Bismarck, A., Lee, K.Y., 2017. Plant fibre-reinforced polymers: where do we stand in terms of tensile properties? International Materials Reviews 62, 441–464.

Galletti, A.M.R., D'Alessio, A., Licursi, D., Antonetti, C., Valentini, G., Galia, A., o Di Nasso, N.N., 2015. Midinfrared FT-IR as a tool for monitoring herbaceous biomass composition and its conversion to furfural. Journal of Spectroscopy 2015, 1–12.

Garrote, G., Dominquez, H., Parajo, J.C., 1999. Hydrothermal processing of lignocellulosic materials. Holz als Roh- und Werkstoff 57, 191–202.

Hanausek, T.F., 2012. Lehrbuch der Technischen Mikroskopie. Salzwasser.

Hospodarova, V., Singovszka, E., Stevulova, N., 2018. Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials. American Journal of Analytical Chemistry 09, 303–310.

Jain, S., 2019. Global Potantial of Biogas. The World Biogas Association.

Königsberger, S., Deorte, M., Reuland, G., 2019. EBA Statistical Report 2018. European Biogas Association.

Kozlowski, R., Baraniecki, P., Barriga-Bedoya, J., 2005. Bast fibres (flax, hemp, jute, ramie, kenaf, abaca), in: Blackburn, R. (Ed.), Biodegradable and Sustainable Fibres. Woodhead Publishing, pp. 36 – 88.

Lütz, M., Hügel, M., Milwich, M., Gresser, G.T., 2019. Investigation of fermentation residue of biogas plants for the production of sustainable fiber reinforced composites. Materials Today: Proceedings 31, 5242–5246.

Macatangay, P., Mangundayao, E., Rosales, C., 2012. Utilization of agricultural wastes in the manufacture of composite boards. ASEAN Journal on Science and Technology for Development 29, 129–140.

Mishra, S.C., Nayak, N.B., 2010. An Investigation of Dielectric Properties of Chicken Feather Reinforced Epoxy Matrix Composite. Journal of Reinforced Plastics and Composites 29, 2691–2697.

Ramamoorthy, S.K., Persson, A., Skrifvars, M., 2014. Reusing textile waste as reinforcements in composites. Journal of Applied Polymer Science 131.

Riedel, U., Nickel, J., 2000. Konstruktionswerkstoffe aus nachwachsenden rohstoffen (Bio-Verbunde), in: Tagungshandbuch - 3. Internationale AVK-TV Tagung für Verstärkte Kunststoffe und Duroplastische Formmassen, pp. 493–498.

Riley, A., 2012. Paper and paperboard packaging, in: Emblem, A., Emblem, H. (Eds.), Packaging Technology. Woodhead, pp. 178 – 239.

Sauer, M., 2019. Composites-Marktbericht 2019 - Der globale CF- und CC-Markt 2019 -. Carbon Composites e. V.

Schenek, A., 2001. Naturfaser-Lexikon. Deutscher Fachverlag.

Schimpf, U., Hanreich, A., Mänert, P., Unmack, T., Junne, S., Renpenning, J., Lopez-Ulibarri, R., 2013. Improving the Efficiency of Large-Scale Biogas Processes: Pectionalytic Enzymes Accelerate the Lingocellulose Degradation. Journal of Sustainable Energy & Environment 4, 53–60.

Sergion., M., Terrones, L.A.H., Lopes, F.P., d'Almeida, J.R.M., 2005. Mechanical Strength of Polyester Matrix Composites Reinforced with Coconut Fiber Wastes. Revista Matéria 10, 571–576.

Siebel, T., 2020. Naturfasern eignen sich für den karosseriebau. https://www.springerprofessional.de/biowerkstoffe/karosserie/naturfasern-eignen-sich-fuer-den-karosseriebau/18695956 visited on 21.2.2020.

Ulrich, H., 1956. Handbuch der chemischen Untersuchung der Textilfaserstoffe: Zweiter Band Chemismus, Eigenschaften und Einsatz der textilen (nicht veränderten) Faserstoffe und ihre Prüfung. Springer.

Van Soest, P.J., Robertson, J.B., 1970. Systems of analysis for evaluating fibrous feeds, in: Pigden, W.J., Balch, C.C., Graham, M. (Eds.), Standardization of Analytical Methodology for Feeds, pp. 49–60.

Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., Santas, R., 2003. Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Industrial Crops and Products 19, 245–254.

Vogt, D., 2006. Studie wood plastic composites, Holz-Kunststoff-Verbundwerkstoffe. Landwirtschaftsverlag.

4 Composites based on Biogas Digestate

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Abstract

The extraction of fibres from digestate can enhance the profitability of biogas stations. Furthermore, fibre from digestate can be an environmentally friendly alternative to commonly used fibres. In this study a nonwoven of the solid fibrous components of biogas digestate was used. The nonwoven was infiltrated and consolidated with a biobased thermoset matrix by a hot-pressing process. Multiple processing parameters were varied (matrix amount, pressing conditions) to evaluate mechano-physical properties. A pressure of 4.5 MPa resulted in a high-quality composite with a matrix ratio of 47 % by weight. A young's modulus of approximately 5500 MPa and a strength of approximately 70MPa is reached Different applications are conceivable, e.g. indoor furniture or decorative surfaces.

Keywords: Biobased composites, Digestate, Waste usage, Furniture, Compression moulding

4.1 Introduction

Due to their high strength and stiffness to weight ratio, fiber reinforced plastics (FRP) are increasingly used for many applications like automotive, aerospace or sports equipment (Martin, 2006). FRP consist of a fibre or textile reinforcement to bear the load and a polymer matrix to establish the shape of the composite and initiate the load into the fibres. The fibre reinforcement ranges from short fibres to nonwoven-, woven-, unidirectional- or tailored fabrics, depending on the application (Zweben, 2015). The main applications today are based on glass fibre composites or natural fibre composites with a fibre content by weight between 45 % to 75 % (glass fiber reinforced plastics (GFRP)) or 50 % to 70 % (natural fiber reinforced plastics (NFRP)) (Schürmann, 2007).

Natural fibre for composites are obtained from fibre plants like flax, jute, kenaf or hemp, but also wood particles and fibres can be used (Vogt, 2006; Stark et al., 2004). Those fibre plants are grown on agricultural land and compete partially with food production (Grundmann, 2007; Rana and Fangueiro, 2016). A possible ecological and also economical alternative is to obtain fibres from plant residues.

Different studies have investigated the use of agricultural plant waste as fibre reinforcement for composites, e.g. the non-edible fibrous mesocarp of coconuts (Bradley and Conroy, 2019), the invasive grass *Arundo donax* (Suárez et al., 2019; Ortega et al., 2021), fibrous parts of the date palm (Bourmaud et al., 2017) or the sea grass *Posidonia oceania*, which is a problem in the Mediterranean Sea (Scaffaro et al., 2018). The plant parts of the coconut and the date palm are residues from food production, whereas the sea grass *Posidonia oceania* and *Arundo donax* are plants which destroy the typical environment in the regions they grow in. Currently, these materials are not industrially used. *Posidonia oceania* and *Arundo donax* are dried, ground and mixed with a thermoplastic polymer to form a filled plastic material. The grasses in these composites are not in fibrous shape anymore. In contrast, the coconut fibres and thermoplastic matrix fibres were processed into a nonwoven and hot-pressed to a composite. Other investigated fibres for composite materials are human hair from barbers (Eshwara et al., 2018) or chicken feathers (Mishra and Nayak, 2010). Wood production waste (fibres and particles) are already used in WPC (Vogt, 2006).

So far, the biogenic fibres in the digestate of biogas plants have rarely been investigated for their suitability to produce composites. Biogas plants use microorganisms to convert solid or liquid manure, energy crops or organic residues under anaerobic conditions into methane and carbon dioxide. The by-product of this fermentation process is digestate, which consists of more than 85 % water. In addition to minerals, the digestate also con-

tains fibres of the initial substrates that are not degradable under anaerobic conditions. This digestate is mostly used as fertiliser (Koszel et al., 2017). The main substrate of biogas stations is plant-based biomass (Daniel-Gromke et al., 2017), which naturally contains lignocellulose (Biernacki et al., 2013; Schimpf et al., 2013). In contrast to animal residues, plant residues or energy crops contain high proportions of undigestible fibres. The lignocellulose structures of the initial substrates have already been released from the biomass by the microorganisms in the biogas process. In principle, therefore, fermentation residues are an interesting source of fibres for composite production, which has already been investigated. Essel et al. (2015) blended digestate with wood in fibre boards. He finally accomplished a digestate content of 30 %, which results in a cost reduction because of a lower wood content (Essel et al., 2015). Another study was conducted by König (2005). Digestate was mixed into agricultural plastic products to increase their biodegradability (König, 2005). Taurino et al. (2016) added milled digestate particles with a size of 500 µm to unsaturated polyester matrix as a filler.

Compared to other fibres from residues investigated so far, digestate is available in very large quantities. Biogas technology is applied worldwide. Europe alone counts 14000 biogas stations, of which 9000 are in Germany (Königsberger et al., 2019). The majority of biogas stations are fed with agricultural material that includes energy crops, agricultural waste, and excrements (Torrijos, 2016).

The goal of this study is to investigate the manufacturing of composites with a high ratio of digestate fibres as reinforcement. In contrast to the other studies mentioned, the fibres are not grinded. The digestate fibres are used as a nonwoven textile, produced with a fast and comparatively low cost nonwoven technology. The further steps to produce the final composites should also be fast and low cost. The hot-pressing technology was chosen, which is widely used in composite mass production.

4.2 Material and Methods

4.2.1 Material

The digestate originated from a biogas station in southern Germany which feeds lignocellulose rich hop vines as the main substrate. The solid part of the digestate was separated, washed and dried. The material has a broad range of fibre length and is comparably coarse. A detailed description of the digestate is given in (Gebhardt et al., 2021a,b; Lütz et al., 2019). The investigated fibre component was a nonwoven material based on biogas digestate and abaca pulp. Pulp is commonly used for paper-making and nonwoven products (e.g. medical compresses, tissues) (Russell, 2006). The pulp functions as a

fibrous binder, so no chemical binders are necessary. Abaca pulp has longer fibres than common wood pulp and a high wet stability (Materialarchiv.de, 2020). The nonwoven material was made by a wet laying process (Fuchs and Albrecht, 2012). The digestate fibres and 12 % of pulp are mixed with water in a vat.
The matrix was the partly bio-based epoxy resin GreenPoxy56 together with the hardener SZ8525 (both from Sicomin, Châteauneuf-les-Martigues, France). The biobased part in the epoxy matrix is 45 %. This matrix system is commercially available and suitable for the hot-pressing process due to the short reaction time. The recommended curing conditions are 10 min at 100 °C. An advantage for hot-pressing is the low viscosity (90 mPa s at 60 °C). The low viscosity allows the matrix to penetrate the textile and wet it uniformly before curing. No information on the chemical resistance of the matrix were available.

4.2.2 Composites Manufacturing

The composites were manufactured with a hot press VCP 500 from Lauffer (Horb, Germany). To secure full impregnation and to produce composite parts without dry spots, hot-pressing requires a matrix surplus. In the pressing process the matrix surplus drains out of the die and is removed from the composite afterwards. To gain fully impregnated and cured parts, two different pressing test series were executed: (1) constant pressure with different amount of matrix (called matrix addition), and (2) constant amount of matrix with different pressures:

1. Setting
    - Pressure: $p_{\max}$= 6 MPa
    - Matrix addition (relative to weight) 30 %, 45 %, 50 %, 55 % and 70 %
2. Setting
    - 60 % matrix addition (relative to weight)
    - Pressure variation: 1.5 MPa, 3 MPa, 4.5 MPa and 6 MPa

The general procedure was kept constant for both settings. Before pressing the nonwovens were dried at 105 °C for 2 h. One layer of nonwoven material with dimensions of 250 mm times 250 mm was positioned in an aluminium pressing die. One half of the matrix was spread on the nonwoven material. A second layer and the remaining matrix were added. The die was closed and put in the hot press. First it was operated for 60 s with lower pressure. Then the maximum pressure was applied. The pressing conditions were 10 min at a form temperature of 100 °C, following the recommendation of the matrix manufacturer.

4.2.3 Water Absorption

The water absorption was calculated according to DIN EN ISO 53923. The samples were stored in a standard climate (20 °C, rel. humidity 65 %) for 24 h before testing. Small samples (20 mm times 20 mm) made from the composite plates were weighed and then put into deionised water. The water absorption was measured after 1 min and after 10 min. After being given time to drain for one minute, it was weighed again. With the relationship between the weights before m_{climate} and after submerging in water m_{wet}, the water absorption was calculated (see equation (4.1)). The measurement was repeated five times (Arnold et al., 2013).

$$\text{water absorption}\% = \frac{m_{\text{wet}} - m_{\text{climate}}}{m_{\text{climate}}} \tag{4.1}$$

In Gebhardt et al. (2021a) the water absorption over 24 h was investigated. In addition a drop test was made. A drop of water was put on the composite and the time until it was absorbed by the specimen was measured. After 10 min the measurement was stopped due to the test specification.

4.2.4 Bending Test

To measure strength and young's modulus, a 3-point bending test according to DIN EN ISO 14125 was performed. A sample size of 60 mm times 15 mm was chosen and the test speed set to 2 mm/ min. For this test, a testing machine from ZWICK-ROELL, Ulm, Germany was used. Nine repetitions were tested.

4.2.5 Resistance against Chemicals

The knowledge of the chemical resistance helps to find proper application for the new material. The sample with 70 % matrix pressed with 6 MPa was chosen for the chemical resistance tests. Again, samples of a size of 60 mm times 15 mm were used. The samples were placed in different chemicals for 48 h each. After the storage in chemicals a bending test was performed. Three repetitions where tested for each of the chemicals. The chemicals chosen were formic acid 98 %, 6 M hydrochloric acid, 35 % nitric acid, sulphuric acid 60 %, soda solution 20 %, and caustic potash solution 40 %.

The chemicals were selected according to Wang et al. (2016), representing a proper mixture of acids and bases. After testing, pictures of the cross section and the surface structure were taken using a digital microscope VHX 2000 from KEYENCE (Neu-Isenburg, Germany).

4.2.6 Additional Measurements

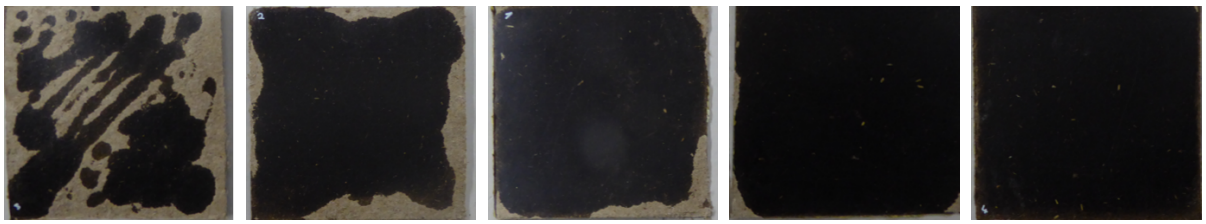
The thickness of the composites was measured using a calliper gauge, on samples randomly taken from the entire composite plate. The matrix ratio of the composite describes the weight of the matrix m_{nonw} relative to the weight of the composite plate m_{comp} (equation (4.2)).

$$\text{mass ratio}\% = \frac{m_{\text{comp}} - m_{\text{nonw}}}{m_{\text{comp}}} \tag{4.2}$$

4.3 Results

4.3.1 Overview

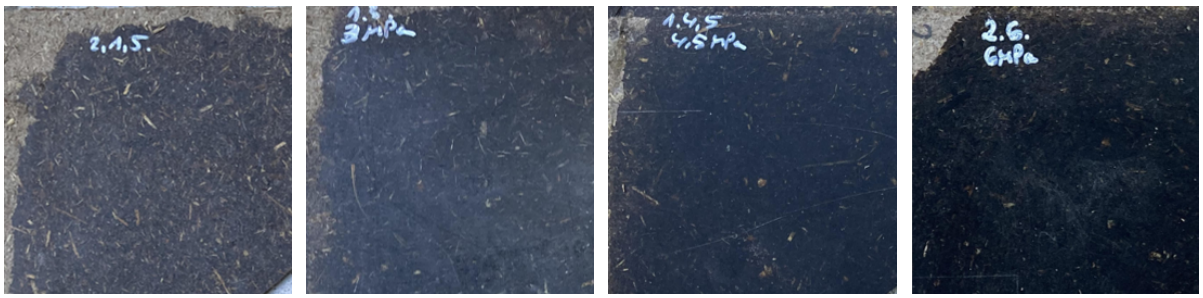
A uniform impregnation with matrix is essential for the mechanical properties of the composites. Figure 4.1 and Figure 4.2 show the results of variations in matrix addition and pressure. Figure 4.1 show the result of Setting 1 processed with a constant pressure of 6 MPa. A fully impregnated plate was achieved with a matrix addition of 55 % or higher.



(a) 30 % **(b)** 45 % **(c)** 50 % **(d)** 55 % **(e)** 70 %

Figure 4.1: Matrix distribution with 6 MPa pressure and matrix addition from 30 % to 70 % (Setting 1)

Figure 4.2 shows the samples with a constant matrix addition of 60 % (Setting 2). An even and full matrix distribution was achieved by applying a pressure of at least 4.5 MPa. When applying lower pressure, the plates turned out to be brittle and showed loose fibres.

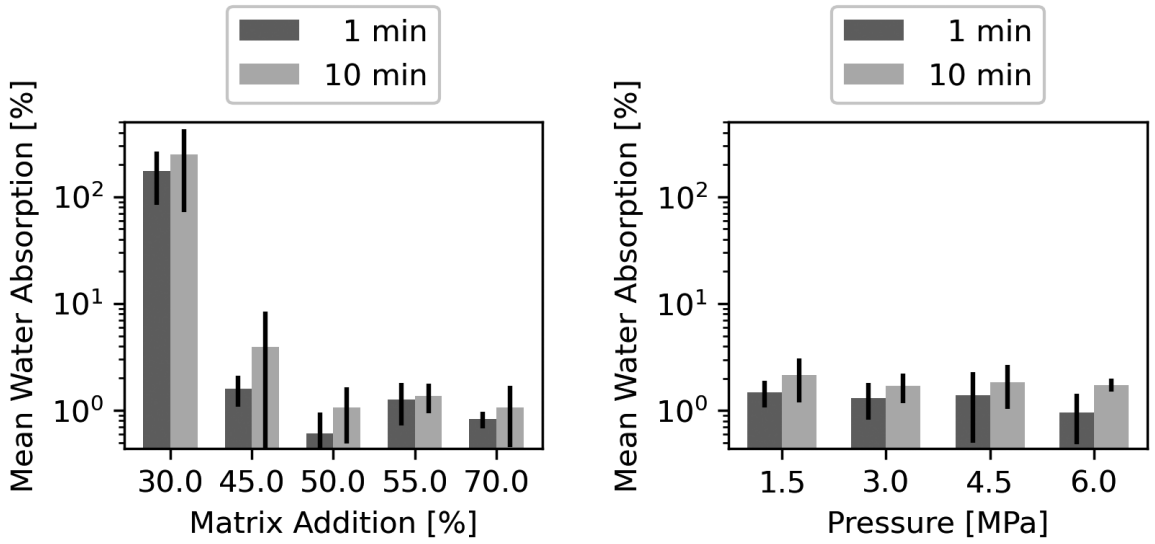


(a) 1.5 MPa **(b)** 3.0 MPa **(c)** 4.5 MPa **(d)** 6.0 MPa

Figure 4.2: Matrix distribution with 60 % matrix addition and pressure from 1.5 MPa to 6.0 MPa (Setting 2)

4.3.2 Water Absorption

The water absorption of the composites produced with the two pressing settings is shown in Figure 4.3. A matrix addition of at least 45 % led to a lower water absorption after 1 min and after 10 min compared to the variant with a lower matrix proportion. The sample with 30 % matrix addition was swollen at the not fully impregnated spots. All other samples did not show any modification in shape or aspect ratio. A higher addition did not lead to other results, which means that the composite was saturated. The pressure had only a minimal influence on the water absorption. The pressure of 6 MPa showed the lowest water absorption and the smallest deviation.



(a) 6 MPa pressure and matrix addition from 30 % to 70 %% (Setting 1)

(b) 60 % matrix addition and pressure from 1.5 MPa to 6.0 MPa (Setting 2)

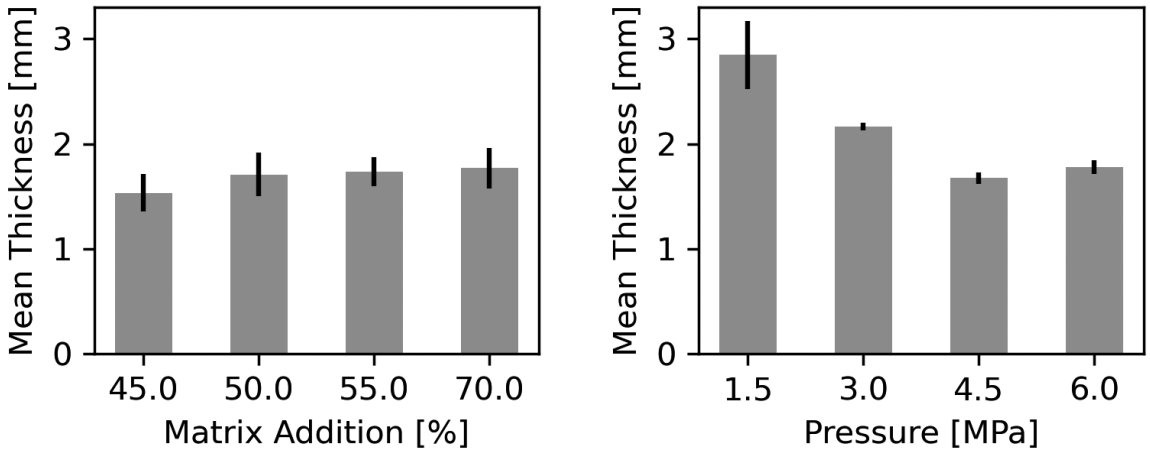
Figure 4.3: Mean water absorption of the composites after 1 min and after 10 min for the composites with different matrix addition and pressure

The water absorption after 10 min was around 0.5 % higher, which can be observed for all variations. This proves that the fibres were not perfectly covered within the matrix. The water flowed inside of the samples because of the open edges caused by the cutting. This problem is well known from all kinds of natural fibre composites.

The drop tests showed that only the samples with 30 % matrix addition and 1.5 MPa pressure had dry parts on the surface. The reason was the unequal impregnation with matrix. All other samples had closed surfaces which were resistant to water. This confirms that the water absorption was caused by the open cut edges. The water absorption test showed that at a pressure of 6 MPa, a matrix addition of at least 45 % is needed, while for a matrix addition of 60 %, a minimum pressure of 3 MPa is necessary.

4.3.3 Thickness

Figure 4.4 shows the thickness of the composites from the two production settings. For the composites made with a constant pressure, the thickness varied between 1.5 mm (45 %) and 1.8 mm (70 %). The amount of matrix addition had almost no influence on the thickness. The sample with only 30 % matrix was not completely soaked and thus could not be measured.



(a) 6 MPa pressure and matrix addition from 30 % to 70 % (Setting 1)

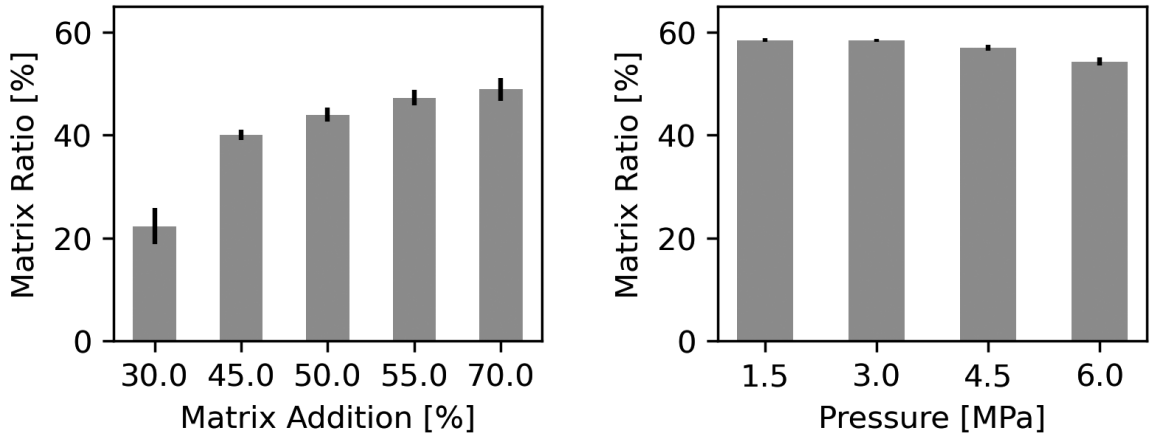
(b) 60 % matrix addition and pressure from 1.5 MPa to 6.0 MPa (Setting 2)

Figure 4.4: Thickness of the digestate composites for the composites with different matrix addition and pressure.

In comparison to the matrix addition, the pressure had a significant influence on the thickness. Increasing the pressure from 1.5 MPa to 4.5 MPa resulted in a decrease in the thickness from 2.7 mm to 1.7 mm, where 1.7 mm was the final thickness with both pressing settings. A further increase in the pressure did not cause thinner composites. Although the nonwoven is a compressible material, it behaves like an incompressible material as soon as all imperfections in the laminate are eliminated under pressure and thus could not be pressed further (block height). For two layers, the minimum resulting thickness was 1.7 mm because it was defined by the number of nonwoven layers.

4.3.4 Resulting Matrix Content

To secure fully impregnation and to produce composite parts without dry spots, hot pressing or wet-pressing technique require to work with a certain matrix excess. As described, the excess matrix was removed from the composite edges, the matrix ratio calculated with equation (4.2). The following diagrams in Figure 4.5 show the matrix ratio of the composite plates produced with Setting 1 and Setting 2.



(a) 6 MPa pressure and matrix addition from 30 % to 70 % (Setting 1)

(b) 60 % matrix addition and pressure from 1.5 MPa to 6.0 MPa (Setting 2)

Figure 4.5: Matrix ratio of the digestate composites for the composites with different matrix addition and pressure

A higher matrix addition in the process led to a higher matrix ratio in the composite plate up to a final saturation with a matrix addition of 55 % (compare Figure 4.5a). A matrix addition of 55 % led to a matrix ratio in the plate of approx. 47 %. This matrix ratio could not be increased by enhancing the matrix addition.

The variation of the applied pressure had a minor influence on the matrix ratio of the composite (compare Figure 4.5b), which was around 55 % to 60 % for all pressures. A pressure of 6 MPa led to a small decrease of the matrix ratio.

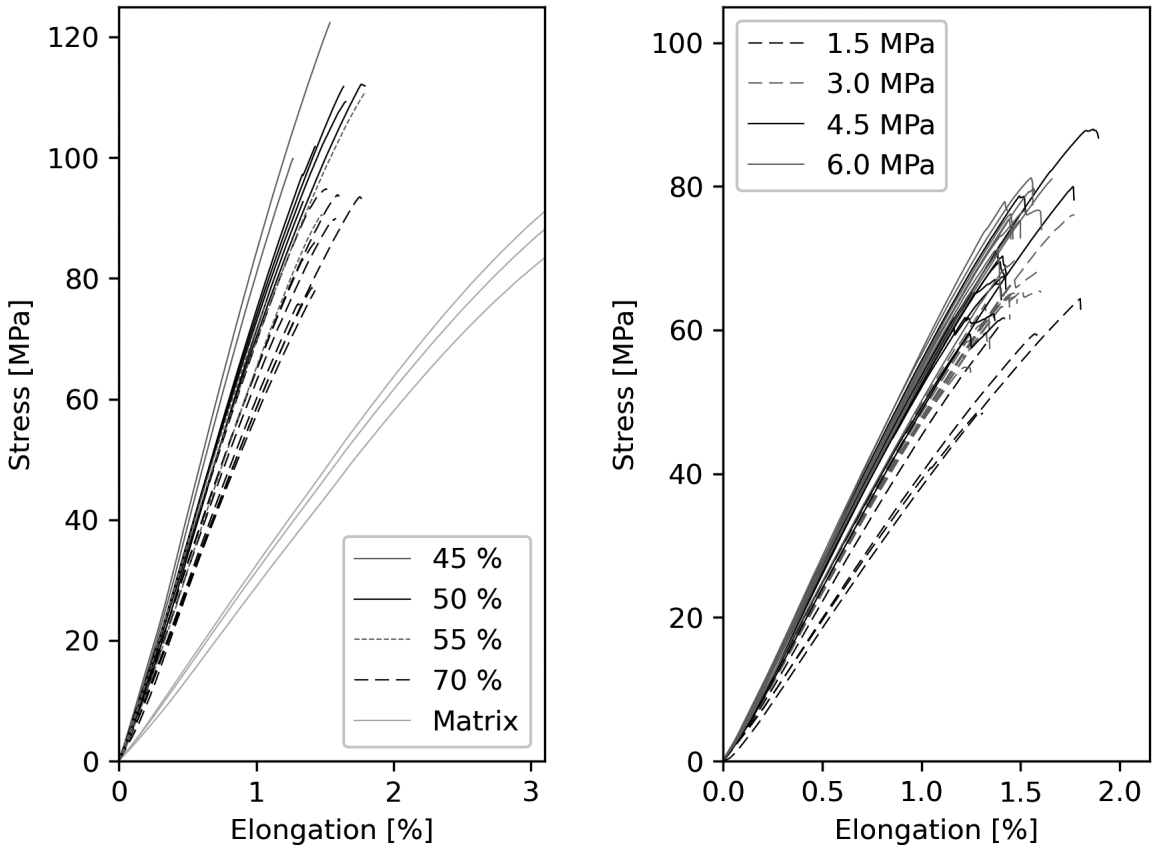
Summarizing the results, a pressure of 4.5 MPa and a matrix addition of 55 % led to a uniform and reproducible matrix ratio of approximately 50 % in the composite. A typical value for composites with nonwoven reinforcement. The slight differences in the results of Setting 1 and Setting 2 were presumably caused by deviation in the nonwoven, which was produced on different days.

4.3.5 Bending Test

Figure 4.6 presents the results of the 3-point bending tests. For the sake of clarity, not all tested samples are plotted. The outliers were identified and the samples with less than 15 % deviation from the maximum stiffness were plotted in the figure.

The young's modulus respectively stiffness is an important property for fibre reinforced plastic. The diagram of Figure 4.6a is limited to 2 % elongation due to multiply reason: 1. Improve the presentability 2. Showing the influence of reinforcement on the stiffness 3. Technical non-relevant due to nonlinear behaviour. Figure 4.6b presents the results of

the experiments with variation in the matrix addition. The mean strength of the pure matrix was 110 MPa, the mean young's modulus was 2970 MPa. The sample with 30 % matrix addition could not be tested because of an inhomogeneous impregnation.



(a) 6 MPa pressure and matrix addition from 30 % to 70 % (Setting 1)

(b) 60 % matrix addition and pressure from 1.5 MPa to 6.0 MPa (Setting 2)

Figure 4.6: Stress-elongation diagrams of the digestate composites with different matrix addition and pressures

The stiffness of all samples was higher than the stiffness of the matrix. The highest stiffness results were seen in the sample with 45 % matrix addition. The stiffness of the samples with 50 %, 55 % and 70 % matrix addition were quite similar (5289 MPa, 5139 MPa, 4770 MPa). The strength followed the same trend, but it was lower than the matrix strength. The highest mean strength has the sample with 50 % matrix addition with 83 MPa. With a higher matrix addition, the deviation of the results decreased. A higher matrix addition led to a better impregnation and caused the composites to show more homogeneous properties.

Figure 4.6a presents the results of the experiments with variation in the pressure. A higher pressure results also in a better and uniform impregnation and led to a higher stiffness of the composites. A pressure of 3 MPa resulted in a young's modulus of 5064 MPa, and

the mean pressure of the 6 MPa sample was 5732 MPa. The difference between 4.5 MPa and 6 MPa was only 231 MPa, which was in the range of the standard deviation of both variations. A pressure above 4.5 MPa increased the stiffness significantly. An increasing pressure led to a higher strength caused by a better impregnation. With the exception of 1.5 MPa, the differences in the mean strength of the samples were small compared to the standard deviation. The mean strength of the 3 MPa samples was 64 MPa, and the result of the 6 MPa sample was 76 MPa. The standard deviation was 5 MPa (3 MPa sample) and 4 MPa respectively.

The pure matrix has a high elasticity, reducing the matrix ratio resulted in stiffer composite material. All composite variations showed a higher stiffness as well as a lower strength and elongation compared to the pure matrix. A high stiffness is characteristic of fibre composites. This underlines that the digestate nonwoven material acts as reinforcement material. The *Arundo donax* composite from Suárez et al. (2019) has a lower strength and stiffness than the investigated digestate composite. The strength of a WPC material with 50 % wood flour is about two times smaller than that of the digestate composite (Stark et al., 2004). The digestate composite is comparable to other construction materials. Because of different fibre contents and polymers this comparison has only a low expressiveness. The change of the polymer and the fibre content can change the properties. Digestate is a natural product with inhomogeneous ingredients and properties. This is one reason for the high deviation of the mechanical properties. A further reason is the nonwoven itself. Its thickness and weight per area vary between different batches. The amount and mixture of the plants variegate in the digestate. This fact causes differences in the fibre composition and therefore in the textile quality. These variations directly influence the properties of the composite.

4.3.6 Resistance aginst Chemicals

The composites after treatment with the acids and bases are shown in Figure 4.7. All chemicals, except for soda solution, strongly affected the composites. The cross-section showed fractures, and the surface tended to be rougher. Formic acid affected the composite more strongly than the other chemicals. It seems like the matrix was partly dissolved. The nonwoven material was swollen but retained its shape. After exposure to formic acid and nitric acid the colour changed. The first fractures were visible on the surface after a one-hour exposure.

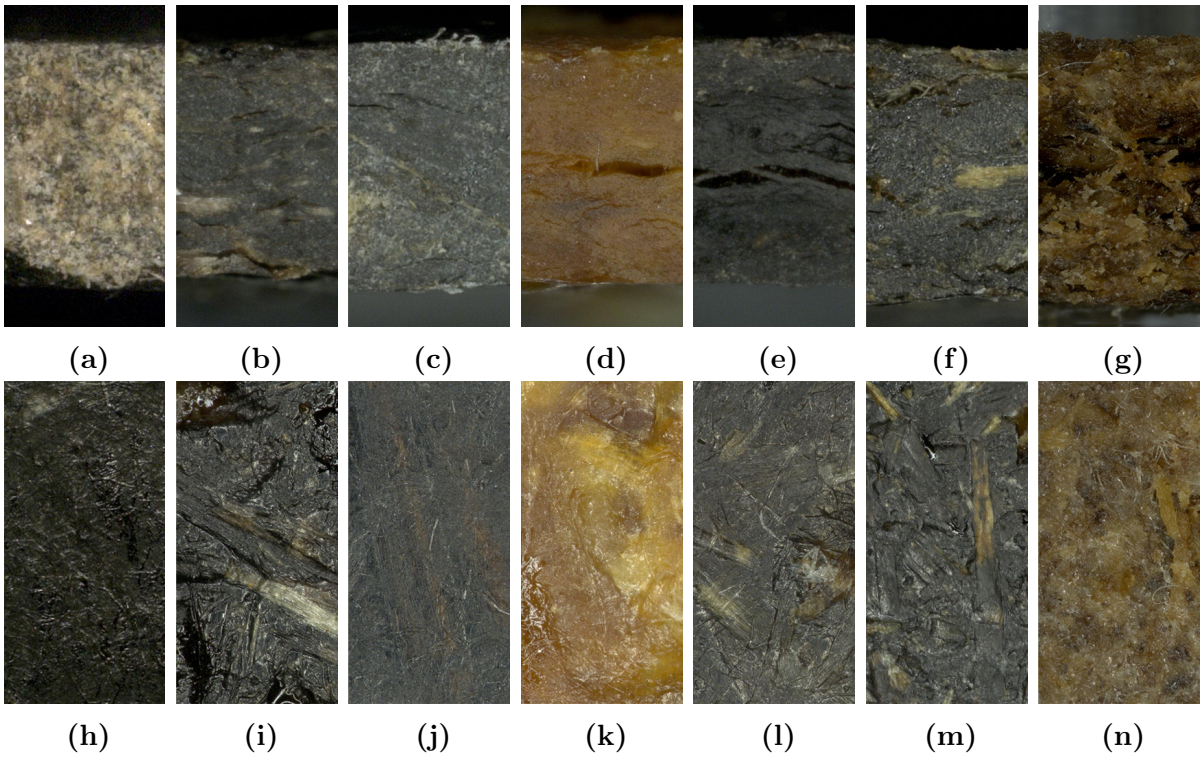


Figure 4.7: Influence of chemical treatment (cross section a-g, top h-n); Untreated (a,h), Sulphuric Acid (b,i), Soda Solution (c,j), Nitric Acid (d,k), Hydrochloric Acid (e,l), Caustic Potash (f,m), Formic Acid (g,n)

The treatment with the acids and bases, except for soda solution, led to a drastic loss of mechanical properties, see Figure 4.8. The sample treated with formic acid was almost destroyed, thus it was not possible to test it. Compared to the non-treated sample, the strength of the caustic potash sample was 87 % and the stiffness 98 %. Nitric acid led to the highest loss of mechanical properties: stiffness and strength only reached 17 % of the original composite. The other three samples showed a strength and stiffness of around 40 % of the untreated sample.

The elongation was higher, which is an effect of the matrix degradation and cannot be regarded as an advantage. Single fibres were partly loose and therefore acted more like a textile.

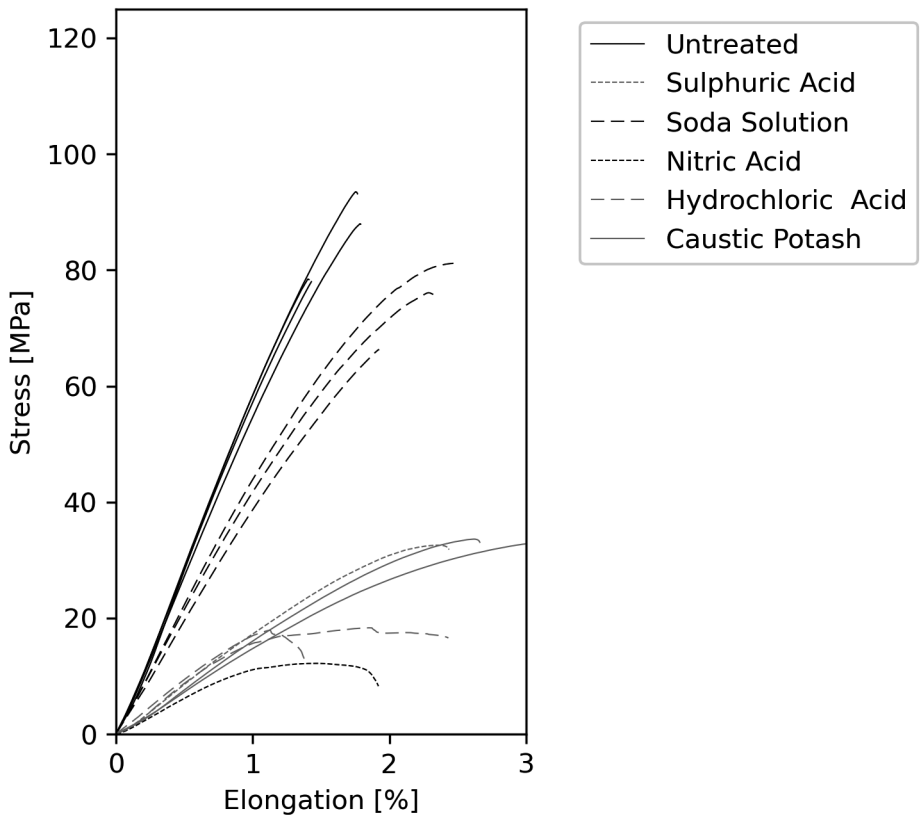


Figure 4.8: Stress-elongation diagram of the composites produced with 70 % matrix addition and 6 MPa pressure after treatment with different chemicals for 48 h

4.4 Conclusions

The study presented shows, that it is feasible to produce a biobased thermoset composite with digestate fibres as the main reinforcing component. To reach a fully impregnated uniform composite a matrix addition of 55 % to 60 % combined with a pressure of at least 4.5 MPa were found to be the best process parameters. The matrix ratio is in the range of composites which are already used. The composites have better a stiffness than the unreinforced matrix. Further improvement of the properties could be reached with a lower matrix ratio. To improve the infiltration behaviour the manufacturing of the nonwoven material could be investigated. One possibility is to reduce the amount of pulp binder. Based on the results of the different tests, the digestate composite could be applied as a furniture material. For example, as decorative layer for kitchen furniture as the tests show that water absorption is not an issue. Another possible application could be car interior. Here environmentally friendly material is desired and the chemical surrounding fits to the properties of the digestate composite.

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References

Arnold, J., Dittrich, J.H., Finnimore, E., Haase, J., Hempel, P., 2013. Prüfverfahren in der Textil- und Bekleidungstechnik. Springer.

Biernacki, P., Steinigeweg, S., Borchert, A., Uhlenhut, F., 2013. Application of anaerobic digestion model no. 1 for describing anaerobic digestion of grass, maize, green weed silage, and industrial glycerine. Bioresource Technology 127, 188–194.

Bourmaud, A., Dhakal, H., Habrant, A., Padovani, J., Siniscalco, D., Ramage, M.H., Beaugrand, J., Shah, D.U., 2017. Exploring the potential of waste leaf sheath date palm fibres for composite reinforcement through a structural and mechanical analysis. Composites Part A: Applied Science and Manufacturing .

Bradley, W.L., Conroy, S., 2019. Using Agricultural Waste to Create More Environmentally Friendly and Affordable Products and Help Poor Coconut Farmers. E3S Web of Conferences 130, 1–10.

Daniel-Gromke, J., Rensberg, N., Denysenko, V., Stinner, W., Schmalfuß, T., Scheftelowitz, M., Nelles, M., Liebetrau, J., 2017. Current developments in production and utilization of biogas and biomethane in germany. Chemie Ingenieur Technik 90, 17–35.

Eshwara, P.K., Divakara, R.P., Udaya, K.C., 2018. Experimental Studies on Behavior of Keratin Based Human Hair Fiber - A New Reinforcing Material for Composites. International Journal of Engineering & Technology 7, 459–463.

Essel, R., Breitmayer, E., Carus, M., Pfemeter, A., Bauermeister, U., 2015. Stoffliche Nutzung lignocellulosehaltiger Gärprodukte für Holzwerkstoffe aus Biogasanlagen. Nova-Institut.

Fuchs, H., Albrecht, W. (Eds.), 2012. Vliesstoffe. Wiley-VCH.

Gebhardt, M., Milwich, M., Gresser, G.T., Lemmer, A., 2021a. Impact of long-term weathering on the properties of a digestate-based biocomposite. Materials Circular Economy 3.

Gebhardt, M., Wanek, N., Lemmer, A., Gresser, G.T., 2021b. Comparison of fibers from hop rich biogas digestate with natural fibers as raw material for composites. Journal of Natural Fibers , 1–11.

Grundmann, E., 2007. Faserpflanzen aus ökologischem Anbau Anbau - Verarbeitung - Markt. Lebendige Erde.

König, Ulich; Fudel, A., 2005. Verfahren zur Herstellung von Naturfasern aus Biogasanlagen und deren Verwendung. DE 10 2005 034 586 B3.

Königsberger, S., Deorte, M., Reuland, G., 2019. EBA Statistical Report 2018. European Biogas Association.

Koszel, M., Przywara, A., Jakubowska, M.K., Kraszkiewicz, A., 2017. Evaluation of the use of biogas plant digestate as a fertilizer in field cultivation plant, in: Farm Machinery and Processes Management in Sustainable Agriculture.

Lütz, M., Hügel, M., Milwich, M., Gresser, G.T., 2019. Investigation of fermentation residue of biogas plants for the production of sustainable fiber reinforced composites. Materials Today: Proceedings 31, 5242–5246.

Martin, J., 2006. Materials for Engineering. Elsevier.

Materialarchiv.de, 2020. Abaca bananenfasern. `https://materialarchiv.ch/de/ma:material_2136/?q=abaca` visited on 18.08.2022.

Mishra, S.C., Nayak, N.B., 2010. An Investigation of Dielectric Properties of Chicken Feather Reinforced Epoxy Matrix Composite. Journal of Reinforced Plastics and Composites 29, 2691–2697.

Ortega, Z., Romero, F., Paz, R., Suárez, L., Benítez, A.N., Marrero, M.D., 2021. Valorization of invasive plants from macaronesia as filler materials in the production of natural fiber composites by rotational molding. Polymers 13.

Rana, S., Fangueiro, R. (Eds.), 2016. Fibrous and Textile Materials for Composite Applications. Springer.

Russell, S.J., 2006. Handbook of Nonwovens. Woodhead.

Scaffaro, R., Lopresti, F., Botta, L., 2018. PLA based biocomposites reinforced with posidonia oceanica leaves. Composites Part B: Engineering 139, 1–11.

Schimpf, U., Hanreich, A., Mänert, P., Unmack, T., Junne, S., Renpenning, J., Lopez-Ulibarri, R., 2013. Improving the Efficiency of Large-Scale Biogas Processes: Pectionalytic Enzymes Accelerate the Lingocellulose Degradation. Journal of Sustainable Energy & Environment 4, 53–60.

Schürmann, H., 2007. Konstruieren mit Faser-Kunststoff-Verbunden. Springer.

Stark, N.M., Matuana, L.M., Clemons, C.M., 2004. Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites. Journal of Applied Polymer Science 93, 1021–1030.

Suárez, L., Paz, R., Ortega, Z., Díaz, N., Monzón, M., Marrero, M.D., Benítez, A.N., 2019. Ecofibras project: a strategy to improve ecosystems affected byinvasive plant species in macaronesia, in: ICNF 2019. TecMinho.

Taurino, R., Lancellotti, I., Tatàno, F., Carchesio, M., Pozzi, P., 2016. Mechanical and chemical resistance of composite materials with addition of anaerobic digestate. Composites Part B: Engineering 92, 259–264.

Torrijos, M., 2016. State of development of biogas production in europe. Procedia Environmental Sciences 35, 881–889.

Vogt, D., 2006. Studie wood plastic composites, Holz-Kunststoff-Verbundwerkstoffe. Landwirtschaftsverlag.

Wang, H., Song, X., Xu, L., Li, X., Wang, J., Zhao, Y., Cai, Z., 2016. Fabrication of acid-resistant fabrics with fluoropolymer/SiO2 nanocomposites for the application of protective clothing. Journal of Industrial Textiles 47, 727–740.

Zweben, C., 2015. Materials and Engineering Mechanics. John Wiley & Sons, Inc.. chapter Composite Materials. pp. 1–37.

5 Impact of Long-Term Weathering on the Properties of a Digestate-Based Biocomposite

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Abstract

Natural fibre composites are increasingly used. For many applications the long-term stability of the mechanical properties is crucial. Therefore, the effects of weathering of a bio composite made from fibrous digestate and bio-based thermoset is investigated. The fibre component of the composite comes from digestate of a German biogas stations which processes hop vines as main substrate. The matrix is a plant-oil-based epoxy resin. The samples were alternately exposed to UV radiation and moisture for various length of time. Afterwards the material strength and water absorption were tested. As a result, the weathering leads to a decrease of strength but not to a high increase of water uptake.

Keywords: Agricultural waste, Accelerated weathering, Bio-composites, Sustainability, Biogas

5.1 Introduction

5.1.1 Natrual fibre composites

Fibre-reinforced plastics consist of a fibre component and a plastic matrix. The fibres are usually present as a textile and absorb the tensile and flexural forces. The matrix protects against environmental influences and gives the material its shape (Schürmann, 2007). Natural fibres are more and more used in composites. Especially natural plant fibres are increasingly used due to their good specific properties and their ecological advantages, compared to synthetic fibres (Riedel and Nickel, 2000). Examples for the use of Natural fibres as reinforcement in composites are NFRP with so called endless fibres like woven fabrics or nonwovens. A further example are the WPC (Carus et al., 2015). WPC are mostly made of synthetic thermoplastic polymers and wood fibre, particle or flour. (Vogt, 2006). Although natural fibres are renewable, the fact that they are specially cultivated makes them less sustainable than they could be (Grundmann, 2007; Gessner, 1955; Rana et al., 2014). There is a lot of research to use alternative fibre sources, such as fibrous waste materials like wooden saw dust, coconut fibre or invasive plants (Fitri et al., 2017; Dhakal et al., 2018; Bradley and Conroy, 2019).

5.1.2 Durability of composites in general

One main objective of sustainable materials is that they are made from environmentally friendly raw materials with low energy costs. Another important thing is that the product life time is as long as possible. In case of plastics and reinforced plastics the durability is important. Plastics do not have an unlimited shelf life. Environmental influences cause irreversible changes in their chemical and mechanical properties (Bonnet, 2009). Aging of polymers is a complex process and is divided in chemical and physical aging, whereas the physical aging leads to decreasing mechanical properties (Barbosa et al., 2017). This is the interesting type of aging for the presented study. The aging of fibre-reinforced composites is dominated by the aging of the polymer (Blaga, 1978; Kammerhofer, 2018). Thermoset polymers are not sensitive to environmental influences, except of ultra violet (UV) radiation. The presence of UV radiation and oxygen leads to photooxidative degradation. In general polymers with higher service temperature show a better UV stabilisation (Bonnet, 2009). For thermoset polymers the glass transition temperature is an indication for the service temperature (Schürmann, 2007).

Epoxy resins loose mechanical properties after exposure to environmental influences because of matrix degradation (Pschorr and Cianciarulo, 1965; Kumar et al., 2002). Epoxy coatings show the same behaviour (Kotnarowska, 1999). Roylance (1978) made weather-

ing tests with glass-fibre-epoxy-composites. The used epoxy has a glass transition temperature from 180 °C. After storage at the outside in the city panama (hot-wet) the tensile strength decreased to 70 % of the original strength (Roylance, 1978). Information on the sunshine duration and rain fall is not given. Accelerated weathering tests from Barbosa et al. (2017) do not show any influence on the breaking force of carbon fibre reinforced plastics after weathering for 3 month (Barbosa et al., 2017). In both studies high performance endless-fibre reinforcements are used.

5.1.3 Durability of natural fibre reinforced plastics

As example of natural fibre reinforced plastics with outdoor applications WPC are investigated in different studies. There is no clear information about the aging of WPC, because it depends on the material and additives. It is found that WPC (wood and Polyethylen) loses approx. 30 % of the original stiffness after 2000 h weathering with UV and moisture (Vogt, 2006). The composite surface is rougher after the weathering periods than before. Friedrich and Luible (2016) summarize different studies on accelerated weathering of WPC. They point out, that the strength of the materials decreases through artificial weathering, even if the values differ depending on the used material and weathering method (Friedrich and Luible, 2016). The aging of Jute-epoxy-composites was investigated by Nizin et al. (2019). The material shows 33 % of the original strength after 12 month of outdoor storage.

Natural fibre composites have the major disadvantage that they are hygroscopic. The swelling of the fibre causes a degradation of the composite (Koolen and van Vuure, 2019). Special fibre treatments and a complete enclosure with the polymer matrix help to prevent water absorption. Natural fibres are lignocellulosic materials with cellulose being the main component in most of the classic fibres with textile use. Most of the fibre plants are non-wooden plants and lignin makes only a small part of the fibres. In wooden plants the lignin content is 20 % to 35 % depending on the origin tree of the wood (Knackstedt, 1939). On the other hand, Lignin is a natural UV absorber which leads to a good UV stability of wood (Sadeghifar and Ragauskas, 2020; Wang et al., 2019; Sandermann and Schlumborn, 1962).

5.1.4 Motivation and goal

Composites based on digestate from biogas stations (agricultural waste) appear very advantageous from an ecological point of view. While the production of these composites has already been described in single articles, all information about the long-term stability of such materials and their potential product lifetime is missing so far. The Knowledge about the stability and potential product lifetime is important for estimating the sus-

tainability of the new material because sustainability has three parts: ecology, economy and sociology. The origin of material and its processing is important for the ecology of a product (Pufe, 2012). For the social acceptance and the economic part, the lifetime plays a major role.

To focus more on the social and economic parts of sustainability the United Nations General Assembly set 17 sustainable development goals sustainable development goals (SDG). These goals should lead to a better future for all people. The goals are: No Poverty, Zero Hunger, Good Health and Well-being, Quality Education, Gender Equality, Clean Water and Sanitation, Affordable and Clean Energy, Decent Work and Economic Growth, Industry, Innovation and Infrastructure, Reducing Inequality, Sustainable Cities and Communities, Responsible Consumption and Production, Climate Action, Life Below Water, Life on Land, Peace, Justice, and Strong Institutions, Partnerships for the Goals (Nations, 2021). The digestate composite helps to avoid over fertilization and this leads to less pollution of ground water. In this work the weather stability is investigated. The goal of the presented work is to observe the environmental durability of the digestate composite by weathering tests to get more data for assessing the sustainability and possible applications of this new material. The study should answer the question, if the developed composite can address the goal of responsible consumption and production.

5.2 Material and Methods

5.2.1 Material

The investigated bio-composites consist of a bio-based matrix and specially treated solid fraction of digestate. Digestate is a fibrous agricultural waste from biogas plants with a dry matter content less than 15 %. Using a screw press, the digestate can be separated in a liquid fraction, which is used as fertilizer, and a solid, fibrous fraction, which can be used as fibre reinforcement for composites. The composition of the digestate is highly dependent on the input materials used in the station. The biogas plant from which the digestate was obtained mainly uses chopped hop vines, and smaller amounts of grass silage and maize, which resulted in a solid phase with a high fibre content after separation. The solid fraction of digestate is washed, grinded, dried and sieved before using for the composite production. The solid fraction of the digestate has a lignin and cellulose content of approximately 30 %. The material is called digestate fiber because after washing and grinding most particles have a significantly higher length than width. The main part of the cleaned digestate fibers has a length between 2 mm and 17 mm. With a density of 1.46 $\mathrm{g\,cm^{-3}}$ (Gebhardt et al., 2021). The digestate is further processed to a wet laid

nonwoven with pulp as binder leading to a completely bio-based material. The process is similar to paper making and the resulting nonwoven is completely bio-based.

The matrix is a vegetable oil based epoxy system with 100 % bio based carbon in the resin component. As main component of the hardener is a polycarboxylic acid anhydride. The viscosity at 120 °C is 20 mPa s, which is advantageous for the pressing process. The glass transition temperature is 110 °C. The curing temperature of the resin system is between 100 °C and 190 °C and the curing time depends on the temperature. With higher temperature the curing is faster. The composite is produced by hot pressing. Two layers of nonwoven are impregnated with the matrix by hand lay-up and then put into the die. To spread the matrix and consolidate the composite, it is pressed with 155 °C and 6 MPa for 10 min. The composite has a fibre-weight-ratio of approx. 40 %. Figure 5.1 shows the production process of the composites beginning from the biogas station.

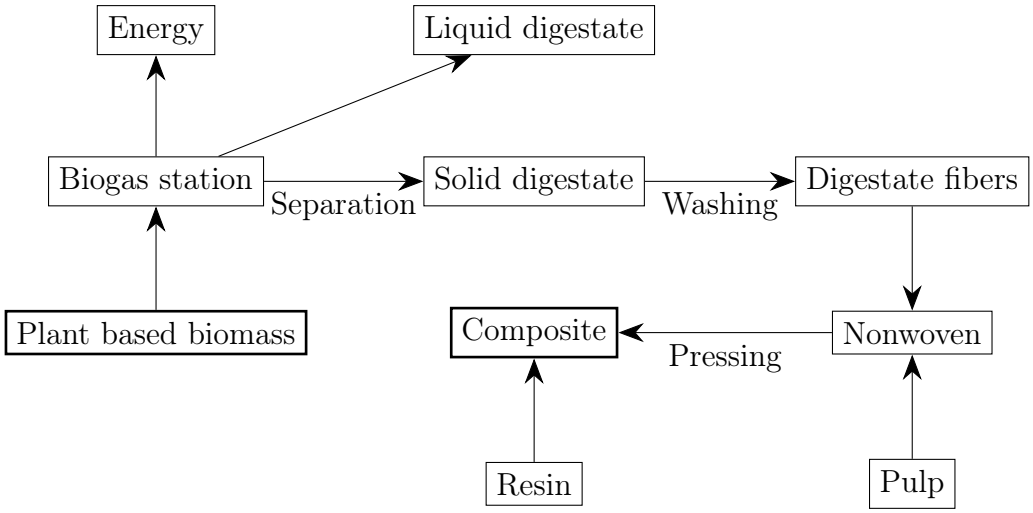


Figure 5.1: Flow diagram of the composite production out of digestate

5.2.2 Methods

To observe the durability of the composite, it is artificially weathered. The weathering is done according to ISO 4892-3 with an QUV-accelerated weathering tester by Q-Lab, Saarbrücken, Germany. The samples (15 mm × 60 mm) are alternately exposed to UV radiation (8 h) and moist air (4 h), at room temperature over test periods of 1000 h and 2000 h testing with UV radiation corresponds with one year of sunshine in Germany. Due to the test machine, only one side of the sample is exposed to the UV radiation. In addition, an untreated, dry and dark stored sample is used as reference.

To measure the strength and the elongation after aging 3-point-bending-tests are made using a testing machine from ZWICK-ROELL, Ulm, Germany according to DIN EN ISO 14125. The sample size is 15 mm times 60 mm and three repetitions are measured. The

average aging velocity is calculated as interpolation between the strength of the 0 h weathering and the 2000 h weathering samples.

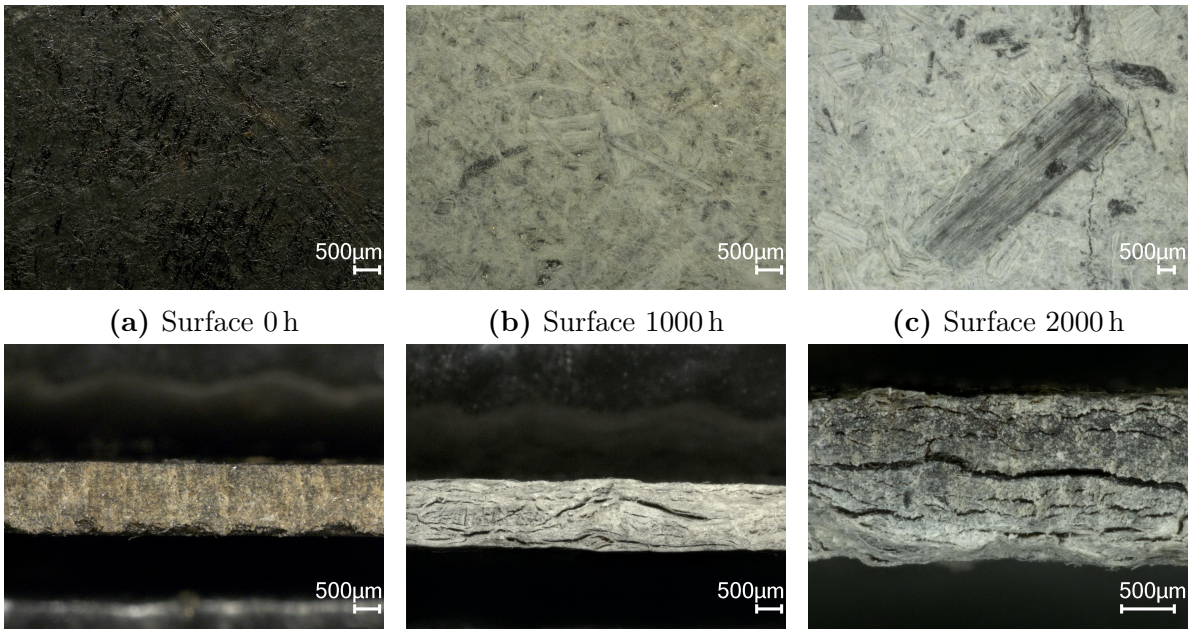
The water uptake is calculated according to DIN EN ISO 62:2008-05. The main change compared to the standard is, that additionally the water uptake after 10 min is measured. Small samples from the composite plates are put into deionized water for 10 min and 24 h. The sample is weighed before and after storage in water. The water uptake is observed as additional test with a small sample quality (n=3), for this reason no statistics are made.

Microscopic pictures of surfaces and cross sections were made using a KEYENCE VHX 2000, Neu-Isenburg, Germany to observe changes in the composite structure. The observed cross section is cut and polished before weathering and not treated again.

5.3 Results and Discussion

5.3.1 Composite structure

Figure 5.2 shows the micrographs of the surface and the cross section of the different samples. The first observation is that the surface of the exposed side is white after 1000 h and 2000 h of treatment. The surface of the weathered composite is wavy after the UV and moisture treatment but still closed, whereas the cross section shows bigger differences in the form of delamination and cracks. The damage is not only at the surface of the cross section but goes to the inside of the material and not only near the exposed surface. The cross section of the parts which are cut before the weathering are white. When comparing those visible effects on matrix and fibres, it can be stated, that the colour changing, and the cracks are the result of a degrading polymer matrix and that the fibre seems to be intact. As described in the literature, the observations show that the decomposition process of the composite is determined by the polymer. The relatively high lignin content of the digestate can be a reason for the stability of the fibres.



(a) Surface 0 h **(b)** Surface 1000 h **(c)** Surface 2000 h

(d) Cross Section Area 0 h **(e)** Cross Section Area 1000 h **(f)** Cross Section Area 2000 h

Figure 5.2: Micrographs of surface and cross section of the original and weathered samples

5.3.2 Flexural strength

The mechanical properties of the weathered samples differ from the untreated samples, this can be taken from figure 5.3 and table 5.1. In table 5.1 the average values are given and figure 5.3 shows the strength elongation-diagrams. After a weathering period of 1000 h the strength is reduced to approx. 70 % of the original strength and after 2000 h even to approx. 40 %. The strength can be predicted using the average aging velocity. This leads to the equation y=0.014x+51, with x equals the exposure duration in h and y equals the predicted strength in MPa. The elongation of the composite decreases from 2.6 % to 1.9 % after 1000 h of weathering and increases to 2.2 % after the weathering of 2000 h. The scattering of the values for the weathered samples is smaller than of the original samples. The scattering can be seen with the help of the lines of the single samples. For the weathered samples the lines are much closer together. UV light and humidity have no evidently influence on the elongation of the examined material.

The fracture pattern is not influenced by the UV and moisture treatment. The samples show a brittle failure without splintering and a complete break. The samples show a light tendency to a more ductile behaviour after 2000 h of weathering.

The digestate composite shows a faster loss of strength than the materials described in the literature. The differences can be rather assigned to the polymer used than to the type of

reinforcement fibre. The reaction kinetics of bio-based polymers are different to synthetic polymers so this can be a reason for the faster degradation. In comparison studies endless fibre reinforcements are used. An endless fibre bundle of carbon or glass fibres has a higher strength than a nonwoven of naturals fibres. When the matrix is destroyed the aligned fibres can better carry the load. The glass transition of the used epoxy is not very high compared to other systems which can be another explanation for the faster degradation.

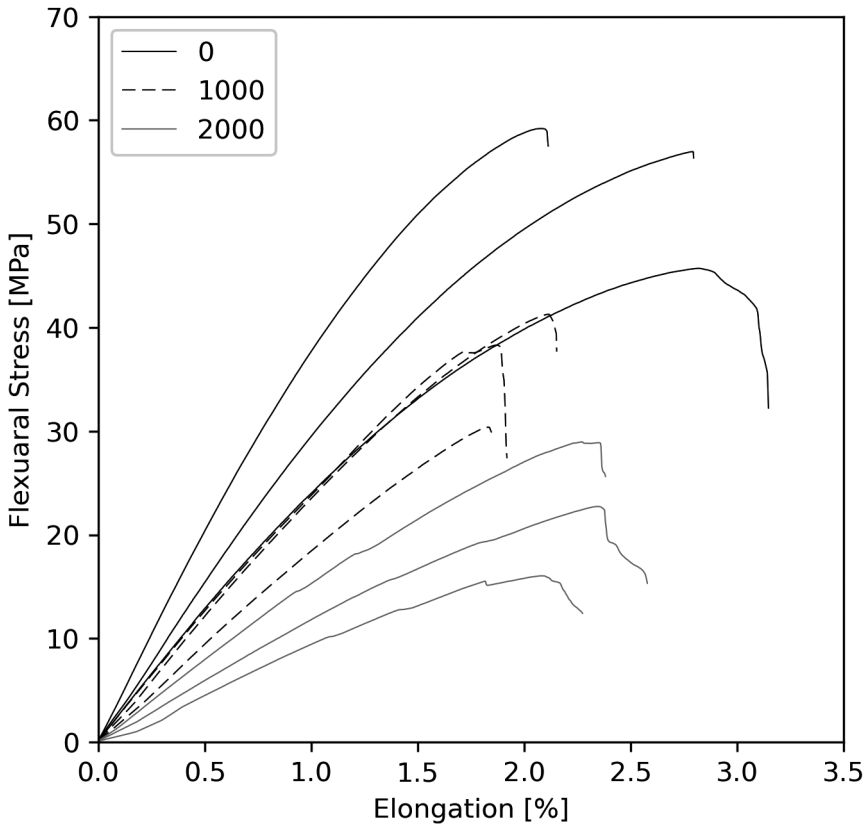


Figure 5.3: Strength-elongation-diagram of the variations with 0 h, 1000 h, 2000 h of accelerated weathering. For every variation the result of all three tested samples is plotted

Table 5.1: Results of the bending test: average values for E-modulus, strength and elongation

Parameter		0 h	1000 h	2000 h
E-Modulus	[GPa]	3.3	2.2	1.1
Strength	[MPa]	54.0	36.7	22.6
Elongation	[%]	2.6	1.9	2.2

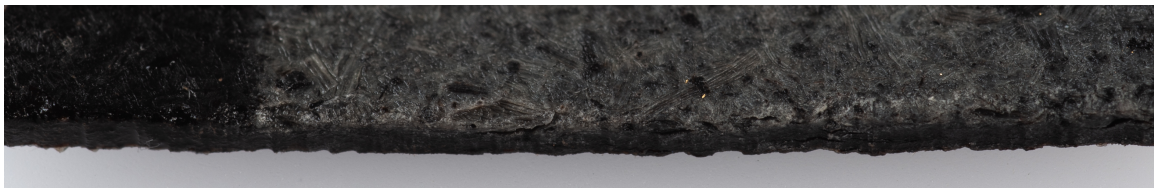
The non-linear behaviour of the elongation is a result of the matrix degradation. The matrix itself has a lower elongation than the nonwoven. The nonwoven structure is still intact and the fibre seem not to be degraded. This can be a result of the high lignin content of the digestate. The nonwoven, as a textile, is able to elongate before failing.

When the matrix is partly destroyed the fibres are no longer fixed and the composite elongation is higher.

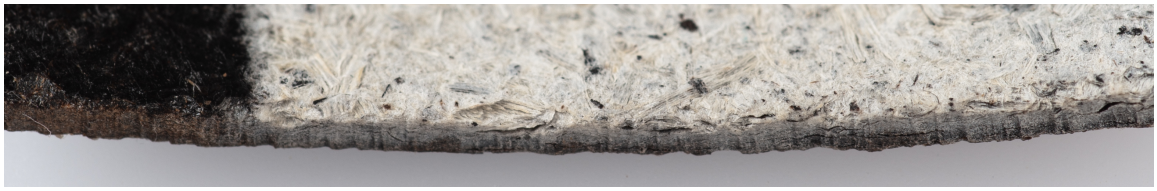
5.3.3 Water absorption after weathering

The results of the water uptake are presented in table 5.2. The 10 min water uptake shows between the three weathering conditions bigger differences than the 24 h water uptake. The 2000 h weathered sample has a higher 10 min water uptake than the untreated original sample, whereas the 24 h water uptake shows a smaller increase (from 10 % to 13 %). A possible explanation could be, that in case of short time water uptake, water flows fast into the cracks. This water uptake decreases over time because after initially filling the cracks, the matrix takes up water much slowly. The fibres are still surrounded with resin, so they also show a low tendency to adsorb water. Figure 5.4 shows a 2000 h sample before and after the water storage. All pictures are taken under the same artificial light conditions After water storage no optical changes can be seen. The composite is not widened or deformed. This is another indication for a proper saturation with resin, even after weathering.

(a) Sample before water storage



(b) Sample directly after water storage (wet)



(c) Sample after drying again for 12 h at room temperature

Figure 5.4: Sample 2000 h before and after water storage

Table 5.2: Results of water uptake after 10 min and 24 h of the weathered and unweathered samples

Sample	10 min	24 h
0 h	2 %	10 %
1000 h	4 %	12 %
2000 h	6 %	13 %

5.3.4 Influence on the material sustainability

Because the sustainability is influenced by the test results their relevance should be discussed. The high decrease of the strength leads to a restricted product use time for outdoor applications. The changes in the composite structure and surface are also reasons for a faster replacement of the material, which is a negative point regarding to the sustainability. The water uptake is the only parameter, which has no negative influence. The long time water uptake (24 h) is not negatively influenced by the aging.

5.4 Conclusions

The material properties of the digestate bio epoxy composite decrease due to the accelerated weathering. As described and according to the literature, this seems to be dominated by the degrading polymer matrix. Therefore, UV stabilised matrices or the use of another matrix can enhance the durability of the composite. The fibre itself seems to have no significant influence on the weathering stability. Fibres obtained from biogas digestate can thus be an interesting starting material for the production of composites. With the material the SDG 12 should be addressed. The fiber itself has a great potential to be a sustainable fiber resource. But to reach the goal of a sustainable consumer product some problems must be solved. At the present state of the development an indoor use is preferred to address all parts of the sustainability. With additives or coatings, the weather stability can be improved. This should be investigated in further studies.

Declaration

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Competing Interests

The authors declare that they have no competing interests.

Availability of Data

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Author Contribution

MG did the experiments and wrote the main part of the article. MM was the project coordinator and wrote parts of the article. GTG helped planning the project and necessary experiments. AL planed the experiments. All authors read and approved the final manuscript.

References

Barbosa, A.P.C., Fulco, A.P.P., Guerra, E.S., Arakaki, F.K., Tosatto, M., Costa, M.C.B., Melo, J.D.D., 2017. Accelerated aging effects on carbon fiber/epoxy composites. Composites Part B: Engineering 110, 298–306.

Blaga, A., 1978. Grp composite materials in construction: properties, applications and durability. Indian Forum 9, 27–32.

Bonnet, M., 2009. Kunststoffe in der Ingenieuranwendung verstehen und zuverlässig auswählen. Vieweg + Teubner.

Bradley, W.L., Conroy, S., 2019. Using Agricultural Waste to Create More Environmentally Friendly and Affordable Products and Help Poor Coconut Farmers. E3S Web of Conferences 130, 1–10.

Carus, M., Eder, A., Scholz, L., 2015. Bioverbundwerkstoffe Naturfaserverstärkte Kunststoffe (NFK) und Holz-Polymer-Werkstoffe (WPC).

Dhakal, H., Bourmaud, A., Berzin, F., Almansour, F., Zhang, Z., Shah, D.U., Beaugrand, J., 2018. Mechanical properties of leaf sheath date palm fibre waste biomass reinforced polycaprolactone (PCL) biocomposites. Industrial Crops and Products 126, 394–402.

Fitri, S.P., Zaman, M.B., Priyanta, D., Hidayat, M., 2017. Application waste sawdust as mixed polyurethane insulation in traditional cold storage of fishing vessel. International Journal of Marine Engineering Innovation and Research 1, 46–50.

Friedrich, D., Luible, A., 2016. Investigations on ageing of wood-plastic composites for outdoor applications: A meta-analysis using empiric data derived from diverse weathering trials. Construction and Building Materials 124, 1142–1152.

Gebhardt, M., Wanek, N., Lemmer, A., Gresser, G.T., 2021. Comparison of fibers from hop rich biogas digestate with natural fibers as raw material for composites. Journal of Natural Fibers , 1–11.

Gessner, W., 1955. Naturfasern Chemiefasern. Fachbuchverlag Leipzig.

Grundmann, E., 2007. Faserpflanzen aus ökologischem Anbau Anbau - Verarbeitung - Markt. Lebendige Erde.

Kammerhofer, P.P., 2018. Analyse der Haltbarkeit von Werkzeugen aus carbonfaserverstärkten Kunststoffen. phdthesis. Technischen Universität München.

Knackstedt, W., 1939. Untersuchung über pflanzliche Bastfasern. Ph.D. thesis. Technische Hochschule Carolo-Wilhelmina zu Braunschweig.

Koolen, G., van Vuure, A., 2019. The effect of silicone coatings on the durability of natural fibrecomposites when subjected to hygrothermal aging, in: ICNF 2019, pp. 64–65.

Kotnarowska, D., 1999. Influence of ultraviolet radiation and aggressive media on epoxy coating degradation. Progress in Organic Coatings 37, 149–159.

Kumar, B.G., Singh, R.P., Nakamura, T., 2002. Degradation of carbon fiber-reinforced epoxy composites by ultraviolet radiation and condensation. Journal of Composite Materials 36, 2713–2733.

Nations, U., 2021. The 17 goals. `https://sdgs.un.org/goals` visited on 10.4.2021.

Nizin, D.R., Nizina, T., Selyaev, V., Chernov, A., Gorenkova, A., 2019. Natural climatic aging of epoxy polymers taking into account the seasonality impact. Key Engineering Materials 799, 159–164.

Pschorr, F.E., Cianciarulo, A.N., 1965. Weathering of epoxy resins systems. Polymer Engineering and Science , 166–170.

Pufe, I., 2012. Nachhaltigkeit. UVK.

Rana, S., Pichandi, S., Parveen, S., Fangueiro, R., 2014. Natural plant fibers: Production, processing, properties and their sustainability parameters, in: Textile Science and Clothing Technology. Springer, pp. 1–35.

Riedel, U., Nickel, J., 2000. Konstruktionswerkstoffe aus nachwachsenden rohstoffen (Bio-Verbunde), in: Tagungshandbuch - 3. Internationale AVK-TV Tagung für Verstärkte Kunststoffe und Duroplastische Formmassen, pp. 493–498.

Roylance, D., 1978. Weathering of fiber-reinforced epoxy composites. Polymer Engineering and Science 18.

Sadeghifar, H., Ragauskas, A., 2020. Lignin as a UV light blocker—a review. Polymers 12, 1134.

Sandermann, W., Schlumborn, F., 1962. On the effect of filtered ultraviolet light on wood - part 1: Photometric and chromatographic investigations on wood powders. Holz als Roh- und Werkstoff 7, 245–252.

Schürmann, H., 2007. Konstruieren mit Faser-Kunststoff-Verbunden. Springer.

Vogt, D., 2006. Studie wood plastic composites, Holz-Kunststoff-Verbundwerkstoffe. Landwirtschaftsverlag.

Wang, Y., Xiao, X., Wang, S., Li, K., Jiang, Y., Ma, Y., Zhang, T., Ran, R., 2019. Exploration on UV-blocking performance of lignin from palm (trachycarpus fortunei) fiber. Journal of Natural Fibers 18, 71–79.

6 Discussion

6.1 Fiber quality and output

In the biogas process, microorganisms degrade biomass under anaerobic conditions, releasing methane and carbon-dioxide. The extraction of fibers from plants for material use is equally based on the degradation of the non-lignified parts of the biomass to obtain fiber bundles or single fibers (Sisti et al., 2017). In principle, the digestate from biogas plants thus represents a very interesting raw material for the simple extraction of plant fibers. Although the digestate consists of degraded biomass, the fiber bundles and plant parts are still undamaged and no single fiber can be observed in it, see figure 1.4. In order to utilize the digestate as fibers, a further extraction is necessary. Mechanical fiber extraction methods are common (Sisti et al., 2017; Lee et al., 2020). The Hollander beater is comparable to a mechanical extraction (Tedesco et al., 2014; Zhou et al., 2018). Therefore, it was also used in this study to prepare the digestate, for the nonwoven production process. The mechanical extraction refines the fiber pattern, see figure 1.5. The beaten fibers show a high number of fibers with a length around 2 mm, the untreated fibers show more longer fibers, see figure 1.5. Therefore, the anaerobic digestion should be combined with a mechanical method to break the plant material and loosen the fibers for further technical applications.

To produce fiber composites with a high quality, the constitution of the fiber material is important. The length, slenderness and composition determine the quality of the fibers. To measure the length and slenderness, the fibers are divided into batches and are scanned in high resolution. The images were evaluated manually using an image processing software (Rueden et al., 2017). Fully automated methods exploit specific properties of fibers and can therefore not be used for fibers of different types (Saville, 1999), in particular the irregularity of digestate fibers poses a problem here. The method of determining the slenderness of fiber is only fully applicable for round fibers (Saville, 1999). However, the digestate fibers have no round or regular diameter, as well the thickness cannot be measured, due to the 2D scan. Therefore, the slenderness of the digestate is only a rough estimation. Nevertheless this type of measurement is used in other studies for determining the fineness or fiber diameter (Razali, 2015; Correia and Valera, 2019). All investigated

digestates show coarse particles which can be defined as fiber or fiber like structure because they have a slenderness ratio of at least 3 (DIN, 2001). These measurements were compared to literature data of other natural fibers, see section 2.1 and 3.1. The digestate fibers are comparable to wood fibers. The slenderness ratio is thus approximately 20 times smaller than the slenderness ratio for wood fibers (Carus et al., 2015; Ververis et al., 2003). A slenderness ratio of 1000:1 is necessary for conventional textile production processes such as spinning (Schenek, 2001). Woven or tailored textiles need a roving or yarn. The highest slenderness ratio of the digestate fibers is approximately 40:1 furthermore the median of the length distribution is around 7.5 mm, see figure 2.4. Such fibers can only be used for the production of nonwoven (AVK, 2013; Schürmann, 2007; Fuchs and Albrecht, 2012). The results of the analysis of the cell wall components according to van Soest, see chapter 2 and 3, demonstrate that the lignin content of the digestate fibers with about 20 % to 40 % (depending on the substrate mix) is similar to wood (e.g. softwood 29 %) and higher than that of classic fibers (e.g. flax 2 %).The washing which is investigated in chapter 3 halves the content of soluble contents (37 % to 17 %) and therefore increases the lignocellulose content of the digestate. Higher lignin content can be beneficial for later composite application, since lignin is a natural UV-blocker (Wang et al., 2019). Overall, the digestate provides fibers with advantageous quality for composites production.

To assess the technical feasibility of fiber recovery from digestate, it is necessary to know the fiber yield. Since most of the biogas plants are fed with a mixture, the influence of the initial substrates on the mass of extractable fibers is investigated. Determination of dry matter content and sieving analysis were used to evaluate the potential output. All fibers over 1 mm are considered as usable fibers. The maximum fiber output is achieved with the investigated excrement free substrate mix. In this case, 80 % of the digestate's dry mass is considered to be usable as fiber. In Germany animal excrements are a common substrate, only 12 % of the biogas plants do not use it. An increasing share of animal excrements leads to a decreasing fiber output. About 70 % of the German biogas plants are fed with between 0 % and 49 % animal excrements (Daniel-Gromke et al., 2020). The output of usable fibers decreases significantly (from 70 % to 30 %) when the ratio of animal excrements increases from 45 % to 55 %, see figure 2.5. For fiber production, biogas plants with low share of excrements should be considered. The results show that the upper boundary for excrements should not extend 50 % in the substrate. The assessment of fiber output via sieving is not very precise. Sieving is a method of classifying a material into different sizes (Liu, 2009). The issue with sieving fibers is that they are very long and thin. The fibers can get through a sieve with a specific width because of their diameter, even if they are much longer (Madyan et al., 2020). The results for the sieving fractions are not perfect. The real share of small fibers is smaller than measured, which results in a larger real ratio of long, usable fibers. Alternative sorting methods are manually or by airflow.

The manual sorting is comparable to the described analysis of fiber dimension, see chapter 2. It is only capable to handle small sample sizes. Sorting by air is based on aerodynamic behaviour (Saville, 1999; Berthet et al., 2017). Mass and size are consequently only sorted implicit. Therefore, the density of each individual fiber has to be identical, an unproven assumption.

6.2 Composite production

To assess the suitability of the fibers from the digestate, the individual steps in the production of composites based on nonwoven were investigated. The evaluation of process parameters is important to achieve constant product properties and a repeatable process. In this study, the compression moulding with a hot press was used because 95 % of the natural fiber composites for automotive application are produced using with this process (Paul, 2006; Carus et al., 2015). The textile was placed in a die and the matrix (an epoxy resin) was spread before closing the press. It is consolidated with pressure and heat. The results of chapter 5 show that the compression moulding is suitable for digestate-nonwovens. With a pressure of at least 4.5 MPa and a matrix addition of 55 % to 60 % related to weight, fully impregnated composites could be produced, see section 4.3.1. A pressure of 6 MPa was investigated as positive for natural fiber composites by Yamamoto (2005). In the study of Yamamoto (2005) a matrix content of 22 % by weight was reached. The digestate composite reached a matrix ratio of 47 %. The difference of matrix ratio in the composites is probably a result of the used textiles. Especially the pulp in the digestate nonwoven might be responsible. The composites produced were tested for their durability. The low water absorption of about 1 % underlines that the textiles were completely enclosed by the matrix. The variation of the mechanical properties decreases with higher matrix addition and pressure, see figure 4.6. Consequently, the found process parameter led to reproducible product properties. Compression moulding is a well-known manufacturing process but there are other options (Schürmann, 2007). It should be proven if other manufacturing processes are also feasible with the digestate fibers. For small series or unique parts, the vacuum infusion process is used. In the vacuum aided laminating processes (and vacuum infusion) depression is used to distribute the matrix over the textile. The exact depression depends on the matrix system, textile and geometry (Schürmann, 2007). For example Born (2020) used a 100 mbar reduction of the ambient pressure for glass fiber and epoxy resin. For this process, porous materials are needed (AVK, 2013). Preliminary test with hand layup and vacuum infusion showed, that the matrix could not penetrate the nonwoven bases on digestate fibers because it is too thick and dense. A common process for the production of short glass fiber composites is the bulk molding compound (BMC) (Hull, 1996). A doughy mix of fiber (mostly glass fibers) and matrix polymer is pressed into a complex shape (AVK, 2013). There is an increasing

interest in the combination of natural fibers and BMC. Sreenivasan et al. (2018) uses kenaf fibers, which are typically 6 mm to 12 mm long. It was shown by Lütz et al. (2019) that digestate fibers can be processed in a similar way to BMC if the length is shorter than 12 mm. The produced composites showed air inclusions and a low fiber matrix bonding, which reduces the material quality. Matrix polymers differ in viscosity and reaction kinetics (Domininghaus, 2008). For this reason, additional test series are necessary to find the process parameter for each individual polymer. The discussed results show that compression moulding is a suitable manufacturing process for the digestate fibers.

6.3 Composite properties

To determine potential applications for the digestate composites, their properties must be evaluated and compared to those of currently used materials. Without knowing mechanical properties, it is not possible to find an application for the digestate composite. Destructive and non-destructive material test were used to evaluate the produced composites. A bending test was performed to measure the strength. The strength of the digestate (83 MPa) is four times higher than the strength of MDF, and the young's modulus (around 5000 MPa) is around two times higher (Holzforschung Austria, 2017). A typical WPC is filled with 50 % wood flour and has a flexural strength of 40 MPa (Stark et al., 2004). The grass/polyethylene composites with 20 % of Arundo donax (see chapter 1) have a strength of 12 MPa and a young's modulus of 600 MPa (Ortega et al., 2021). The large variation in mechanical properties is particularly problematic for technical applications. The variation of the mechanical properties of the investigated composites is up to four times higher than that of the unfilled matrix, see figure 4.6. The comparison of the digestate composite properties to other composites is only conditionally useful because other polymer matrixes and fiber ratios are used (Hull, 1996). Both parameters influence the material properties. As mentioned, the mechanical properties of the investigated composite are comparable to WPC and MDF, and therefore similar application are suitable. The high deviation of the mechanical properties is caused by the inhomogeneous fiber material. Due to the fact that the material data fluctuates, no parts with safety concern should be designed with this material.

The durability of a composite material is crucial for finding applications and for the sustainability of a product. To determine the durability of the digestate composite, it was exposed to UV radiation and several chemicals. After 200 h of artificial weathering, WPC showed about 70 % of its original stiffness (Vogt, 2006; Stark et al., 2004) while the stiffness of digestate composite decreased to 40 % compare to the initial stiffness. the strength and stiffness reduce to 30 % and less of the original properties after storage in chemicals, except for the soda solution treatment. Natural weathering would yield

results which are closer to the real long-term behaviour of the composites then immersion in chemicals and artificially weathering. Nevertheless the artificial test lead to results comparable to other experiments using artificial weathering (Friedrich, 2018). According to the loss of properties through UV radiation, indoor furniture is a possible application of the digestate. Water absorption is another important property to find an application for the novel material. For measurement of water absorption, the material is immersed in water for a defined time. The water absorption for the digestate composite was lower than 2 % of the original mass and no swelling was observed, see chapter 3. MDF typically shows a swelling of about 50 % after water storage (Krug, 2010; Vetter et al., 2010). The behaviour under the influence of water was observed after 1 min and 10 min of immersion. To get results for the long-term water resistivity, an immersion for 24 h would be useful (Vetter et al., 2010). MDF is a typical material for furniture, especially in kitchens. The digestate composite showed similar mechanical properties and better water resistivity. Overall, furniture seems to be the most promising application for the digestate composites.

6.4 Sustainability

Sustainability has three parts: ecology, economy and social impact (Pufe, 2012). A product or process is sustainable, if all three parts are addressed. The ecological part of sustainability is particularly dependent on the source material. If the same plant is used for several applications, the land use conflict can be defused (Rösch et al., 2010). Such a concept is pursued by the biorefinery, and the biogas plant is especially suitable for its implementation (Andersen et al., 2018). The biogas plant can produce simultaneously energy, liquid fertilizer and fibers. Therefore, the solid fraction of the digestate provides the fibers, as already discussed.

During the pressing process a matrix overdose of 10 % to 15 % is necessary, this causes polymer waste, see chapter 4. The used epoxy system consists only of 45 % bio-based raw materials and it is not degradable (Sicomin, 2016). These facts are negative regarding the ecology, especially combined with the low durability, which is shown by the weathering experiment. At the present state of the development, the economic viability cannot be evaluated. An enquiry of potential costumers showed that there is interest of products out of digestate. It is also not possible to evaluate the social impact without a real production.

7 Conclusions

The presented study demonstrates that digestate can be used as a raw material for thermoset composites. The qualification of the digestate for use in composite materials is divided into three parts: fiber extraction, composite production and composite properties. The investigated digestates have a low slenderness ratio and are therefore suitable for composite material production, but not for textile production. Additional washing and defibration of the digestate improves the fiber quality. The composition and length of the fibers are similar to wood fibers. To achieve a high yield of fibers, biogas plants with a low proportion of animal excrements are preferable. A nonwoven was produced from digestate fibers using the wet laying technique, which is the starting material for the fiber composite. To ensure complete impregnation of the nonwoven with the thermoset matrix, an excess of matrix was used. The nonwoven was consolidated in a hot press at 4.5 MPa and 100 °C. The quality of the material and its field of application were evaluated in detail by the properties analysed. The composite material has a stiffness of about 5000 MPa and a strength of about 80 MPa, which is comparable to other natural fiber reinforced plastics. However, the chemical and weather resistance could be improved. Biogas plants with a low excrement content offer the highest potential for fiber production. The material properties are comparable to those of common furniture materials such as MDF. Due to the better results in water absorption, the application in kitchen furniture is to be emphasized.

Bibliography

3N Kompetenzzentrum, 2022. Naturfaserverbundwerkstoffe. https://www.3-n.info/themenfelder/stoffliche-nutzung/naturfaserverbundwerkstoffe.html visited on 09.06.2022.

Ahmed, Z., Akhter, F., 2001. Jute retting: an overview. Online Journal of Biological Science 7, 685–688.

Aleksendrić, D., Carlone, P., 2015. Introduction to composite materials, in: Soft Computing in the Design and Manufacturing of Composite Materials. Elsevier, pp. 1–5.

Andersen, L., Lamp, A., Dieckmann, C., Baetge, S., Schmidt, L.M., Kaltschmitt, M., 2018. Biogas plants as key units of biorefinery concepts: Options and their assessment 283, 130–139.

Arnold, J., Dittrich, J.H., Finnimore, E., Haase, J., Hempel, P., 2013. Prüfverfahren in der Textil- und Bekleidungstechnik. Springer.

AVK, 2013. Handbuch Faserverbundkunststoffe/Composites. Springer.

Barbos, J.D.V., Azevedo, J.B., da Silva M. Cardoso, P., da Costa Garcia Filho, F., del Rio, T.G., 2020. Development and characterization of wpcs produced with high amount of wood residue. Journal of Materials Research and Technology 9, 9684 – 9690.

Barbosa, A.P.C., Fulco, A.P.P., Guerra, E.S., Arakaki, F.K., Tosatto, M., Costa, M.C.B., Melo, J.D.D., 2017. Accelerated aging effects on carbon fiber/epoxy composites. Composites Part B: Engineering 110, 298–306.

Berger, W., Faulstich, H., Fischer, P., Heger, A., Jacobasch, H.J., 2011. Textile Faserstoffe. Springer.

Berthet, M.A., Mayer-Laigle, C., Rouau, X., Gontard, N., Angellier-Coussy, H., 2017. Sorting natural fibres: A way to better understand the role of fibre size polydispersity on the mechanical properties of biocomposites. Composites Part A: Applied Science and Manufacturing 95, 12–21.

Biernacki, P., Steinigeweg, S., Borchert, A., Uhlenhut, F., 2013. Application of anaerobic digestion model no. 1 for describing anaerobic digestion of grass, maize, green weed silage, and industrial glycerine. Bioresource Technology 127, 188–194.

Blaga, A., 1978. Grp composite materials in construction: properties, applications and durability. Indian Forum 9, 27–32.

BMBF, 2020. National bioeconomy strategy. `https://www.bmbf.de/SharedDocs/Publikationen/de/bmbf/FS/31617_Nationale_Biooekonomiestrategie_Langfassung_en.pdf?__blob=publicationFile&v=5` visited on 23.06.2022.

Bonnet, M., 2009. Kunststoffe in der Ingenieuranwendung verstehen und zuverlässig auswählen. Vieweg + Teubner.

Born, L., 2020. Grundlagen für die Auslegung und Gestaltung eines Hybridmaterials für außen liegende, adaptive Fassadenbauteile aus Faserverbundkunststoff. Ph.D. thesis. Universität Stuttgart.

Bourmaud, A., Dhakal, H., Habrant, A., Padovani, J., Siniscalco, D., Ramage, M.H., Beaugrand, J., Shah, D.U., 2017. Exploring the potential of waste leaf sheath date palm fibres for composite reinforcement through a structural and mechanical analysis. Composites Part A: Applied Science and Manufacturing .

Bradley, W.L., Conroy, S., 2019. Using Agricultural Waste to Create More Environmentally Friendly and Affordable Products and Help Poor Coconut Farmers. E3S Web of Conferences 130, 1–10.

Campbell, F.C., 2010. Structural Composite Materials. ASM International.

Cantero, G., Arbelaiz, A., Llano-Ponte, R., Mondragon, I., 2003. Effects of fibre treatment on wettability and mechanical behaviour of flax/polypropylene composites. Composites Science and Technology 63, 1247 – 1254. Eco-Composites.

Carus, M., Eder, A., Scholz, L., 2015. Bioverbundwerkstoffe Naturfaserverstärkte Kunststoffe (NFK) und Holz-Polymer-Werkstoffe (WPC).

Cherif, C. (Ed.), 2011. Textile Werkstoffe für den Leichtbau. Springer.

Cherubini, F., 2010. The biorefinery concept: Using biomass instead of oil for producing energy and chemicals. Energy Conversion and Management 51, 1412–1421.

Cichosz, S., Masek, A., 2020. IR study on cellulose with the varied moisture contents: Insight into the supramolecular structure. Materials 13, 4573.

Correia, C.A., Valera, T.S., 2019. Cellulose nanocrystals and jute fiber-reinforced natural rubber composites: Cure characteristics and mechanical properties. Materials Research 22.

Crowther, J. (Ed.), 1995. Oxford Advanced Learner's Dictionary of Current English. Oxford Universty Press.

Daniel-Gromke, J., Rensberg, N., Denysenko, V., Barchmann, T., Oehmichen, K., Beil, M., Beyrich, W., Krautkremer, B., Trommler, M., Reinholz, T., Vollprecht, J., Rühr, C., 2020. Optionen für Biogas-Bestandsanlagen bis 2030 aus ökonomischer und energiewirtschaftlicher Sicht. Umweltbundesamt.

Daniel-Gromke, J., Rensberg, N., Denysenko, V., Stinner, W., Schmalfuß, T., Scheftelowitz, M., Nelles, M., Liebetrau, J., 2017. Current developments in production and utilization of biogas and biomethane in germany. Chemie Ingenieur Technik 90, 17–35.

Deepanraj, B., Sivasubramanian, V., Jayaraj, S., 2014. Biogas generation through anaerobic digestion process: An overview. Research Journal of Chemistry and Environment 18, 80–93.

Dhakal, H., Bourmaud, A., Berzin, F., Almansour, F., Zhang, Z., Shah, D.U., Beaugrand, J., 2018. Mechanical properties of leaf sheath date palm fibre waste biomass reinforced polycaprolactone (PCL) biocomposites. Industrial Crops and Products 126, 394–402.

DIN, 2001. DIN 60001-1:2001-05 Textile Fibres - Part 1: Natural Fibres and Letter codes.

DIN, 2004. DIN EN ISO 1183-2 Kunststoffe- Verfahren zur Bestimmung der Dichte von nicht verschäumten Kunststoffen.

DIN, 2006. EN ISO 16472:2006 Animal feeding stuffs – Determination of amylase-treated neutral detergent fibre content (aNDF).

DIN, 2008. EN ISO 13906:2008 Animal feeding stuffs – Determination of acid detergent fibre (ADF) and acid detergent lignin (ADL) contents.

DNFI, 2018. Forecast world fibre production bremen cotton report 05/06. `https://textile-network.com/en/Technical-Textiles/Fasern-Garne/Forecast-world-fibre-production` visited on 26.4.2020.

Domininghaus, H., 2008. Kunststoffe. Springer.

Eshwara, P.K., Divakara, R.P., Udaya, K.C., 2018. Experimental Studies on Behavior of Keratin Based Human Hair Fiber - A New Reinforcing Material for Composites. International Journal of Engineering & Technology 7, 459–463.

Essel, R., Breitmayer, E., Carus, M., Pfemeter, A., Bauermeister, U., 2015. Stoffliche Nutzung lignocellulosehaltiger Gärprodukte für Holzwerkstoffe aus Biogasanlagen. Nova-Institut.

FAO, 2021. Data - crops and livestock products - fiber plants. `https://fenixservices.fao.org/faostat/static/bulkdownloads/Production_Crops_Livestock_E_All_Data.zip` visited on 12.1.2021.

Fettweis, Kühl, 2010. Comparative Tests for the Purposes of a Crude Fibre Analysis using both the Official VDLUFA Method and FibreBag Technology (C. Gerhardt), in: Landschaftselement oder Rohstofflieferant - zur Multifunktionalität des Grünlandes, VDLUFA-Verlag. pp. 804–810.

Fitri, S.P., Zaman, M.B., Priyanta, D., Hidayat, M., 2017. Application waste sawdust as mixed polyurethane insulation in traditional cold storage of fishing vessel. International Journal of Marine Engineering Innovation and Research 1, 46–50.

Foreest, F., 2012. Perspectives for biogas in Europe. The Oxford Institute for Energy Studies.

Fortea-Verdejo, M., Bumbaris, E., Burgstaller, C., Bismarck, A., Lee, K.Y., 2017. Plant fibre-reinforced polymers: where do we stand in terms of tensile properties? International Materials Reviews 62, 441–464.

Friedrich, D., 2018. Comparative study on artificial and natural weathering of wood-polymer compounds: A comprehensive literature review. Case Studies in Construction Materials 9, e00196.

Friedrich, D., Luible, A., 2016. Investigations on ageing of wood-plastic composites for outdoor applications: A meta-analysis using empiric data derived from diverse weathering trials. Construction and Building Materials 124, 1142–1152.

Frigge, M., Hoaglin, D.C., Iglewicz, B., 1989. Some implementations of the boxplot. The American Statistician 43, 50–54.

Fuchs, H., Albrecht, W. (Eds.), 2012. Vliesstoffe. Wiley-VCH.

Galletti, A.M.R., D'Alessio, A., Licursi, D., Antonetti, C., Valentini, G., Galia, A., o Di Nasso, N.N., 2015. Midinfrared FT-IR as a tool for monitoring herbaceous biomass composition and its conversion to furfural. Journal of Spectroscopy 2015, 1–12.

Garrote, G., Dominquez, H., Parajo, J.C., 1999. Hydrothermal processing of lignocellulosic materials. Holz als Roh- und Werkstoff 57, 191–202.

Gebhardt, M., Milwich, M., Gresser, G.T., Lemmer, A., 2021a. Impact of long-term weathering on the properties of a digestate-based biocomposite. Materials Circular Economy 3.

Gebhardt, M., Wanek, N., Lemmer, A., Gresser, G.T., 2021b. Comparison of fibers from hop rich biogas digestate with natural fibers as raw material for composites. Journal of Natural Fibers , 1–11.

Gessner, W., 1955. Naturfasern Chemiefasern. Fachbuchverlag Leipzig.

Gries, T., 2015. Textile Fertigungsverfahren: Eine Einführung. Hanser.

Grundmann, E., 2007. Faserpflanzen aus ökologischem Anbau Anbau - Verarbeitung - Markt. Lebendige Erde.

Hanausek, T.F., 2012. Lehrbuch der Technischen Mikroskopie. Salzwasser.

Hasegawa, T., Sands, R.D., Brunelle, T., Cui, Y., Frank, S., Fujimori, S., Popp, A., 2020. Food security under high bioenergy demand toward long-term climate goals. Climatic Change 163, 1587–1601.

Holzforschung Austria, 2017. Mdf. `https://www.dataholz.eu/fileadmin/dataholz/media/baustoffe/Datenblaetter_de/mdf.de_01.pdf` visited on 11.06.2022.

Hospodarova, V., Singovszka, E., Stevulova, N., 2018. Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials. American Journal of Analytical Chemistry 09, 303–310.

Hull, D..C.T., 1996. An introduction to composite materials. Cambridge University Press.

Jain, S., 2019. Global Potantial of Biogas. The World Biogas Association.

Kammerhofer, P.P., 2018. Analyse der Haltbarkeit von Werkzeugen aus carbonfaserverstärkten Kunststoffen. phdthesis. Technischen Universität München.

Knackstedt, W., 1939. Untersuchung über pflanzliche Bastfasern. Ph.D. thesis. Technische Hochschule Carolo-Wilhelmina zu Braunschweig.

König, Ulich; Fudel, A., 2005. Verfahren zur Herstellung von Naturfasern aus Biogasanlagen und deren Verwendung. DE 10 2005 034 586 B3.

Königsberger, S., Deorte, M., Reuland, G., 2019. EBA Statistical Report 2018. European Biogas Association.

Koolen, G., van Vuure, A., 2019. The effect of silicone coatings on the durability of natural fibrecomposites when subjected to hygrothermal aging, in: ICNF 2019, pp. 64–65.

Koszel, M., Przywara, A., Jakubowska, M.K., Kraszkiewicz, A., 2017. Evaluation of the use of biogas plant digestate as a fertilizer in field cultivation plant, in: Farm Machinery and Processes Management in Sustainable Agriculture.

Kotnarowska, D., 1999. Influence of ultraviolet radiation and aggressive media on epoxy coating degradation. Progress in Organic Coatings 37, 149–159.

Kozlowski, R., Baraniecki, P., Barriga-Bedoya, J., 2005. Bast fibres (flax, hemp, jute, ramie, kenaf, abaca), in: Blackburn, R. (Ed.), Biodegradable and Sustainable Fibres. Woodhead Publishing, pp. 36 – 88.

Krug, D., 2010. Einfluss der Faserstoff-Aufschlussbedingungen unddes Bindemittels auf die Eigenschaften vonmitteldichten Faserplatten (MDF) für eine Verwendung imFeucht- und Außenbereich. Universität Hamburg.

Kumar, B.G., Singh, R.P., Nakamura, T., 2002. Degradation of carbon fiber-reinforced epoxy composites by ultraviolet radiation and condensation. Journal of Composite Materials 36, 2713–2733.

Lee, C.H., Khalina, A., Lee, S.H., Liu, M., 2020. A comprehensive review on bast fibre retting process for optimal performance in fibre-reinforced polymer composites. Advances in Materials Science and Engineering 2020, 1–27.

Liu, K., 2009. Some factors affecting sieving performance and efficiency. Powder Technology 193, 208–213.

Lütz, M., Hügel, M., Milwich, M., Gresser, G.T., 2019. Investigation of fermentation residue of biogas plants for the production of sustainable fiber reinforced composites. Materials Today: Proceedings 31, 5242–5246.

Macatangay, P., Mangundayao, E., Rosales, C., 2012. Utilization of agricultural wastes in the manufacture of composite boards. ASEAN Journal on Science and Technology for Development 29, 129–140.

Madyan, O.A., Wang, Y., Corker, J., Zhou, Y., Du, G., Fan, M., 2020. Classification of wood fibre geometry and its behaviour in wood poly(lactic acid) composites. Composites Part A: Applied Science and Manufacturing 133, 105871.

Martin, J., 2006. Materials for Engineering. Elsevier.

Materialarchiv.de, 2020. Abaca bananenfasern. `https://materialarchiv.ch/de/material_2136/?q=abaca` visited on 18.08.2022.

Mellor, P., Lord, R., João, E., Thomas, R., Hursthouse, A., 2021. Identifying non-agricultural marginal lands as a route to sustainable bioenergy provision - a review and holistic definition. Renewable and Sustainable Energy Reviews 135.

Mishra, S.C., Nayak, N.B., 2010. An Investigation of Dielectric Properties of Chicken Feather Reinforced Epoxy Matrix Composite. Journal of Reinforced Plastics and Composites 29, 2691–2697.

Moretto, G., Russo, I., Bolzonella, D., Pavan, P., Majone, M., Valentino, F., 2020. An urban biorefinery for food waste and biological sludge conversion into polyhydroxyalkanoates and biogas. Water Research 170.

Nations, U., 2021. The 17 goals. `https://sdgs.un.org/goals` visited on 10.4.2021.

Naupert, A., Prager, E., Menzel, K.C., Hoffmann, L., Rockstroh, E., Hofmann, W., Döcke, W., Fischer, H., 1967. Textile Faserstoffe. Fachbuchverlag Leipzig.

Niewöhner, J., Bruns, A., Haberl, H., Hostert, P., Krueger, T., Lauk, C., Lutz, J., Müller, D., Nielsen, J.Ø., 2016. Land use competition: Ecological, economic and social perspectives, in: Land Use Competition. Springer, pp. 1–17.

Nizin, D.R., Nizina, T., Selyaev, V., Chernov, A., Gorenkova, A., 2019. Natural climatic aging of epoxy polymers taking into account the seasonality impact. Key Engineering Materials 799, 159–164.

Obeng, G.Y., Amoah, D.Y., Opoku, R., Sekyere, C.K.K., Adjei, E.A., Mensah, E., 2020. Coconut wastes as bioresource for sustainable energy: Quantifying wastes, calorific values and emissions in ghana. Energies 13.

Ortega, Z., Romero, F., Paz, R., Suárez, L., Benítez, A.N., Marrero, M.D., 2021. Valorization of invasive plants from macaronesia as filler materials in the production of natural fiber composites by rotational molding. Polymers 13.

Paul, N., 2006. Datensammlung "Formpressen und Spritzgießen mit Naturfasern" in Vorbereitung. `https://news.fnr.de/fnr-pressemitteilung/datensammlung-formpressen-und-spritzgiessen-mit-naturfasern-in-vorbereitung` visited on 09.06.2022.

Pfeiffer, D., Thrän, D. (Eds.), 2015. Messmethodensammlung Biogas. DBFZ.

Pschorr, F.E., Cianciarulo, A.N., 1965. Weathering of epoxy resins systems. Polymer Engineering and Science , 166–170.

Pufe, I., 2012. Nachhaltigkeit. UVK.

Ramamoorthy, S.K., Persson, A., Skrifvars, M., 2014. Reusing textile waste as reinforcements in composites. Journal of Applied Polymer Science 131.

Rana, S., Fangueiro, R. (Eds.), 2016. Fibrous and Textile Materials for Composite Applications. Springer.

Rana, S., Pichandi, S., Parveen, S., Fangueiro, R., 2014. Natural plant fibers: Production, processing, properties and their sustainability parameters, in: Textile Science and Clothing Technology. Springer, pp. 1–35.

Razali, Nadlene; Sapuan, S.J.M.I.M.R., 2015. Material characterization of rosellefibre (hibiscus sabdariffa l.) as potentialreinforcement material for polymercomposites. Fibres and Textiles in Eastern Europe 23, 23–30.

Riedel, U., Nickel, J., 2000. Konstruktionswerkstoffe aus nachwachsenden rohstoffen (Bio-Verbunde), in: Tagungshandbuch - 3. Internationale AVK-TV Tagung für Verstärkte Kunststoffe und Duroplastische Formmassen, pp. 493–498.

Riley, A., 2012. Paper and paperboard packaging, in: Emblem, A., Emblem, H. (Eds.), Packaging Technology. Woodhead, pp. 178 – 239.

Rösch, C., Jörissen, J., Skarka, J., Knapp, M., 2010. Strategies to reduce land use competition and increasing the share ofbiomass in the german energy supply, in: 18th European Biomass Conference and Exhibition„ pp. 34–39.

Roylance, D., 1978. Weathering of fiber-reinforced epoxy composites. Polymer Engineering and Science 18.

Rueden, C.T., Schindelin, J., Hiner, M.C., DeZonia, B.E., Walter, A.E., Arena, E.T., Eliceiri, K.W., 2017. Imagej2: Imagej for the next generation of scientific image data. BMC Bioinformatics 18.

Russell, S.J., 2006. Handbook of Nonwovens. Woodhead.

Sadeghifar, H., Ragauskas, A., 2020. Lignin as a UV light blocker—a review. Polymers 12, 1134.

Salit, M.S., Jawaid, M., Yusoff, N.B., Hoque, M.E. (Eds.), 2015. Manufacturing of Natural Fibre Reinforced Polymer Composites. Springer International Publishing.

Sandermann, W., Schlumborn, F., 1962. On the effect of filtered ultraviolet light on wood - part 1: Photometric and chromatographic investigations on wood powders. Holz als Roh- und Werkstoff 7, 245–252.

Sathish, S., Karthi, N., Prabhu, L., Gokulkumar, S., Balaji, D., Vigneshkumar, N., Farhan, T.S.A., AkilKumar, A., Dinesh, V., 2021. A review of natural fiber composites: Extraction methods, chemical treatments and applications. Materials Today: Proceedings 45, 8017–8023.

Sauer, M., 2019. Composites-Marktbericht 2019 - Der globale CF- und CC-Markt 2019 -. Carbon Composites e. V.

Saville, B., 1999. Physical Testing of Textiles. Woodhead.

Scaffaro, R., Lopresti, F., Botta, L., 2018. PLA based biocomposites reinforced with posidonia oceanica leaves. Composites Part B: Engineering 139, 1–11.

Scarlat, N., Dallemand, J.F., Fahl, F., 2018. Biogas: Developments and perspectives in europe. Renewable Energy 129, 457–472.

Schenek, A., 2001. Naturfaser-Lexikon. Deutscher Fachverlag.

Schimpf, U., 2014. Enzymatischer Abbau des Lignocellulosekomplexes in Energiepflanzen unter besonderer Berücksichtigung der Silierung und der Biogasproduktion. Ph.D. thesis. Humboldt-Universität zu Berlin.

Schimpf, U., Hanreich, A., Mänert, P., Unmack, T., Junne, S., Renpenning, J., Lopez-Ulibarri, R., 2013. Improving the Efficiency of Large-Scale Biogas Processes: Pectionalytic Enzymes Accelerate the Lingocellulose Degradation. Journal of Sustainable Energy & Environment 4, 53–60.

Schmidt, P., Körber, R., Coppers, M., 2003. Sieben und Siebmaschinen. Wiley-VCH.

Schneider-Götz, N., Mastel, K., 2007. Gärreste aus Biogasanlagen - Nähr- und Schadstoffe,Einsatzmöglichkeiten im Ackerbau.

Schuldt, A., Dinse, R., 2010. Übungen zur Tierernährung im Rahmen des Moduls Tierernährung und Futtermittelkunde.

Schürmann, H., 2007. Konstruieren mit Faser-Kunststoff-Verbunden. Springer.

Sergion., M., Terrones, L.A.H., Lopes, F.P., d'Almeida, J.R.M., 2005. Mechanical Strength of Polyester Matrix Composites Reinforced with Coconut Fiber Wastes. Revista Matéria 10, 571–576.

Shevlyakov, G., Andrea, K., Choudur, L., Smirnov, P., Ulanov, A., Vassilieva, N., 2013. Robust versions of the tukey boxplot with their application to detection of outliers, in: International Conference on Acoustics, Speech and Signal Processing, IEEE. pp. 6506–6510.

Sicomin, 2016. Technisches Datenblatt SR GreenPoxy 56 / SZ8525.

Siebel, T., 2020. Naturfasern eignen sich für den karosseriebau. https://www.springerprofessional.de/biowerkstoffe/karosserie/naturfasern-eignen-sich-fuer-den-karosseriebau/18695956 visited on 21.2.2020.

Sisti, L., Totaro, G., Vannini, M., Celli, A., 2017. Retting process as a pretreatment of natural fibers for the development of polymer composites, in: Lignocellulosic Composite Materials. Springer, pp. 97–135.

Sörgel, C., Mantau, U., Weimar, H., 2006. Standorte der Holzwirtschaft – Aufkommen von Sägenebenprodukten und Hobelspänen.

Sreenivasan, S., Sulaiman, S., Ariffin, M.K.A.M., Baharudin, B.H.T., Abdan, K., 2018. Physical properties of novel kenaf short fiber reinforced bulk molding compounds (BMC) for compression moulding. Materials Today: Proceedings 5, 1226–1232.

Stark, N.M., Matuana, L.M., Clemons, C.M., 2004. Effect of processing method on surface and weathering characteristics of wood-flour/HDPE composites. Journal of Applied Polymer Science 93, 1021–1030.

Steffen, R., Szolar, O., Braun, R., 1998. Feedstocks for Anaerobic Digestion.

Steinbach, D., 2020. Umsetzung von Lignocellulosen zu Hydroxymethylfurfural in einer hydrothermalen Bioraffinerie zur. Ph.D. thesis. Karlsruher Instituts für Technologie (KIT).

Suárez, L., Paz, R., Ortega, Z., Díaz, N., Monzón, M., Marrero, M.D., Benítez, A.N., 2019. Ecofibras project: a strategy to improve ecosystems affected byinvasive plant species in macaronesia, in: ICNF 2019. TecMinho.

Taurino, R., Lancellotti, I., Tatàno, F., Carchesio, M., Pozzi, P., 2016. Mechanical and chemical resistance of composite materials with addition of anaerobic digestate. Composites Part B: Engineering 92, 259–264.

Tedesco, S., Barroso, T.M., Olabi, A., 2014. Optimization of mechanical pre-treatment of laminariaceae spp. biomass-derived biogas. Renewable Energy 62, 527–534.

Tiefenthaller, F., 2006. Futterwerttabelle für Wiederkäuer. Landwirtschaftskammer Oberösterreich Abteilung Tierproduktion/Referat Fütterung.

Torrijos, M., 2016. State of development of biogas production in europe. Procedia Environmental Sciences 35, 881–889.

Ulrich, H., 1956. Handbuch der chemischen Untersuchung der Textilfaserstoffe: Zweiter Band Chemismus, Eigenschaften und Einsatz der textilen (nicht veränderten) Faserstoffe und ihre Prüfung. Springer.

Van Soest, P.J., Robertson, J.B., 1970. Systems of analysis for evaluating fibrous feeds, in: Pigden, W.J., Balch, C.C., Graham, M. (Eds.), Standardization of Analytical Methodology for Feeds, pp. 49–60.

Ververis, C., Georghiou, K., Christodoulakis, N., Santas, P., Santas, R., 2003. Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production. Industrial Crops and Products 19, 245–254.

Vetter, L.D., den Bulcke, J.V., Acker, J.V., 2010. Envelope treatment of wood based materials with concentrated organosilicons. European Journal of Wood and Wood Products 69, 397–406.

Vogt, D., 2006. Studie wood plastic composites, Holz-Kunststoff-Verbundwerkstoffe. Landwirtschaftsverlag.

Wang, H., Song, X., Xu, L., Li, X., Wang, J., Zhao, Y., Cai, Z., 2016. Fabrication of acid-resistant fabrics with fluoropolymer/SiO2 nanocomposites for the application of protective clothing. Journal of Industrial Textiles 47, 727–740.

Wang, Y., Xiao, X., Wang, S., Li, K., Jiang, Y., Ma, Y., Zhang, T., Ran, R., 2019. Exploration on UV-blocking performance of lignin from palm (trachycarpus fortunei) fiber. Journal of Natural Fibers 18, 71–79.

Wulf, S., Roth, U., 2018. Verfahren zur Aufbereitung von Gärresten.

Yamamoto, T. ; Medina, L.S.R., 2005. Tensile properties of natural fibre reinforced thermoset composites. Advanced Compoistes Letters 14.

Zeng, T., Büchner, D., Bischoff, J., Schneider, A., 2012. Beurteilung der thermischen Nutzung von Biomassepellets aus Gärresten. DBFZ Deutsches Biomasse Forschungs Zentrum.

Zethner, G., Pfundtner, E., Humer, J., 2002. Qualität von Abfällen aus Biogasanlagen. Umweltbundesamt.

Zhou, S., Li, Y., Huang, L., Chen, L., Miao, Q., 2018. Enhancedreactivity of kraft-based viscose-grade dissolving pulp by hollander beating treatment. Bioresources.com 13, 2861–2870.

Zweben, C., 2015. Materials and Engineering Mechanics. John Wiley & Sons, Inc.. chapter Composite Materials. pp. 1–37.