frontiers in Energy Research

REVIEW
published: 27 November 2020
doi: 10.3389/fenrg.2020.579577

Beyond Sugar and Ethanol Production: Value Generation Opportunities Through Sugarcane Residues

*Steffi Formann[1†], Alena Hahn[2,3†], Leandro Janke[4], Walter Stinner[5,7], Heike Sträuber[6], Washington Logroño[6] and Marcell Nikolausz[6]**

[1] Department of Thermochemical Conversion, Deutsches Biomasseforschungszentrum Gemeinnützige GmbH (DBFZ), Leipzig, Germany, [2] Department of Bioenergy Systems, Deutsches Biomasseforschungszentrum Gemeinnützige GmbH (DBFZ), Leipzig, Germany, [3] Department of Bioenergy, Helmholtz Centre for Environmental Research—UFZ, Leipzig, Germany, [4] Department of Energy and Technology, SLU-Swedish University of Agricultural Sciences, Uppsala, Sweden, [5] Department of Biochemical Conversion, Deutsches Biomasseforschungszentrum Gemeinnützige GmbH (DBFZ), Leipzig, Germany, [6] Department of Environmental Microbiology, Helmholtz Centre for Environmental Research—UFZ, Leipzig, Germany, [7] Hefei University, Hefei, China

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***Correspondence:**
Marcell Nikolausz
marcell.nikolausz@ufz.de

[†]These authors contributed equally to the work.

Specialty section:
This article was submitted to Bioenergy and Biofuels, a section of the journal Frontiers in Energy Research

Received: 03 July 2020
Accepted: 22 September 2020
Published: 27 November 2020

Citation:
Formann S, Hahn A, Janke L, Stinner W, Sträuber H, Logroño W and Nikolausz M (2020) Beyond Sugar and Ethanol Production: Value Generation Opportunities Through Sugarcane Residues. Front. Energy Res. 8:579577. doi: 10.3389/fenrg.2020.579577

Sugarcane is the most produced agricultural commodity in tropical and subtropical regions, where it is primarily used for the production of sugar and ethanol. The latter is mostly used to produce alcoholic beverages as well as low carbon biofuel. Despite well-established production chains, their respective residues and by-products present unexploited potentials for further product portfolio diversification. These fully or partially untapped product streams are a) sugarcane trash or straw that usually remain on the fields after mechanized harvest, b) ashes derived from bagasse combustion in cogeneration plants, c) filter cake from clarification of the sugarcane juice, d) vinasse which is the liquid residue after distillation of ethanol, and e) biogenic CO_2 emitted during bagasse combustion and ethanol fermentation. The development of innovative cascading processes using these residual biomass fractions could significantly reduce final disposal costs, improve the energy output, reduce greenhouse gas emissions, and extend the product portfolio of sugarcane mills. This study reviews not only the state-of-the-art sugarcane biorefinery concepts, but also proposes innovative ways for further valorizing residual biomass. This study is therefore structured in four main areas, namely: i) Cascading use of organic residues for carboxylates, bioplastic, and bio-fertilizer production, ii) recovery of unexploited organic residues via anaerobic digestion to produce biogas, iii) valorization of biogenic CO_2 sources, and iv) recovery of silicon from bagasse ashes.

Keywords: anaerobic digestion, anaerobic fermentation, biogenic silicon, carbon capture and utilization (CCU), carboxylates, methane production, sugarcane, power-to-x

INTRODUCTION

Sugarcane (*Saccharum officinarum*) is cultivated in tropical and subtropical regions and it is the most produced agricultural commodity worldwide. It is primarily used for the production of sugar and ethanol, with the latter being mostly used to yield alcoholic beverages and low carbon biofuels. In 2018, the top producers of sugarcane were Brazil (747 Mt), India (377 Mt), China (109 Mt), Thailand (104 Mt), and Mexico (57 Mt) (FAOSTAT 2019). However, besides sugar and ethanol production, there are further untapped potentials and options for improvement within the sugarcane industry, in particular with regard to environmental issues associated with the handling of waste products of the traditional process chains (Oliveira et al., 2017; Oliveira B. G. et al., 2020).

Depending on the regional context, sugarcane mills present different production setups, targeting specific products. For instance, in Brazil, due to local policies for promoting the production and use of biofuels, industrial facilities with both sugar and bioethanol production capacities are often found in an integrated refinery setup, referred to as annexed sugarcane mills. In contrast, distilleries that only produce bioethanol (i.e., autonomous mills) are not as widely spread in Brazil. In other sugarcane growing countries, stand-alone sugar mills can also be found. Regardless of the product being produced, the different types of sugarcane mills have some operational features in common, such as harvesting, milling, juice clarification, and bagasse-based cogeneration. It is important to note that, depending on the harvesting technique used, straw composed of tops and leaves (also known as sugarcane trash) becomes available as a source of biomass (mechanized harvesting system) or is burned on the fields prior to manual sugarcane harvesting. The latter one can cause severe air pollution due to particulate matter emissions (Leal et al., 2013). After the sugarcane juice clarification, important differences in the industrial process between autonomous and annexed mills are observed. While in autonomous mills the juice is solely used for bioethanol production, a more flexible use of this raw material is observed in annexed ones. In this case, market prices and conditions drive the predominant use of juice for either bioethanol and/or sugar production with synergies between both production routes by re-using molasses, i.e., a by-product of the sugar production process that can serve as a source of fermentable sugars for the bioethanol production. Within both production chains, different types of solid, semi-solid, and liquid residues are produced with different characteristics depending on the type of product being produced (sugar or bioethanol) (Renó et al., 2014; Leite et al., 2015a). Similarly, different amounts of carbon dioxide (CO_2) as gaseous emissions are generated, in particular during the ethanol fermentation process and from bagasse combustion. **Figure 1** presents an overview of the sugar, bioethanol, and heat/power production system as well as a simplified mass balance of both autonomous and annexed sugarcane mills. In case of annexed sugarcane mills, the yields of residues are different and vary according to the technology and ratio of the end-products (**Figure 1**).

Despite the maturity of sugarcane processing technologies, there are still many unresolved environmental issues that are to be addressed via a better valorization of waste products in an advanced biorefinery setup that implements circular economy concepts. Six significant waste and by-products streams in the sugarcane industry are straw, bagasse, filter cake, vinasse, molasses, and CO_2. 1) With burnt cane harvest still being in practice in many countries (Silalertruksa et al., 2015; Pongpat et al., 2017), local air pollution persists to occur, causing severe respiratory diseases in the area (Le Blond et al., 2017) and contributing to greenhouse gas (GHG) emissions. While the remaining ash of this burning process could theoretically improve or preserve the soil quality, compounds formed during the incineration also contribute to soil and groundwater contaminations (e.g., polycyclic aromatic hydrocarbons) (Netto et al., 2004). While burnt cane harvest is still the predominant form of harvest in Thailand, the green harvesting of sugarcane is gaining ground in many other countries (Pongpat et al., 2017). With this green harvesting approach, straw remains on the fields that can alternatively be used as feedstock for biogas production via AD. 2) Bagasse is mainly utilized in boilers or cogeneration units to provide heat and power for the milling and distillation process or, in case of larger plants, even to produce electricity to feed it into the grid (De Paoli et al., 2011). However, especially in smaller factories, only a fraction of bagasse is used and the rest causes disposal problems. Selling surplus bagasse is an option but it depends on the market situation and the transportation cost considering the delivery distance between the sugarcane mill and potential bagasse users (Salomon et al., 2011). 3) Filter cake or press mud is usually spread on the fields as fertilizer but is also associated with leaching and GHG emissions during the decomposition of the filter cake (Elsayed et al., 2008; Janke et al., 2015). To avoid these detrimental effects on the groundwater quality and the climate, alternative filter cake uses are to be investigated. 4) Vinasse is mainly used for fertirrigation (also called fertigation), which is the irrigation with liquids contributing to increased soil fertility. However, temporary storage of the vinasse in open storage ponds and lagoons leads to methane emission (de Oliveira et al., 2015) and the fertirrigation has further negative effects on the soil quality (de Oliveira et al., 2013; Fuess et al., 2017c). For instance, it increases the salinity and heavy metal accumulation in the soils with overall adverse effects on the crop yields (Christofoletti et al., 2013). 5) Molasses derived from the sugar production has still high energetic value and it is often used as a substrate for ethanol production, as feed additive or as food ingredient. 6) At most current sugarcane refineries, CO_2 from bagasse combustion and sugarcane juice fermentation is simply vented to the atmosphere. However, by capturing the CO_2, it can be a valuable, renewable carbon source for material applications in various industries as well as, when combined with hydrogen, a renewable fuel for transportation. Alternatively, the biogenic CO_2 from the sugarcane industry can also be stored geologically in view of generating negative emission credits.

A potential improvement of the sugarcane industry is a better implementation of circular economy approaches via the cascading use of the above-mentioned wastes and residues to foster bioeconomy concepts. In contrast to the traditional take-make-use-dispose strategy of a linear economy, circular economy tries to minimize wastes and pollution by keeping products and materials in cascading use to create the most economic value out of these by-products and to maximize their recycling and reuse (Hysa et al., 2020). Cascading use is based on a hierarchical, efficient use of bio-based resources focusing first on higher value products and ending with energy recovery (Keegan et al., 2013). As such, circular economy is not only a scientific idea (D'Amato et al., 2017; Korhonen et al., 2018), but it has become an

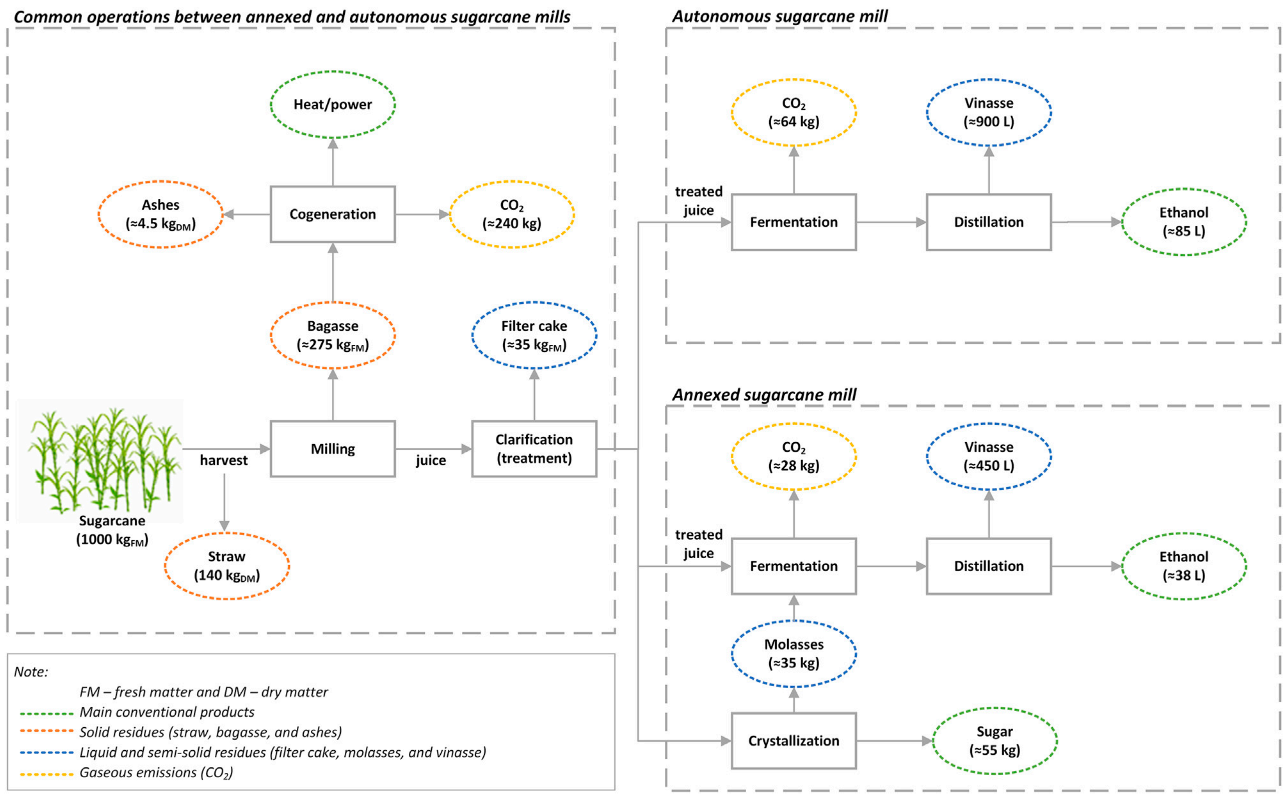

FIGURE 1 | Scheme of the sugar and bioethanol production process from sugarcane with the associated waste production.

important basis for economic development in various countries and regions, such as in important economic areas like the European Union (European Comission, 2020). In a transition away from fossil carbon sources, the bioeconomy plays an increasingly important part under the broader circular economy perspective (D'Amato et al., 2017).

Therefore, the present review discusses not only the state-of-the-art sugarcane biorefinery, but also proposes innovative ways for further valorizing residual biomass by cascading use, including the recovery of silicon from bagasse ashes, the cascading use of organic residues for carboxylates, bioplastic and bio-fertilizer production, the recovery of unexploited organic residues via anaerobic digestion (AD) to produce biogas, as well as the valorization of biogenic CO_2 sources. Such improved biorefinery approach could further diversify the product range of traditional sugarcane mills by including higher value products making the sector more profitable and less dependent on price fluctuation of competing products based on fossil fuels.

CASCADING USE OF ORGANIC RESIDUES FOR CARBOXYLATES, BIOPLASTICS, AND BIO-FERTILIZER PRODUCTION

Carboxylate Platform

Residues from the sugarcane industry with high water content such as sugarcane filter cake (SFC) or vinasse are predestined for biotechnological processes, notably for the production of chemicals or bioenergy with the help of microbial communities. Dryer biomass, such as straw or bagasse, might be co-fermented with vinasse or other aqueous waste streams to increase their moisture content and thus make them suitable for biological degradation processes.

For the production of carboxylates, which are valuable basic chemicals with a broad application spectrum, anaerobic fermentation of sugarcane residues by microbiota can be conducted. The produced carboxylates can be used directly in the chemical industry or be converted to secondary products via (electro)chemical or biological processes, e.g., for production of bioplastics, fuel, food and feed additives, pharmaceuticals or cosmetics. The carboxylate production can also be combined with AD in a cascading process: After recovery of the carboxylates from the anaerobic fermentation step, remaining undesired fermentation products and recalcitrant substrate residues are turned into biogas in the subsequent AD step. This enables a coupled material and energetic use of biomass which is more sustainable than sole energetic utilization or composting.

The product spectrum of anaerobic fermentation by microbiota includes short- (SCC; C2-C4) and medium-chain carboxylates (MCC; C5-C8). SCC such as acetate and butyrate can be produced by primary fermentation from all sorts of sugarcane residual biomass (Janke et al., 2016a; Rabelo et al., 2018; Moraes et al., 2019). Pre-treatment of lignocellulosic biomass can increase the amount of soluble compounds and thus enhance production rates and yields (Ratti et al., 2015; Janke et al., 2016a; Janke et al., 2018; Ong et al., 2019; Soares et al., 2019).

For the production of more valuable MCC such as caproate and caprylate, the carbon chain of SCC is extended in several steps by so-called microbial chain elongation (Angenent et al., 2016). Recently, MCC production from fermented sugarcane molasses was reported (Cavalcante et al., 2020). In addition, primary fermentation and chain elongation can be combined in one reactor, without being more elaborate than the production of SCC. However, an additional compound (typically ethanol or lactate) is necessary for microbial chain elongation serving as electron donor. This electron donor limits the whole process of MCC production. The addition of electron donors as chemical reactants is economically not feasible (Liebetrau et al., 2017). Rather, co-fermentation with ethanol or lactate containing side-streams of other processes is possible. Alternatively, electron donors are derived from sugarcane residues or could be directly produced within the fermentation process.

As ethanol is one main product of the sugarcane industry, it is available in big amounts, however not applicable for MCC production. Residual ethanol concentrations in vinasse are too low for reaching high MCC titers. For a worthwhile MCC production from vinasse alone or in combination with SFC, straw or bagasse, more ethanol would need to remain in this side-stream. The other typical electron donor lactate is not an integral part of most sugarcane residues, which restricts the production of chemicals by anaerobic fermentation to SCC production. As an exception, considerable lactate concentrations of up to 12.7 g/L were found in vinasse (Santos et al., 2014b), which turns this residual stream into a suitable substrate for MCC production. For the other sugarcane residues, lactate might be easily produced from these substrates by lactic fermentation prior to MCC production. In this case, an additional substrate pre-treatment step with favorable process conditions for lactic acid bacteria should be included into the process chain. Sugarcane residues with convenient moisture content and soluble carbohydrates are suitable biomass for ensiling. Ensiling is a widespread, conventional and cheap preservation technology for moist biomass, e.g., used for food (e.g. sauerkraut, kimchi), feed (e.g. grass, corn silage), or as substrate for biogas production (e.g., whole plant silage). Ensiling can be considered as biological pre-treatment that improves the biodegradability of the biomass and concurrently increases the lactate content (Janke et al., 2019). Ensiling is mainly established for the entire sugarcane plant in regions where it is used as valuable fodder for livestock during dry season. As for sugarcane residues, ensiling of sugarcane tops is state-of-the-art, because they are easy to ensile without ensilage helpers and provide a palatable silage (Getahun et al., 2018; Kumar et al., 2018). SFC can be used as ensiling agent or ensiled together with dry leaves, thus contributing to the needed moisture and texture for an optimized ensilage process (Kumar et al., 2018). The ensilage of bagasse was investigated (Pereira et al., 2009); however, as bagasse contributes most to the energy consumption of sugarcane plants, this process has no significance at industrial scale. While the ensiling process can increase lactate content of sugarcane residues, current studies do not report any achieved lactate concentration, given that they focused on preservation for fodder and not on further utilization in a biotechnological production process. Accordingly, more research is necessary for developing an appropriate ensiling process and embedding this into a biorefinery process for MCC production from sugarcane residues.

As alternative to ethanol or lactate, hydrogen (H_2) and/or carbon monoxide (CO) could also be applied as electron donors for microbial chain elongation. Hydrogen and CO are compounds of synthesis gas (syngas, $H_2/CO/CO_2$ in low amounts CH_4 and C_xH_y) or water-shifted syngas (H_2/CO_2). Using a thermochemical process, the generation of syngas requires the partial oxidation of solid dry biomass in three alternative ways: i) at high temperature and at near atmospheric pressure with oxygen or steam, ii) pyrolytic gas release in the absence of active agents, or iii) catalytic gasification in supercritical water at moderate temperature and at high pressure (Prakash et al., 2015). Via biomass gasification, recalcitrant lignocellulose fractions can be made available to anaerobic bacteria via syngas fermentation including the Wood-Ljungdahl pathway. On the syngas platform, syngas can be turned into acetate, i.e., the main electron acceptor for chain elongation, but also into ethanol or butyrate. By merging the syngas platform with the carboxylate platform, i.e., combining syngas fermentation with fermentation of organic substrate, dry and moist or liquid biomass can be integrated in an optimal way. Thereby, MCC product yields and productivities are increased and product portfolios can even be expanded to bioalcohols (Baleeiro et al., 2019; Chowdhury et al., 2019).

Two-stage processes consisting of anaerobic fermentation in the first and AD in the second stage were investigated for sugarcane tops (Kumari and Das, 2016), vinasse (Mota et al., 2013; Fuess et al., 2018b) as well as mixtures of vinasse and SFC (Janke et al., 2018) or food waste (Náthia-Neves et al., 2018) as substrates. Although these systems did not aim to a targeted production of carboxylates, they can be used as basis for further development to biorefineries.

A biorefinery setup for producing SCC or MCC from sugarcane residues must comprise downstreaming of the produced chemicals and treatment of residual streams. For downstreaming, membrane filtration or extraction are suitable for separation of SCC or MCC from the fermentation broth. Prior to this, depending on the type of feedstock, residual substrate particles and other solids have to be removed from the broth, resulting in a more complex cascade of product separation. Residual streams of the downstreaming step contain solids and high amounts of water, which in turn should be treated in an AD process where the more recalcitrant substrate fraction and undesired fermentation products can be converted into bioenergy. The produced biogas can contribute to covering the energy demand of the biorefinery and the whole sugarcane processing industry. Digestate, the residue of AD, can be used as valuable and safe fertilizer, thus nutrient cycles are closed. Furthermore, this process can replace a fossil-based production of mineral fertilizer (see also the section below on bio-fertilizer production).

Nowadays, different companies are developing bioprocesses aiming at carboxylate production for future commercialization, such as Sekab, Corbion, Galactic, and GF Biochemicals. Based on the current technological readiness level (TRL), acetic and lactic acid production (TRL of 8–9) are the closest to reach a commercial application. Even though their market price is considered to be low, 617 and 1,450 USD/ton for acetic and lactic acid, respectively, their market sizes are relatively high at 8.3 billion USD/a for acetic acid and 6.8 billion USD/a for lactic acid (Silveira et al., 2018). In contrast, the market prices for MCC (such as caproic acid) are much higher than for SCC, thus having a competitive advantage. Economic viability of biorefinery processes with MCC and ethanol as co-products was recently shown (Scarborough et al., 2018), and several pilot plants with residual and waste biomass as substrates and including downstreaming of caproic acid have been launched.

Bioplastics and Biopolymers

Lactate production is so far not an integral part of any sugarcane biorefinery but it is considered as an electron donor for the chain elongation and as a preservation agent of biomass to prevent spoilage during storage (see previous section). However, lactate can also be considered as a major product itself, namely as a monomer of polylactic acid (PLA) or polylactate (Nampoothiri et al., 2010). The biological production of PLA is currently based on starch from renewable agricultural feedstocks, such as corn starch via fermentation and polymerization. Sugarcane juice is also used for PLA production in Thailand at commercial scale (Morão and de Bie, 2019), however, the utilization of sugarcane wastes for this purpose is less developed. As an example, L-lactic acid production was optimized with *Lactobacillus casei*, grown on a mixture of sugarcane bagasse and cassava starch (Rojan et al., 2005). Despite some physical shortcomings and production issues (Nagarajan et al., 2016), PLA is gaining popularity, especially by the widespread application of 3D printing. The economic potential and manufacturing cost estimates of several PLA-related products and process options are presented by (Datta et al., 1995).

Polyhydroxyalkanoates (PHAs) are biologically produced polyesters, synthetized by various microorganisms, and serve as intracellular energy and carbon storage. PAHs are usually produced by the cells under certain nutrient limited growth conditions such as excess supply of carbon and lack of one or more essential nutrients and/or trace elements (Hazer and Steinbuchel, 2007). Among many attractive properties, they are UV stable, biocompatible and biodegradable. Poly-β-hydroxybutyrate (PHB) and poly-β-hydroxyvalerate (PHV) are the most common types of PHA produced by microorganisms (Luengo et al., 2003). The production of PHAs can be incorporated into a biorefinery concept utilizing cheap biomass waste streams. An interesting application is to use volatile fatty acid-rich effluents from a biohydrogen producing reactor as main substrate (Mohan et al., 2010; Passanha et al., 2013; Amulya et al., 2014). Recently, sugarcane molasses was used successfully as a substrate by a *Bacillus* strain (Santimano et al., 2009). Sugarcane vinasse (stillage) was also tested as a substrate by mixed microbial cultures in a sequencing batch reactor under increasing organic loading rates (de Oliveira et al., 2019). In addition, middle-chain-length PHAs exhibiting thermoelastomeric properties were produced from sucrose-derived carbohydrates and decanoic acid by a genetically engineered *Pseudomonas* strain (Oliveira G. H. D. et al., 2020). However, the substitution of petrochemical-based materials by bioplastics is hindered by the higher market price that is between 2.4 and 5.5 US$/kg in case of PHAS compared to 1.2 US$/kg for synthetic plastic (Crutchik et al., 2020). Traditionally, PHAs are produced by pure cultures using expensive carbon sources that contribute up to 30–50% of the total costs. These costs can, however, be reduced by using instead low-cost substrates, such as waste streams (Morgan-Sagastume et al., 2016).

Cellulose nanofibrils (CNFs) are promising high-strength polymeric fibrils derived from renewable resources with promising characteristics such as low-cost, significant barrier and colloidal properties, biodegradability, good potential for recycling, which make them useful material for the preparation of green electronic products. CNFs result from the disintegration of cellulose fibers under high shearing and impact forces. Wood is currently the most important industrial source of CFNs but recently sugarcane bagasse was also considered as potential feedstock and extensively studied (Heidarian et al., 2016; Feng et al., 2018; Heidarian et al., 2018; Tao et al., 2019; Zhang et al., 2019; Marcondes et al., 2020). The recent advances on production of cellulose nanofibrils was reviewed elsewhere (Nechyporchuk et al., 2016).

Bio-Fertilizer Production

The concept of circular economy is based on cycles, which can be organized in long cascades and include the different spheres like soil, atmosphere and water bodies. For example, carbon is taken by plants from the atmosphere in form of CO_2, while hydrogen is taken from water directly or from soil storage. Building up the biomass and releasing O_2 into the atmosphere by photosynthesis brings these elements into the bioeconomy cycle. While the raw biomass can be used in several cascades for material purposes, final residues can be turned into biofuels for energetic use, releasing CO_2 and water vapor into the atmosphere. With regard to the plant nutrients, such as N, P, K, S, Ca, and the micro-nutrients, the principle of closed cycles within the system of cropping and biomass use is of fundamental importance. Outflows (e.g., N in form of N_2O and NH_3 into the atmosphere, NO_3 into water bodies, S-oxides into the atmosphere, all nutrients in case of other form of transfer into the environment) are pollutants, causing direct (N_2O) or indirect (NH_3) greenhouse effects (Robertson et al., 2000; Denmead et al., 2008; Snyder et al., 2009), water pollution, or eutrophication (Galli and Abe, 2017; Nieder et al., 2018). For the cropping systems, outflows of these nutrients are mostly lost. As mining options for these nutrients are limited, especially in case of P (Elser and Bennett, 2011; Cordell and White, 2014; Nedelciu et al., 2020), or as provision in large quantities depends on cheap fossil energy in case of N (Lin et al., 2017; Harchaoui and Chatzimpiros, 2019), this results in a limitation of nutrient supply for future crop production. A high level of biomass production and especially a high yield per hectare without overshooting natural limitations is required, as the transition to bioeconomy needs additional biomass resources, i.e., additional to the rising demand for food and feed due to rising population and changing diets. As a consequence, a strict nutrient cycling with high nutrient efficiency is one prerequisite of sustainable intensification in agricultural systems for the future (Jurgilevich et al., 2016; Mohan et al., 2016; Trimmer and Guest, 2018). This approach of closed cycles is very challenging. However, there is a strong need for a differentiated view. For instance, in the case of food chains, material flows from the cropping systems to the final consumers (often located in urban areas) are always bound with nutrient flows (like N, P, K, etc.), material flows (like sugar, ethanol, pure oils, fats and starch), and pure cellulose flows (containing C, O, and H). Closing the nutrient cycles within the food sector therefore also needs a coordinated management and regulation of urban mass flows (e.g., feces, urine, wastewater/sludge, food wastes, and other bio-wastes). Such an approach requires the integration of final consumers, despite them having low interest in these mass flows. Otherwise, there is always a risk of pollution, e.g., by heavy metals, plastics, or endocrine substances.

Translating this circular economy concept and its mass flows to the sugar industry shows that the outgoign products are sugar (sucrose) and ethanol, both based on CO_2 and water. All plant nutrients harvested from the plantations are found in the residues (tops and trash, bagasse, filter cake and vinasse). This means, a closed nutrient cycle is completely in the responsibility of the management of plantations, harvest, processing, and recycling of residues. This has a big impact on its life cycle assessment results (Cherubini et al., 2009; Davis et al., 2009; Hoefnagels et al., 2010; Rocha et al., 2014) and therefore impacts the marketability of ethanol, which has to obey to stringent compliance criteria, especially in export markets (Corbiere-Nicollier et al., 2011). Despite the fact that there is no export of fertilizer nutrients within the main products of the sugarcane industry, there is usually a need of mineral fertilizer application on the sugarcane plantations (Singh et al., 2007; Allen et al., 2010; Franco et al., 2011; Delgadillo-Vargas et al., 2016). Especially in case of combined fertilization with undigested organic fertilizers, enhanced N_2O-emissions occur, as reported earlier (do Carmo et al., 2013). Nitrogen fertilizer application is usually quickly resulting in nitrate, independent from the N-form applied. In case of urea or ammonia application, these fertilizers are transformed into nitrate by nitrification processes. Supplementing easily degradable carbon, as in vinasse (e.g., organic acids), tops and trash without previous digestion provide easy to utilize carbon sources for denitrifying bacteria enhancing the N_2O-emissions (do Carmo et al., 2013).

The use of residues of sugarcane industry to improve soil quality, such as vinasse fertirrigation, is quite common. Vinasse could be biodigested before irrigation or concentrated by evaporation, microfiltration, and reverse osmosis before using it as fertilizer (Marafon et al., 2020). The big advantage of this not yet widespread option is a better transportability thanks to its higher concentration. On the other hand, the evaporation and other concentration technologies require a lot of energy, which needs to be in accordance with the plant's concept of mass-flow and energy management. Another, even less used option so far is the composting of the residual mass-flows to generate a valuable organic fertilizer as shown (Xavier et al., 2019). Similar to AD, the composting process also delivers an organic fertilizer with a high humification index, which generates more stable humus effect thanks to biologic degradation within the process. However, the AD delivers further benefits by substituting fossil energy sources with the produced biogas. Another more technical option are organomineral fertilizers, called "BIOFOM" (Gurgel et al., 2015), which is processed from concentrated vinasse, filter cake, boiler ash, soot from chimneys and supplemented with mineral fertilizers. However, even this option requires evaporation and thus additional energy to concentrate the vinasse. While bagasse cogeneration could theoretically deliver this energy, most of its heat energy is already consumed for different processes of the core sugar or ethanol processing, thus not available for the generation of organic fertilizer with high humification index.

BIOGAS PRODUCTION AND UTILIZATION

Anaerobic Digestion

AD offers an excellent solution for the treatment of sugarcane waste streams. While the core product of AD is biogas, the process can also be partially steered toward the production of carboxylates as discussed above. Biogas can directly be utilized for electricity and heat production by using combined heat and power (CHP) units or it can be upgraded to high-quality biomethane (more than 98% purity) by various technologies reviewed elsewhere (Angelidaki et al., 2018; Adnan et al., 2019). Such high-quality methane can be injected into a natural gas grid, if available in close vicinity, or it can be utilized for residential and industrial applications. Furthermore, biomethane can also be used as fuel for light-duty vehicles or as feedstock for the synthesis of platform chemicals and other fuels through CO_2 utilization (e.g., via super-dry reforming of CH_4 (Verbeeck et al., 2018)). Overall, biomethane could replace large amounts of natural gas, therefore it has the potential to considerably reduce GHG emissions.

The conversion of biomass into methane-rich biogas through AD is a complex anaerobic biochemical process carried out by synergistic interactions among the members of a diverse microbial community (Wei, 2016). It has four major steps, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis, which is often a rate-limiting step (Nikolausz et al., 2013). In case of lignocellulosic substrates, such as bagasse, hydrolysis can also be a rate-limiting step. The process occurs in a controlled engineered system called anaerobic digester or biogas reactor with defined operational parameters, such as temperature, mixing, hydraulic retention time, and solid retention time. The reactor configuration and the process design mainly depend on the characteristics of the substrate used. This technology is frequently applied for solid wastes and wastewater treatment and preferred over aerobic treatment processes due to the better energy balance and associated GHG emission reduction, and much lower amounts of sludge generation (Liebetrau et al., 2017).

The waste products of the sugarcane bioethanol industry were characterized in detail from the biogas process design point of view by previous studies (De Paoli et al., 2011; Gonzalez et al., 2013; Santos et al., 2014a; Leite et al., 2015a; Janke et al., 2015; Fuess et al., 2018a). They observed high heterogeneity and even seasonal variations. The waste types can be grouped according to their total solid (TS) and volatile solid (VS) content, which mainly determines the appropriate reactor design and process type. Straw, bagasse and even filter cake (press mud) have relatively high TS and VS contents and are also considered to be recalcitrant due to the higher lignocellulose content; therefore, longer solid and hydraulic retention time (SRT and HRT) with higher reactor volume is preferred. Biogas reactors based on the continuous stirred tank reactor (CSTR) or plug flow reactor designs are suggested for such solid wastes. Vinasse, on the other hand, has low TS and VS content relative to the other waste fractions. As large vinasse volumes are produced during the sugarcane mill operation period, high-rate reactors with biomass immobilization systems (e.g., biomass granulation, fixed/fluidized bed) are recommended with relatively short HRT to avoid excessive large reactor volumes. Although the TS and VS content of vinasse is relatively high compared to other typical wastewater types, the well-established technologies have been applied for its treatment. Examples of high-rate systems applied to treat vinasse dates back decades ago by applying UASB reactors (Costa et al., 1986; Craveiro et al., 1986) followed by other pilot-scale applications (Souza et al., 1992; Del Nery et al., 2018). Connection of two UASB systems in a row as two-stage systems were also evaluated under mesophilic (Barros et al., 2016) and thermophilic conditions (Ferraz et al., 2016; Fuess et al., 2017b). Alternative options for biomass retention in high-rate anaerobic vinasse treatment systems are to apply anaerobic fluidized bed reactor (AFBR) (Siqueira et al., 2013) or fixed-bed reactors (de Aquino et al., 2017).

Further challenges associated with the AD of sugarcane wastes are due to the fact that the compositions of these residues are not completely appropriate for biogas production. In addition, waste compositions are also influenced by the cultivar, the region, soil quality, the technology used by the industry, and quality variations year by year (Fuess et al., 2018a; Santos et al., 2019). The ranges of characteristics of wastes are summarized in **Table 1**. Straw and bagasse have high lignin contents; therefore, pre-treatment is recommended for a better digestibility. The various options for physical, chemical and biological options for pre-treatment of lignocellulosic biomass are reviewed elsewhere (Mosier et al., 2005; Hendriks and Zeeman, 2009). Pre-treatment of sugarcane residues to improve disintegration and/or enhance the biogas yield were investigated by previous studies applying mechanical treatment (Leite et al., 2015a; Janke et al., 2017b), chemical treatments (Leite et al., 2015a; Thite and Nerurkar, 2019) especially alkaline treatments (Janke et al., 2016a; de Carvalho et al., 2016; Talha et al., 2016), or combination of treatments (de Carvalho et al., 2015; Janke et al., 2017b; Mustafa et al., 2018; Sanchez-Herrera et al., 2018). Another interesting approach is to use sequential combinations of supercritical CO_2 and alkaline hydrogen peroxide at mild conditions for the pre-treatment of sugarcane bagasse (Phan and Tan, 2014). Pre-treatments applied for second-generation bioethanol production, such as steam explosion (Rocha et al., 2012; Oliveira et al., 2013) can also be used for the enhancement of the AD process. From macroelements, nitrogen, sulfur and phosphorus addition is recommended in case of mono-digestion, while supplementing a mixture of trace-elements including Fe, Ni, Co, Mo, W, Mn, Cu, Se, and Zn is also advised achieving an optimal bioprocess (Janke et al., 2015). Filter cake has a more balanced composition, therefore requiring only S, Mo, W, and Se addition. Vinasse is often treated separately using technologies from high-rate wastewater treatment processes with biomass retention. Even though chemical analyses indicated a potential lack of P, Fe, Ni, Co, Mo, W, Mn, Cu, Se, and Zn, previous studies achieved effective performance without macro and trace-elements addition (Siqueira et al., 2013; Janke et al., 2015; Ferraz et al., 2016; Fuess et al., 2017b). However, special attention must be taken to avoid the use of expensive alkaline reagents to counteract the low pH of vinasse, which could potentially make the AD process economically non-viable for full-scale applications (Fuess et al., 2017a). In contrast, trace element supplementation showed stimulatory effects on methanogenesis during mesophilic AD of vinasse, and together with an alternative alkalizing strategy based on urea it could stabilize the process and at the same time enrich digestate with nitrogen for further fertirrigation on sugarcane fields (Janke et al., 2016b). Further problems associated with the relatively high concentration of sulfate in vinasse supporting the sulphate-reduction process. Sulphate-reducing bacteria compete with methanogenic archaea for hydrogen and the end-product of the process, namely H_2S, has a toxic effect on many microorganisms and it may cause corrosion in the treatment facilities (Leite et al., 2015a). Co-digestion is a frequently used strategy to balance the composition and lack of macro- and micronutrients of various substrates, and livestock manure is frequently used for this purpose. However, sugarcane factories are often located in remote places far from animal husbandry and locally produced wastes can only be combined to a certain extent. Despite the fact that filter cake can be combined with other waste products such as straw, optimal biogas production still requires macronutrient supplementation (Janke et al., 2017a). Start-up of a new AD system is also a challenge. In countries where biogas plants are frequent and well developed, a biogas reactor can be started with inocula from an already operating system to overcome the start-up challenges (Kobayashi et al., 2009). In countries with few AD plants separated by long distances such as Brazil, arranging proper inocula is difficult. This was successfully addressed by the evaluation of reactor inoculation with fresh cattle manure as a locally available, alternative inoculum (Janke et al., 2016c; Leite et al., 2016). Animal manure is rich in microorganisms from animal digesting system, as well important macronutrients and trace elements (Feng et al., 2020).

Another challenge is associated with the seasonality, which is a problem affecting the whole biorefinery approach relying on a single seasonal crop without cover crop production. The availability of the substrate in case of sugarcane industry is limited to around 200–240 days per year. This is one reason, beside low incentives to produce bioenergy, hindering the implementation of the biogas process for waste treatment in countries like Brazil. The concept of using vinasse during the sugarcane season and preserving/storing filter cake to be used as substrate during the off-season period was evaluated (Janke et al., 2016b). However, treatment of filter cake requires a different

TABLE 1 | Composition and major characteristics of the wastes produced by the sugarcane industry.

Parameter	Unit	Straw	Filter cake	Bagasse	Vinasse
pH	—	—	—	—	3.8–5.1[a,b,c,d]
TS	$\%_{FM}$	46–94[c,e]	22–32[b,c]	45–57[b,c,e]	1–4[b,c]
VS	$\%_{TS}$	68–92[c,e]	62–83[b,c,f]	92–97[b,c,e]	67–80[b,c]
COD	$g{\cdot}L^{-1}$	—	—	—	16–40[a,b,c,d]
TKN	$g{\cdot}kg_{TS}^{-1}$	2.9–5.5[c]	17–22[c]	2.5–3.3[c]	21–72[c]
Cellulose	$\%_{TS}$	21–39[c]	10–29[b,c]	28–45[b,c]	2.6–7.0[c]
Lignin	$\%_{TS}$	13–19[c]	8.5–13[b,c]	6.4–17[b,c,e]	3.2–6.7[c]
hemicellulose	$\%_{TS}$	21–24[c]	14–30 [b,c]	16–37[b,c]	8.1–36[c]
NFC	$\%_{TS}$	6.7–15[c]	1.4–27[b,c]	2.4–33[b,c]	21–40[c]
Raw protein	$\%_{TS}$	1.8–5.5[c,e]	11–18[b,c]	1.1–4.3[b,c,e]	14–16[c]
Raw fat	$\%_{TS}$	0.7–1.0[c,e]	3.9–4.4[b,c]	0.4–0.9[b,c,e]	0.01–0.1[c]
Carbon (C)	$\%_{TS}$	37–51[c,e]	34–47[c,f]	44–50[c,e]	37–39[c]
Nitrogen (N)	$\%_{TS}$	0.5–1.1[c,e]	1.5–1.9[c,f]	0.4–0.7[c,e]	1.8–3.2[c]
Phosphorous (P)	$\%_{TS}$	0.3–0.1[c]	0.3–1.1[c,f]	0.02–0.06[c]	0.3–0.8[c]
Sulfur (S)	$\%_{TS}$	0.05–0.08[c]	0.16–0.19[c]	0.02–0.07[c]	0.5–2.1[c]
Silicon (Si)	$mg{\cdot}kg_{TS}^{-1}$	107–352[c]	315–1,500[c]	270–400[c]	400–3,800[c]
Calcium (Ca)	$mg{\cdot}kg_{TS}^{-1}$	2000–5,000[c]	9,000–17,000[c]	600–1700[c]	4,000–21,000[c]
Sodium (Na)	$mg{\cdot}kg_{TS}^{-1}$	4–75[c]	0–42[c]	4–44[c]	200–900[c]
Potassium (K)	$mg{\cdot}kg_{TS}^{-1}$	2,600–8,300[c]	1,200–3,300[c]	1,300–5,600[c]	18,000–152000[c]
Magnesium (Mg)	$mg{\cdot}kg_{TS}^{-1}$	1,200–2000[c]	2,600–4,300[c]	400–1,100[c]	2,800–24,000[c]
Aluminum (Al)	$mg{\cdot}kg_{TS}^{-1}$	785–33,300[c]	12,600–55,200[c]	455–2,570[c]	105–587[c]
Cobalt (Co)	$mg{\cdot}kg_{TS}^{-1}$	0.43–8[c]	2.4–4.9[c]	0.2–0.7[c]	0.2–1.2[c]
Iron (Fe)	$mg{\cdot}kg_{TS}^{-1}$	856–50,000[c]	12,800–55,700[c]	716–3,700[c]	117–690[c]
Manganese (Mn)	$mg{\cdot}kg_{TS}^{-1}$	88–293[c]	405–773[c]	36–56[c]	55–275[c]
Molybdenum (Mo)	$mg{\cdot}kg_{TS}^{-1}$	0–1.0[c]	0–1.5[c]	0.3–1[c]	0.5–1.1[c]
Nickel (Ni)	$mg{\cdot}kg_{TS}^{-1}$	3.5–14.9[c]	9.5–20.8[c]	0.5–6.6[c]	0.4–3.7[c]
Tungsten (W)	$mg{\cdot}kg_{TS}^{-1}$	0–0.2[c]	0–0.8[c]	0–0.2[c]	0–0.1[c]
Methane yield	$mL_N{\cdot}g_{VS}^{-1}$	79–234[c,e]	160–281[b,c,f]	226–326[b,c]	223–302 [b,c,g]

[a](Santos et al. (2014a).
[b]Leite et al. (2015a).
[c]Janke et al. (2015).
[d]Fuess et al. (2018a).
[e]De Paoli et al. (2011).
[f]Gonzalez et al. (2013).
[g]*In case of vinasse methane yield is given as* $mL_N g_{COD}^{-1}$.

reactor type as discussed earlier. This challenge was addressed by the strategy of decoupling the AD of filter cake into two steps during the off-season period. Filter cake was initially hydrolyzed/fermented in an acidogenic CSTR at short HRT followed by solid-liquid separation and the existing UASB reactor used for vinasse treatment was used as a methanogenic reactor for biogas production from the separated liquid fraction (Janke et al., 2018). A recent study described the successful ensiling of whole sugarcane biomass enabling the storage up to 6 months without loss of biogas potential (Hoffstadt et al., 2020). However, a better implementation of ensiling of sugarcane residues to improve storage without carbon loss should be further investigated. The seasonality issues can also be addressed by growths of legume intercrops between the cropping periods of cane for improvement of soil fertility and to provide alternative biomass for the biogas production. Production of corn (*Zea mays* L.) was suggested to diversify the substrate spectrum of the Brazilian ethanol sector and due to the better storability of grains it might solve current seasonality issues (Eckert et al., 2018).

Even though the use of sugarcane waste for biogas production is not considered to be the common practice within this industrial sector, few implementations of large-scale AD plants driven by different reasons do exist. For instance, in Brazil, a 5,000 m^3 thermophilic UASB reactor has been operating since the 1990s aiming at the use of biogas as fuel in the process of yeast drying (São Martinho biogas plant). A low-cost anaerobic reactor based on a lagoon system has been developed for the digestion of vinasse, in which the produced biogas is used for electricity production in a 1 MWe CHP unit (McCabe and Schmidt, 2018). The use of solid fractions of sugarcane waste has been targeted since 2012 by the company Geo Energética which operates a biogas plant based on a CSTR and production capacity of up to 4 MWe (GeoEnergética, 2020). Recently, even larger facilities of 20 MWe are being commissioned aiming at the year-round electricity production by Raízen Bonfim. In such implementations, the feasibility of projects is certainly influenced by favorable scale-effects since the selling price of electricity of Raízen Bonfim project [0.07 €/kWh (Euro 2016)] is much lower than practiced in countries like Germany (23.73 €/kWh for plants up to 75 kWe) where small-scale biogas plants are incentivized (Blumenstein et al., 2016; Borin et al., 2019). If policies and incentives to promote biogas production are not in effect in cane growing countries, it is unlikely that the full utilization of sugarcane waste would occur, in particular for straw since an additional cost of 50 USD/ton_{DM} to recover from the fields is incurred (Pierossi and Bertolani, 2018).

BIOGAS UPGRADING

AD of filter cake co-digested with bagasse reported a biogas composition of CH_4: 54–61% and CO_2: 46–39% (Leite et al., 2015b). Digesting sugarcane stillage produced biogas with a methane content as high as 68.4 ± 7.2%–74.5 ± 6.0% (Ramos and Silva, 2020). Other studies digesting sugarcane vinasse showed different methane contents such as 68.8 ± 7.14% (Del Nery et al., 2018), 55.0 ± 0.3–74.5 ± 0.4% (de Aquino et al., 2017), 78% (Costa et al., 1986), 60% (Craveiro et al., 1986), and 64–85% (Barros et al., 2016). Hence prior to utilization the raw biogas needs downstream processing such as cleaning (where mainly H_2S removal is targeted when biogas is used for combustion) or upgrading (where increasing the gas purity is targeted and is achieved by CO_2 removal) if used as a fuel or chemical precursor (Angelidaki et al., 2018). If upgrading is the subsequent process choice, it can be done in a chemical or biological fashion. Biogas upgrading involving physicochemical processes such as absorption, adsorption and membrane separation removes CO_2 from the raw biogas, so that CH_4 can reach a composition ≥96% which is comparable to natural gas (Angelidaki et al., 2018). As a result, CH_4 is highly enriched but the CO_2 share of biogas is unutilized. Alternatively, H_2 produced from other renewables can be coupled to the AD process of the sugarcane industry (or other point CO_2 sources of the industry) in a process called biological biogas upgrading. This process is advantageous because it allows energy storage of surplus electricity in a chemical form and methane is produced from the CO_2 contained in the biogas or other CO_2 sources from the sugarcane industry process. Biological biogas upgrading exploits the CO_2 reductive pathway of hydrogenotrophic methanogens and three approaches have been described, namely *in situ*, *ex situ* and hybrid biological biogas upgrading (Kougias et al., 2017). *In situ* is the process where H_2 is directly injected to the AD reactor but this poses a risk to the reactor because only limited amounts of H_2 can be effectively injected. The *ex situ* process means that CO_2 from biogas or other sources are combined with H_2 in a separate reactor to produce CH_4, with the biocatalytic activity of pure cultures (Rittmann, 2015) or mixed cultures (Kougias et al., 2017; Angelidaki et al., 2018; Logrono et al., 2020). The hybrid process consists of the combination of the two previously aforementioned methods (Kougias et al., 2017; Angelidaki et al., 2018; Corbellini et al., 2018). A proposed scheme for the combination of renewable H_2 integration with the AD technology of sugarcane industry is shown in **Figure 2**.

According to the literature, various reactor configurations such as CSTR (*in situ* and *ex situ*), UASB (*in situ* and *ex situ*) and trickle-bed reactors (TBR; *ex situ*) have been used for biological biogas upgrading (Angelidaki et al., 2018; Lecker et al., 2017; Rittmann et al., 2015). *In situ* biomethanation studies have achieved a lower CH_4 enrichment than *ex situ* biomethanation (Angelidaki et al., 2018; Lecker et al., 2017). In addition, the methane evolution rate (MER) in *ex situ* biomethanation with mixed cultures is higher than that in *in situ* processes. Conversely, *ex situ* biomethanation with pure cultures shows remarkably higher MER than that of mixed cultures, but the obtained CH_4 percentage is lower (Lecker et al., 2017). A comparison of different reactor systems is presented in **Table 2**. Clear differences exist from the microbiological point of view between the different types of biomethanation systems. The *in situ* process relies on the hydrogenotrophic methanogens from the AD process. The *ex situ* process can be performed with very specific hydrogenotrophic mixed cultures (enrichment cultures or digestate sludge) or pure cultures. A disadvantage of mixed cultures is shown by homoacetogenesis as a competing reaction in both the *in situ* and *ex situ* process since homoacetogenic bacteria produce acetate from H_2/CO_2 (Lecker et al., 2017; Angelidaki et al., 2018); however, this could be controlled by refining the medium composition in order to achieve a selective production of CH_4 (Logrono et al., 2020).

HYDROGEN PRODUCTION

The remarkable declining costs of renewable energy sources like solar photovoltaic (PV) offer new opportunities for the development of hybrid systems integrated within the sugarcane industry as many emerging countries in the global South receive high solar irradiance, which significantly increases the performance of solar projects. In the case of the sugarcane industry, solar PV systems could be strategically deployed on marginal lands within sugarcane plantations to produce together with bagasse-fueled cogeneration plants electricity for feeding the grid. At times of unfavorable prices on the spot market, the electricity produced would be used for H_2 production via water electrolysis (**Eq 1**) (Götz et al., 2016; Janke et al., 2020).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (1)$$

As a flexible energy carrier, H_2 can be used directly as fuel for mobility or in a variety of processes to produce gaseous (e.g., CH_4 and NH_3) and liquid fuels (e.g., methanol and dimethyl ether), as building block molecule for bio-based chemical production (e.g., carboxylic acids and alcohols), or even for microbial protein production (e.g., yeast) (De Vrieze et al., 2020). This concept of electricity-based hydrogen production with subsequent transformation into other products is therefore frequently referred to as power-to-x (PtX). Thanks to its ability of using surplus electricity for its operation, it can provide various energy services like grid balancing, energy storage, and reduction of curtailment of variable renewable energy. In addition, it further contributes to a reduction of GHG emissions, in particular by synthesizing H_2 with CO_2 to renewable, non-fossil based products (**Eq 2**). Such a use of CO_2 is also referred to as carbon capture and utilization (CCU), which will be explored in the section below (Thauer, 1998; Angelidaki et al., 2018)

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O; \Delta H = -130.7kJ \qquad (2)$$

Different water electrolysis technologies have been proposed for PtX applications such as alkaline electrolysis (AEL), proton exchange membrane electrolysis (PEMEL), anion exchange membrane electrolysis (AEMEL), and solid oxide electrolysis (SOEL). While AEL is characterized by relatively low capital costs compared to other technologies due to the avoidance of

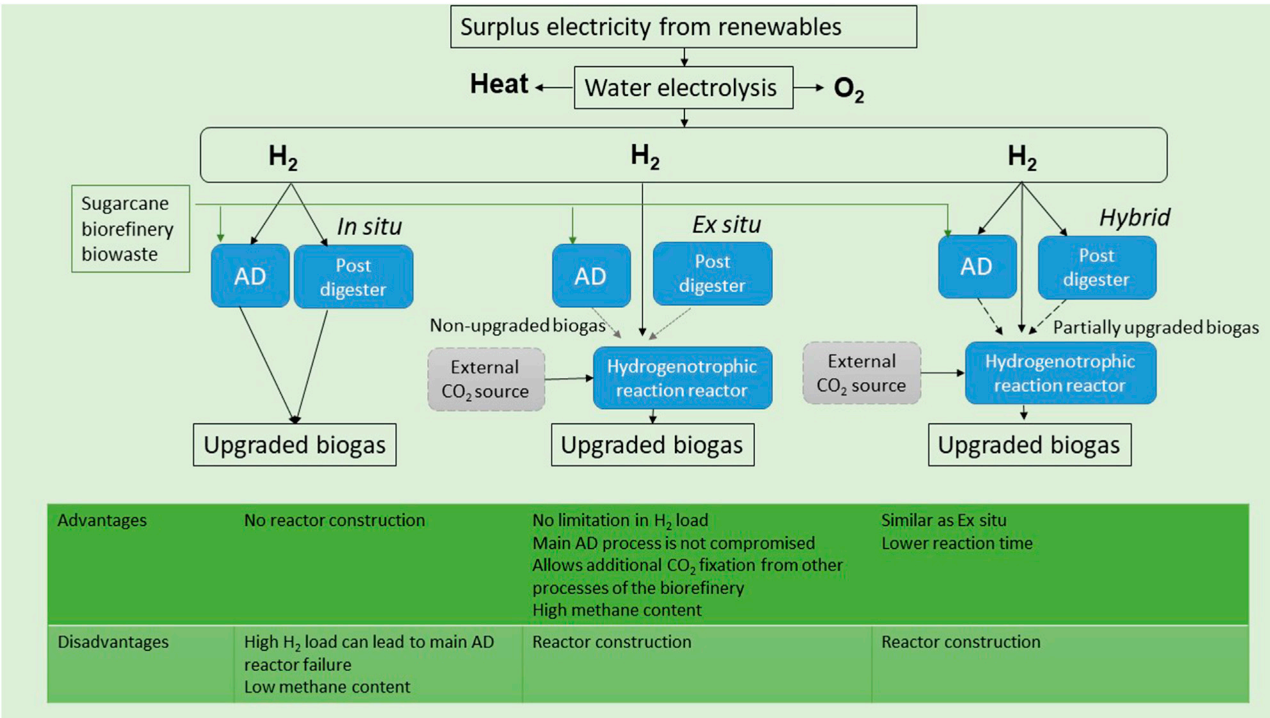

FIGURE 2 | P2G integration with the anaerobic digestion (AD) process of the sugarcane industry. Gray dotted arrow: Non-upgraded biogas and black dashed arrow: Partially upgraded biogas. Heat from the electrolyzer can be used for heating units and O_2 can be used for aerobic treatment or sold.

TABLE 2 | A comparison of *in situ* and *ex situ* biomethanation with different reactor setups.

Type of bioprocess	Reactor type	Reactor volume (L)/working volume (L)	Temperature (°C)	Gases and ratio	Type of biocatalyst	MER L/L/d	CH_4 (%)	References
In situ	CSTR	1/0.6	55	H_2/1:4	Sludge	0.38	96	(Luo and Angelidaki, 2013)
In situ	UASB	–/1.4	55	H_2/1:4	Enrichment culture	0.18	82	(Bassani et al., 2016)
Ex situ	TBR	7.54/5.78[a]	37	H_2:Biogas/1:4	Enrichment culture	1.56	98.26	(Rachbauer et al., 2016)
Ex situ	CSTR	1/0.6	55	H_2,CH_4:CO_2 (60:25:15)	Enrichment culture	1.5	95	(Luo and Angelidaki, 2012)
Ex situ	UASB	–/1.4	55	H_2:CH_4:CO_2 (62:23:15)	Anaerobic digestate	–	98	(Kougias et al., 2017)
Ex situ	CSTR	1.5/–	65	H_2:CO_2/1:4	*M. thermautotrophicus*	288	96	(Peillex et al., 1988)
Ex situ	TBR	136/–	65	H_2:CO_2/1:4	*M. thermautotrophicus*	123	58	(Jee et al., 1988)

[a]*Carrier material volume.*

precious materials, PEM requires expensive electrodes catalysts (e.g. platinum and iridium) and membrane materials (e.g., Nafion). In contrast, PEM has a more compact design and simpler system without the need for corrosive electrolytes as required in AEL (e.g., KOH). In addition, PEM offers faster response times to ramp-up and higher flexibility to operate in part- or overload (Buttler and Spliethoff, 2018). Both AEL and PEM are the most suitable technologies for short-term implementation thanks to their higher TRL. For implementation within the next 5–10 years, AEMEL proposes to combine the advantages of both AEL and PEM in a single system by replacing the use of expensive platinum-based catalyst by non-noble metal catalyst (e.g., Ce_2-La_2O_3) as well as providing the option of using distilled water or diluted KOH as electrolyte. Such characteristics will result in lower costs and higher stability for H_2 production when AEMEL becomes commercially available (Vincent and Bessarabov, 2018). In the long-term, SOEL will be able to provide even better grid balancing services since this electrolyzer technology allows the operation in reverse mode as fuel cell, converting H_2 back into electricity. It will also have the advantage of reaching higher electrical efficiencies (74–90%) compared to other technologies (56–80%) (IEA, 2019). However, due to its high operating temperatures (700–900 °C), SOEL technology currently still faces low durability and high investment costs (Buttler and Spliethoff, 2018).

Regardless the efficiency of converting electricity into H_2, low-temperature waste heat (50–90°C) is generated as a by-product of AEL, PEM, and AEMEL technologies, which could be recovered for use in the ethanol distillation process, thus representing an important synergy for further increasing the overall efficiency of the system. In addition, O_2 could also be recovered for use at the sugarcane biorefinery. In this case, oxyfuel combustion could take place in the cogeneration process, improving the efficiency of the process since less air would be used for combustion. Furthermore, the oxyfuel combustion process would facilitate carbon capture and utilization since a more concentrated flue gas would be generated (Stanger et al., 2015).

The cost of H_2 production will primarily depend on the price of the electricity and the capacity factor of the electrolyzer (Janke et al., 2020). In addition, technological developments are likely to drastically reduce CAPEX and OPEX of H_2 production based on water electrolysis. Together with anticipated cost reductions for solar PV of around 50% in the next decades, electrofuels based on H_2 could become competitive with fossil fuels in regions of high solar irradiance. Furthermore, as mentioned in previous sections, CO_2 can be a valuable resource when combined with H_2 to produce carboxylic acids or synthetic carbohydrates.

VALORIZATION OF BIOGENIC CO_2 SOURCES

Within sugarcane biorefineries, instead of venting CO_2 into the atmosphere, it can be captured either from bagasse combustion, sugarcane juice fermentation, or biogas upgrading (in case of biogas production from sugarcane residues and upgrading to biomethane for grid injection, see respective section above). The CO_2 thus obtained can be a valuable resource for various other industries, notably when combined with hydrogen to produce synthetic carbohydrates.

CO_2 CAPTURE

Fermentation of Ethanol Production Process

Considering that the sugarcane fermentation results in 0.75 kg of CO_2 for each liter of ethanol produced (Hornafius and Hornafius, 2015), recovering this by-product for subsequent use can reduce emissions while simultaneously representing an additional revenue stream for the biorefinery. Recovering CO_2 from ethanol production is considered a low-hanging fruit, especially as the CO_2-rich streams from the fermentation step come with a purity of higher than 99%, consisting only of CO_2, H_2O, and small amounts of sulfur and organic compounds (Barbosa et al., 2017). This CO_2 can therefore be purified, dehydrated and compressed by using already commercially proven and relatively low-cost technologies (Sanchez et al., 2019). A common CO_2 capture and purification method is cryogenic distillation where non-condensable impurities are separated from the exhaust gas via a physical-chemical process. This process is particularly suitable for gas streams that already have a high CO_2 content (de Assis et al., 2013), which is the case for sugarcane-based ethanol production. Thanks to the high purity of the CO_2 side-stream, one of the major barriers for subsequent CO_2 utilization is removed, namely the cost of processing diluted CO_2 streams from other point sources (Bachu, 2008). In fact, for the entire carbon capture process, cost estimates range for bioethanol plants between US\$ 11/t CO_2 and US\$ 21.3–27.3 per t CO_2 (Irlam, 2017), being among the lowest of all CO_2 point sources.

Combustion of Bagasse

Merschmann and co-workers claimed that CO_2 capture is only viable from sugarcane fermentation (Merschmann et al., 2016). However, Carminati et al. (2019) demonstrated for an integrated sugarcane biorefinery with ethanol production and bagasse cogeneration that the bulk of CO_2 emissions is linked to bagasse cogeneration, representing up to 94% of the refinery's CO_2 emissions (Carminati et al., 2019). Therefore, a considerable CO_2 capture potential is linked to the combustion stage even if technically more challenging than recovering CO_2 from fermentation. Three different types of carbon capture processes exist, namely pre-combustion capture, post-combustion capture (PCC) and oxyfuel capture (OFC). For bagasse combustion, the latter two ones are best suited. The major advantage of PCC technologies is that they can be retrofitted on brownfield plants, functioning as add-on to the combustion step. For the specific use of bagasse combustion with low CO_2 levels, amine-based CO_2 absorption systems are particularly suitable as PCC flue gas treatment option. For instance, applying this technology setup to a hypothetical integrated sugar mill operating with 500 tons of sugarcane per hour, an electricity supply is needed of 46.5 MWe for flue gas treatment and compression, resulting in a CO_2 purity of up to 99.6% (Barbosa et al., 2017). The required power for the capture process can be provided either by the cogeneration plant, by renewable energy sources installed on-site or by the grid. In contrast, oxyfuel capture requires alterations in the combustion process, being not carried out under air, but instead using a stream of high oxygen concentration. By condensing the water contained in the OFC flue gas, the remaining gaseous stream then consists mostly of CO_2. The CO_2 thus obtained is partially recirculated to maintain the combustion temperature close to air-firing mode (Möllersten et al., 2003). Equipping a sugarcane refinery with an electrolyzer for H_2 production (as suggested in previous section), the O_2 side-stream of the latter process can be fed into the OFC process, without additional O_2 supply cost. Besides this synergy, OFC has the advantage of not being reliant on solvent-based systems (such as some PCC options), thus reducing its upstream emissions close to zero and improving its GHG balance.

CO_2 Utilization

In future defossilized energy systems, sustainable sources of carbon, such as captured as sugarcane refineries, are likely to play a crucial role both for energetic use (via the production of synthetic hydrocarbons) and material use (e.g., in the chemical industry), allowing to reduce GHG emissions while increasing the energy yield and/or carbon efficiency from the same unit of land used for sugarcane plantation (Barbosa et al., 2017). Interesting CCU pathways for CO_2 obtained from polygeneration sugarcane plants are on-site juice clarification and power-to-gas/power-to-liquid production (see previous section on biomethanation for more details). In the sugar industry, the sugarcane juice purification is traditionally carried out via the sulphitation method. However, periodic sulfur price increases as well as food safety and environmental concerns related to the use of sulfur have given considerations to replacing sulfur dioxide with carbon dioxide, i.e. relying on a carbonation process (Saska et al., 2010). Although carbonation is not yet widely used in the sugarcane industry, it is a common method for beet juice purification in which the raw juice is treated with lime and carbon dioxide to separate non-sugar substances (Lambert et al., 2018). This thus presents an opportunity for on-site utilization of the previously captured carbon.

Beyond on-site use of CO_2 for juice clarification and/or PtX processes, sugarcane refineries can also sell the CO_2 to other industries that are in need of carbon supply. For example, CO_2 is used in the food industries for various carbonation processes such as for carbonated soft drinks, water and beer. Even carbonated sugarcane juices exist which could theoretically be integrated in the portfolio of a sugarcane refinery. CO_2 can also be used in form of dry ice for various refrigeration systems. Other promising areas of CO_2 utilization are to be found in the chemical, pharmaceutical and cosmetics industry such as in polymer processing, for the synthesis of urea and the production of acyclic carbonates, formic acid and renewable methanol (Xu et al., 2010; Aresta et al., 2016).

CO_2 Storage

Besides CO_2 valorization via CCU, the captured CO_2 can also be stored underground in geological formations. Already in 2003, Möllersten et al. discussed CO_2 capture and storage (CCS) for the sugarcane-based ethanol production (Möllersten et al., 2003). Qualified as "market niche" at the time, the ethanol industry became the pioneer for bioenergy with carbon capture and storage (BECCS). In fact, all five operating BECCS facilities are fully or partially based on CO_2 captured from bioethanol plants (Consoli, 2019). While all of these use corn as feedstock for the ethanol production, the techno-economic realities are similar to sugarcane-based ethanol production. In order to finance the CO_2 capture unit, four out of five BECCS projects sell the captured CO_2 to enhanced oil recovery (EOR) operators that inject the CO_2 into oil reservoirs to increase the resource extraction. The BECCS business case also strongly depends on local conditions, more refined analysis on country and regional level have been proposed for the sugarcane industry in Brazil (Moreira et al., 2016; Tagomori et al., 2018), Australia (Pour et al., 2018), and Tanzania (Hansson et al., 2019).

With 411 sugarcane biorefineries being currently located in Brazil, a significant amount of CO_2 is emitted each year from fermentation and bagasse combustion (Carminati et al., 2019). Up to 28 Mt of these CO_2 emissions could be captured and stored from the sugarcane fermentation alone (Moreira et al., 2016). Extending the scope to both fermentation and cogeneration, Restrepo-Valencia and Walter (2019) conducted a techno-economic assessment of BECCS for sugarcane mills with integrated PCC systems (Restrepo-Valencia and Walter, 2019). Four different refinery sizes and set-ups, they determine emission avoidance costs of 45–80 €/t CO_2, with larger plants of 8 Mt/y milling capacity presenting the most favorable conditions. In the Brazilian case, CO_2 transportation costs to offshore injection sites are a considerable cost factor. To guarantee sufficient and regular CO_2 flows, Tagomori et al. (2018) demonstrate that CO_2 from the ethanol production would need to be pooled together with the bagasse cogeneration plants as well as other closely located fossil point sources to enable the development of the necessary CO_2 transportation infrastructure in Brazil (Tagomori et al., 2018). However, this comes at the expense of higher levelized abatement costs for the entire BECCS system as more emitters would need to be equipped with capital-intensive CO_2 capture units.

In Australia, Pour et al. (2018) modeled four BECCS systems for the power sector, using four different biomass feedstocks and conversion technologies (Pour et al., 2018). With respect to sugarcane bagasse combustion in circulating fluidized bed reactors, they considered brownfield plants with a total capacity of around 400 MW with a CO_2 capture retrofit via PCC technology. With this setup, they found a technical bagasse-based BECCS potential in Australia of $-3.43\ Mt_{CO2}$/year from a lifecycle perspective. Scaled up to the global level, the authors identified a negative emissions potential of 0.5 Gt CO_2 per year based on bagasse-CCS. The techno-economic assessment revealed that a carbon price higher than $125/t CO_2 would be needed for BECCS to become competitive in the Australian power sector with coal-fired power plants. However, as CCS costs are expected to significantly decrease by 2050, BECCS could be a viable option even at lower carbon prices. Furthermore, cost savings can be achieved when creating CCS clusters that share CO_2 transport and storage infrastructure (Brownsort et al., 2016).

In contrast to this positive outlook, the conclusions of Hansson et al. (2019) on the Tanzanian case point toward a non-implementation of CCS in the domestic sugarcane-based energy production (Hansson et al., 2019). Their analysis revealed that despite feedstock availability and technical feasibility, large-scale deployment of ethanol-based CCS in Tanzania is not advisable as the country lacks adequate formal institutional capacities to regulate and monitor sensitive issues related to potential land-use conflicts, resource trade-offs and broader sustainability concerns. In consequence, distrust among local communities both in the government and in foreign investors and ad hoc informal governance to cope with the absence of formal institutions result in an unstable investment environment for BECCS.

Recovery of Biogenic Silica From Bagasse Ashes

Sugarcane being a graminaceous culture plant, it accumulates silicon (Si) in its exterior cell structures (Park et al., 2003; Nguyen et al., 2014). While only approx. 20% of this silicon is present in the harvested products, roughly 80% of the Si accumulation remains in the crop residues cane trash (Haynes, 2017). With an average of 14 tons of sugarcane trash per hectar along the sugarcane value chain, notably from cultivation and harvesting (Hassuani et al., 2005), this represents a significant amount of biogenic silica. Being the second most abundant element in the

Earth crust (Szulc et al., 2019), Si is ubiquitously available in the soil and important for plant growth and plant health (Yan et al., 2018). The sugarcane plant benefits fundamentally from the widespread element Si and its accumulation and inclusion (Coskun et al., 2019). In the soil, silicon exists in solid and liquid phases (Elsokkary, 2018). The availability of silicon in form of silica ($Si(OH)_4$) from the soil solution depends on the soil property, sorption and desorption processes, and the soil pH (Szulc et al., 2019). While the bioavailable silicon, i.e. mono-silicic acid, is absorbed and accumulated by plants (Exley, 1998), Si is accumulated as silica-gel via the apoplastic pathway into epidermal tissue and polymerizes as monosilicic acid or amorphous silica (Taiz and Zeiger, 2008; Nguyen et al., 2014; Phonde et al., 2014; Bhatt and Sharma, 2018). The accumulated form of Si in plant tissues are often different amorphous phases like silicon double layers and microscopic bodies of Opal-A ($Si(OH)_2{\cdot}nH_2O$) with enclosed co-boundings, called phytoliths (Hodson et al., 2005; Schaller and Struyf, 2013). This accumulated Si converts inside the living cells into biogenic silica, which is a bioavailable form of Si and for more easily accessible for living organisms (Fraysse et al., 2006; Sommer et al., 2006). In previous studies, an accumulation rate of 380 Kg ha^{-1} Si into sugarcane tissue over 12 months was reported (Savant et al., 1999). To enable the uptake and transport of Si from the soil solution via the roots to the shoots inside the plant and the plant tissue, a group of proteins and genes are responsible (Ma and Yamaji, 2006). Furthermore, several transporters in the plasma membrane of plant cells regulate this Si influx and efflux (Elsokkary, 2018). Si thus plays an important physiological and morphological role for growth, especially for the generation of plant cells. Despite Si considered as non-essential element in these circumstances, it serves as functional element for optimal growth and development of the sugarcane plant. Beneficial effects for plant growth and development as well as increases in crop yield and disease resistance are described for agricultural crops (Phonde et al., 2014). Furthermore, Si improves the ability of the plant to treat salt and drought stress, temperature fluctuations, radiation and UV-B damage, pathogen attack and metal toxicity (Liang et al., 2007; Etesami and Jeong, 2018; Katz, 2019).

Content of Biogenic Silica in Sugarcane Residues and Bagasse Ashes

Silicon contents of sugarcane dry matter vary greatly among various plant families from 0 to 10 wt% (Hodson et al., 2005; Katz, 2015; Trembath-Reichert et al., 2015). For comparison, natural silicon content in grass dry matter range between 0.1 and 12.4 wt% (Epstein, 1999; Ma et al., 2001; Liang et al., 2007). Plants from the *Saccharum* genus, especially *Saccharum officinarum*, accumulate high amounts of Si in their shoots and leaves (Hodson et al., 2005). Depending on regional specificities in terms of soil properties, season and growth stage of the plant, the Si content might differ in the sugarcane. Potential residues with high amounts of biogenic Si are, in descending order, straw > bagasse > filter cake > vinasse. The highest amounts of biogenic silica of up to 4,006 mg/kg dry weight have been reported for sugarcane bagasse (origin Cuba, ECN, The Netherlands). Generally, the bagasse is used in boilers or cogeneration units to provide heat and steam for further milling and distillation processes (Baker, 1977). After combustion, bagasse ashes remain as non-volatized mineral fractions, including a high fraction of biogenic silica (Valmari et al., 1998; Parr et al., 2001). The quantity of SiO_2 content of the bagasse dry ash amounts to 41.9–72.3 wt% (Miles et al., 1995; Turn et al., 2006). Therefore, biogenic silica can be obtained in high quality (up to >98 wt%) from agricultural residues, which allows a combined energetic and material utilization (Nguyen et al., 2014; Schliermann et al., 2018), and thus with options to receive high purities >98 wt% and provide a sustainable and renewable source for biogenic silica (Beidaghy Dizaji et al., 2019). The production process includes three main preparation steps under controlled conditions: pre-treatment of the biomass, thermo-chemical conversion of surpluses and post-treatment of biogenic silica enriched ashes and raw materials (Schliermann et al., 2018; Schneider et al., 2020). Furthermore, a removal of inorganics before oxidizing the organic matter to obtain high-grade biogenic silica is beneficial to the silica's quality (Schneider et al., 2020).

APPLICATION POTENTIALS FOR BIOGENIC SILICA

The advanced application prospects for biogenic silica is multifaceted and finds usage among others as drug delivery carrier, catalyst, addition in construction material or industrial applications, concrete, backing material etc. (Nair et al., 2008; Bharti et al., 2015; Patel and Raijiwala, 2015; Kumar et al., 2016; Tchakoute et al., 2016; Beidaghy Dizaji et al., 2019). Value added products like solar-grade silicon, nano-silicon, Si/nitrogen-doped carbon/carbon nanotubes (SNCC) and nano/microstructured spheres for enhanced Li-ion batteries or SiC are well described from biogenic Si-raw material sources as well (Wong et al., 2014; Marchal et al., 2015; Zhang et al., 2016). Further applications for sugarcane derived Si can be soil amendments. In fact, silicon-rich residues from crop production can mitigate toxicity stresses of plants in acidic conditions, deficiency of P as well as Al and Mn overloads (Pontigo, et al. 2015). Finally, sugarcane-straw derived biochar can immobilize the accumulation of heavy metals like Cd, Pb, and Zn through sorption processes (Puga et al., 2015).

CONCLUSION AND PERSPECTIVES

A simple biorefinery concept has already been implemented in the sugarcane industry by extending the product portfolio from sugar only to ethanol, electricity and in some cases also including biogas and PLA production. The present review discussed further potentials to improve the circular economy approach by fostering a better utilization of waste and residue streams. To provide an even more diversified portfolio, other innovative chemical production pathways, material utilization of biogenic silica recovered from sugarcane residues, as well as CCU/S approaches of CO_2 valorization were therefore included in the review. The scheme of this complex biorefinery is shown in **Figure 3**. However, the design and implementation of such complex system is very challenging and several downstream

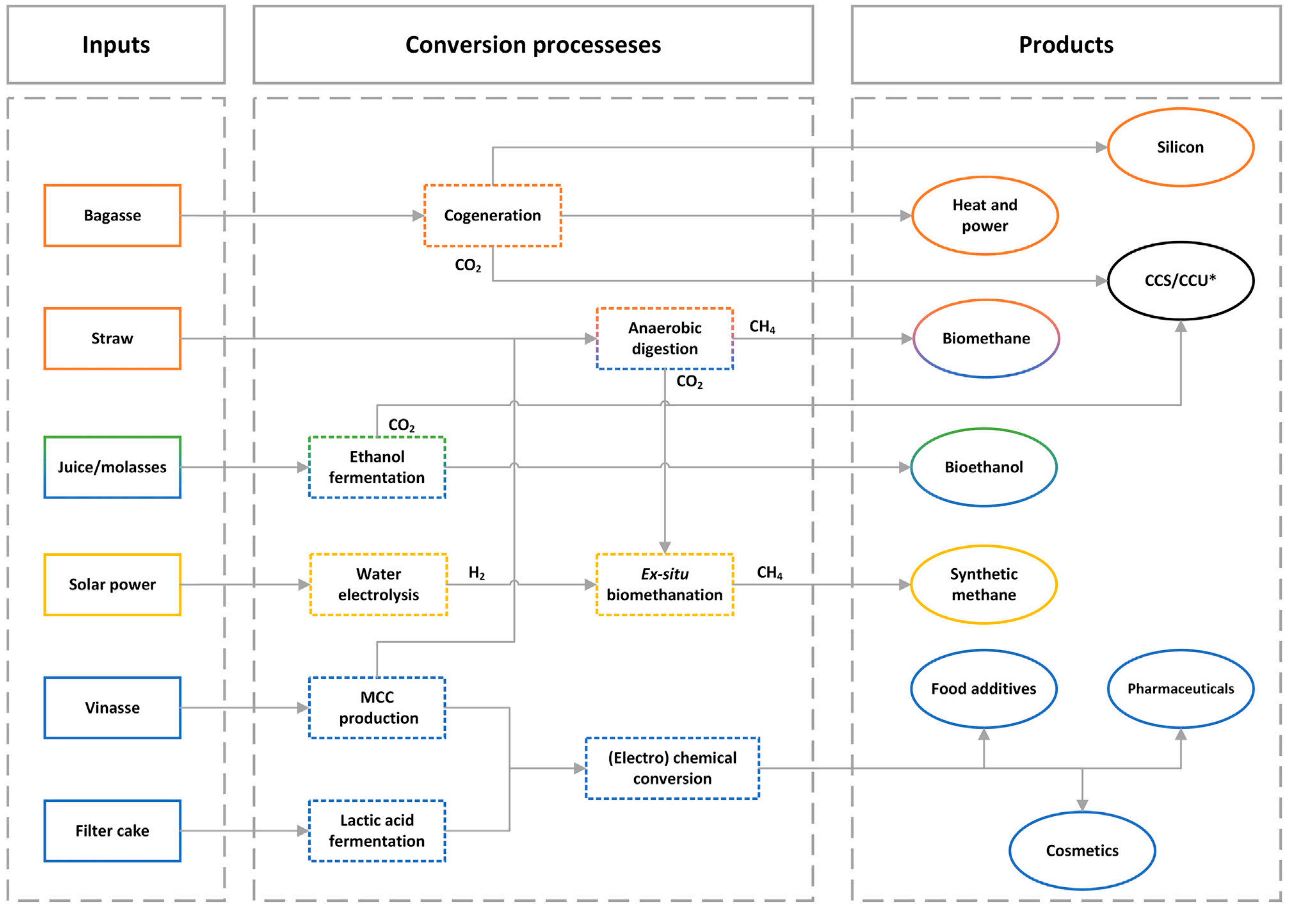

FIGURE 3 | Simplified scheme of future sugarcane biorefinery fully implementing the circular economy concept * other CCU than synthetic methane.

technologies (e.g., separation of fermentation products, CO_2 capture units) should be improved for a successful deployment of integrated biorefineries in the future. The techno-economic feasibility assessment of these technologies was beyond the scope of this article, and it is partially reviewed elsewhere (Mandegari et al., 2017; Meghana and Shastri, 2020). Nevertheless, the mitigation of environmental impacts, especially the reduction of GHG emissions should also be taken into account when considering economic feasibility. Therefore, by implementing better CO_2 utilization or even sequestration, the circular sugarcane economy might play an important role in defossilizing other industry branches that can take advantage of the renewable biomaterials obtained by exploiting the sugarcane wastes and residues to their full extent, thus substituting fossil resources. However, long-term detrimental effects on soil quality are to be prevented by adequate nutrient management and fertilization technique, by recirculating urban mass flows, as well as by growing legume intercrops between the sugarcane cropping seasons. All in all, the sugarcane value chain extensions, cascading processes and circular bioeconomy concepts highlighted in this paper by optimizing the use of sugarcane by-products, wastes and residues highlights how valorization of agricultural lands still exhibits further, yet untapped potentials.

AUTHOR CONTRIBUTIONS

SF initiated the writing process and wrote the recovery of silicon section. AH wrote the CCS and CCU sections, and proofread the manuscript. LJ contributed to the biogas section and wrote the hydrogen production section, created **Figure 1** and **3** and contributed to **Table 1**. WS wrote the bio-fertilizer production section and contributed to the introduction. HS wrote the carboxylate platform section. WL wrote the biogas upgrading section and created **Figure 2** and **Table 2**. MN formulated the article and wrote the introduction, bioplastic, biogas production, conclusion and perspectives sections, contributed to the **Figure 1** and **3** and **Table 1**, reviewed and compiled the whole article. All authors contributed to the article and approved the submitted version.

FUNDING

The authors would like to acknowledge the financial support from BMBF-German Federal Ministry of Education and Research (# 01DN19018).

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

GLOSSARY

AEL alkaline electrolysis
AEMEL anion exchange membrane electrolysis
AD anaerobic digestion
CCU carbon capture and utilization
CCS carbon capture and storage
CH_4 methane
CHP combined heat and power
CNF cellulose nanofibril
CO carbon monoxide
CO_2 carbon dioxide
COD chemical oxygen demand
CSTR continuous stirred tank reactor
ECN energy research center of The Netherlands
GHG greenhouse gas
H_2S hydrogen sulfide
HRT hydraulic retention time
VS volatile solids
KOH potassium hydroxide
MCC medium-chain carboxylate
MER methane evolution rate
Mt metric ton
MW megawatt
NFC natural fiber composites
NH_3 ammonia
N_2O nitrous oxide
NO_3 nitrate
NPV net present value
OFC oxyfuel capture
PCC post-combustion capture
PEM proton exchange membrane
PEMEL proton exchange membrane electrolysis
$PtCH_4$ power-to-methane
PtX (or P2X) power-to-x
PV photovoltaic
SCC short-chain carboxylate
SFC sugarcane filter cake
SiC silicon carbide
SiO_2 silicon oxide
$Si(OH)_4$ silica
$Si(OH)_2 \cdot nH_2O$ opal-A
SOEL solid oxide electrolysis
SRT solid retention time
TKN total Kjeldahl nitrogen
TRB trickle-bed reactor
TRL technology readiness level
TS total solids
UASB upflow anaerobic sludge blanket
VRE variable renewable electricity