Chapter

Bioenergy Recovery from Cotton Stalk

Rafat Al Afif, Christoph Pfeifer and Tobias Pröll

Abstract

Cotton stalk (CS) plant residue left in the field following harvest must be buried or burned to prevent it from serving as an overwintering site for insects such as the pink bollworm (PBW). This pest incurs economic costs and detrimental environmental effects. However, CS contains lignin and carbohydrates, like cellulose and hemicelluloses, which can be converted into a variety of usable forms of energy. Thermochemical or biochemical processes are considered technologically advantageous solutions. This chapter reviews potential energy generation from cotton stalks through combustion, hydrothermal carbonization, pyrolysis, fermentation, and anaerobic digestion technologies, focusing on the most relevant technologies and on the properties of the different products. The chapter is concluded with some comments on the future potential of these processes.

Keywords: cotton stalk, thermochemical, biochemical, bioenergy

1. Introduction

Worldwide energy demand and greenhouse gas (GHG) emissions are predicted to increase by 70 and 60%, respectively, between 2011 and 2050 according to the International Energy Agency (IEA) [1]. An increase in GHG emissions is unequivocally the largest anthropogenic contributor to exacerbating climate change [2]. Currently, the majority of energy is derived from fossil fuels. As reported in 2017, it is estimated that if consumption of fossil fuels persists at 2016 levels, reserves of coal, gas, and oil will last only 153, 52.5, and 50.6 more years, respectively [3]. Therefore, other forms of energy such as biomass have significant potential to offset traditional energy sources [4]. Biomass, as a zero CO_2 emission fuel, can offer one solution in the reduction of CO_2 atmosphere content. In 2016 renewable energy accounted for 18.2% of the 576 exajoules (EJ) of total primary energy supply (TPES), of which 13% came from biomass [1, 5]. Biomass provided 46.4 EJ of TPES in 2016, and expert scientific analysis predicts that by 2050 the bioenergy share of TPES could reach 100–300 EJ per year (year^{-1}) with the highest theoretical share proposed at 500 EJ year^{-1} [5, 6]. Although renewable energy makes up only a small percentage of current TPES, it has the theoretical potential to provide all of the human energy requirements on earth [7]. By 2035, biofuels could realistically provide at least a quarter of the estimated world's TPES of 623 EJ. To increase the proportions of renewables in the TPES, innovative feedstocks or inputs are required [8]. A significant source of biomass for renewable energy is available globally in the form of agricultural waste. Agricultural wastes pose expensive and challenging issues for crop producers. With exception to the fraction of residues tilled back into the soil to increase soil organic carbon (SOC) content and enhance other soil physical characteristics, many of these wastes have little to negative value, and knowledge of revenue streams are sparse [9, 10]. For example, cotton biomass waste is an abundant and available waste from agricultural production at a high estimate of roughly 50 million tons annually [11]. Similarly, other crops produce even more abundant waste, such as rice husks which sum up to 822 million tons of waste with no real end of use application [12].

It has been reported that cotton residues left during harvest are carriers of the pest; therefore, adequate disposal of these residues is necessary [13]. However, it is worth considering that one of the major complications of cotton production is the management of the pink bollworm (PBW) (*Pectinophora gossypiella*). It is considered one of the most detrimental cotton pests because of its hardiness to insecticides [14]. PBW's life cycle consists of four stages: egg, larva, pupa, and adult. During the first stage, females lay 200–500 tiny eggs in single or small groups of 5–10 each on cotton plants which hatch 3–4 days later. During the second and most destructive stage, the larvae bore into the bolls to grow before cotton boll blossoming occurs. Here the larvae feed on seeds for 12–15 days where they mature to 12 mm long as a fully developed larva. The most significant damage occurs to the seed and lint. Before pupation, the larva experiences diapause during the winter for 2–4 months in which they do not feed or move. They may be found in bolls, in stems, or in the soil in which they are safe in a silken cocoon until spring. During the pupation stage, spring conditions cause the larva to drop to the soil beneath the cotton plants where they pupate; the pupa is roughly 7 mm long and brown, and the pupal period is between 7 and 8 days. During the adult stage in spring, first-generation adults develop from the pupae and are gray brown small moth which mate and lay eggs. In the summer, larvae from the previous generation fall to the soil, pupate, and emerge as second-generation moths, completing the life cycle. The entire cycle from egg to egg takes roughly 32 days, and the PBW can persist, on average, for up to six summer cycles [15, 16]. This pest is distributed globally where cotton is grown and is considered the key cotton pest. Its main effect on cotton crops is preventing flowering buds to open, shedding of the fruit, seed loss, and damage to lint. Trials in the USA have shown that the potential loss of harvest without control was 61%, whereas losses of 9% were estimated when the pest was controlled through insecticide application. In 1998, the total US crop yield of cotton was reduced by 2.7%, while in Egypt it is estimated that the PBW causes losses of about 10–20% of cotton crop annually [13, 15]. In 2014, it was reported that the PBW had been eradicated from California, Arizona, New Mexico, and Texas in the USA as well as Chihuahua in Northern Mexico. The eradication is attributed to a combination of insecticides and genetic modification of the cotton crop as well as releases of sterile PBW throughout the region [17]. In countries without robust pest management strategies, the most common method of PBW prevention is through burning the residues in the field or by shredding and plowing the residues to a depth of 6 inches into the soil, the latter of which is time and energy intensive [11, 15]. In light of the global challenges associated with cotton agricultural residuals, a promising method of cotton waste disposal is through their utilization as an energy source.

Studies indicate that undebarked cotton stalks are unsuitable for the production of fine paper and dissolving pulps [18, 19]. Furthermore, cotton stalks and other agricultural residues are unsuitable for hardboard and particle board due to their high water absorption and thickness swelling (deteriorated dimensional stability) [20, 21].

In contrast, the usage of cotton waste as an energy feedstock has become a subject of numerous studies in recent years [22–24]. Researchers generally focused on the production of biogas, ethanol, and the production of fuel pellets or briquettes. Several studies on the subject of cotton waste pyrolysis indicate that pyrolysis of cotton stalks is deemed to have potential as one of the technological solutions for its management.

The purpose of the study is to review current bioenergy conversion technologies and to provide quantitative data and interpretation of the heating value, proximate and elemental analysis, and product yields specific to bioenergy recovery from CS. The hypothesis is that resulting data will be consistent with past research proving that CS residues have a high potential for use as an energy source. Moreover, some products from the conversion (e.g., biochar from pyrolysis) can be used as soil additive to recover nutrients and carbon to the soil. The latter can additionally act as water storage. This subject is important because there are significant quantities of CS waste from agricultural production globally, which is a potential source of revenue. Furthermore, other risks associated with cotton waste such as farm hygiene by pesticide remnants and soilborne pathogens can be addressed. Therefore, utilizing CS biomass has the potential to be a significant source of energy and an opportunity to reduce their environmental issues and financial costs [11]. This study contributes to the needed understanding of energy derived from thermal and biological conversion products of cotton stalks.

2. Cotton stalk residues for energy

Cotton stalks are a common agricultural residue with little economic value. They may be utilized without direct competition to food or feed provision. It is a renewable lignocellulosic biomass produced during cotton production. Daud et al. report values of 58.5% cellulose, 14.4% hemicellulose, and 21.4% lignin, which makes it a particularly attractive feedstock for thermochemical conversion processes [25]. Based on biomass classifications, cotton agricultural waste is a primary residue and herbaceous biomass fuel [26, 27]. Cotton crop cultivation occurs between July and February, while harvesting occurs from October to March [28]. Cotton agricultural wastes consist of the main stem, branches, bur, boll rinds, bracts, peduncle, roots, petioles, and leaf blades (**Figure 1**) left as residual biomass after harvesting the floral cotton bolls for commercial purposes, equivalent to roughly 3–5 times the weight of the produced cotton. The roots are 23.2% of the whole plant in average with the measured values ranging between 14.3 and 29.1%. However, based on observations of the amount of the soil stacked on the roots during fieldwork, it was decided in most studies to investigate the possibility of collecting only the aerial part of the residue, leaving the roots in the field. It was anticipated that the collected

Figure 1.
Cotton residual wastes after harvesting.

material would be free of soil and with less moisture content. These factors would make its storage easier and its use for energy production by thermal conversions more attractive [29].

The separated CS consists of the main stem, branches, burs, boll rinds, bracts, and peduncles [28, 30]. The stem has an outer fibrous bark weighing 20% of the weight of the stalk as well as an inner pith [11, 31]. It reaches between 1 and 1.75 m long, and the diameter above ground varies between 1 and 2.5 cm. On average depending upon species and crop conditions, 2 to 3 tons of CS are generated per each hectare of land annually; it's worth noting that the moisture content was found to drop from 50% to under 20% when the stalks were left in the field, after harvesting, for 3 weeks [28].

According to the US Department of Agriculture (USDA), the total global production of cotton was roughly 26.9 million metric tons for the reporting year of 2018 from August 1, 2017, to August 1, 2018, which has been relatively steady for the last 5 years of data collection. The three largest global producers of cotton in 2018 were India, China, and the USA. India produced 6.3 million metric tons of cotton, China produced 6.0 million tons, and the USA produced 4.5 million tons. The remaining countries produce less than 2 million tons year^{-1} [32].

To determine the total CS residue or collectable dry residue from the cotton production values, several factors are required. These are the annual production, residue to the crop factor, dry weight factor, and the availability factor [33]. The annual production is reported yearly by each respective country and collected by the USDA [32]. The residue factor is based on the ratio of the fresh weight of residue to the grain weight harvested at field moisture. It describes the relationship between crop grown for product and the residual biomass leftover after harvest. The relationship is specific to the type of crop variety [33, 34]. As mentioned previously, the residue typically weighs three to five times the harvested cotton [31]. Klass and co-workers estimate the residue factor to be 2.45 [33]. The availability factor is based on the end use of the CS residue and how much is available for collection. The availability of crop residues may be limited due to tilling some residues into the soil to reduce erosion risk; to provide structure; to preserve fertility; to use as a fertilizer, as fibrous material for various agricultural uses; or to feed to livestock [34]. Therefore, it can be best described as the sustainable removal rate of a residue [35]. Typically, in areas with low SOC, more crop residues will be tilled into the soil, while in areas with high SOC, more crops can be sustainably removed [34]. Many studies assume roughly 25% of total available agricultural residues can be recovered; however, recovery percentages may be higher or lower depending on the crop [35, 36]. It is estimated that in the USA, up to 70% of the residues are tilled back into the soil for nutrient cycling and soil health, whereas in India 15% is used for fuel, while the remainder is burned in the field [28, 30]. Klass et al. report a residue factor of 0.6 for cotton agriculture. Lastly, the dry weight factor is the amount of moisture in the freshly harvested cotton residue. Therefore, collectable dry biomass can be calculated with all of these values [33]. It is worth noting that harvesting crop residues for energy has been shown to be efficient and the energy required to collect and process residues is a small percentage of the energy content of the residue itself [37].

3. Characterization of cotton stalks for determination of energy potential

In order to get an overview of the main fuel properties of cotton stalks, proximate as well as ultimate analyses need to be performed. Schaffer et al. [24] compared data from cotton stalks to data for wheat straw and beechwood (**Table 1**). In

Properties		Unit	Basis	Biomass		
				Cotton stalks	Wheat straw	Wood (beech)
Proximate analysis	Ash	wt%	Dry	5.51	4.35	0.82
	Volatile matter	wt%	Dry	73.29	79	84
	Fixed carbon	wt%	Dry	21.20	17	15
Ultimate analysis	Carbon	wt%	Dry	47.05	47.82	48.26
	Hydrogen	wt%	Dry	5.35	5.29	5.80
	Nitrogen	wt%	Dry	0.65	0.47	0.29
	Sulfur	wt%	Dry	0.21	0.08	0.03
	Oxygen	wt%	Dry	40.77	41.59	44.80
Lower heating value (LHV)		MJ/kg	Dry	17.1	17.7	17.4

Representative values based on analyses reported in the literature [29, 38, 39]

Table 1.
Fuel properties of cotton stalks, wheat straw, and wood on a dry basis.

comparison with wood, the agricultural by-products are characterized by higher ash contents. The lower heating value (LHV) of dry cotton stalks is equivalent to poor-quality wood and varies from 16.4 to 18.26 MJ/kg [38]. Compared with wheat straw (LHV of 17.28–18.41 MJ/kg [38]), the cotton stalk can be considered as a biofuel with respect to its energy content. However, a clean and energy-efficient utilization in combustion plants is counterindicated by high contents of elements like Cl, K, and Na that decrease the ash melting point of SiO_2 and lead to fouling and corrosion in the boiler plant. Although straw and stalks are, therefore, not suitable for conventional combustion plants, low-temperature thermochemical conversion could be applied with the effect to yield biologically stable biochar containing the critical ash constituents and also plant nutrients, while the ash-free volatiles can be used in high-temperature conversion routes such as combustion in gas boilers or cofiring in pulverized coal boilers. In this respect, it is important to notice that the fixed carbon content obtained in the proximate analysis is higher for cotton stalks than wheat straw and beechwood. This observation holds true also when looking at other fuel samples available in the literature cited in **Table 1**. Furthermore, it is seen that cotton stalks possess high amounts of carbon (47.05%) and oxygen (40.77%) and its composition is relatively similar to wheat straw and wood. The presence of these elements in biomass leads to more char formation as well as to the high calorific value of the product. Therefore, because cotton stalks, wheat straw, and wood have high carbon and oxygen contents, they are suitable for energy production and could be combined with the supply of biochar.

Proviso studies have shown that raw CS provides higher combustion efficiency and longer burn time than some other agricultural residuals; furthermore, the energy needed to collect and process these residues is a small percentage of the energy contained within them [11]. To summarize, cotton stalk can be considered a typical biofuel with respect to its energy content.

4. Bioenergy conversion technologies

Bioenergy carriers are solid, liquid, or gaseous fuels which can be obtained from the available technologies. Liquid fuels are commonly used in transportation vehicles but can also be used in stationary engines especially turbines. Solid fuels are directly combusted to obtain heat, power, or combined heat and power (CHP). Gaseous fuels can be applied to the full range of end uses. As CS calorific value is equivalent to poor-quality woody biomass. A method of increasing the calorific value of the feedstock while simultaneously utilizing the residue is the technological processing through thermal and bioconversions to yield high-energy-content products which can be more easily transported and stored for use at a later time [11, 22]. CS can be converted into several useful forms of energy using different processes (conversion technologies). Bioenergy is the term used to describe energy derived from CS feedstocks. Several processing steps are required to convert raw CS into useful energy using mainly the two main process technology groups available: biochemical and thermochemical. Biochemical conversion encompasses two primary process options: anaerobic digestion (to biogas) and fermentation (to ethanol). For the thermochemical conversion routes, the four main process options presented here are pyrolysis, gasification, combustion, and hydrothermal processing (basically hydrothermal carbonization (HTC)). **Figure 2** provides a broad classification of energy conversion processes for CS.

4.1 Thermochemical conversion

Thermochemical conversion of biomass is the process of utilizing heat and, in some cases, chemical reagents, to create more energetically useful products. The output from the process is heat, gaseous, liquid, or solid fuels [40]. The four major thermal processes for converting biomass to useful energy are combustion, gasification, pyrolysis, and hydrothermal processes (see **Figure 2**). Hydrothermal processes summarize three distinct processes such as hydrothermal carbonization, liquefaction, and gasification. Hydrothermal carbonization is the process which fits best to cotton stalks and is the most developed, and therefore the focus is here on this conversion route. Pyrolysis, gasification, and combustion can be seen as state-of-the-art technologies, although not implemented in demonstration scale for cotton stalks yet. All processes can be implemented in similar plant configurations (fix bed, fluidized bed, entrained flow). Pyrolysis seems to be the most promising thermochemical conversion route due to its robustness, flexibility, and the possibility to provide a method to recover nutrients. Thus, pyrolysis is described in more details.

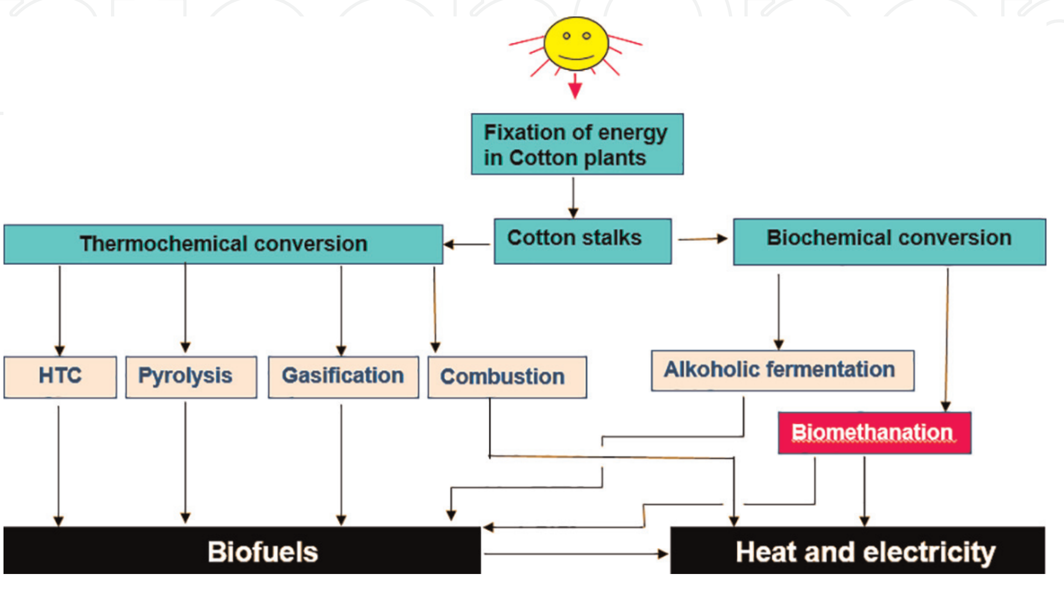

Figure 2.
Schematic diagram of the processes of energy conversion of cotton stalks.

4.1.1 Combustion

Combustion, or direct burning, of biomass consists of full oxidation of combustibles in air or oxygen-enriched air. Generally, biomass combustion produces a variety of pollutants and particulate matter (PM), as well as flue gas which requires special treatment of unburned particles. In comparison to gasification and dependent on the feedstock used for fuel, combustion can release the acid rain contributing pollutants sulfur oxides (SO_x) and nitrogen dioxide (NO_2) at roughly 40 times and 9 times, respectively [41]. Combustion of biomass with high ash content has several drawbacks in comparison with low-ash biomass. The remnant ash content is left deposited on the internal heating surfaces, which forms slags and causes fouling to the process, affecting the heating rate negatively and decreasing process efficiency [9]. The inorganic compounds in the biomass feedstock may lead to an increase in particulate matter (PM) concentrations, such as crystalline silica, which has detrimental health effects in the air [9, 42]. With consideration to the detrimental impacts of ash on combustion processes, the ash content of the CS is relatively high with 5.5 wt% db. Although straw and stalks are, therefore, not suitable for conventional combustion plants, the ash problem can be avoided by separating it into biochar through pyrolysis at low temperatures prior to combustion [9]. This can be also done by air staging in the boiler to separate the oxidation of the gases from contact to the ash. However, it has been reported in a number of studies that CS provides the highest burning efficiency and longest burn time compared to corn stover and soybean residues. The greater the density, the longer the duration of combustion. This could lead to the necessity to pelletize the feedstock for certain applications. In the study by Coates [37], it was shown that cotton plant residue could be incorporated with pecan shells to produce commercially acceptable briquettes. However, changeover of the existing factories to facilitate utilization of CS would require an initial infusion of capital. This should be compensated by lower raw material costs in a reasonable period of time.

4.1.2 Gasification

Gasification is the thermochemical conversion of biomass by partial oxidation with O_2 and the reformation by steam, carbon dioxide, or other gasification agents, producing syngas as a chemical product or fuel. The biomass is exposed to less O_2 than in combustion but more than in conditions of pyrolysis. Gasification may be allo- or autothermal; therefore, the heat required for endothermal processing is provided by ex or in situ combustion of char or gas [43]. Gasification is one of the most efficient methods for converting the chemical energy stored in biomass into heat and other useful forms of energy. Estimates of overall exergetic efficiency range from high estimates between 80.5 and 87.6% [44]. It is closely related to pyrolysis, in which both processes undergo devolatilization of biomass in the absence of O_2 or air to yield suitable products for energy without entire combustion. However, the process is optimized for maximum gas yield through oxidation and subsequent reduction [41, 44]. Gasification is processed at temperatures of typically 750–900°C for fixed and fluidized bed, 1200–1500°C for entrained flow, and up to 3000°C for plasma applications.

The products yielded by gasification include a high proportion of gases, namely, carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), water (H_2O), hydrogen (H_2), gaseous hydrocarbons, minimal char residue, and condensed oil and tar. An oxidizing agent is added to the reaction in the form of air, O_2, or steam; and the gaseous tar or oil in the gas is condensed to acquire the desired product, producer gas. The gas may have a low energy content for autothermal operation, between 3 and 5 MJ/m^3, 10% of the heating value of natural gas; however, it is enough to power gas engines and increases the value of feedstocks that would otherwise be considered wasteful [41, 44]. For allothermal operation heating values of 12–14 MJ/m^3 are achieved. The relatively low temperature of the process leaves a char residue, which can subsequently be gasified through burning it at a high temperature, such as at 1000°C, while simultaneously injecting steam into the process. This breaks down the steam into oxygen (O_2) and hydrogen (H_2) which react with the carbon (C) from the char to create CO and H_2. By using O_2 rather than air, high-quality syngas can be produced from the CO and H_2 yield of the reaction, after impurities such as sulfur (H_2S), ammonia (NH_3), and tar have been removed. This syngas has the potential to be synthesized into methanol (CH_3OH), a high value liquid fuel, as well as other types of hydrocarbon compounds through the Fischer-Tropsch process. The efficiency of the overall process varies from 40% in simple designs to roughly 75% in processes which are well designed [41]. Allesina et al. [45] indicate that cotton residue gasification represents the basis for local circular economy models.

4.1.3 Pyrolysis

Pyrolysis is the process of thermochemical decomposition of a substance in the absence of O_2 [46]. Pyrolysis is a similar process to gasification; however, gasification controls the O_2 more precisely and generally; pyrolysis produces a significantly larger portion of biochar and is therefore sometimes called carbonization [47]. Pyrolysis is typically operated at 400–600°C. Pyrolysis produces a bio-oil liquid which can be used directly as a fuel and as a pretreatment intermediate step for converting biomass into a high-energy liquid which may be processed for power, heat, biofuels, and chemicals. Compared to the other technologies, pyrolysis is expected to offer more versatility, environmental stewardship, and higher efficiency [48]. Economically, periods of the energy crisis and fluctuating prices and availability have made biomass pyrolysis a more significant technology for development and research [49].

4.1.3.1 Pyrolysis product yields

Cotton stalk pyrolysis in a fixed-bed reactor has been studied to demonstrate products yield variation for different temperature regions [50]. They indicate that temperature increase from 650 to 800°C favored gas production, while char production decreased from 66.5 to 26.73 wt%, as the temperature increased from 250 to 650 C. This effect can be thought of as more volatile material being forced out of the char at higher temperatures, thereby reducing yield but increasing the proportion of carbon in the char. As far as the liquid fraction of the products is concerned, there is an optimum temperature at which maximum oil yield obtained (41% at ~550°C). Further temperature increases resulted in tar and liquid cracking into gases, and hence a high gas production is achieved. Similar results are also reported by [51]. The higher heating value (HHV) of pyrolysis oil is 16–23 MJ/l compared to fossil fuel which is 37 MJ/l. Pyrolysis oil has a low pH value of around 3, which must be taken into account in its handling and use. The (hydrophilic) bio-oil has water contents of typically 15–35 wt%. Typically, phase separation does occur when the water content is higher than about 30–45%.

4.1.3.2 Pyrolysis system

Pyrolysis reactors can be operated in continuous or batch mode. Typical continuous pyrolysis reactors include fluidized-bed pyrolysis, auger/screw-type pyrolysers, and rotary kilns. These reactors involve continuous input of feedstock and output of biochar, bio-oil, and syngas and often result in higher biochar yields and operational efficiencies than batch processes [52]. Compared to batch reactors, continuous reactors are more complex and expensive to design and operate and may require a reliable source of electricity [52, 53]. Therefore, continuous reactors are ideal for medium- to large-scale biochar production systems relying on centralized large quantities of feedstock. Additional information about the particularities of different pyrolysis systems can be found in the literature [48]. Nevertheless, some continuous reactor types are suitable for application in small to medium scale, too [53–56].

For the present study with cotton stalks as the feedstock, the continuously operated, indirectly heated rotary kiln reactor has been recommended according to **Figure 3**. The reasons for this decision are:

- The technology is robust and industrially proven not only for biomass but also for waste [57].

- Small- to medium-scale technology is readily available for distributed application in cotton-producing countries.

The elements chlorine and potassium, which are critical for combustion systems, remain quantitatively in the pyrolysis char fraction [55], and about 50% of the primary fuel energy can be exported with the gas and oil fraction, while less than 50% of the primary fuel energy stays in the char fraction. Thus, if the char is not further converted but returned to the soil, the problematic compounds may even have positive effects as nutrients and the related carbon will not be released as CO_2. Therefore, researchers consider the potential application of the pyrolysis char as a soil additive to increase crop yield [56, 59] or as a negative emission technology [24, 60].

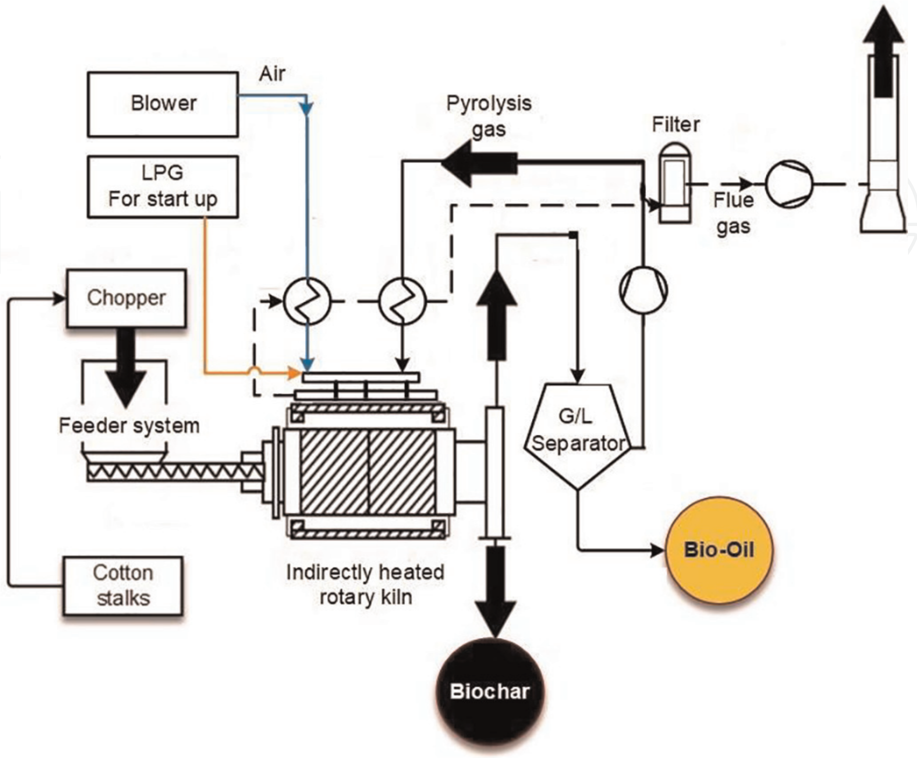

Figure 3.
Example of an indirectly heated rotary kiln pyrolysis process scheme [58].

4.1.3.3 Char utilization from cotton stalks for sustainable soil enhancement and carbon storage

Currently, the cotton stalks are often burnt on the fields causing high local pollution. However, the solid residues of the stalks remain on the field supplying nutrients. The same effects can be reached by the application of biochar from stalks. Cotton crops typically grow in hot regions on sandy soils, where biochar addition has been reported to enhance the soil fertility [59]. Mild conversion conditions below 600°C avoid ash melting and keep nutrients available for microorganisms and plants. With respect to the carbon storage effect, biochar from pyrolysis at >500°C shows sufficiently low O/C ratios to promise longevity in the soil [61]. Generally, slow pyrolysis is preferred for increased char yield [40]. The steady-state process simulation environment IPSEpro was used by Schaffer et al. [24] to assess a virtual pyrolysis conversion of cotton stalks, and they indicated that 52.8% of the carbon contained in the biomass accumulates in the biochar, whereas 38% of the input energy can be exported as heat energy at temperature levels suitable for electricity generation or industrial heat supply. The pyrolysis char shows a low molecular O/C ratio of 0.07 and an H/C ratio of 0.26. The expected half-lives of biochar in the soil are in the order of 1000 years for O/C ratios below 0.2. This makes the presented approach an interesting low-tech negative emission option. The predicted net negative emissions through stored carbon amount to 2.42 t CO_2 per hectare and year (**Figure 4**). The overall CO_2 emission avoidance effect can be increased if fossil fuel is substituted by the energy exported from the pyrolysis process.

From **Figure 5** one can see that 52.8 wt% of the total amount of carbon stored in cotton stalks is converted to char. Furthermore, the inorganic matter contained in the char, which includes important nutrients, remains in the char. The nutrients are then available for the new generation of plants if the char is used as soil additive.

The remaining part of carbon in pyrolysis gas and oil can be used for energy production as shown in the energy flow diagram in **Figure 6**. Energy streams are

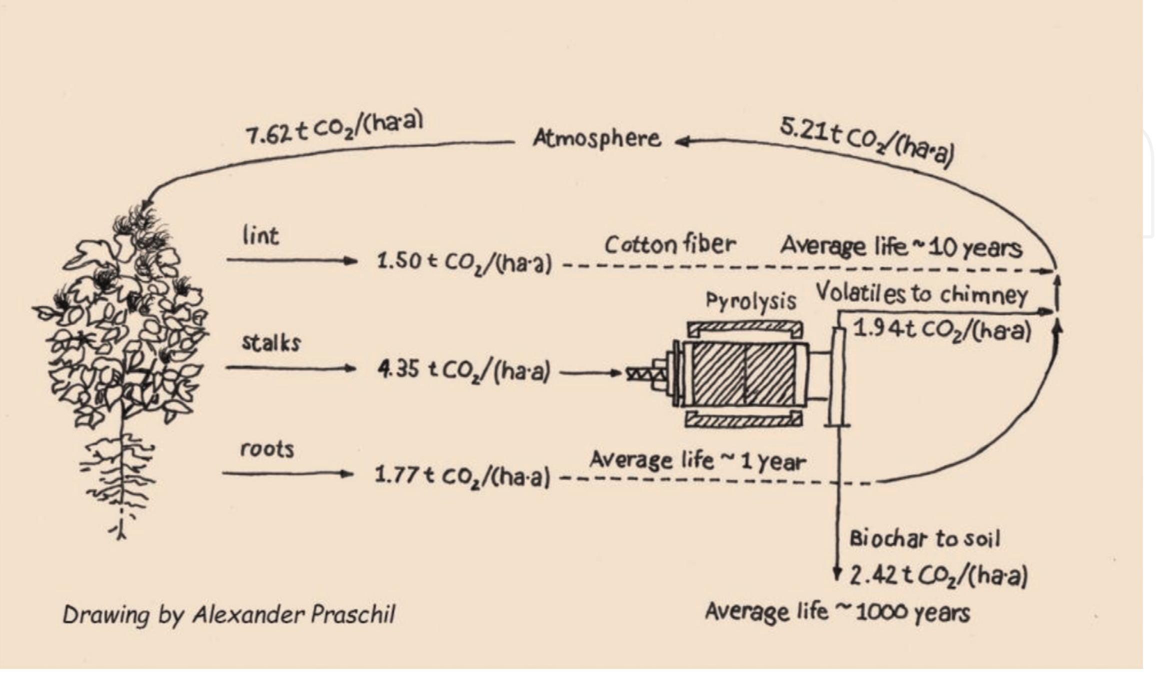

Figure 4.
Net carbon removal from the atmosphere through pyrolysis of cotton stalks and soil application of the pyrolysis char [24].

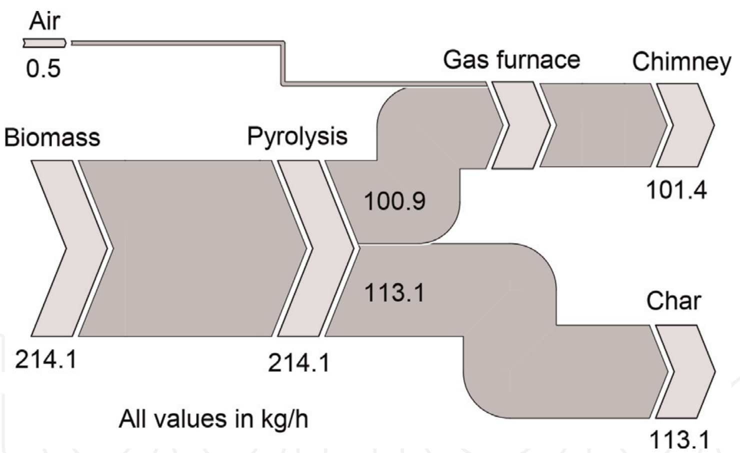

Figure 5.
Carbon mass flow diagram for an indirectly heated rotary kiln pyrolysis process without condensation of pyrolysis oil [24].

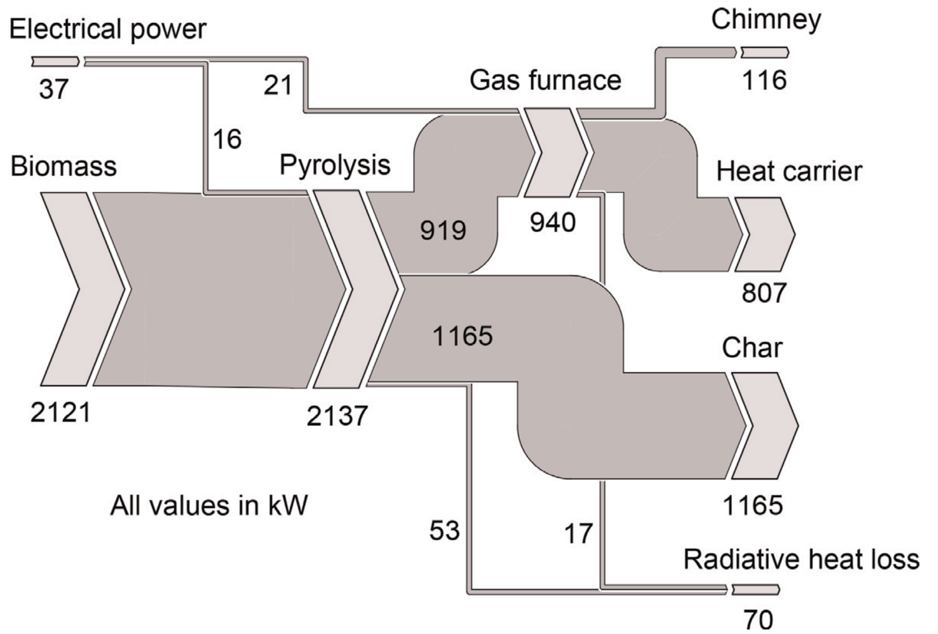

Figure 6.
Energy flow through an indirectly heated rotary kiln pyrolysis process without condensation of pyrolysis oil [24].

assessed based on the lower heating value and sensible heat with a reference temperature (sensible heat of zero) of 273.

In conclusion, the use of agricultural wastes such as cotton stalks in distributed, small- to medium-scale, energy-autonomous pyrolysis plants will allow for quasi-permanent soil storage of a part of the carbon contained in the biomass without the need for CO_2 storage sites. As a side-effect, it is expected that soil quality can be maintained and even improved by the application of biochar.

4.1.4 Hydrothermal carbonization

Nowadays hydrothermal carbonization is mentioned as a promising technology to convert biomass into a high-quality bioproduct, namely, hydrochar, as well as process water to recover nutrients (e.g., P, N, K, Si, etc.). Carbonization depletes compounds rich in oxygen and hydrogen and thereby increases the carbon content in the coal compared to the starting material. The depleted compounds are found essentially in the so-called process water and at low levels in the resulting process gas again. The product hydrochar is more hydrophobic than the source material, and the drainage is less energy intensive than the dewatering of fresh biomass. In addition, essential reactions are exothermic, and upon carbonization, after initial energy input, heat energy is released. Due to the increased carbon content of the hydrochar, the heating value increases. The hydrothermal carbonization, e.g., of CS, kills the eggs of the pink bollworm and other pathogens. There is still a need for research in the area of reduction of impurities and in the accumulation of nutrients in the coal. The distribution of nutrients between the solid, liquid, and gaseous phase can be adjusted via the process conditions (pressure, temperature, residence time, heating rate, pH, additives, catalysts, etc.). The considered process is shown in **Figure 7**.

Al Afif et al. [62] investigate the use of HTC in the production of hydrochar from CS. They concluded that hydrothermal carbonization is a promising conversion technology to provide bioenergy from CS. And there was a strong dependence between the residence time and the char quality, as the LHV of the hydrochar from CS increased with increasing residence time, whereas the total amount of hydrochar was decreased.

4.2 Biochemical conversion

Cotton stalk, as lignocellulosic biomasses, is difficult to hydrolyze due to its complex structure and a large amount of lignin present in it. Basic steps involved in bioconversion process of lignocellulosic biomass are pretreatment (physical, chemical, biological, and their combination) for cell wall destruction for biogas production, hydrolysis (acid or enzymatic) for soluble sugar release, and fermentation (bacteria or yeast) for ethanol production. Due to recalcitrant nature of lignin and its binding with holocellulose, a pretreatment step is required for fractioning of different cell wall components. Pretreatment exposes the cellulose surface for enzymatic attack and improves enzymatic digestibility and subsequent processes. Pretreatment identifies one of the major economic costs in the biochemical conversion process [63]. Generally, both process routes as discussed in the following are technically feasible, but techno-economic assessments are missing.

4.2.1 Ethanol production

The six-carbon sugars, or hexoses, glucose, galactose, and mannose, can be fermented to ethanol by many naturally occurring organisms. Baker's yeast, or *Saccharomyces cerevisiae*, has been traditionally used in the brewing industry to produce ethanol from hexoses. Recently, engineered yeasts have been reported to efficiently ferment xylose and arabinose, as well as mixtures of xylose and arabinose. In order to effectively utilize cotton stalk as a feedstock for ethanol

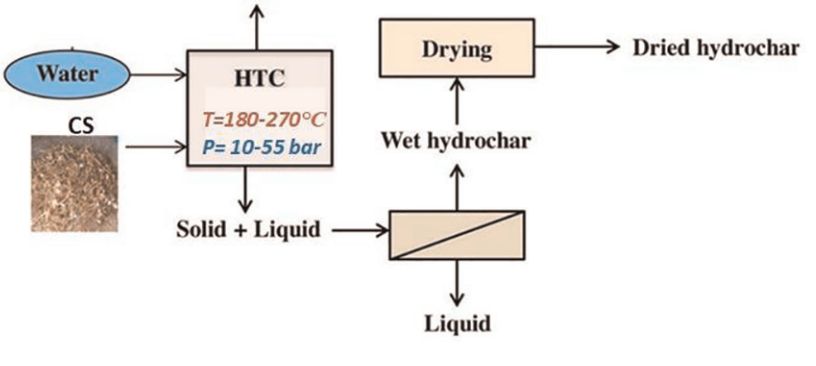

Figure 7.
System boundaries of the considered hydrothermal carbonization process.

production, optimal pretreatment is required to render the cellulose fibers more amenable to the action of hydrolytic enzymes. Generally, alkaline pretreatment is found to be more effective on agricultural residues and herbaceous crops such as cotton [64]. Christopher et al. [65] indicate that a hydrolytic efficiency of 80% was achieved for alkali-treated biomass using cellulase supplemented with beta-glucosidase and concluded that cotton stalks have great potential as a bioethanol feedstock.

4.2.2 Biogas production

Anaerobic digestion is a technology widely used for treatment of organic waste for biogas production. Biogas is a combustible gas derived from decomposing biological waste in the absence of oxygen. Biogas normally consists of 50–60% methane. It is currently captured from landfill sites, sewage treatment plants, livestock feedlots, and agricultural wastes. There were only a few studies on the subject of biogas production from cotton wastes. Isci and Demirer [23] studied the biogas production potential of cotton wastes. They indicated that cotton wastes can be digested anaerobically yielding 65–86 lN CH_4 kg^{-1} VS $(24 \text{ days})^{-1}$. A two-stage digestion technique for biogas production from co-fermentation of organic wastes (rice, maize, cotton) was also investigated [66]. This study indicated that under anaerobic conditions from the main components in CS, the cell wall carbohydrates were well preserved, while the level of soluble carbohydrate was low. Pretreatment of lignocellulosic biomass is a necessary step to overcome the hindrance of lignin and to increase solubilization [67]. Al Afif et al. [22] investigated the anaerobic digestion of cotton stalk (CS) using organosolv plus supercritical (SC) carbon dioxide pretreatment of cotton stalks for methane production. Results indicated that supercritical carbon dioxide pretreatment of CS is a potential option for improving the energy output, as the pretreatment of CS samples with organosolv plus SC-CO_2 increased the methane yield up to 20% compared with the untreated samples. The highest methane yield of 177 lN kg^{-1} VS was achieved by pretreatment with organosolv plus SC-CO_2 at 100 bars and 180°C for 140 minutes. It is worth noting that the quality of biogas was good and increased with pretreatment from 50 to 60% CH_4. To summarize, cotton stalks can be digested anaerobically and is a good source of biogas; nevertheless, pretreatment of cotton stalks is a necessary step to increase solubilization hence the methane production.

4.3 Future perspectives

This study contributes to enhancing our understanding of the feasibility of bioenergy recovery from cotton stalks. The findings have the potential to lead to a sustainable solution for the treatment of cotton stalks.

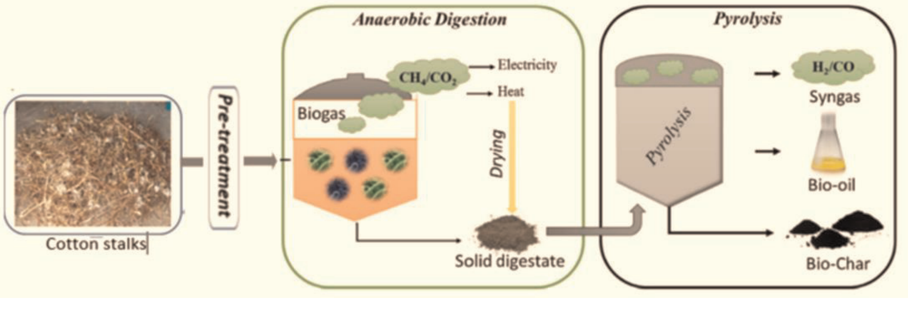

Figure 8.
The system boundary of coupling anaerobic digestion and pyrolysis process.

However, for higher bioenergy recovery, a study of the techno-economic feasibility of the integrated processes of anaerobic digestion and pyrolysis is recommended (see **Figure 8**).

5. Conclusions

It has been shown in this study that:

- CS is an agricultural residue with low economic value, and there is no direct competition to food or feed provision.
- CS contains lignin and carbohydrates, like cellulose and hemicelluloses, which can be converted into a variety of usable forms of energy.
- CS is more appropriate for the production of energy pellets due to its woody structure; however, due to the ash content of the CS which is relatively high with 5.5 wt% db, the ash problem can be avoided by separating it into biochar through pyrolysis at low temperatures prior to combustion.
- The use of pyrolysis and hydrothermal processes for CS treatment would result in the conversion of the major amount of carbon to char, which would mean a significant decrease in CO_2 release, compared to the state-of-the-art treatment paths. Also using biochar in the soil will reduce the need for mineral fertilizer since nutrients return to the soil with the char.
- CS can be digested anaerobically and is a good source of biogas or fermented to produce ethanol. However, pretreatment of cotton stalks is a necessary step to increase solubilization hence the methane and ethanol production.

The findings have the potential to lead to a sustainable solution for the treatment of cotton stalks. However, for higher bioenergy recovery more studies are needed to prove the effectiveness of cotton waste utilization.

Author details

Rafat Al Afif*, Christoph Pfeifer and Tobias Pröll
Institute of Chemical and Energy Engineering, University of Natural Resources and Applied Life Sciences, Vienna, Austria

*Address all correspondence to: rafat.alafif@boku.ac.at

References

[1] International Energy Agency (IEA). Key world Energy Statistics. Paris: International Energy Agency; 2016. Available from: https://www.iea.org/publications/freepublications/publication/KeyWorld2017.pdf

[2] Budinis S, Mac Dowell N, Krevor S, Dixon T, Kemper J, Hawkes A. Can carbon capture and storage unlock 'unburnable carbon'? Energy Procedia. 2017;**114**:7504-7515. ISSN 1876-6102

[3] BP. BP Statistical Review of World Energy June 2017. 2017. Available from: https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-full-report.pdf

[4] Tripathi M, Sahu JN, Ganesan P. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. Renewable and Sustainable Energy Reviews. 2016;**55**:467-481

[5] Renewable Energy Policy Network for the 21st Century (REN21). Renewables 2018: Global Status Report. Paris: REN21 Secretariat; 2018. Available from: http://www.ren21.net/wp-content/uploads/2018/06/17-8652_GSR2018_FullReport_web_final_pdf

[6] Edenhofer O, Pichs R, Madruga Sokona Y, Seyboth K, Matschoss P, Kadner S, et al. editors. Special report on renewable energy sources and climate change mitigation. Intergovernmental Panel on Climate Change. ISBN: 978-92-9169-131-9.2012

[7] Gasparatos A, Doll CNH, Esteban M, Ahmed A, Olang TA. Renewable energy and biodiversity: Implications for transitioning to a Green Economy. Renewable and Sustainable Energy Reviews, Volume. 2017;**70**(2017): 161-184. ISSN 1364-0321

[8] Xu J, Li M. Innovative technological paradigm-based approach towards biofuel feedstock. Energy Conversion and Management. 2017;**141**:48-62. ISSN 0196-8904

[9] Dunnigan L, Ashman PJ, Zhang X, Kwong CW. Production of biochar from rice husk: Particulate emissions from the combustion of raw pyrolysis volatiles. Journal of Cleaner Production. 2018;**172**: 1639-1645. ISSN 0959-6526

[10] Obour PB, Jensen JL, Lamandé M, Watts CW, Munkholm LJ. Soil organic matter widens the range of water contents for tillage. Soil and Tillage Research. 2018;**182**:57-65. ISSN 0167-1987

[11] Hamawand I, Sandell G, Pittaway P, Chakrabarty S, Yusaf T, Chen G, et al. Bioenergy from cotton industry wastes: A review and potential. Renewable and Sustainable Energy Reviews. 2016;**66**: 435-448. ISSN 1364-0321

[12] Dunnigan L, Morton BJ, Ashman PJ, Zhang X, Kwong CW. Emission characteristics of a pyrolysis-combustion system for the co-production of biochar and bioenergy from agricultural wastes. Waste Management. 2018;**77**:59-66. ISSN 0956-053X

[13] CABI. Invasive Species Compendium: *Pectinophora gossypiella* (Pink Bollworm). 2018. Available from: https://www.cabi.org/isc/datasheet/39417#7BD9E856-BD8A-4AA5-9060-4E6504EC8EEC

[14] Lykouressis D, Perdikis D, Samartzis D, Fantinou A, Toutouzas S. Management of the pink bollworm *Pectinophora gossypiella* (Saunders) (Lepidoptera: Gelechiidae) by mating disruption in cotton fields. Crop Protection. 2005;**24**(2):177-183. ISSN 0261-2194

[15] El Saeidy E. Renewable Energy in Agriculture in Egypt: Technological Fundamentals of Briquetting Cotton Stalks as a Biofuel. Master [thesis]. Humboldt University of Berlin; 2004. Available from: https://edoc.hu-berlin.de/bitstream/handle/18452/15724/El-Saeidy.pdf?sequence=1

[16] Ellsworth P, Moor L, Allen C, Beasley B, Henneberry T, Carter F. Pink Bollworm Management. 2003. Available from: http://ag.arizona.edu/crops/cotton/insects/pbw/NCCPBWnewsNo2.pdf

[17] Blake C.. Western Farm Press: Pink Bollworm Eradication in Cotton in 2017? 2014. Available from: https://www.westernfarmpress.com/cotton/pink-bollworm-eradication-cotton-2017

[18] Heilmann S, Davis H, Jader L, Lefebvre P, Sadowsky M, Schendel F, et al. Hydrothermal carbonization of microalgae. Biomass & Bioenergy. 2010; **34**:875-882

[19] Bridgwater A. Biomass fast pyrolysis. Thermal Science. 2004;**8**: 21-49

[20] Algin H, Turgot P. Cotton and limestone powder wastes as brick material. Construction and Building Materials. 2008;**22**:1074-1080

[21] Zhang Y. Hydrothermal liquefaction to convert biomass into crude oil. In: Blaschek HP, editor. Biofuels from Agriculture Wastes Byproduct. Oxford: Blackwell Publishing; 2010. pp. 201-232

[22] Al Afif R, Wendland M, Krapf LC, Amon T, Pfeifer C. Organosolv plus supercritival carbon dioxide pre-treatment of cotton stalks for methane production. In: Proceedings of the 10th International Conference on Sustainable Energy and Environmental Protection, Bioenergy and Biofuels. University of Maribor Press; 2017. pp. 22-33. ISBN: 978-961-286-048-6

[23] Isci A, Demirer G. Biogas production potential from cotton wastes. Renew Energy. 2007;**32**(5): 750-757

[24] Schaffer S, Pröll T, Al Afif R, Pfeifer C. A mass- and energy balance-based process modelling study for the pyrolysis of cotton stalks with char utilization for sustainable soil enhancement and carbon storage. Biomass and Bioenergy. 2019;**120**: 281-290

[25] Daud Z, Hatta MZM, Kassim ASM, Awang H, Aripin AM. Analysis the chemical composition and fiber morphology structure of corn stalk. Australian Journal of Basic and Applied Sciences. 2013;**7**(9):401-405. ISSN 1991-8178

[26] European Commission. Intelligent Energy Europe. Biomass Energy Centre. Solid Biofuels. Fuel Specifications and Classes. Graded Non-woody Pellets: Solid Biofuels. Fuel Specifications and Classes. Graded Non-woody Pellets. 2014. Available from: https://ec.europa.eu/energy/intelligent/projects/sites/iee projects/files/projects/documents/whs_summary_of_woodfuel_standards_en.pdf

[27] Khan AA, de Jong W, Jansens PJ, Spliethoff H. Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology. 2009;**90**(1):21-50. ISSN 0378-3820

[28] Patil PG, Gurjar RM, Shaikh AJ, Balasubramanya RH, Paralikar KM, Varadarajan PV. Cotton Plant Stalk—An Alternative Raw Material to Board Industry. 2007. Available from: https://wcrc.confex.com/wcrc/2007/techprogram/P1506.HTM.

[29] Wang X, Qin G, Chen M, Wang J. Microwave-assisted pyrolysis of cotton stalk with additives. BioResources. 2016; **11**(3):6125-6136

[30] He Z, Zhang H, Tewolde H, Shankle M. Chemical characterization of cotton plant parts for multiple uses. Agricultural & Environmental Letters. 2017;**2**: 110044. DOI: 10.2134/ael2016.11.0044

[31] Reddy N, Yang Y. Innovative Biofibers from Renewable Resources. Heidelberg, New York, Dordrecht, London: Springer; 2015. ISBN 978-3-662-45136-6

[32] United States Department of Agriculture (USDA). Cotton: World Markets and Trade 2018. Available from: https://apps.fas.usda.gov/psdonline/circulars/cotton.pdf

[33] Klass DL. Chapter 5—Waste biomass resource abundance, energy potential, and availability. Biomass for Renewable Energy, Fuels, and Chemicals, Academic Press, Pages. 1998: 137-158. ISBN 9780124109506

[34] European Commission (EC). 2016. Maximising the yield of biomass from residues of agricultural crops and biomass from forestry. Available from: https://ec.europa.eu/energy/sites/ener/files/documents/Ecofys%20%20Final_%20report_%20EC_max%20yield%20biomass%20residues%2020151214.pdf

[35] Scarlat N, Martinov M, Jean-François Dallemand JF. Assessment of the availability of agricultural crop residues in the European Union: Potential and limitations for bioenergy use. Waste Management. 2010;**30**(10): 1889-1897. ISSN 0956-053X

[36] Hoogwijk M, Faaij A, van den Broek R, Berndes G, Gielen D, Turkenburg W. Exploration of the ranges of the global potential of biomass for energy. Biomass and Bioenergy. 2003;**25**(2): 119-133. DOI: 10.1016/S0961-9534(02)00191-5

[37] Coates WE. Using cotton plant residue to produce briquettes. Biomass and Bioenergy. 2000;**18**:201-208

[38] ECN. Phyllis2—Database for Biomass and Waste. 2019. Available from: www.ecn.nl/phyllis2

[39] Ahmed FA, Abdel-Moein NM, Mohamed AS, Ahmed SE. Biochemical studies on some cotton by products Part I—Chemical constituents and cellulose extraction of Egyptian cotton stalks. Journal of American Science. 2010;**6**: 1306-1313

[40] Bridgwater AV. Pyrolysis—State of the art. In: Bridgwater AV, editor. Success & Visions for Bioenergy: Thermal Processing of Biomass for Bioenergy, Biofuels and Bioproducts. Newbury, Berks, UK: CPL Press; 2007

[41] Boyle G. Renewable Energy: Power for a Sustainable Future. Oxford, England: Oxford University Press in association with the Open University; 2012

[42] Johansson LS, Tullin C, Leckner B, Sjövall P. Particle emissions from biomass combustion in small combustors. Biomass and Bioenergy. 2003;**25**(4):435-446. ISSN 0961-9534

[43] Salatino P, Solimene R. Mixing and segregation in fluidized bed thermochemical conversion of biomass. Powder Technology. 2017;**316**:29-40. ISSN 0032-5910

[44] Puig-Arnavat M, Bruno JC, Coronas A. Review and analysis of biomass gasification models. Renewable and Sustainable Energy Reviews. 2010; **14**(9):2841-2851. ISSN 1364-0321

[45] Allesina G, Pedrazzi S, Allegretti F, Morselli N, Puglia M, Santunione G, et al. 2018. Gasification of cotton crop residues for combined power and biochar production in Mozambique. Applied Thermal Engineering. 2018; **139**(5):387-394

[46] Kung CC, Zhang N. Renewable energy from pyrolysis using crops and

agricultural residuals: An economic and environmental evaluation. Energy. 2015; **90**(Part 2):1532-1544. ISSN 0360-5442

[47] Mohan D, Pittman C, Steele P. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy. 2006;**20**:848. DOI: 10.1021/ef0502397

[48] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy. 2012;**38**:68-94. ISSN 0961-9534

[49] Qi Z, Jie C, Teijun W, Ying X. Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management. 2007;**48**:87-92

[50] Chen Y, Yang H, Wang X, Zhang S, Chen H. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: Influence of temperature. Bioresource Technology. 2012;**107**: 411-418. ISSN 0960-8524

[51] Kantarelis E, Zabaniotou A. Valorization of cotton stalks by fast pyrolysis and fixed bed air gasification for syngas production as precursor of second generation biofuels and sustainable agriculture. Bioresources Technology. 2009;**100**:942-947

[52] Brown R. Biochar production technology. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science and Technology. London: Earthscan; 2009. pp. 127-139

[53] Duku MH, Gu S, Hagan E. Biochar production potential in Ghana—A review. Renewable and Sustainable Energy Reviews. 2011;**15**:3539-3551

[54] Halwachs M, Kampichler G, Kern S, Pröll T, Hofbauer H. Rotary kiln pyrolysis—A comprehensive approach of operating a 3 MW pilot plant over a period of two years. In: Bridgwater AV, editor. Proceedings of the Bioten Conference on Biomass, Bioenergy and Biofuels. Newbury: CPL Press; 2010. p. 2011

[55] Kern S, Halwachs M, Kampichler G, Pfeifer C, Pröll T, Hofbauer H. Rotary kiln pyrolysis of straw and fermentation residues in a 3 MW pilot plant—Influence of pyrolysis temperature on pyrolysis product performance. Journal of Analytical and Applied Pyrolysis. 2012;**97**:1-10

[56] Pandit NR, Mulder J, Hale SE, Schmidt HP, Cornelissen G, Cowie A. Biochar from Kon-Tiki flame curtain and other kilns: Effects of nutrient enrichment and kiln type on crop yield and soil chemistry. PLoS One. 2017;**12**: e0176378. DOI: 10.1371/journal.pone.0176378

[57] Meier M, Schmid K, Heger S. Pyrolyseverfahren in Burgau—eine Betrachtung aus Sicht der Überwachungsbehörde. In: Thomé-Kozmiensky KJ, Beckmann M, editors. Energie aus Abfall (in German). Vol. 11. Nietwerder, Germany: TK Verlag; 2014. pp. 780-795

[58] Pröll T, Al Afif R, Schaffer S, Pfeifer C. Reduced local emissions and long-term carbon storage through pyrolysis of agricultural waste and application of pyrolysis char for soil improvement. Energy Procedia. 2017; **114**:6057-6066

[59] Schmidt HP, Pandit BH, Cornelissen G, Kammann CI. Biochar-based fertilization with liquid nutrient enrichment: 21 Field trials covering 13 crop species in Nepal. Land Degradation & Development. 2017;**28**:2324-2342

[60] Pröll T, Zerobin F. Biomass-based negative emission technology options with combined heat and power generation. Mitigation and Adaptation Strategies for Global Change. 2019. DOI: 10.1007/s11027-019-9841-4

[61] Spokas KA. Review of the stability of biochar in soils: Predictability of O:C

molar ratios. Carbon Management. 2010;**1**:289-303

[62] Al Afif R, Pfeifer C, Ramadan M. An experimental study on hydrothermal carbonization of cotton stalks. In: Proceedings of the 11th International Conference on Sustainable Energy & Environmental Protection, Bioenergy and Biofuels. Glasgow, UK; 2018

[63] Alvira P, Tomás-Pejó E, Ballesteros MM, Negro J. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. Bioresource Technology. 2010;**101**:4851-4861

[64] Silverstein RA, Chen Y, Sharma-Shivappa RR, Boyette MD, Osborne J. A comparison of chemical pretreatment methods for improving saccharification of cotton stalks. Bioresource Technology. 2007;**98**:3000-3011

[65] Christopher M, Mathew AK, Kumar KM, Pandey A, Sukumaran R. A biorefinery-based approach for the production of ethanol from enzymatically hydrolysed cotton stalks. Bioresource Technology. 2017;**242**: 178-183

[66] El-Shinnawi MM, El-Houssieni M, Aboel-Naga SA, Fahmy S. Chemical changes during a two-stage digestion technique for biogas production from combinations of organic wastes. Resour Conserv Recycling. 1990;**3**:217-230

[67] Zheng Y, Shi J, Cheng Y. Principles and development of lignocellulosic biomass pretreatment for biofuels. Advances in Bioenergy. 2017;**2**:1-68