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Approaches for adding value to anaerobically digested dairy fiber

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ABSTRACT

One of the consequences of the increase of large dairy concentrated feeding operations (CAFOs) is the abundance of dairy manure that needs to be disposed of or used in some way. CAFOs can become bio-refineries, harnessing the manure for heat, power, fuel, chemicals, fertilizers, fiber, wood composites, and biochar for production of multiple value-added co-products. The objective of this paper is to review options for using dairy manure fiber and its corresponding anaerobically digested (AD) fiber. Bedding for cows remains a common choice for employing the separated AD fiber. However, research has shown that AD fiber has potential for using it as a component of growth substrates used in container plant production systems, for producing composite materials, or as a feedstock for both chemical and thermochemical operations. Potential uses of AD fiber such as composite materials and liquid fuels are proposed based on experiences employing the manure and its fiber (both without a previous AD step and after AD). Thermochemical processing (e.g., liquefaction and pyrolysis) of AD fiber for fuels and chemicals has been conducted at laboratory level and still needs further study at larger scale. Gasification of AD fiber is a promising option since there is potential for integration of current methane production with methane produced from thermal gasification.

1. Introduction

Dairy farmers in several places worldwide are facing the difficulty of managing large amounts of dairy manure on concentrated animal feeding operations (CAFOs). In the United States (US), the midpoint size of dairies has risen from 275 to 900 cows, resulting in roughly 1800 large CAFO dairies with a wet-cow equivalent (WCE) herd size of 1000 or greater (many on the order of 5000, 10,000 or even 20,000). These large CAFOs produce over 50% of the milk supply [1]. With a production rate of 64–69 kg wet manure per cow per day (14–18% dry weight), these CAFOs, can produce a remarkable amount of manure and manure wastewater.

At such large scales, these dairy CAFOs are capable of becoming bio-refineries, harnessing the manure for heat, power, fuel, chemicals, fertilizers, fiber, wood composites, and chars/carbons, while mitigating climate, air, water and human health concerns associated with the manure [2,3]. A baseline for many CAFO bio-refinery visions is an anaerobic digestion (AD) operation for production of biogas and its resulting revenues from either combined heat and power (CHP) or renewable, compressed natural gas fuel (CNG), while also yielding significant environmental benefits related to methane capture and conversion, pathogen and odor destruction, and organic matter stabilization [4,5]. Unfortunately, adoption of even a baseline AD model on CAFOs within the US is currently limited to around 244 farms [6]. While several hurdles exist, a key limit to adoption rests on business economics with revenue from the most traditional biogas off-take, electrical power, simply not enough to supply a preferred return on investment [7,8]. However, incorporation of additional co-products and their revenues can have profound impacts towards financial viability. These additional revenue items can include tipping fees (as well as additional biogas/power) from off-farm organics, carbon credits, and of importance to this review paper, sales from the digested fibrous solid and/or its value-added products.

A key component within dairy manure is recalcitrant fibrous solids (fiber) surviving the cow's digestion process, which comprises roughly 40–50% of total solids (TS) in the as-produced manure [9,10]. This

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Table 1
Some characteristics of AD dairy fiber (dry basis).

Parameter	Unit	Value	
		Ref [10]	Ref [12]
TS (total solids)	%	24.43	–
VS (volatile solids)	%TS	92.00	–
Density	kg/m^3	400.56	–
C	%	–	39.1 ± 0.4
N	%	1.42	3.3 ± 0.2
P	%	0.28	1.1 ± 0.0
K	%	0.68	1.4 ± 0.0
Ca	%	1.44	4.8 ± 0.6
Mg	%	0.28	0.8 ± 0.1
Na	%	0.27	–
S	%	0.50	1.0 ± 0.0
Cu; Zn; Mn; Fe; B	ppm	99.33; 98.67; 929.33; 27.83	–
C/N[a]	–	36.70	–
Ash	%	–	13.7 ± 0.1
Extractives	%	–	11.7 ± 0.1
Cellulose (Glucose)		35.7 ± 1.4	23.6 ± 0.3
Hemicelluloses (Galactose, Arabinose, Xylose, Mannose)	%	9.2 ± 1.0	17.5 ± 0.5
Acid soluble lignin	%	–	1.8 ± 0.0
Acid insoluble lignin	%	27.7 ± 0.7	27.6 ± 0.1

fiber remains for the most part intact and undigested after incorporation in typical mesophilic AD units, representing, in its mechanically separated form, approximately 40% of the AD effluent TS [11]. This fiber can be an important raw source for value-added processing and product development. Table 1 presents a summary of some characteristics of AD dairy fiber according to two works. The values suggest that AD characteristics depend on the origin of the material. Although hemicellulose degradation is expected during the AD process, it is seen that an important portion of it remains intact. Nitrogen content in AD dairy fiber is high when compared with other lignocellulosic materials such as wood.

Pretreatment through various biological, chemical, mechanical, and thermal methods [13–15], and subsequent incorporation of the fiber for a second run at the AD process could allow for greater access to its biogas potential. For example, Biswas et al. [16] reported that a wet explosion process, calculated in conjunction with known US AD and fiber operational data, could increase AD methane production by up to 41%. While an impressive increase in gas productivity as well as potential electrical or CNG sales, net revenues resulting from the pretreatment costs and extra biogas should be compared to other value-added uses for the digested fiber. Recognizing this pretreatment pathway as a viable route (especially if value of the produced biogas and final energy/fuel product increases) is of merit but in addition, continuing down the alternate path of obtaining value to the existing AD fiber appears as a promising pathway for complete use of the fiber and for providing dairy farmers with strategies to increase revenues.

Although recent works [17,18] review some options for adding value to AD agricultural and food waste, there is a lack of works focusing on AD dairy fiber. The objective of this paper is to summarize the literature regarding numerous existing and potential value-added uses for AD dairy fiber. Some discussions rely on processing and use of the non-digested fiber fraction or the whole dairy manure. It is expected that the review will provide information to those interested in planning strategies for adding value to AD dairy fiber.

2. AD fiber for bedding/soil amendment/peat replacement

2.1. Manure and/or AD fiber as feedstock for dairy bedding and soil amendments

Bedding for cows remains a common first choice for using the separated AD fiber [19,20]. From a mass balance perspective, a WCE produces approximately 7–9 m^3/year of wet digested fiber (70–75% moisture content–MC) from the back end of the digester and liquid/solids separation [11]. Simple mechanical screens with scale variable capital ($45–80 per cow) and operating ($8–16 per cow per year) costs can effectively separate the fiber from the manure and/or wastewater [21]. The digestion process both reduces pathogens (2–3 log reduction) [11] and stabilizes the organic carbon in the effluent fiber, yielding a product that currently represents approximately 300,000 WCE in the US [22]. Typical revenues calculated from offset savings of not purchasing and using sawdust, straw, or other materials for bedding are on the order of $6–8 per wet m^3 ($21–27 per wet t), although in some states and regions with high feedstock costs this range could be higher [23]. Farm mass balances show an approximate internal need for 50% of the produced fiber while the remaining 50% could be used for other value-added processing or sold as bedding to nearby dairies without a digester [11]. Several companies have entered the marketplace with additional treatment and drying technologies that further prepare the digested or even non-digested fiber for use as animal bedding. These, among others, include Eco-Composites (Holland, MI), who through a patented drying and treatment process, produces a Perfect Cycle® Natural Bedding that is sold in pelletized form to regional dairies, rabbit breeders and horse stables [24,25] and Nutrient Control Systems (Chambersburg, PA) who selectively target longer fiber particles from non-digested, separated fibrous solids and treats them in short-cycle in-vessel composters.

After separation, another common method to add value to AD fiber is to apply basic compost processing methods—adding aeration and space under controlled conditions for sufficient time to compost the fiber [20]. As part of the AD process, carbon is partially converted into methane, thus AD fiber can have carbon to nitrogen ratios lower than raw manure, but still within the range and with the necessary moisture content for successful composting, especially if the fiber is co-composted with other materials to obtain even more advantageous carbon to nitrogen ratios and other compost properties [26]. While AD fiber may already have reduced pathogen content, hot composting practices can give additional assurance of pathogen reduction and prevent regrowth of pathogens during storage [26]. Composting stabilizes the carbon and other nutrients in the fiber material, darkening the fiber, making it look more like soil. It also reduces the volume and can drive off some of the moisture, producing a product that is easier to handle and with less weight. After composting, the darker composted fiber can be marketed for higher value, either alone or as a desirable ingredient in blended nursery and garden soil mixes [10,26,27]. Typical price points for bulk sales of composted dairy manure/fiber containing appreciable concentrations of nitrogen (~15 kg N/t) are around $20/t with an additional $10/t charge for large-scale field application [28].

A more specialized form of composting with practical application using composted whole dairy manure and/or dairy fiber is vermicomposting [29,30]. Vermicompost is a process in which specialized worms are grown in the presence of organic residuals using a variety of continuous production systems, such as low-cost floor beds, containers or boxes, and raised gantry-fed beds, for production of a greater population of earthworms (e.g., animal or fish protein) or for production of earthworm castings or vermicompost [30]. Research has established the favorable conditions for using earthworms to process cattle or dairy manure solids, as well as bio-solids resulting from AD of wastewater [30]. The earthworms fragment and consume the fibrous organic matter obtaining nutrition from the microorganisms that grow on the feedstock [29].

2.2. AD fiber as a component of growth substrates used in container plant production systems

Greenhouse and nursery production of high-value crop plants is a specialized segment of the horticulture industry. Both woody and herbaceous plants are grown in tightly controlled environments [31] and nearly 80% of the plants are grown in containers [32]. The growth substrates used in container production are typically soilless and at least 70–80% of the ingredients are organic materials [32]. The standard organic components of container substrates have been peat and bark from various softwood and hardwood tree species [33–37]. Both substrates, however, are experiencing sustainability and/or price pressures, with sphagnum peat experiencing environmental concerns, production and transportation costs price hikes, as well as reduced availability [37–39]. Bark is also becoming scarce due to demand from other uses, reduced timber harvests, and rising prices [40,41]. The demand for sustainable alternatives to peat and bark has prompted research to develop alternative substrates [35,37,42–48].

Properly treated, typically by composting or AD, organic wastes have the potential to substitute for peat and bark as components of the growth substrates in containerized plant production systems [37,46–48]. Specific to AD fiber, there is a small but growing body of research showing that AD fiber has the potential to meet the requirements for a component of high-quality growth substrates [49–55]. To produce container crops according to schedule, greenhouse and nursery growers must have reliable source of high quality growth substrates that are consistent over time and that have appropriate physical and chemical properties for their crops [34,46,56,57]. Key physical properties of the substrate include: total porosity, water-holding capacity, air-filled porosity, pH, soluble salts content, and cation exchange capacity. Most organic substrates have 75–85% pore space [34]. Although requirements may vary by crop, a generally accepted range for water holding capacity is 20–60% while 10–20% air-filled porosity is typically considered desirable [33]. The pH range for plants grown in organic soils and soilless substrates is about 1.0–1.5 units lower than for mineral soils [33], with the recommended pH range for most container substrates being 5.5–6.5 [58,59]. Additionally, substrates for growing plants in containers must be standardized, reproducible, available, and economical. The substrates must be free from diseases, pests, harmful chemicals, heavy metals and dangerous foreign materials, easy to work with, and have no objectionable odor.

Early research to determine the potential for the fibrous material from AD dairy manure to act as a peat substitute in soilless growth substrates has been conducted in Israel [49,60]. Chen et al. [60]) sieved and leached the digested slurry to produce a fibrous material resembling peat that was given the commercial name *cabutz*. Tests of its physical and chemical properties indicated *cabutz* was a well-aerated growth substrate with high water and nutrient holding capacities, albeit with slightly basic pH 7.0–7.6) and very high electrical conductivity (EC, a measure of soluble salts), necessitating leaching before use as a growth substrate [60]. In a series of experiments, Raviv et al. [49] tested *cabutz* as a peat substitute for plant growth substrates, for a seed germination medium and for rooting media. As a growth substrate *cabutz* produced marketable size *Philodendron wendlandii* plants a month earlier and 34% larger than plants grown in peat (3 versus 4 months). For other plants there were no growth differences between the *cabutz* and peat substrates.

In 28 greenhouse experiments with petunia plants conducted over several years, MacConnell and Collins [50] used AD fiber as a one-to-one replacement for peat moss in container substrates. The authors found dairy fiber to have physical properties (aeration porosity and water holding capacity) similar to peat but the average pH of 8.4 and EC of 3.5 dS/m were much higher than peat moss. The authors found that amending AD fiber with elemental sulfur to lower the pH produced petunia shoot growth and leaf greenness equal to peat when used as a one to one replacement (70% by volume) but that the addition of gypsum along with the sulfur was needed to produce both shoot and root systems equal to peat.

Krucker et al. [51] compared several locally available peat substitutes, including AD fiber, for greenhouse production of chrysanthemum 'Shasta' at two nitrogen fertilizer rates using conventional overhead irrigation and a capillary mat sub-irrigation system. A commercially formulated, bagged peat-perlite substrate consisting of 70–80% sphagnum peat moss was the control. AD fiber was used alone or mixed 1 to 1 (50%) by volume with Douglas-fir bark. Analysis of chemical and physical properties showed the EC of the dairy fiber was very high, 8.3 dS/m, and even when mixed 1 to 1 with bark the EC was 5.4 dS/m, above the recommended range for container substrates. Leaching the AD fiber with a volume of water equal to four times the volume of the substrate lowered the fiber EC to 3.6 dS/m and the fiber to bark mix to 2.3 dS/m. After leaching, the AD fiber and fiber to bark substrates had pH values of 7.8 and 6.7, respectively. Nine weeks after transplant 'Shasta' chrysanthemums were ready to market and data was collected on root and shoot growth, plant visual quality, and number of flower buds [51]. Results of statistical comparisons for low and high N fertilized chrysanthemums in both the overhead and sub-irrigation treatments indicated there were only two significant differences for any of these measurements between the peat perlite control and either of the AD fiber substrates. The two significant differences indicated visual quality of the overhead and sub-irrigated AD fiber grown plants fertilized at the low N rate was higher than the plants growing in peat-perlite control. Root growth of plants in the experimental substrates was similar to the controls in both irrigation systems. In two recent works, Lamont and Elliot [54,55] evaluated the effect of potting media containing bark-peat-perlite and bark-AD dairy fiber-perlite on the growth of several types of ornamental plants and the nutrients availability in the potting soil. Plants tested were "Jack Frost" brunnera (*Brunnera macrophylla* I.M. Johnst), "Moonbeam" coreopsis (*Coreopsis verticillata* L.), "Whoopsa-Daisy" Shasta daisy (*Leucanthemum × superbum* Bergmans ex J.W. Ingram), "Kobold Original" liatris (*Liatris spicata* (L.) Willd.), "David" phlox (*Phlox paniculata* L.), and Poinsettias (*Euphorbia pulcherrima*). Results showed that AD fiber can be effective for substituting part (e.g., up to 50%) of peat in potting media for a diversity of ornamental plants.

Hummel et al. [53] compared growth and quality of containerized 'Little Hero Flame' marigold and 'Golden California Wonder' pepper plants in an experimental substrate made of dairy manure-food waste AD solids mixed 1 to 1 by volume with Douglas-fir bark to the same commercially available peat:perlite substrate as used by [51]. At the time of harvest, all plants were considered marketable but results were not consistent across species [53]. Marigolds in the digester soilds:bark substrate fertilized with 200 ppm N every-other-day were not significantly different in shoot growth index, dry weight or visual quality but did have more flower buds than marigolds in the peat-perlite control substrate. The peppers had similar shoot growth index and flower bud numbers, but their dry weight and visual quality were lower in the digester solids:bark substrate. When the nitrogen rate was lower (i.e., 200 ppm N every-fourth-day), marigolds in the digester solids:bark and peat-perlite substrates were similar in all measured parameters except that visual quality of plants in peat-perlite was slightly higher. At the low N rate, analysis of pepper measurements indicated plants in the peat-perlite control were larger of higher quality and had 15 rather than 10 flower buds. Although all plants in this experiment were marketable, the results indicate the need to test experimental substrates on a wide range of plant species under different growing conditions.

Crippa et al. [52] tested the solid fraction of AD effluent from digestion of cow manure and pig slurry for its potential as a container substrate. The AD solid was used alone and in combination with sphagnum peat at 25% and 50% by volume to germinate cress and barley seeds and to grow lettuce plants. The authors found that reducing the salinity and lowering the pH of the AD solids was necessary and did so by mixing it with peat. Their results indicated the AD solids could be a valuable component in plant growth substrates replacing up to half of the peat amount.

Although not anaerobically digested, screened solids from a 1600-cow Florida dairy were processed through a horizontal drum digester

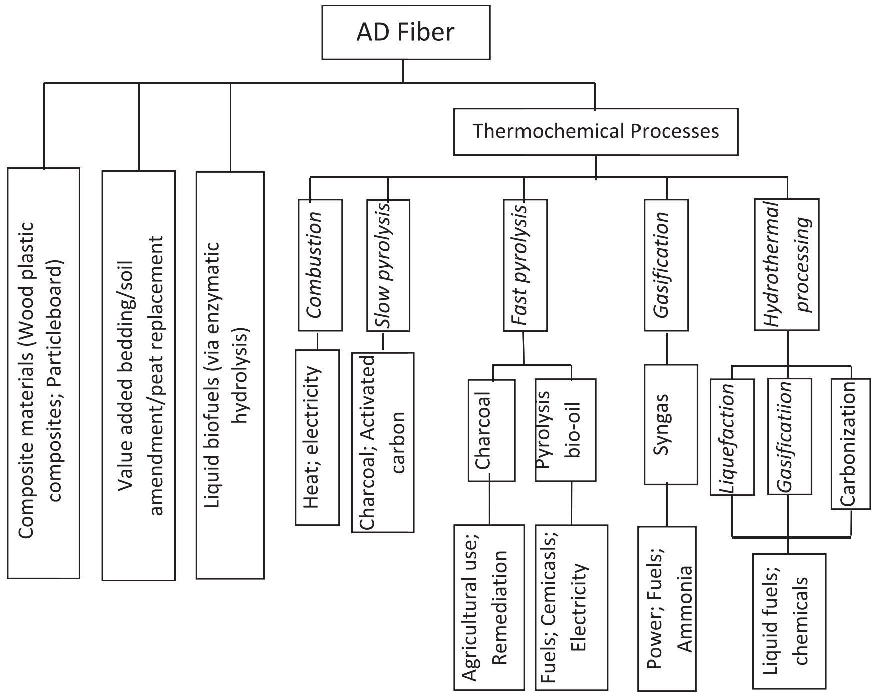

Fig. 1. Options for adding value to anaerobically digested dairy fiber and some expected products.

or composter to produce a dairy manure peat-substitute marketed as *cowpeat* [61]. In experiments with foliage plants, Li et al. [62] replaced peat with *cowpeat* at 10% increments from 10% to 60% in the propagation substrate for germinating *Asparagus densiflorus* seeds and for rooting cuttings of *Epipremnum aureum*, *Philodendron scandens* ssp. *oxycardium* and *Ficus benjamina* 'Florida Spire'. Results indicated that all cuttings rooted and seed germination rates of *cowpeat*-substituted substrates were greater than or similar to the peat substrates. Li et al. [62] concluded that there was potential to use *cowpeat* in foliage plant propagation and for foliage plant production. Shober et al. [63,64]) used *cowpeat* obtained from the same source at about the same time as [62] as a peat substitute in substrates for the container production of three annual bedding plants and three woody landscape shrubs. Their results indicated substrates formulated with *cowpeat* appeared to be commercially acceptable for production of container-grown bedding plant and woody landscape shrub species based on growth and quality [63]. *Cowpeat* is a commercially available peat substitute [65].

Determining the volume and constituents of soilless growth substrates used in container plant production is difficult [47]. The most reliable data comes from the European Union (EU) where the volume of growth substrate constituents produced in 13 EU countries was determined in a survey by [39] for the year 2005. Results indicated a total production of 34.6 million m^3 with 77.4% of the total being peat, 5.1% other organics and 9.1% composted materials. Germany was the largest producer of growth substrates surveyed with a reported total of 9.1 million m^3, 93% of which was peat. Italy was the second largest producer with 5.27 million m^3 total constituents comprising 74% peat. The use of composted biodegradable waste was increasing in many of the countries surveyed and was significant in Italy, amounting to 5% of the total constituents. Unfortunately, the volume of substrate constituents used in North America is difficult to estimate [47]. Recent data are not available but Carlile et al. [47] reported in 2002 to 2003 the Canadian Peat Moss Association estimated its members supplied approximately 8.7 million m^3 of peat to the United States. Canada is the source of most of the peat used in the U.S.

According to Carlile et al. [47] growth substrates used by the greenhouse and nursery industry fall into three general categories: 1) substrates for propagation either by seeds or cuttings and production in small containers; these substrates are typically 50–70% peat by volume with an inorganic component like vermiculite and/or perlite comprising the other component; 2) substrates for large container plant production in the greenhouse that are usually 70% peat:30% perlite by volume; and, 3) substrates for outdoor container nursery plant production, which are typically 60–80% bark with various other materials, including recycled organic wastes, comprising the rest of the substrate. Bilderback et al. [46] indicated there is general agreement among U.S. researchers that alternative substrate components must be able to replace peat or bark by up to 30% or more (by volume) in substrates for container-grown plants.

Transportation costs, environmental considerations, and alternative uses will continue to put upward pressure on the price of peat and bark. A check of suppliers in Pierce County, Washington, indicated spring 2015 grower prices for Canadian sphagnum peat and fine-grade Douglas-fir bark for potting were $101.28 and $29.99 per cubic yard, respectively. These prices do not include delivery or sales tax and can vary with the quantity of material purchased.

3. Other options for using AD fiber: composites, biofuels, and products derived from thermochemical processing operations

Other important options that hold potential for supplanting or supplementing value-added use for AD dairy fiber consist of: a) production of composite materials, b) liquid biofuels, and c) products derived from thermochemical processing. Thermochemical processes include: combustion, gasification, pyrolysis, and hydrothermal operations (hydrothermal liquefaction and hydrothermal gasification), as presented in Fig. 1 (which includes the uses discussed in Section 2). While combustion requires excess of oxygen, gasification is conducted in the presence of limited amounts of air. Pyrolysis and hydrothermal operations, conversely, occur in the absence of air. Potential products include: heat (for steam and/or electricity generation) in combustion, gases (for fuels and chemicals) in gasification, and liquids and solids (which is the case of pyrolytic bio-oil and charcoal) in the case of pyrolysis. This section describes some works that report potential uses of manure fiber and its corresponding AD fiber for producing these products.

3.1. AD fiber as feedstock for composite materials

Possibilities for producing composite materials using AD dairy manure have been reported by [66] (referred to by [67]), [68,69] and, more recently, by Ferraz et al. [70]. Winandy and Cai [67] mentioned that the characteristics of AD fiber (e.g., size and geometry) could make it suitable to substitute either fiber for medium density fiberboard (MDF) or wood particles for particleboard. The authors found that particleboard panels produced with AD fiber, either alone or combined with wood particles, satisfy the requirements for H-1 grade commercial particleboard [71] and MDF [72]. However, water sorption was high, which was attributed to the absence of wax in the formulations used for producing the composites. An associated publication [68] presented an economic analysis of the use of AD dairy fiber for manufacturing particleboard in the State of Wisconsin. Moreover, Dvorak and Hunt [69] have patented a method to produce composites from AD biomass, including AD dairy manure fiber, without adding resins, waxes, or sizing components.

In the work of Ferraz et al. [70], the authors used AD fiber and, after a hot water extraction (HWE) process at 160 °C for 60 min, they produced wood plastic composites (WPCs) via extrusion. The mass lost during HWE was 21.0% of the original material. Fig. 2 shows SEM pictures of AD dairy fiber and its corresponding HWE fiber, indicating morphological changes on the fibers. For extrusion, the formulation contained 58% of untreated or HWE AD fiber, 32% HDPE (high density polyethylene), 3% lubricant (zinc stearate), 2% zinc borate, and 5% talc. WPCs produced with HWE AD fiber exhibited increased mechanical strength (36%) and stiffness (30%), and reduced strain at break (15%) compared to composites produced with untreated AD fiber. Water sorption and thickness swelling were reduced by 39% and 36%, respectively, after immersion in water for 98 days. Results evidence that a viable approach to enhance water resistance and mechanical properties of WPCS produced from AD fiber is by conducting an additional thermal treatment operation, which has also been found effective for other types of lignocellulosic materials [73,74]. Additional works on using the fibers in the whole dairy manure (i.e., without the AD prior step) for composites manufacture have been reported by [75–77]. These works could be of interest for comparison of the differences of using dairy manure fibers with and without the AD process.

3.2. AD fiber as feedstock for liquid biofuels

AD dairy fiber has also been investigated as feedstock for producing liquid biofuels via enzymatic hydrolysis. Several studies have demonstrated that AD is capable of producing a fibrous solid with high cellulose and less hemicellulose content [9,78–80]. The compositional and structural changes of the AD fiber can be realized through the biological action of the microbial consortium that is rich in carbohydrate degraders including *Clostridium* and *Bacteroidetes* species [81]. After these changes, the AD fiber shows an ability to hydrolyze similar to other energy crops and residues such as switchgrass and corn stover. As in the case of dairy manure, the corresponding AD fiber can therefore be used for liquid biofuel production [12,78–80,82–85].

Yue et al. [79] applied alkali pretreatment and enzymatic hydrolysis to convert AD dairy fiber into fermentable sugars for yeast ethanol fermentation, resulting in ethanol yield of 7.7% (w/w dry basis). In another work, a combination of sodium hydroxide and ammonium hydroxide pretreatment (at different concentrations) of AD dairy manure improved the delignification and enzymatic digestibility of the fiber for ethanol production [12]. These works show that, after AD, additional effort could be required for efficient transformation of dairy fiber into sugars for biofuels.

Zhong et al. [85] demonstrated a self-sustaining lignocellulosic biodiesel production system utilizing AD fiber and corn stover as co-feedstock for fungal lipid accumulation. A combined hydrolysis was applied to convert AD fiber and corn stover into mono-sugars, and then an oleaginous fungal strain –*Mortierella isabelina* was cultured on the mono-sugars to accumulate lipids for biodiesel production. The process generated 1 L biodiesel from 24 kg dry biomass (12 kg AD fiber and 12 kg corn stover). The fuel property analysis showed that the fungal-lipid based biodiesel is a good alternative to fossil diesel [86]. These studies delineated a new application of AD fiber for liquid biofuel production and offered an alternative route to establish an AD-based bio-refinery. Liao et al. [87]) reported an integrated farm-based bio-refining concept that implements AD as the base unit operation for power generation and AD fiber production (feedstock for ethanol fermentation), and integrates it with yeast ethanol fermentation and algal cultivation to create a closed-loop system for agricultural residue treatment and utilization [87]. They reported that approximately 118 million dry tons of animal manure from 1.2 million cattle farms in the U.S. could be mixed with 30 million dry tons of corn stover as the feedstock for the farm-based bio-refining operation. The system could be able to generate 11 GWh/year of electricity, 1.7 billion gallons/year of ethanol, and 12 Mt/year of dry algal biomass. The potential for

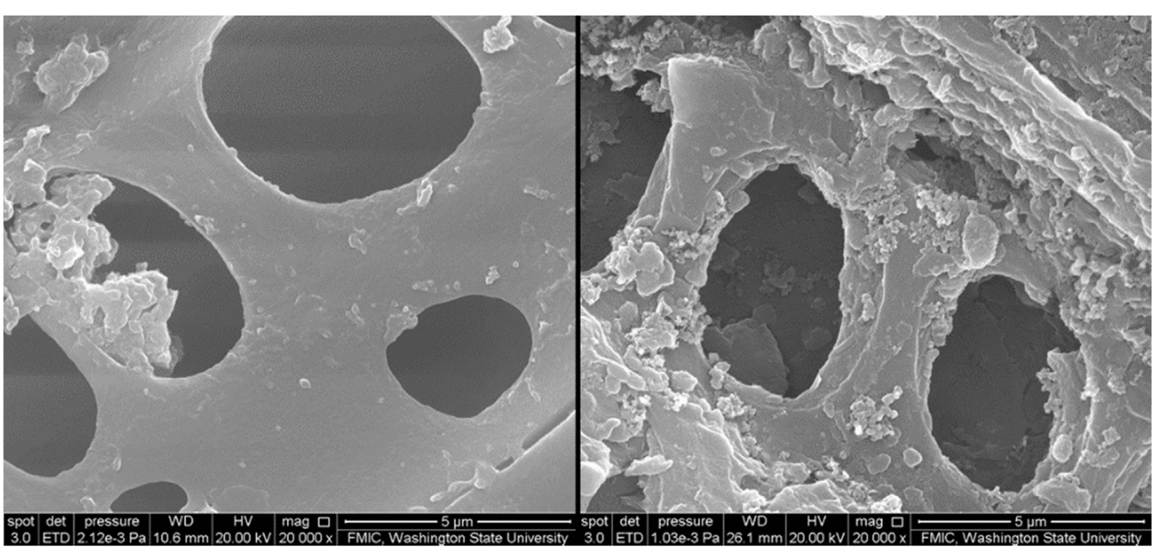

Fig. 2. SEM images of AD fiber (left) and its corresponding hot water extracted fiber at 160 °C for 30 min (right) (20,000×) [70].

combining AD of dairy fiber with algae cultivation has also been assessed by Wang et al. [88], who demonstrated that AD dairy manure can effectively serve as a nutrient supplement for growing oil-rich green microalgae *Chlorella* sp.

3.3. Production of biochar from AD fiber for agricultural use and remediation

Several works have been published on the production of biochar from AD dairy fiber, either for agricultural use or for remediation [89–97]. Streubel [89] and Streubel et al. [90,91] investigated the use of biochar for P recovery in dairy lagoons and for amendment of five soil types in the State of Washington. The authors' evaluated four types of feedstocks (wood pellets, softwood bark, switchgrass straw, and AD fiber) for biochar production. In the case of AD fiber, the material was first pelletized into 5-mm diameter pellets and the pellets were subjected to pyrolysis at 500 °C for 4 h [91]. The biochar was then used for testing its capacity for sequestering P from dairy lagoons and to measure its impact on a sandy soil. The biochar reduced P in dairy effluent by 32%. The sequestered P was predominantly in plant-available inorganic orthophosphate. The resulting fiber-coated biochar increased C mineralization, sodium bicarbonate (Olsen), and water-extractable P levels. Results showed that biochar from AD can reduce P from dairy effluent and that the P-coated biochar may be a viable source of alternative P fertilizer. For soil amendment, the biochar was produced at 500 °C for 30 min, using a continuous auger reactor [90]. The resulting biochar had a similar effect on soil than biochar produced from the other raw materials. The rate of biochar amendment and the change in C content of the soil showed a linear relationship. Soil pH increased with biochar amendments among all soil types and biochar feedstocks. Moreover, the feedstock was not a significant factor in raising pH or C content in the five types of soils the authors studied.

In another work, Inyang et al. [95] studied the ability of AD fiber biochar to sorb heavy metals from aqueous solutions. The biochar was produced at 600 °C for 2 h using nitrogen in a furnace. For the sorption tests, the authors used a mixture of four heavy metals, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}, and lead (Pb) only. Results showed that the biochar was effective for metals sorption and that its Pb sorption capacity was comparable to that of some commercial activated carbons.

An exhaustive work comparing several properties of charcoal produced from different types of feedstocks has been reported by [92]. Specifically, the work examined how feedstock and pyrolysis conditions impact some biochar properties that are of interest for agronomic use. The authors used bull manure with sawdust and dairy manure with rice hulls, besides corn stover, hazelnut shells, oak wood, pinewood, poultry manure with sawdust, grass clippings, paper waste, and food waste. The work also included AD manure and composted dairy manure. These materials were pyrolyzed at temperatures ranging from 300 to 600 °C, using a slow pyrolysis reactor (Daisy reactor). Characterization of the resulting biochars included proximate analysis, elemental analysis, total metals, pH, and organic C. Results showed that the highest ash content (up to 32%) was found in animal manure (including both bull manure and AD dairy fiber) and waste biochars. Both volatiles and fixed carbon content varied in wide ranges, depending on the raw material and the conditions of the pyrolysis (carbonization) process. The pH of biochars also varied in a very wide range (from 4.5 to 11.6), depending on the feedstock. Biochars obtained from animal manure (including dairy manure, AD dairy manure, and composted dairy manure) had pH values above 7.5. The total N, P, Ca, Mg, and Na concentrations also varied greatly among the types of raw material. The authors found that it is difficult to predict the agronomic performance of biochars due in part to the variability of biochar properties. Therefore, they suggested that for a rational use of biochar it is important to define the limiting factors of a particular soil-crop-climate situation. A related work [97] studied how type of feedstock and pyrolysis temperature can affect the aromaticity and the condensation of these aromatic structures in biochar.

The impact of adding different amounts of biochar to a specific type of soil on corn growth (during a 46-day test) has been investigated by [93]. The authors produced biochar from several types of feedstocks (some also used by [92]), including AD dairy manure and poultry manure, at similar temperatures than in the work of [92]. As in the work of [92], the highest pH values were verified in biochar produced from animal manure. Both animal manures increased biomass yield of soil amended by up to 43% compared with soil without amendment. Plant growth was identified to be positively affected by biochar produced at temperatures of 500 °C and nutrient content was found as the main factor responsible for positive crop growth response. However, feedstock type had more effect on plant growth than pyrolysis temperature. According to the authors, post-treatment could be an approach for improving the properties of biochar for use under specific conditions of soil and crop type.

Kirk et al. [96] and Graydon et al. [94] have patented a method for producing biochar from AD fiber and using the resulting biochar for scrubbing hydrogen sulfide (H_2S) from biogas. The process consisted of heating the AD fiber into a tube furnace at temperatures ranging from 400 to 900 °C for 1 h, using nitrogen as a carrier gas. Alternatively, the nitrogen for pyrolysis was humidified (using water) and AD fiber samples were heated at temperatures ranging from 500 to 850 °C. The biochars were then tested to determine the corresponding H_2S absorption capacity. Results showed that: 1) the materials pyrolyzed at 400 °C, 500 °C, and 700 °C, without humidification, showed absorption capacities of 0.3, 2.2, and 4.1 mg H_2S per gram of biochar, respectively, which were considered low, 2) the addition of oxygen or air to the biogas that was tested increased the absorption capacity of biochar. In particular, it was observed that the addition of up to 2% of air increased the absorption capacity at the break through time (i.e., the time at which H_2S was detected in the gas after the biochar column absorption) to 35.8 mg H_2S per gram of biochar, 3) the addition of moisture to the carrier gas had an important effect on the absorption capacity of biochar. For example, AD fiber was pyrolyzed in the presence of humidified nitrogen at 850 °C for 1 h (the humidification process was conducted by bubbling the gas through water at room temperature). The biochar was then tested for H_2S absorption capacity. The result showed that the absorption capacity increased to 330 mg H_2S per gram of biochar.

4. Experiences on thermochemical processing of dairy manure and potential of using these with AD fiber

While the focus of this review paper relates to the use of AD fiber, a discussion of thermochemical processing utilizing both the dairy manure and AD fiber is provided. There is a relatively rich experience on thermochemical processing of the non-digested dairy manure and the fibrous fraction of cow manure. Lessons learned from the whole manure studies can inform on potential uses for the AD fiber as well as conclusions for moving forward.

4.1. Combustion for heat production

Cow manure has been used as a fuel for heat production since ancient times as a substitute of wood fuel [98–100]. In the US, research on using dairy manure for heat production started apparently in the 1970s [101]. At that time, it was estimated that the cost of manure incineration could be similar to that of municipal solid waste incineration [102]. Renewed interest on using animal manure for fuel is due in part to the necessity of disposing large amounts of manure [103–106]. Studies on using dairy manure for heat production, as an alternative to AD or composting, have been reported in several publications [103–117].

A very descriptive report showing several fuel properties of dairy manure, options for thermochemical processing and experiences at pilot scale has been prepared by [104]. Some properties of dairy manure of interest for combustion and pyrolysis (particularly carbonization) have been investigated by [118]. Cantrell et al. [119] showed how thermogravimetric analysis can be employed for proximate analysis of livestock wastes (e.g., dairy manure). Sweeten et al. [105] compared the fuel properties of untreated dairy manure solids with the material after composting. The heating value decreased in composted material and in the materials that have been stored for a “long” time (e.g. eleven months). The relative ash content increased in the composted material, which explains in part the reduction of heating value. Low energy, high MC, and high ash content of dairy manure have been mentioned as factors that limit its use for combustion [104,105,109,113,120].

Thermochemical processes could be more efficient if the manure MC were reduced by spontaneous evaporation (e.g., in dry environments) [121]. However, spontaneous evaporation is normally a slow process. Drying and pretreatment operations could help to increase the efficiency of thermochemical processing such as combustion. Pretreatment operations to improve the fuel value of dairy manure can include torrefaction [105]. According to the same author [105], for torrefaction, the fiber can be subjected to a washing and a drying step, followed by a briquetting process. Nevertheless, adding extra steps to the process and using extra energy for briquetting and water for washing could be a limitation for the economics of the process. Using extra water could also face environmental restrictions.

The combustion efficiency can be improved by using, for example, fluidized bed combustion units [108] or by co-firing with coal [109,110,119]. Co-firing with coal has been suggested since the 1970s [102] and seen as a method to compensate the difficulty of supplying high amounts of manure to operate large thermal power plants. Successful tests of co-firing of municipal solid waste with dairy manure have also been reported. A limiting factor is the presence of salts in manure, which could contribute to corrosion of boilers for combustion [103]. Co-firing can also be a strategy for reducing NOx emissions (co-firing 10% of dairy manure with coal can reduce NOx emissions by approximately 10%) and for increasing financial returns to dairy operators [104]. However, co-firing may require reconfiguring the boilers used for combustion. Research showed that biomass fuels ignite at higher temperatures than coal despite the fact that biomass pyrolysis has lower activation energy [104]. The authors hypothesized that “the increased volatile content of biomass fuels carries away a portion of the heat required for biomass ignition thereby delaying the onset of ignition”.

4.2. Carbonization of dairy manure

Although there are evidences that research on using charcoal (the term biochar is newer) for agricultural applications began approximately one century ago, as shown in works of [122] and later works of [123–126], investigation on using charcoal from animal manure is relatively new. A work of [121] shows results on the pyrolysis of dairy manure, in which charcoal was one of the products. This charcoal was considered as a potential fuel. However, it possessed very high ash content (~50%), resulting in low calorific value (approximately half that of coal). This result explains in part why most current research on charcoal from manure has not considered energy (heat) production from charcoal. Massie [121] mentioned that no works on pyrolysis of manure were found prior to his publication. In fact, interest on employing dairy manure and its fiber for biochar production has been only sporadic. For example, Spokas et al. [127] reviewed literature on the agronomic benefits of using various types of charcoal and mentioned several publications that used manure for biochar production, but only three of them included dairy manure as feedstock.

Recent research on using dairy manure for charcoal has been conducted, for instance, in Japan [128], motivated by the necessity of looking for alternatives to composting and land filling of waste materials, which normally require large spaces. Four raw materials were used in the referred work: sugarcane bagasse, rice husk, animal waste (e.g., dairy manure), and human waste (treated municipal sludge). The pyrolysis (carbonization) was carried out in closed containers, at temperatures that varied from 250 to 800 °C. The authors found that increments on pyrolysis temperature increased surface area, total carbon, ash content, and pH of charcoal, and the density of the product was not affected by the temperature. The yields of biochar produced from dairy manure were higher than those from the other raw materials. Surface area of the biochar obtained from dairy manure was larger than that of wood and sludge, but less than that of sugarcane bagasse. Ash content was highest in dairy manure biochar. Analysis of different properties allowed the authors to conclude that the biochars can be used as soil amenders or adsorbents. The raw material had considerable influence on the properties of the biochar, which has commonly been observed by other authors [92,93,129,130]. Cantrell et al. [128] compared properties of biochar produced from five types of manure (swine separated-solids, paved-feedlot manure, dairy manure, poultry litter, and turkey litter) produced at 350 and 700 °C for 2 h, using an electric box furnace. Biochar produced from dairy manure presented the greatest volatile matter, C, and energy content, along with the lowest ash, N, and S contents.

Cao and Harris [131], Cao et al. [132], and Xu et al. [133] reported works on the direct carbonization of dairy manure for biochar that was used for remediation. In the work of [131], the manure was dried and ground (the resulting particle size was less than 1 mm) prior to carbonization. Biochar was produced using a muffle furnace at temperatures ranging from 100 to 650 °C under abundant air. However, a more effective pathway could be by grinding the produced biochar. Power consumption is greatly reduced if grinding is conducted on thermally modified biomass instead of grinding the biomass as received [73,134,135]. Cao and Harris [131] showed that surface area, ash content, and pH of biochar increased as the temperature in the furnace increased. As expected, combustion of the fiber occurred at temperatures higher than 350 °C, thus leaving high amounts of ash. The biochar showed capability for absorption of Pb and atrazine from aqueous solution, which was confirmed by [132]. The charcoal produced from dairy manure using similar method was also effective for removing other types of heavy metals (Cd, Cu, and Zn) [133]. The mechanism that describes Pb(II) removal has been proposed by [136]. In a related work [137], biochar produced from dairy manure was suggested as an alternative to dairy manure for soil amendment as a method to reduce P in surrounding water.

Additional studies that explored the feasibility of using dairy manure biochar for *remediation* (stabilization of heavy metals) have been published by [138] and [139]. In the work of Uchimiya et al. [138], five different types of manure were employed: dairy, paved feedlot, swine solids, poultry litter, and turkey litter. The pyrolysis process was conducted using a Lindburg electric box furnace, as described by [140], at 350 and 700 °C for 2 h under nitrogen environment. The authors found that dairy manure (along with swine manure) is less effective for stabilization than the biochars produced from the other types of manure. Kinetic and adsorptive characteristics of biochar (produced from dairy manure) in metal ions have been reported by [139]. In the work of [139], biochar was produced at 400 and 600 °C under nitrogen environment. Preliminary studies showed that the amount of Cu(II) ions adsorbed increased when smaller particles were used. Thus, the biochar was ground to obtain material with particle size between 0.420 and 0.600 mm and used for sorption tests of Cu(II), Zn(II), Cd(II) and Pb(II). The effectiveness of Cu(II), Zn(II), Cd(II) and Pb(II) ions removal increased by increasing the initial concentration of biochar and metal ion, pH, as well as phase contact time. Maximum adsorption was observed in the pH range 5.0–6.0. The kinetics of adsorption was found to be pseudo second order with intra-particle diffusion as one of the rate determining steps.

4.2.1. Biochar for soil amendment

Several studies exploring the possibilities of using dairy manure biochar for *soil amendment* have recently been reported [92,129,130,141–143]. Wang et al. [141,142] produced biochar by mixing dairy manure with eucalyptus wood particles. The carbonization process was carried out using a rotating drum kiln at temperatures ranging from 250 °C to 550 °C. The objectives of the works were to determine the phosphorous and nitrogen availability in biochar in the short and in the long term. For this, the biochar was extracted with HCl and the hydrolysable, extracted N (THN), was measured. The ratio of volatile C to THN was used as an indicator of whether net N mineralization or immobilization of N in biochar occurred. Thus, THN could be an adequate estimator of the labile N fraction in biochar in the short term [141].

Domene et al. [143] studied the effect of the pyrolysis conditions of dairy manure biochar for short-term ecological toxicity using basal soil respiration and collembolan reproduction tests. Results showed lack of toxicity at concentrations in the range of usual field biochar applications rates (< 20 t/ha), indicating low short-term toxicity risk of the slow pyrolysis biochars used in the study. Singh et al. [129] evaluated the effect of biochar on soil in the conditions of nutrient-poor soils in Australia. The biochar was obtained from different plants and dairy manure via slow pyrolysis (using a Daisy reactor) at 400 and 500 °C with and/or without steam activation. As expected, biochar properties (e.g., pH, elemental composition, electrical conductivity (EC)) varied among feedstock types and relied on the pyrolysis conditions. However, the pH of dairy manure charcoal remained the same when the pyrolysis temperature was increased. Manure biochar presented the highest ash content but the lowest total C content. The manure based biochar also showed higher N, P, K, S, Ca, Mg, Al, Na, and Cu content than the wood based biochars. The activation process, on the other hand, had little effect on the properties of biochars. Manure biochar presented good to high liming potential.

An additional work that investigated the effect of cow manure biochar on maize productivity and nutrient uptake in sandy soils has been published by Uzoma et al. [144]. Dry dairy manure was used for carbonization at 500 °C for 5 h using a muffle furnace. The resulting biochar was ground for blending with sandy soil for maize production under greenhouse conditions. It was observed that biochar promoted positive effects on total height and number of leaves at different growth stages of maize. Maize grain yield was increased by up to 150% when biochar was applied to soil (compared to control without biochar addition). The results were attributed to the presence of nutrients in cow manure biochar.

The Wisconsin Department of Agriculture, Trade and Consumer Protection [145] has provided information about a project for using dairy manure for producing biochar, gases, and bio-oil via slow pyrolysis, although the bio-oil was not a target product from the process. The bio-oil resulting from the process was consumed in the process as a fuel. Additionally, studies to determine thermodynamic parameters related with the pyrolysis of dairy manure and other materials (rice straw, rice bran, and chicken manure) has been carried out by [146]. The raw materials were dried and ground to particle size less than 0.154 mm (100 mesh) and used for thermogravimetric analysis (TGA). TGA aimed at determining the activation energy of the pyrolysis of each biomass constituent (i.e., cellulose, hemicellulose, and lignin in the fiber). Biochar was produced using a muffle at temperatures ranging from 100 to 700 °C for 6 h for comparison of results obtained via TGA. Results showed that the activation energy was not very different among biomass constituents independent of the feedstock, but in the case of manure, values were visibly affected by the presence of minerals. TGA has also been used for studying the mechanism of the pyrolysis process of cattle manure [147] and for studying the biological stabilization process of this material [148].

4.3. Production of activated carbon

Qian et al. [149,150] explored the feasibility of using the fiber after dairy manure composting for producing activated carbon. After drying, the fiber was ground and subjected to a one-step carbonization and activation process, using chemical activation by zinc chloride. Prior to pyrolysis, the fiber was impregnated with zinc chloride solution. The tests were conducted in a horizontal tubular furnace under nitrogen flow of 300 mL/min. The pyrolysis temperature ranged from 400 to 900 °C with various retention times. The resultant activated carbons were characterized by nitrogen adsorption–desorption (at 77 K). The authors observed that dairy manure compost can adequately be used for activated carbon using zinc chloride. Yields of activated carbon can be up to 47%.

4.4. Pyrolysis for bio-oil production

Pyrolysis processing of dairy manure intending to optimize the yields of liquids (pyrolytic bio-oil) has been reported, to the best of our knowledge, only by Garner and Smith [151]. The authors used livestock waste (steer manure), which was dried, ground, and subjected to pyrolysis. The process was conducted at atmospheric and low pressure. Optimum operating conditions were established by the criteria of maximizing yield of liquid organic products and minimizing the yield of carbonaceous solid residue. Low pressure and a maximum temperature of 400–500 °C showed the best results. A multiple condensation system was employed to collect the condensable fractions from the pyrolysis products. This setup approximated a continuous run. The material from this run was analyzed by a classical organic separation scheme. Typical yields of products are presented in Table 2.

Analysis of the liquid fraction showed that it was constituted by a wide variety of alcohols, aldehydes, ketones, acids, amines and phenols as well as poly-functional compounds, but none was present in sufficient concentration for profitable separation. Therefore, pyrolysis of cattle feedlot wastes was found uneconomical in comparison with incineration. However, it was stated that economic pyrolysis might be feasible if the fresh manure were allowed to spontaneously dry in an arid climate.

It is important to mention other works on "pyrolysis" of livestock wastes (cattle manure) that have been conducted at temperatures that today are more frequent for gasification. For instance, [152] pyrolyzed cow manure at 800 °C, using both wet and pre-dried materials, after grinding (40 mesh particle size). It is evident in this work that the objective was to maximize gases production instead of liquids (pyrolysis bio-oil). However, the authors mentioned that a liquid fraction was recovered through a simple condensation system, although no characterization of this liquid was reported.

4.5. Thermal gasification

Thermal gasification has been perhaps the most studied thermochemical process (in terms of the amount of publications) intending to transform dairy manure into value-added byproducts (e.g., fuel gases and liquids), as reported in a number of works [153–179]. However, as stated by the Midwest Energy Research Center [180], no operational

Table 2
Typical yields of products of the pyrolysis of steer manure (dry weight basis) [151].

Char	35.7%
Ash	9.2%
Carbonaceous residue	26.5% (by difference)
Low-boiling organics	7.3%
Tarry volatile organics	14.2%
Reaction water	16.7%
Noncondensable gases	26.1% (by difference)

farm-scale gasification systems have been identified in the United States but research has been conducted only at laboratory or pilot scale.

Interest on gasification of manure started during the 1970s. Whetstone et al. [102] (p. 68) mentioned that no experimental results on high temperature manure gasification were reported prior 1974. At that time, it was presumed that results of manure gasification could be similar to results from coal gasification, “with appropriate allowance for manure's high ash content and low heating value” [102]. A review carried out by Huffman et al. [163] mentioned that an initial project on gasification of cattle manure was developed in 1971 at Texas Tech University. As a result, a number of works on gasification of dairy manure were conducted during the 1970s [153–155,161–164]. Engler et al. [155] evaluated a concept for gasification of feedlot manure considering the advantages of simultaneously producing gases (which were envisioned that could be used for power generation, raw material for ammonia synthesis, or raw material for methanol production) and ash by-product potentially usable as a fertilizer. The conceptual design was based on a plant with capacity of 1000 t/d of manure (50% of MC). The main sections of the proposed concept included three major steps: preparation, gasification, and gas cleanup. Results showed that only large scale facilities could be attractive from an economic point of view.

In the US, experimental studies on gasification of dairy manure apparently started with a work of Halligan et al. [161], who investigated the potential of using cattle feedlot manure for producing ammonia synthesis gases in a bench scale fluidized-bed reactor. The range of temperatures tested was from 677 to 816 °C. Although relatively high yields of gas were reported, additional desulfurization and reformation processes were suggested to make the gas suitable for the synthesis of ammonia. The potential ammonia production of the reactor could reach 0.5 t of NH_3 per t of dry, ash-free animal manure processed. A scaled-up version of the reactor described by [161], able to process 450 kg/day of manure, was further manufactured. The reactor was a counter-current fluidized one with air-steam mixtures to fluidize and gasify the manure. This pilot plant was used by other authors [153,162,164], who also studied options for producing ammonia synthesis gases from cattle feedlot manure. Results confirmed the feasibility of producing ammonia synthesis gases. In addition, the results showed the feasibility of scaling-up the process for producing medium heating value gas potentially suitable as a fuel. Ethylene was suggested as an additional gas that could be produced from cattle manure gasification [164]. The reactor used by the authors allowed production of ethylene that ranged from 21 to 70 g per kg of dry, ash-free manure, depending on the conditions of the process.

Studies conducted by [168,169] provided information on the effect of gasification temperature, as well as gas velocity and feedstock particle size on gases composition, yield, and high heating value. For the experiments, the authors used a 23 cm internal diameter fluidized bed reactor. The feedlot manure (80% MC) was dried to 8% MC prior to gasification. Particle size ranged from 2 to 40 mesh and the feeding rate was varied from 10 to 20 kg/h. Results showed that temperature is the factor that most affects the properties and yield of the gas produced from feedlot manure since both yield and heating value increased as gasification temperature was augmented. Particle size had a marginal impact on the composition and heating value of the produced gas, while the superficial gas velocity was shown not to affect composition and heating value of the produced gas. The heating value of the gases was up to 19.5 MJ/Nm^3. A mathematical model was later proposed for the gasification process of feedlot manure in the fluidized-bed reactor [170]. Kunzru and Ali [164] also provided data on the effect of particle size of bovine waste on gas yield and properties. Gas yields increased with temperature and varied from 0.5 to 0.65 Nm^3/kg of raw material. However, the heating value of the gas was lower (up to 13 MJ/Nm^3) than in the case of the works of [170].

Fan and Walawender [156] mentioned that one of the problems of using fluidized-bed reactors for biomass gasification is the formation of agglomerates or “clinkers” from the sand used for the fluidization process. The authors proposed utilizing an anti-agglomerating material to prevent deterioration of the fluidizing sand. The effectiveness of the innovation was proven by gasifying different types of feedstocks, including feedlot manure. Pian and Yoshikawa [171,172], on the other hand, proposed a gasification technology referred to as MEET (Multi-staged Enthalpy Extraction Technology). The process used a high-temperature, rapid devolatilization process “to enhance the volatile yields from the fuel and to improve the gasification efficiency. A high-temperature pebble bed filter” was “used to remove the slag and particulates from the synthetic fuel gas. Finally, a novel regenerative air heater” was “used to supply the high temperature air for use to achieve rapid pyrolysis in the gasifier.” The authors mentioned that the system worked adequately with different raw materials, including partially composted cow manure. The portability of the system was also claimed as an important characteristic of the innovation. Additional information on the MEET process characteristics and operation has been provided by Young and Pian [179], who also conducted gasification of dairy manure. Results indicated that gasification efficiencies can reach up to 65–68%, depending on the gasifier operating configuration. The authors suggested that the gases could be used for producing electricity or heat in the farms.

Studies on gasification of dairy manure combined with poultry litter and on co-gasification of dairy manure with coal have been conducted by Priyadarsan et al. [173,174]. The experimental work was conducted using a 10 kW (thermal) fixed-bed counter-current atmospheric pressure gasification reactor. Gasification of dairy manure produced low energy content gas (4.4 ± 0.4 MJ/m^3) and an average product gas composition (dry basis) of H_2: 5.8 ± 1.7%, CO: 27.6 ± 3.6%, CH_4: 1.0 ± 0.5%, CO_2: 6.7 ± 4.3%, and N_2: 59.0 ± 7.1%. Co-gasification of dairy manure with coal, on the other hand, showed that there were no variations on the product gases in terms of composition, irrespectively of the particle size of the raw material or air flow rate. However, higher oxygen content in biomass resulted in slightly higher CO_2 content in the gases. The heating value of the gases was in the range of 4.5–5.1 MJ/kg. The results suggested that blending manure with coal does not affect the heating value of the gas product. Therefore, it was found that it is feasible to co-gasify animal waste-based fuels (high-ash, low-energy content), such as feedlot and chicken litter, with coal.

Other works on gasification of dairy manure have been published by [157–160,175]. These authors have used an adiabatic, fixed bed gasifier, with air and steam as oxidizers. H_2 in gases was reported to be up to 28%. A model to predict the composition of the gases based on the biomass characteristics was additionally provided. An important study on the life cycle assessment (LCA) of greenhouse gas (GHG) emissions of feedlot manure practices, comparing land application and gasification of feedlot manure, has been prepared by [178]. The publication showed that the net GHG emissions in land application was 119 kg CO_2eq for 1 t of dry feedlot manure, which was much higher than the −643 kg CO_2eq for 1 t of dry feedlot manure that resulted from gasification of manure. Therefore, gasification of feedlot manure appeared a more promising approach to reduce GHG emissions than land applications. This work has been further complemented by studies on the design of the process and by providing more insight on the benefits of gasification compared with land application of manure [176,178].

4.6. Hydrothermal processing

This section reviews works in which dairy manure has been used for producing energy (e.g., synthesis gas) and other products (e.g., chemicals) while manure is still in a water slurry. The operations for processing high MC dairy manure are referred to as hydrothermal processes. Hydrothermal processing involves three possible operations: hydrothermal liquefaction, hydrothermal gasification (also known as wet gasification), and hydrothermal carbonization. While hydrothermal liquefaction (water at subcritical conditions) of biomass intends to convert biomass into liquid fuels and chemicals, hydrothermal gasification (either under subcritical or above critical conditions) intends to transform biomass into gases, usually by using a catalyst [167,181]. A variation of this process is hydrogasification, in which hydrogen is used and a catalyst is not required. As in the case of gasification, studies on the hydrothermal processing of dairy manure started during the 1970s, although the interest on this process, using other types of biomass, started in the 1940s [182]. Since drying can be expensive, direct use of high MC manure (without adding extra water) could positively impact the efficiency of the thermal conversion operation.

4.6.1. Hydrothermal liquefaction

Studies on hydrothermal liquefaction of dairy manure have been reported by, for example, [183–185]. Fu et al. [183] processed bovine manure at temperatures of 330, 380, and 425 °C and pressures of 1500–3000 psi (~10–20 MPa). Part of the bio-oil produced was recycled for the hydrothermal process in the presence of a Co-Mo catalyst. The catalyst increased the yields of oil and the temperature was the parameter that most affected the properties of the bio-oil. Mass spectrometry analysis of oil produced at 380 °C suggested that the main compounds in the oil were alicyclic hydrocarbons, N-containing heterocyclic compounds, and alkalyl phenols (C_8–C_{18} range). Cow manure with MC up to 35% was evaluated and found as an acceptable feedstock, without the necessity of adding extra water to the process.

Yin et al. [184] studied the effects of different processing parameters (e.g., temperature, pressure, residence time, and manure to water mass ratio) on the yields of the bio-oil obtained via hydrothermal liquefaction. The process consisted of grinding dairy manure without removing moisture (initial MC was 76%) and subsequently subjecting it to a subcritical hydrothermal liquefaction process using a 1.8 L Parr reactor. Temperatures were varied from 270 to 350 °C, the manure to water mass ratio was changed from 0.25 to 2, and the time was varied from 0 to 40 min (isothermal conditions only). NaOH was added to the reactor. The bio-oils' properties were compared with those of gasoline, ethanol, biodiesel, and pyrolysis bio-oil. The yield of bio-oil was up to 49%, which was obtained at 310 °C, with CO as process gas, residence time of 15 min (at isothermal conditions) and manure to water ratio of 0.25 (mass/mass). The high heating value (HHV) was estimated (based on elemental composition) to be approximately 35.5 MJ/kg on average. Results of the characterization of the bio-oil also showed that it contained function groups of poly-alcohols, carboxylic acids, phenol derivatives, and alpha, beta-unsaturated ketones. The bio-oil did not present C_4–C_{15} constituents, the major components of gasoline and diesel. Non-polar compounds were toluene, ethyl benzene and xylene. These findings suggested that upgrading steps are required for further use of the bio-oil (obtained from dairy manure via hydrothermal liquefaction) as liquid transportation fuel. In another study [185], the authors presented a concept for waste treatment and simultaneous hydrothermal liquefaction of manure. The manure was first dried; then, deionized water was added (4:1 mass/mass water to manure ratio) for the hydrothermal treatment. The temperature in the reactor was varied from 250 to 350 °C (pressures from 5.1 to 20.5 MPa), for 15 min, with varying amounts of Na_2CO_3 as catalyst. CO was used as process gas. The energy efficiency of the process was up to ~68% and the HHV of the bio-oil obtained was up to 32 MJ/kg. Chemical oxygen demand (COD) of the dischargeable slurry, on the other hand, was up to 75%.

4.6.2. Hydrothermal gasification and hydrogasification

Hydrothermal gasification of dairy manure has been conducted by [167,186–188]. Elliot et al. [186] carried out wet gasification in a continuous process in fixed-bed catalytic tubular reactors. The manure slurry used in the process was ground to 60 mesh. The wet gasification process was performed at temperatures from 330 to 360 °C and 21 MPa, using ruthenium metal catalyst. No other oxidizer or reagent than water was added. The analysis of the produced gas was conducted via GC and the liquid effluent was analyzed for chemical oxygen demand (COD) and pH, with spot checks for ammonia, inorganic anions (principally chloride and sulfate), and trace metals. The authors concluded that although good gas production was demonstrated, the presence of trace compounds in biomass caused some processing difficulties. Therefore, careful monitoring and control of feedstock trace components (e.g., calcium, magnesium, sulfur, and phosphorus) are critical for maintaining long-term operability and catalyst activity. Matsumura et al. [167] reviewed the status of wet gasification in near- and supercritical water conditions for processing high MC biomass. In addition, the authors compared some results on hydrothermal gasification of several feedstocks, including dairy manure.

The work of Ro et al. [187] assessed the feasibility of wet gasification for treatment/energy conversion of manure (swine, dairy, paved and unpaved feedlot, and poultry), municipal solid waste (MSW), and raw sludge. The study was based on the analysis of energy production potentials and end products composition. The work also compared relevant costs and benefits of first-generation wet gasification technology to anaerobic lagoon animal manure management technology. The authors observed that high MC materials (swine and dairy manure, and sewage sludge) can be directly gasified (using hydrothermal gasification) to produce an energy rich gas; however, additional water is required for poultry litter, MSW, and feedlot manures to make the feedstock suitable for pumping. Results suggested that municipal solid waste and unpaved feedlot manure would not generate positive energy balance if an efficient heat recovery system (90% efficiency) is not added to the process. The net energy was higher in wet gasification of swine manure, while MSW and unpaved feedlot manure produced the lowest. Yakaboylu et al. [188], on the other hand, investigated the equilibrium partitioning of elements on the basis of compounds and phases in supercritical wet gasification of a mix of pig and cow manure. The interval of temperatures investigated was from 100 to 500 °C and 24 MPa. In addition, the effects of pressure and water fraction on main product gases were explored. Results of the modeling process suggested that hydrothermal gasification above 340 °C would be appropriate under equilibrium conditions.

An alternative process to hydrothermal liquefaction and hydrothermal gasification is *hydrogasification*, in which manure reacts with hydrogen at temperatures similar to those used for hydrothermal gasification, but using higher pressure, and without the necessity of catalysts. The gas produced is rich in methane. This process was used by Kiang et al. [189], who proposed to produce synthetic natural gas, without the need of methanation steps. Both batch and continuous processes were investigated, showing that the manure in the continuous reactor was more reactive. The process was conducted at 550 °C and pressure of approximately 11 MPa. The heating value of the produced gas was approximately 37.7 MJ/m^3. It was found that no tars or oils were produced from manure hydrogasification. A review on economic analyses of the hydrogasification process has been presented by Kreis [190].

4.6.3. Hydrothermal carbonization

Hydrothermal carbonization has been suggested as a process for managing P content in cow manure. Dai et al. [191] used wet cow manure (85% MC) for biochar production using autoclaves that operated at 200 °C for 4, 6, 8, 10, 12, and 24 h. Results indicated that hydrothermal processing retains P (as observed from the relative increase of P in thermally treated manure). Moreover, the retained P presented lower levels of Water-extractable P (WEP) and Mehlich-3-extractable P (MEP), which was attributed to the effect of hydrothermal treatment. Thus, hydrothermal carbonization has been suggested as a viable technology for immobilizing P in cow manure.

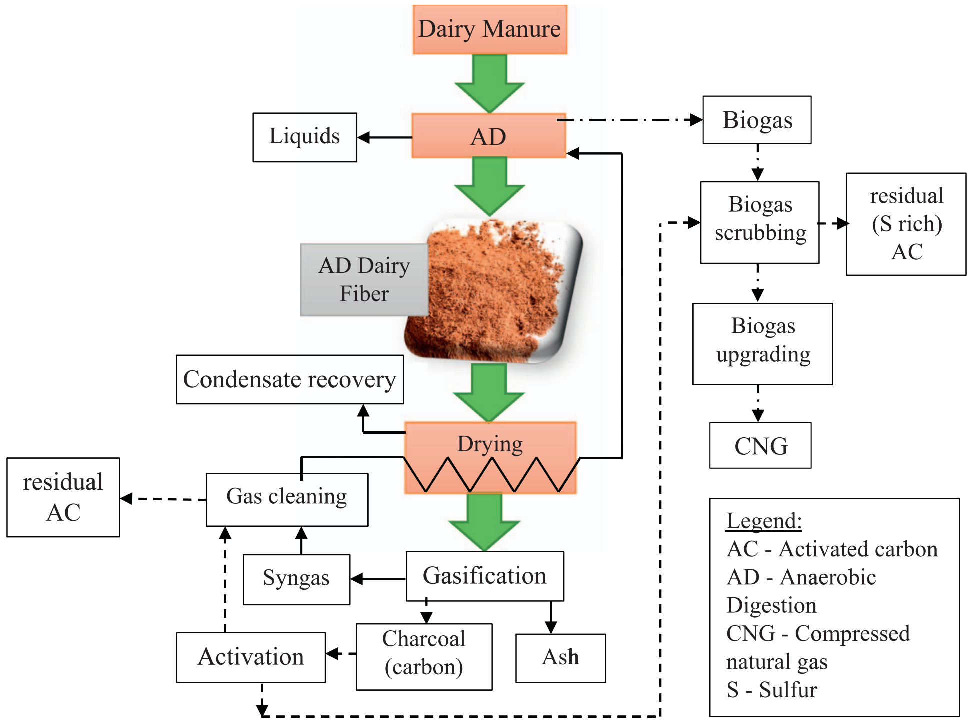

Fig. 3. Scheme of the proposed integration of manure AD with thermal gasification of AD fiber for increasing biogas yields and using bioproducts (e.g., char).

5. Opportunities for adopting thermal operations for adding value to AD fiber

The literature review presented in the previous sections shows that there is a relatively rich experience on using thermochemical processing of dairy manure for producing heat, synthesis gases, or biochar. However, the experience on using AD dairy fiber is more limited. Most of the research has been conducted at laboratory scale and only a few works were conducted at pilot scale. Although adapting these experiences in current dairy farms (that have implemented AD) for processing AD fiber does not seem a straightforward process, thermochemical processing offers a promising pathway for adding value to AD fiber, especially if integration of these technologies with AD is performed. Some obstacles and opportunities for adopting thermochemical processes for livestock residues treatment have been discussed by [192]. This section discusses ideas on why thermochemical operations offer potential for transforming AD fiber into value-added products beyond the present focus on soil amendments and peat/nursery industry.

Possible thermal processes that could be employed for adding value to AD fiber are: fast pyrolysis, hydrothermal processing, combustion, production of fuel pellets, slow pyrolysis for biochar production, and gasification. Both fast pyrolysis (for bio-oil production) and hydrothermal processes are at development stages and, in the case of the pyrolysis bio-oil, refining operations that could allow for its use/upgrading are not commercially available. Combustion, on the other hand, would not be attractive from an economic point of view because using the heat produced in the dairy farm could be possible at a limited scale only. Heat, in fact, may result in a low value-adding strategy due to seasonal uses of heat (at least in temperate regions). In addition, as discussed in previous sections, the high ash content could hinder the operation of systems designed for operating with other types of biomass. Our literature review suggests that no works have been conducted on using AD fiber for combustion.

Research on using manure fiber for pellets production (e.g., for home heating) has not been reported in the literature. Lack of works on combustion and pellets production using AD fiber can in part be justified by the potential problems associated with the use of high ash content AD fiber. Tests we have conducted using a LECO CHN equipment [193,194] showed that the ash content in AD fiber can be as high as 26% (in dry basis) and nitrogen content (in dry and ash free basis) can reach up to 4.4%. Ash content directly affects the combustion process and the quality of fuel pellets. The Pellet Fuel Institute' standard [195] has established that high quality (premium) pellets should contain very low ash content ($<1\%$). Therefore, using AD fiber for fuel pellets is greatly limited by ash content. The production of biochar via slow pyrolysis (carbonization), on the other hand, needs to be accompanied by additional processes in which the biochar has to be produced/modified to comply with characteristics required for specific uses such as agriculture and/or remediation. Therefore, this option sounds attractive only if the dairy farm is committed to including new business models in which biochars designed and produced for specific purposes are targeted products.

5.1. Gasification of AD fiber

The possible limitations of combustion, fast pyrolysis, hydrothermal processing, carbonization, and pelletization can be avoided if the dairy farm adopts thermochemical operations able to produce a product the farmer is more familiar with. Undoubtedly, this product is methane (biogas). Since dairy farmers that currently produce biogas via AD have a long experience on managing/using biogas and infrastructure for using this fuel is available, the ideal business model should be designed to improve the yields of biogas in the dairy farms by using the fibers after AD. From this point of view, currently, thermal gasification presents the best perspectives.

Synthesis gases produced via thermal gasification are a mixture of CO, H_2, CO_2, CH_4, and other gases in less amounts. Interest in using syngas for methanation ($CO+3H_2 => CH_4+H_2O$; $\Delta H° = -206$ kJ/mol) to synthetic natural gas (SNG) has been reported in several studies [196–198]. However, this approach, while technically feasible, may be limited by the necessity of using expensive catalysts and the requirement of cooling the reactors due to the highly exothermic methanation process [198,199]. The use of such catalysts can be avoided if the synthesis gas produced via thermal gasification of the dairy fiber is added to the AD process inside the dairy farm to increase the yields of methane. Josse and Benedek [200] have patented a method for adding syngas to the AD process. The only requirement for adding syngas to the digester is that the temperature of the syngas needs to be lowered. Ideally, the heat released during the cooling process should be used for drying the fiber after AD.

Fig. 3 shows a simplified diagram of the possible integration of AD with thermal gasification in dairy farms. The proposed concept shows that this integration can also allow for a better utilization of another main gasification byproduct, charcoal, and for heat recovery. The charcoal could be prepared and/or activated to comply with specific requirements for cleaning the produced syngas and for biogas scrubbing. The hot gases, on the other hand, can be used for drying the AD fiber and reduce the moisture content. The condensed moisture can also be recovered for several uses in the dairy farm. Moreover, the high ash content of AD fiber is not a limitation in the proposed concept if updraft gasifiers are used. Updraft gasifiers are suitable for feedstocks with high ash (up to 25%) and high MC (e.g. up to 60%) [201].

6. Conclusion

There exists a rich experience, although mostly at laboratory scale, on using dairy manure and the corresponding anaerobically digested fiber for producing an array of products through non-thermal and thermal processes. The products identified include: peat moss substitute, fertilizers, charcoal (via carbonization), sugars for biofuels, syngas (via gasification), wood composites, bio-oil from both fast pyrolysis and hydrothermal operations. Fertilizers and peat moss substitutes produced form AD fiber have reached commercial level. The production of wood composites appears promising if additional thermal treatment is conducted to reduce the natural hygroscopicity of the fiber and, thus, improve composite water resistance. However, this topic deserves further study to evaluate the economics of the process. Thermochemical operations offer options for an integrated use of AD fiber. Among thermochemical processes, both fast pyrolysis (for bio-oil production) and hydrothermal processes are at development stage. Moreover, refining/upgrading operations for pyrolysis bio-oil are not commercially available, thus limiting fast pyrolysis of AD fiber. Combustion would not be attractive from an economic point of view because using the heat produced in the dairy farm could be possible at a limited scale only. The high ash content could hinder operating equipment designed for other types of biomass and for fuel pellets production. Production of biochar needs to be accompanied by additional processes in which the biochar should be produced/modified to comply with characteristics required for specific uses such as agriculture and/or remediation. Therefore, this option sounds attractive if the dairy farm is committed to including new business models in which biochars designed and produced for specific purposes are targeted products. The possible limitations of combustion, fast pyrolysis, hydrothermal processing, carbonization, and pelletization can be avoided if the dairy farm adopts thermochemical operations able to produce a product the farmer is more familiar with, which is the case of biogas. Thus, thermal gasification offers important perspectives. Dairy farmers currently produce biogas via AD and have a long experience on managing/using biogas. Infrastructure for using this fuel is also available and ready. Therefore, the ideal business model could be designed to improve the yields of biogas in the dairy farms by using the fibers after AD.

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