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Potentialities of biotechnological recovery of methane, hydrogen and carboxylic acids from agro-industrial wastewaters

Amanda de Sousa e Silva, Naassom Wagner Sales Morais, Milena Maciel Holanda Coelho, Erlon Lopes Pereira, André Bezerra dos Santos*

Department of Hydraulic and Environmental Engineering, Federal University of Ceará, Fortaleza, Ceará, Brazil

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ABSTRACT

This paper aimed to explore the anaerobic resource conversion from some agro-industrial wastewaters (AWWs) employing three biorefinery platforms (methane, hydrogen, and carboxylic acids). Additionally, it presents the reported quantitative and qualitative characterization of AWWs, bioproduct conversion yields, by which it was possible to estimate the gross value added of the by-products. The studied AWWs showed to have excellent economic potentials for resource recovery, in which the CA platform seems to be more economically advantageous, especially when a chain elongation process is considered. However, the traditional anaerobic digestion is simpler in terms of process control, and methane purification is usually easier and cheaper. Because of the low yields achieved, it seems that hydrogen production is the least attractive technological route. Therefore, it is necessary to analyze other factors such as the gross value-added, consolidation of the production and recovery techniques, among others, to adopt the best choice of resource recovery platform.

1. Introduction

Faced with problems of fossil resources depletion and increased waste generation, alternative production chains involving the use of renewable resources are needed to reduce the dependence on petroleum and mitigate environmental impacts. In this context, biorefineries are fundamental as resource conversion systems. So, various technologies are employed to separate biomass resources into their building blocks (carbohydrates, proteins, triglycerides, and others), which can then be converted into biofuels and other high value-added products (Coma et al., 2017). In general, this system depends mainly on plant biomass, which negatively impacts human food due to the competition for food crops. For this reason, the change of raw materials from first to the second generation has been done, as organic material left over from the primary destination of plants (for example, maize straw and sugarcane bagasse), biomass derivative by-product for which supply far exceeds market demand (e.g., glycerol from biodiesel production), and wastewater in general. Therefore, waste becomes an economic opportunity for the production of valuable bioproducts in biorefineries (Coma et al., 2017; Chandra et al., 2018).

For many wastes, the anaerobic digester is the heart of the biorefinery, and other technologies are added downstream to produce multiple products that can repay the capital and operating costs with the process. In the fermentation process that occurs in traditional anaerobic wastewater treatment plants (WTPs), carboxylic acids (CAs), alcohols and hydrogen (H_2) are naturally formed during acidogenesis and/or acetogenesis stages, and then converted into methane (CH_4), carbon dioxide (CO_2) and hydrogen sulfide (H_2S) as the main end products. CAs can be classified into short (SCCAs - 2 to 5 carbons) and medium (MCCAs - 6 to 12 carbons) carboxylic acids (Grootscholten et al., 2014). In general, the value-added of SCCAs (400–2500 US$ ton^{-1}) is higher than CH_4 (200–600 US$ ton^{-1}) and hydrogen (600–1800 US$ ton^{-1}), but lower than MCCAs market price (2000–2500 US$ ton^{-1}) (Bastidas-Oyanedel et al., 2015; Bhatia and Yang, 2017; Moscoviz et al., 2018; Zacharof and Lovitt, 2013). Therefore, from an economic point of view, it would be more advantageous to invest in the biological production of CAs by acidogenic fermentation than in obtaining CH_4 from conventional anaerobic digestion.

CH_4 is used in various industries such as automotive, chemical, electrical, and aerospace due to its applications as fuel, natural gas, liquefied natural gas, liquid methane rocket fuel, and raw material in chemical industries (Jeanmonod et al., 2019). On the other hand, H_2 also has a variety of applications, for example, in metal processing, glass industry, edible fats and oils, energy, and others (Sarma et al., 2016). Both SCCAs and MCCAs groups have various industrial applications, such as varnishes, perfumes, disinfectants, plasticizers,

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* Corresponding author at: Department of Hydraulic and Environmental Engineering, Campus do Pici, Bloco 713, Pici, CEP: 60455-900 Fortaleza, Ceará, Brazil.
E-mail address: andre23@ufc.br (A. Bezerra dos Santos).

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surfactants, textile auxiliaries, pharmaceuticals, food products, among others (Abdel-Rahman et al., 2013; Liu et al., 2013).

However, MCCAs have broader industrial applications and are also used in the production of dyes and rubber lubricants (Angenent et al., 2016). Moreover, it is noteworthy that their production is generally more complicated than that of SCCAs because a Biological Carboxylic Chain Elongated Process (BCCEP) is necessary (Chwialkowska et al., 2019). Therefore, the value of CAs tends to increase as the number of carbons increases. Among the MCCAs, caproic acid (C6) has been one of the most studied due to its application as a biologically based biofuel precursor, flavoring, and feed supplement for swine and poultry for enteric disease control (Dams et al., 2018). So, the biological production of high value-added compounds during the anaerobic treatment of agro-industrial wastewaters (AWWs) is growing attention, but the information concerning their quantitative and qualitative aspects, bioproduct conversion yields, is very dispersed in the literature. Moreover, it is still necessary to analyze other factors such as the gross value added of the by-products, consolidation of the production and recovery techniques, the production scales, and the possibility of installation in urban and rural environments to adopt the best choice of resource recovery platform.

In this context, this paper aims to explore the anaerobic resource conversion from some agro-industrial wastewaters (AWWs) employing three biorefinery platforms (methane, hydrogen, and carboxylic acids). Additionally, it presents the reported quantitative and qualitative characterization of AWWs, bioproduct conversion yields, by which it was possible to estimate the gross value added of the by-products, seeking to point out which one is more advantageous. Therefore, mechanisms and operational parameters of anaerobic digestion, as they are widely covered in the literature, will not be addressed in this review.

2. Wastewaters from the agro-industrial system

Agribusiness is understood as the sum of four segments: inputs for agriculture, primary agricultural production, agroindustry, and agro services. This work will focus on the generation of wastewaters from the agroindustry, as it is the stage that produces effluents with the most significant pollutant potential in quantitative and qualitative terms. Agroindustry accounts for more than 50% of manufacturing value-added in low-income countries and 30% in middle-income countries (FAO, 2017). Brazil is one of the leading players in the agribusiness worldwide. In 2017, about 21.6% of the Brazilian Gross Domestic Product (GDP) came from the agribusiness, with 2.7% growth of the agroindustry (CEPEA, 2018).

Thus, given the continuous growth of agroindustry, large amounts of wastewater are generated in the processes of raw material transformation, often causing several environmental impacts, a lot of them of high magnitude (Cheng et al., 2019; Pereira et al., 2014). Therefore, it is essential to know the characteristics of the agro-industrial wastewaters to identify their potential not only to solve the environmental problems caused by their improper disposal but also to add economic value to these wastes. Among the agro-industrial activities with the highest pollutant potential are cattle and swine slaughterhouses, coffee processing, pulp and paper production, beer, milk and derivatives, ethanol (vinasse generation), and biodiesel (residual glycerol generation). Table 1 summarizes the main quantitative and qualitative characterizations of important agro-industrial activities and the calculated annual production of pollutants (ton).

Regarding the volume of AWWs produced, pulp and paper, as well as milk and dairy products, represent the major concerns. In terms of organic matter, expressed as biochemical oxygen demand (BOD) and chemical oxygen demand (COD), biodiesel and ethanol AWWs have higher concentrations, but with lower pollutant loads and lower COD/BOD ratio, the latter indicating easier biodegradation. On the other hand, regarding the presence of nutrients, the highest concentrations of N and P are found in swine slaughter and ethanol production AWWs.

AWWs of cellulose and paper, and those generated of milk and dairy production, have the highest gross polluting organic load. Considering the population equivalent organic load rate of 44 kg COD inhabitant^{-1} year^{-1} for domestic effluent, the polluting potential of cellulose and paper AWWs is equivalent to about 4.7 billion people (Nowak et al., 2015). In other words, this single effluent has the same polluting potential as 60% of the world's population. The population equivalent data, which were chosen only to highlight the pollution capacity in terms of COD load for the examined AWWs, are presented in Fig. 1.

3. Obtaining methane, hydrogen and carboxylic acids via anaerobic digestion

Traditional anaerobic digestion (AD) is divided into four steps (hydrolysis, acidogenesis, acetogenesis, and methanogenesis), where the complex substrate is transformed into CH_4, CO_2, and H_2S. However, when the focus is on the production of intermediate compounds, such as H_2 and CAs, methanogenesis must be inhibited, as can be seen in Fig. 2.

3.1. Methanization route

A traditional AD has methane as a final product in the form of biogas (biomethane) from the conversion of acetate, carbon dioxide, and hydrogen compounds by methanogenic archaea (methanogenic step – Fig. 2) (Duda et al., 2015). Owing to the fact that CH_4 has applications as fuel and as a raw material in chemical industries, maximize the production of methane in the anaerobic reactor and promote biogas recovery is indeed an attractive strategy to meet the growing need for renewable energy sources and to reduce greenhouse gas emissions (Dollhofer et al., 2018; Yousef et al., 2019). Europe is the world's largest biomethane producer, accounting for around 1362 million m^3 in 16,606 biogas plants in 2015. In this year, the total electricity capacity exceeded 10,100 MW, i.e., 67% of the global biogas capacity (Scarlat et al., 2018).

The amount and the quality of biogas produced in anaerobic systems vary according to several factors, such as wastewater or raw material type, pretreatment technology (when present), temperature, reactor configuration, among others (Achinas et al., 2017; Dollhofer et al., 2018). In qualitative terms, it usually contains 40–75% methane (natural gas has 87–97% methane), often requiring purification to use it as a source of bioenergy in electricity production, heat and steam generation in homes and industries, injection into the natural gas, and vehicular fuel network (Kadam and Panwar, 2017).

Technologies commonly used commercially for biogas purification are pressure swing adsorption, high-pressure water wash, organic solvent wash, amine scrubbing, membrane separation, and cryogenic separation. This is the most expensive step in the overall process; therefore, for a proper choice, it is important to consider the efficiency and economy of a specific application. More information on biogas treatment processes can be found in the review by Ullah Khan et al. (2017).

3.2. Hydrogen production route

Although CH_4 is considered the main AD product, hydrogen gas, which is an intermediate product of this process (Fig. 2), has a higher added value. However, in systems operating under normal conditions, H_2 produced in traditional anaerobic digesters is rapidly consumed by methanogenic archaea and homoacetogenic bacteria. Even in hydrogen-producing reactors, H_2 production is accompanied by CO_2 production. The proportions may vary from 30 to 60% for H_2 and 40 to 70% for CO_2, with possible traces of CH_4 and/or H_2S. Thus, when the focus is on biohydrogen production, ways to either eliminate or suppress hydrogen-consuming microorganisms, or to reduce the amount of

Table 1
Quantitative and qualitative characterization of important agro-industrial activities and the calculated annual production of pollutants (ton).

Activity (Agro-industrial wastewater typology)	Agro-industrial wastewater description	Annual output of the activity	AWW production	Pollutants concentrations (mg L^{-1})	Annual production of pollutants (ton)	Brazil's contribution to the activity (%)	References
Cattle slaughterhouse (bovine slaughterhouse wastewater)	Main contamination: stomach and intestinal blood and mucus. Distribution of its production: 36% slaughter room, 40% other dependencies (bushes, guts, tallow etc.), 24% external attachments (courtyards and corrals)	$3.0 \cdot 10^8$ slaughtered cattle	$0.7–3.0 \cdot 10^3$ L/slaughtered cattle	BOD 420–5770 COD 500–15.900 N 50–1.300 P 9–200	$1.7 \cdot 10^6$ $4.4 \cdot 10^6$ $3.6 \cdot 10^5$ $5.6 \cdot 10^4$	10.3	Banks and Wang (2006), Beux et al. (2007), Bustillo-Lecompte and Mehrvar (2015), Fia et al. (2015), IBGE (2019), Pereira et al. (2016), Scarassati et al. (2003), Wang et al. (2018a, 2018b)
Pig slaughterhouse (swine slaughterhouse wastewater)	Distribution of its production: 25% in the killing room, 33% in the other facilities, 42% in the external annexes.	$1.5 \cdot 10^9$ slaughtered pigs	160–541 L/slaughtered pigs	BOD 1.500–8.700 COD 3.000–30.000 N 600–6.000 P 100–1.400	$2.3 \cdot 10^6$ $4.1 \cdot 10^6$ $1.5 \cdot 10^6$ $3.4 \cdot 10^5$	2.9	Banks and Wang (2006), Cheng et al. (2018), Ding et al. (2017), FAOSTAT (2017), Islam et al. (2011), Scarassati et al. (2003), Suto et al. (2017), Valmir et al. (1998), Waki et al. (2018)
Coffee processing (coffee beans processing wastewater)	High concentrations of pollutants resulting from the process of stripping the flesh of the fruit (mesocarp when peeled) and mucilage.	$1.0 \cdot 10^{10}$ kg of coffee	8.3 L de AR/kg of coffee	BOD 457–37.600 COD 812–64.467 N 19–71 P 60–186	$1.6 \cdot 10^6$ $2.7 \cdot 10^6$ $3.7 \cdot 10^3$ $1.0 \cdot 10^4$	38.0	Campos et al. (2014), Chanakya and De Alwis (2004), da Silva et al. (2011), Fia et al. (2010), International Coffee Organization (2019), Novita (2016), Rattan et al. (2015)
Pulp and paper production (pulp and paper processing wastewater)	The wastewater varies with the raw material and the manufacturing stage. The effluent from the pulping process (black liquor) is rich in lignin, the bleaching (larger volume and pollutant load) is rich in toxic compounds.	$4.0 \cdot 10^{11}$ kg of paper	5–100 L/kg of paper	BOD 26–13.088 COD 426–115.000 N 2–350 P 1–36	$1.3 \cdot 10^6$ $5.4 \cdot 10^6$ $5.8 \cdot 10^4$ $4.4 \cdot 10^3$	2.5	Kamali et al. (2016), Pokhrel and Viraraghavan (2004), STATISTA (2019), Toczyłowska-Mamińska (2017)
Milk and dairy products (dairy wastewater)	It mainly results from cleaning transport lines and equipment between production cycles, and tank trucks, washing milk silos and equipment malfunctions or operating errors.	$8.0 \cdot 10^{11}$ L of milk	0.2–10 L/L of milk	BOD 40–48.000 COD 80–95,000 N 14–380 P 9–280	$9.8 \cdot 10^7$ $1.9 \cdot 10^8$ $8.0 \cdot 10^5$ $5.9 \cdot 10^5$	4.4	Daneshvar et al. (2019), Elangovan and Sekar (2012), Embrapa Gado de Leite (2018), Lu et al. (2016), Silva et al. (2019)
Brewery industry (brewery wastewater)	Distribution of its production by sector: 38% in packaging, 25% in production, 20% in utilities and 17% in wineries	$2.0 \cdot 10^{11}$ L of brewery	3–10 L/L of brewery	BOD 429–3.600 COD 1.778–32.500 N 25–450 P 0.5–220	$2.6 \cdot 10^6$ $2.2 \cdot 10^7$ $3.1 \cdot 10^5$ $1.4 \cdot 10^5$	6.5	Arantes et al. (2017), Bakare et al. (2017), Barth-Haas Group (2017), Herrmann and Janke (2001), Mathuriya and Sharma (2009), Mendes et al. (2005), Simate et al. (2011)
Ethanol production (vinasse)	It is derived from the ethanol distillation step and depends on the raw materials and chemicals used in the alcohol production process.	$1.1 \cdot 10^8$ L of ethanol	9–15 L/L of ethanol	BOD 6.000–96.000 COD 8.200–134.000 N 200–4.200 P 4–3.003	$6.7 \cdot 10^4$ $9.4 \cdot 10^4$ $2.9 \cdot 10^3$ $2.0 \cdot 10^3$	27.3	Chowdhary et al. (2017), España-Gamboa et al. (2017), Hoarau et al. (2018), Lappa et al. (2015), Moraes et al. (2015), Renewable Fuels Association (2019)
Biodiesel production (residual glycerol)	By-product of the transesterification reaction of oils for biodiesel production.	$3.7 \cdot 10^{10}$ L of biodiesel	0.08 L of glycerol/L of biodiesel	BOD 900.000–1.200.000 1.023.000–1.900.000 COD 0–500 53 N P	$3.1 \cdot 10^6$ $3.4 \cdot 10^6$ $7.4 \cdot 10^2$ $1.6 \cdot 10^2$	11.6	ANP (2018), Dams et al. (2018), OECD/FAO (2016), Oliveira et al. (2015), Pan et al. (2019), Pereira et al. (2017), Sittijunda and Reungsang (2012), Xie et al. (2011), Yazdani and Gonzalez (2007)

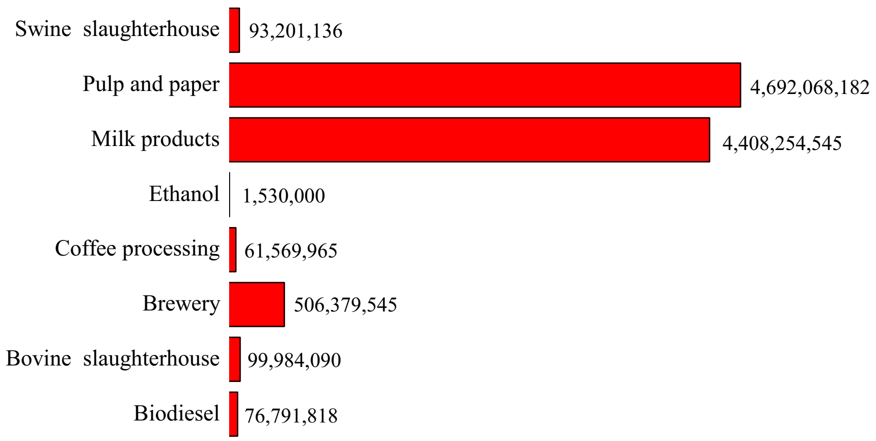

Fig. 1. Population equivalent based on COD load of agro-industrial wastewaters.

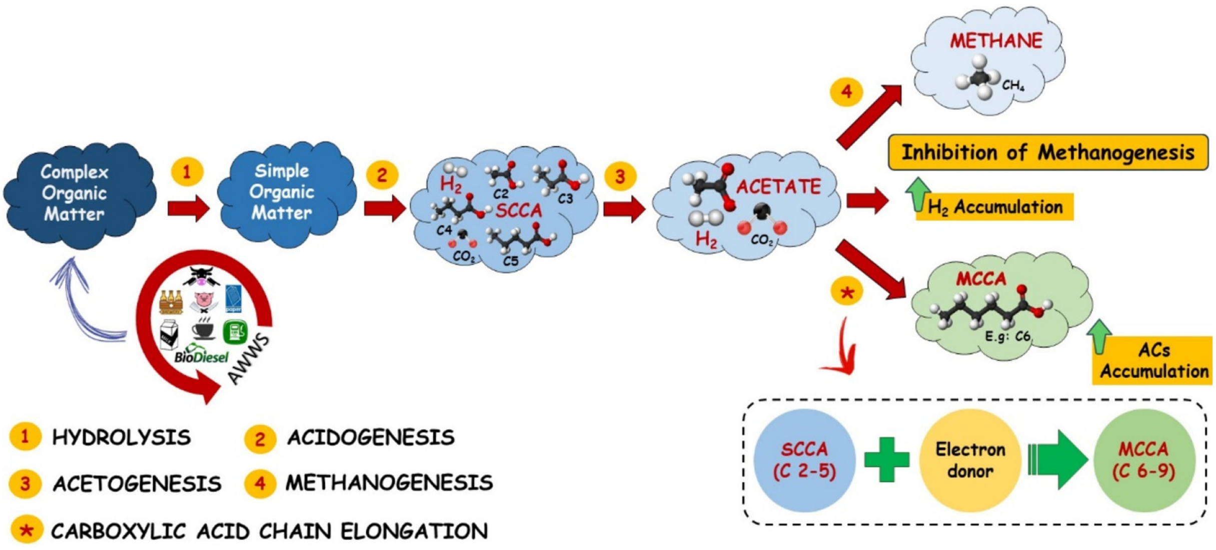

Fig. 2. Traditional and modified anaerobic digestion.

CO_2 by stripping or microbial consumption, should be sought to increase the content of H_2 in the biogas. However, the hydrogen partial pressure (HPP) in anaerobic systems should be controlled, because high values cause operational disturbances in the hydrogen-producing microorganisms themselves, such as acidogenic and acetogenic bacteria, or even hydrolytic bacteria, negatively affecting all the process (Yan et al., 2019). This control could be done by some physical removing methods such as releasing gases and exhausting gases by sparging other gas to reduce the HPP (Zhou et al., 2017).

H_2 can be formed in different metabolic pathways that depending on the type of inoculum, substrate, and operating conditions, can lead to different yields and subsequent HPP (Arantes et al., 2017). The fatty acid relative production is assumed to be dependent on the potential redox or equivalently on the ratio $[NADH]/[NAD^+]$ (Kleerebezem et al., 2015). This ratio is made a function of the HPP in the gas phase. Apart from the acidogenic bacteria, HPP also influences the acetogenic growth rate, since high values inhibit (thermodynamically) the generation of propionic and butyric acids (Lyberatos and Skiadas, 1999). High HPP favors the production of reduced fermentation products, particularly propionate and higher volatile fatty acids. Propionate is only degraded at an HPP below 10 Pa. The production of H_2 is kinetically and thermodynamically less favored when the HPP is higher than 60–100 Pa (Rugerri et al., 2015).

For the biogas produced, there is a need for employing hydrogen separation technologies, such as pressure oscillation adsorption and membrane permeation technology. Even though a biohydrogen separation step is not a technological issue, it remains one of the most expensive steps in the global process. More information about a metabolic route of hydrogen production and its extraction can be obtained in the review by Moscoviz et al. (2018).

3.3. *Carboxylic platform route*

Concomitantly with the production of H_2, there is the formation of CAs, products also derived from the acidogenic and/or acetogenic stages of the anaerobic digestion (Wainaina et al., 2019). The carboxylic platform also requires the elimination or suppression of microorganisms that transform CAs into end products such as CH_4 and H_2S. Several types of pretreatments have been investigated for this purpose, such as thermal, thermochemical, chemical, enzymatic etc. (Grootscholten et al., 2013). As previously mentioned, SCCAs are naturally formed in the stage of acidogenesis. However, the MCCAs production requires a Biological Carboxylic Chain Elongated Process (BCCEP), where a smaller organic material (electron donor) provides electrons for SCCAs bioconversion into MCCAs (Grootscholten et al., 2013). Therefore, one of the strategies to enhance BCCEP is the addition of electron donors, such as ethanol, lactic acid, methanol, propanol, peptides, galactitol, and carbohydrates (Coma et al., 2016).

It is known that CAs fermentation is usually inhibited by the products formed in the process, so in situ CAs recovery during fermentation will reduce possible inhibitory effects, resulting in higher productivity (Dahiya et al., 2015). Developing and optimizing in situ product extraction processes can improve the quality of a biorefinery product while reducing costs, the latter accounting for 30–50% of the total costs of obtaining CA per biological pathway (Murali et al., 2017).

For using CAs as raw materials in industrial processes, the downstream process to AD involves the following steps: 1) removal of large particles in clarification; 2) removal of the product from the bulk aqueous solution containing the main impurities in the primary recovery by known separation methods such as liquid-liquid extraction, ultrafiltration, reverse osmosis, electro-dialysis, direct distillation, liquid membrane extraction, anion exchange, precipitation and adsorption. The adsorption and extraction are the most used processes; 3) replacement of a carboxylate cation by H^+ to produce CA on acidification; 4) concentration/purification by removing the bulk solvent or by capturing/separating the CA (Vidra and Németh, 2018). Further details on CAs separation methods can be obtained in the review by Atasoy et al. (2018).

Therefore, the process challenging (metabolic pathways, separation of the CAs from the liquid phase etc.) is to produce a specific CA in a competitive environment and avoid the formation of either lower value-added CAs or other by-products. For instance, sometimes there is the formation of 1,3-propanediol, which is undesirable, despite a wide possibility of use of this last bioproduct after the extraction from the liquid medium and subsequent recovery. A review of the different metabolic pathways of CAs production and BCCEP can be found in the paper of Zhou et al. (2018).

Fig. 3 shows the global process of obtaining CAs via biological processes. Much research is being done to optimize this process, and some companies already produce and market CAs from various wastes, as will be discussed in Section 4.

4. The biorefineries market applied to agro-industrial wastes

The use of AWWs to prospect for chemical inputs in anaerobic processes is an economically attractive strategy that can mitigate environmental impacts caused by improper disposal of these wastes and reduce dependence on the petrochemical sector (Ramió-Pujol et al., 2015). Table 2 presents the yields of mass production of carboxylic acids, hydrogen, and methane obtained in various anaerobic digestion works. In general, studies report CA production of 2 to 6 carbon atoms, except for Chookaew et al. (2015), who obtained 0.5 mg C7 $gCOD_{applied}^{-1}$, and Dams et al. (2018), who obtained 312.7 mg C8 $gCOD_{applied}^{-1}$. This is because the BCCEP becomes more difficult for larger carboxylic chains. The AWWs that obtained the highest yields of mass production of CAs were swine and residual glycerol (1324.0 and 1237.3 mg CAs g $COD_{applied}^{-1}$, respectively) likely because these wastewaters are rich in proteins and lipids, which are mainly responsible for the formation of CAs (Wang et al., 2018b). Residual glycerol was also the AWWs that generated the highest CH_4 production (426 mg CH_4 g $COD_{applied}^{-1}$). The production of H_2 was higher when using the pulp and paper AWW (356.8 mg H_2 g $COD_{applied}^{-1}$).

Table 3 presents an estimation of the gross value added with the recovery of carboxylic acids with and without chain elongation, hydrogen, and methane, from AWWs using anaerobic processes. It can be observed that the production of these bioproducts is quite profitable, varying according to the volume of AWWs generated, the production yield of the compound of interest, and its market value. Moreover, it can be inferred that the carboxylic platform is the most advantageous from a gross value-added point of view (Table 3). For biodiesel wastewater, for example, when compared to hydrogen production, it generates US$ 8.8 billion more per year. This is primarily because H_2 yields are low, and the market value of CAs is slightly higher than H_2. Regarding methane, although its productivity is high, its market value is much lower, resulting in a gross income of US$ 8.9 billion less than the production of CAs.

In addition, it can be noted that the maximum gross value-added of CAs production from residual glycerol with chain-elongating is ten times greater than that of non-chain-elongated production. This is because the elongation process forms higher carboxylic chain acids, and the longer the chain, the higher the value-added. Even so, there is a scarcity of studies in this area, as can be observed in Table 2, where only three of the 38 investigations with AWWs focused on chain-elongation processes. Ullah Khan et al. (2017) present the upgrading biogas costs for different technologies (0.12–0.40 €/Nm^3 of biogas) and the work by Outram and Zhang (2018) presents an economic analysis of the

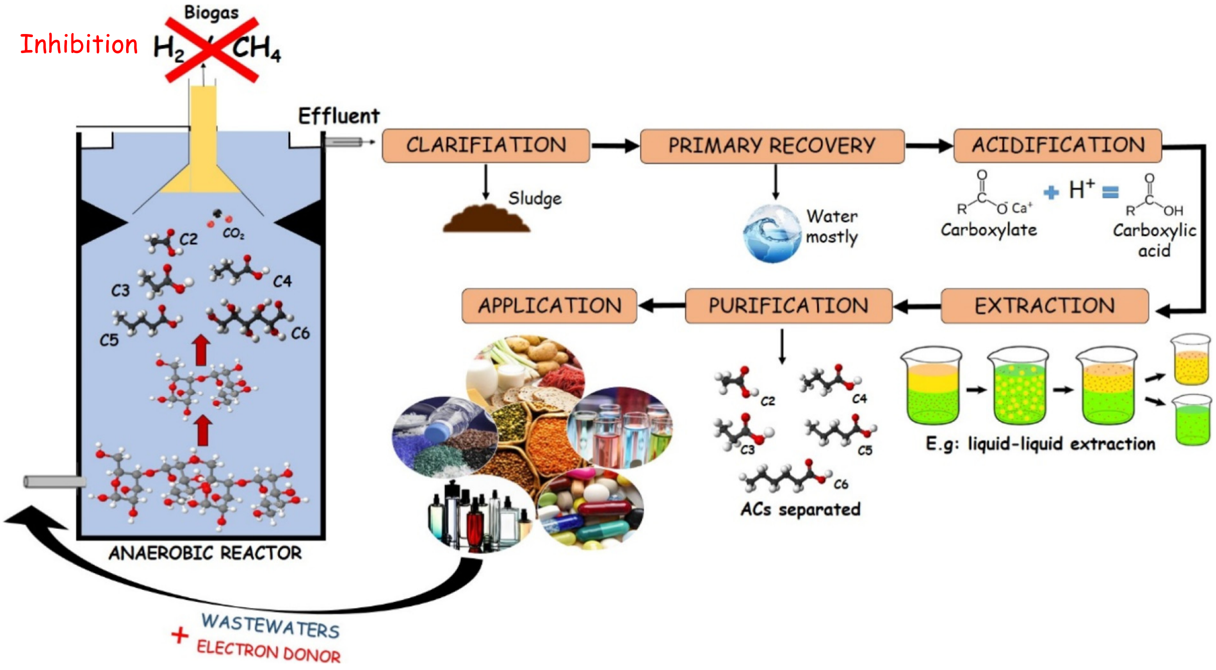

Fig. 3. Schematic diagram of carboxylic acids production and recovery process from agro-industrial wastewaters.

Table 2
Biological production of carboxylic acids, hydrogen, and methane from the anaerobic digestion of some agro-industrial wastewaters (AWW).

Agro-industrial wastewater	C2	C3	C4	C5	C6	CAs	H_2	CH_4	References
	(mg bioproducts/g $COD_{applied}$)[a]								
Bovine slaughterhouse	-	-	-	-	-	-	-	137.1	(Wang et al., 2018a)
	-	-	-	-	-	-	-	259.2	(Jensen et al., 2015)
	112.1	29.1	15.7	-	-	156.9	-	213.7	(Palatsi et al., 2011)
Pig slaughterhouse	43.5	52.9	4.7	11.8	1.2	114.1	-	11.3	(Molinuevo-salces et al., 2018)
	692.0	632.0	-	-	-	1324.0	-	-	(Bayr et al., 2012)
	36.3	38.2	71.9	-	-	146.4	8.0	24.5	(Li et al., 2010)
Coffee beans processing	103.6	64.7	146.5	104.2	96.5	515.5	13.7	-	(Jung et al., 2010)
	25.2	3.9	34.0	2.5	1.5	67.1	1.2	45.9	(Novita, 2016)
	122.1	73.2	88.4	-	114.2	397.9	27.0	213.2	(Jung et al., 2012)
Pulp and paper processing	165.4	104.0	132.4	71.1	-	472.9	-	-	(Tamis et al., 2018)
	82.4	26.1	22.9	-	-	131.4	-	195.7	(Yilmaz et al., 2008)
	-	-	-	-	-	-	-	349.1	(Meyer and Edwards, 2014)
	-	-	-	-	-	-	21.1	-	(Lakshmidevi and Muthukumar, 2010)
	-	-	-	-	-	-	356.8	-	(Xiao et al., 2017)
	-	-	-	-	-	-	-	178.4	(Kamali and Khodaparast, 2015)
Dairy products	-	-	-	-	-	-	5.2	289.3	(Jürgensen et al., 2018)
	-	-	-	-	-	-	9.4	124.6	(Kothari et al., 2017)
	102.8	3.9	7.5	-	3.4	117.6	60.2	238.8	(Silva et al., 2019)
	133.0	41.0	54.5	23.5	13.0	265.0	41.6	78.7	(Yu and Fang, 2001)
	131.8	62	64	22	11	290.8	-	6.6	(Fang and Yu, 2000)
Brewery industry	-	-	-	-	-	-	-	301.8	(Herrmann and Janke, 2001)
	335.0	72.0	45.7	18.8	8.8	480.3	13.5	250.0	(Arantes et al., 2017)
Ethanol (vinasse)	200.7	525.4	96.9	-	-	823.0	11.5	-	(Santos et al., 2014)
	55.2	33.1	80.1	16.6	16.6	201.6	1.4	-	(Ferraz Júnior et al., 2014)
	254.6	140.3	24.0	12.0	-	430.9	-	153.5	(Janke et al., 2016)
	198.1	35.1	678.4	-	-	911.6	31	-	(Sydney et al., 2014)
	-	-	-	-	-	-	-	208.8	(Moraes et al., 2014)
	-	-	-	-	-	-	-	130.6	(Ferraz Júnior et al., 2016)
Biodiesel (residual glycerol)	22.4	34.1	42.5	-	-	99.0	6.0	-	(Reungsang et al., 2013)
	123.6	3.6	88.8	-	-	216.0	-	-	(Forrest et al., 2010)
	92.0	16.2	43.2	0.6	-	152.0	-	-	(Forrest et al., 2010)
	19.5	0.8	4.2	1.4	27.4	53.8	12.8	-	(Chookaew et al., 2015)
	-	-	-	-	-	-	-	426.0	(Baba et al., 2013)
	-	-	-	-	-	-	-	236.4	(Vlassis et al., 2013)
	-	-	-	-	-	-	52.8	-	(Liu et al., 2013)
	-	-	-	-	-	-	93.0	-	(Wu et al., 2013)
Works focusing on carboxylic chain elongation									
Dairy products	101.8	-	51.0	-	90.4	243.2	-	-	(Duber et al., 2018)
Biodiesel (residual glycerol)	116.2	-	8.2	-	10.6	135	-	-	(Leng et al., 2017)
	38.2	90.9	420.0	-	698.2	1247.3	-	-	(Dams et al., 2018)
	-	74.5	94.5	-	694.5	1176.2	-	-	(Dams et al., 2018)

[a] Note: not all of these studies showed yields of bioproducts production, so it was calculated by the equation Y = [bioproduct] / applied COD, where Y is the yield and the unit of measure was standardized in mg bioproducts/gCOD. (-) values not shown or not detected.

Table 3
Gross value-added with recovery of carboxylic acids, hydrogen, and methane from agro-industrial wastewater using anaerobic processes.

Agro-industrial wastewater	[a]Gross value-added with recovery (US\$·year^{-1})			
	CAs No elongation	CAs With elongation	H_2	CH_4
Bovine slaughterhouse	$6.2 \cdot 10^8$	–	–	$2.4 \cdot 10^8$–$4.6 \cdot 10^8$
Pig slaughterhouse	$6.2 \cdot 10^8$–$5.5 \cdot 10^9$	–	$7.5 \cdot 10^7$	$1.9 \cdot 10^7$–$4.0 \cdot 10^7$
Coffee beans processing	$2.8 \cdot 10^8$–$2.7 \cdot 10^9$	–	$7.5 \cdot 10^6$–$1.7 \cdot 10^8$	$5.0 \cdot 10^7$–$2.3 \cdot 10^8$
Pulp and paper processing	$2.8 \cdot 10^{10}$–$1.5 \cdot 10^{11}$	–	$1.0 \cdot 10^{10}$–$1.7 \cdot 10^{11}$	$1.5 \cdot 10^{10}$–$2.9 \cdot 10^{10}$
Dairy products	$1.7 \cdot 10^{10}$–$7.7 \cdot 10^{10}$	$7.6 \cdot 10^{10}$	$2.3 \cdot 10^9$–$2.7 \cdot 10^{10}$	$5.1 \cdot 10^8$–$2.2 \cdot 10^{10}$
Brewery	$1.1 \cdot 10^{10}$	–	$6.9 \cdot 10^8$	$2.2 \cdot 10^9$–$2.7 \cdot 10^9$
Ethanol (vinasse)	$3.2 \cdot 10^7$–$1.5 \cdot 10^8$	–	$3.0 \cdot 10^5$–$6.7 \cdot 10^6$	$4.9 \cdot 10^6$–$7.8 \cdot 10^6$
Biodiesel (residual glycerol)	$3.7 \cdot 10^8$–$9.0 \cdot 10^8$	$3.2 \cdot 10^8$–$9.5 \cdot 10^9$	$4.7 \cdot 10^7$–$7.2 \cdot 10^8$	$3.2 \cdot 10^8$–$5.8 \cdot 10^8$

[a] Note: Value calculated through the equation $V = \Sigma Y \times COD \times Q \times US\$$, where V is the gross aggregate value, Y is the yield of bioproducts (Table 3), COD is the average wastewater COD calculated from Table 2, Q is the AWW production flowrate (Table 2) and US$ is the commercial price of bioproducts (respectively 570, 1499, 2144, 2280, 2500, 2300 and US$ 400 ton^{-1}). (–) could not be calculated due to the lack of data on the production yield of bioproduct.

membrane and extractor cost in CAs recovery. However, further studies are needed considering the costs of other CAs recovery technologies and their separation for individual application of acids, providing information about the cost per mass of purified acid. Regarding the hydrogen platform, Kreutz et al. (2005) estimated the cost of purification in the order of 1 US\$ kg^{-1} H_2.

It is also noteworthy that butyric (C4) and caproic acids (C6) are the most advantageous CAs due to the correlation of market value and yield of mass production. Thus, these two acids are the main focus of CAs research, as acetic acid (C2) is more easily formed and can be elongated

Table 4
Key information on the industrial application, production system, and major manufacturers of carboxylic acids (C2–C6).

Carboxylic acid	Industrial applications/products	Production system and major manufacturers	References
Acetic acid (Ethanoic acid) $C_2H_4O_2$ – C2 EP = $1.7 \cdot 10^7$–$1.8 \cdot 10^7$ MV = 376–764	Vinyl acetate (150 gC2 kg^{-1}), acetic anhydride (cigarette filter - 2.5 kgC2 kg^{-1}), terephthalic acid (synthetic and textile fiber, paints; acetate ester; vinegar - 50–150 mLC2 L^{-1}); chitosan-based antimicrobial films (0.5 L C2 kg^{-1}) solvents; flavoring; plastic; food additive; dyes; drugs; pesticides.	Liquid and gas phase oxidation of petroleum gases, acetaldehyde oxidation, methanol and carbon monoxide reaction or ethanol fermentative oxidation. Manufacturers: BP, Celanese Corporation, Daicel Corporation, Eastman Chemical Company, Lyondellbasell Industries Holdings, SABIC.	Atasoy et al. (2018), Bastidas-Oyanedel et al. (2015), Bhatia and Yang (2017), Du et al. (2015), Moscoviz et al. (2018), Murali et al. (2017), Nayak and Pal (2013), Lewis (2016), Technavio (2018)
Propionic acid (Propanoic acid) $C_3H_6O_2$ – C3 EP = $4.7 \cdot 10^5$ MV = 1425–1573	Preservatives (food and feed industries, agricultural sector - maize, wheat, barley, and sorghum crops); bakery and dairy products; cellulose acetate propionate; synthetic cellulosic fiber; herbicides; Perfumes; drugs; anti fungicide; propionic acid esters; animal food; vitamin E.	Petrochemical synthesis from ethylene, CO and steam (Reppe process) or ethanol and CO (Larson process); by-product of acetic acid manufacturing; chemical processes such as propanol or propanal oxidation and ester hydrolysis; and biotechnological methods. Manufacturers: BASF, The Dow Chemical Company, Eastman Chemical Company, Perstorp, Macco Organiques.	Ahmadi et al. (2017), Bastidas-Oyanedel et al. (2015), Du et al. (2015), Leatherhead Food Research (2014), Moscoviz et al. (2018), Technavio (2017), Wallenius et al. (2015)
Butyric acid (Butanoic acid) $C_4H_8O_2$ – C4 EP = $1.1 \cdot 10^5$ MV = 1904–2383	Pharmaceuticals, poly-3-hydroxybutyrate (PHB) cellulose acetate butyrate plastics, medicine, antibacterial, bioplastics, butyric acid esters (methyl, ethyl and amyl butyrate - food additives and perfume formulation due to their pleasant aromas and flavors), fuels (butanol).	Synthesis of oxo: propylene is oxidized to butyraldehyde, which is converted to butyric acid for example, through the H_2O_2 catalyzed oxidation reaction. Maleic anhydride, butane, but-2-enoic and butanol may be used instead of butyraldehyde. Semi-chemical production: butter extraction (2–4% C4). Manufacturers: BASF, Blue Marble Biomaterials, Eastman, Thermo Fisher, OXEA, Perstorp.	Atasoy et al. (2018), Bastidas-Oyanedel et al. (2015), Brar et al. (2016), Du et al. (2015), Markets and Markets (2018), Moscoviz et al. (2018), Technavio (2016)
Valeric acid (Pentanoic acid) $C_5H_{10}O_2$ – C5 EP = 75[a] MV = $2.8 \cdot 10^6$	Flavorings and perfumes, agricultural chemicals (pesticides), pharmaceuticals, esters (ester-type lubricants, vinyl plasticizers and stabilizers, ethyl valerate, and pentyl valerate - food additives).	Oxo process: butylene process reacts with synthesis gas (CO and H2) in the presence of a catalyst, producing valeraldehyde, which is oxidized to valeric acid. Manufacturers: The Dow Chemical Company, Perstorp Orgnr, Sisco Research Laboratories Pvt. Ltd., Sigma Aldrich, Central Drug House, The good scents Company, Merck KGaA, LKT Laboratories, Neuchatel Chemie Specialties, Yufeng International Co., Ltd.	Persistence Market Research (2019), The Dow Chemical Company (2014), Zauba Technologies PVT LTD (2018)
Caproic acid (Hexanoic acid) $C_6H_{12}O_2$ – C6 EP = $2.5 \cdot 10^4$ MV = 2000–3000	Pharmaceuticals, surfactants (textiles, soaps & detergents, personal care & cosmetics) fungicides, human & animal food additive, antimicrobial, growth promoter, lubricants (synthetic & fluid-cooled for fire-resistant metal machining), fragrances, additives paint, biofuel (decane).	Crude fermentation of C4 or fractional distillation of natural fatty acids. From food crops such as palm and coconut (low in these oils - less than 1%). Its synthetic production is not well established. Manufacturers: P & G Chemicals, Emery Oleochemicals, KLK OLEO, Ecogreen Oleochemicals, Pacific Oleochemicals Sdn Bhd, Oleon NV, Ecogreen Oleochemicals, Timur OleoChemicals e Mosselman S.A.	Bastidas-Oyanedel et al. (2015), Cavalcante et al. (2017), Chen et al. (2017), Future Market Insights (2019), Moscoviz et al. (2018)

MV = Market Value (US\$ ton^{-1}).

[a] EP = Estimated Production for 2020 (ton), 2014.

Table 5
Comparison between methane, hydrogen, and carboxylic acid platforms from agro-industrial wastewater using anaerobic processes.

Platform	Methane	Hydrogen	Carboxylic acids
Gross value-added	+	+ +	+ + +
Production technique consolidation	+ + +	+	+ +
Recovery technique consolidation	+ + +	+ +	+ +
Use for different production scales	+ + +	+	+ +
Possibility for urban installation	+ + +	+ + +	+ + +
Possibility for rural installation	+ + +	+	+

Note: (+) Low (+ +) Medium (+ + +) High.

to C4 and then to C6. The AWWs that C6 was most produced were residual glycerol and coffee processing wastewater. These AWWs also presented low COD/BOD ratios (1.1 and 1.7, respectively), indicating easier biodegradation that favors fermentative microorganisms (Jayakrishnan et al., 2019). In general, a high COD is known to lead to high CAs yields, but at the same time, provides problems related to inhibition of substrate excess and thus the variation of CAs content and profile. AWWs composition (carbohydrate, lipid, and protein) also influences the content and profile of CAs (Jayakrishnan et al., 2019). However, the operating conditions adopted in the AD process are also determinant.

Although the challenges of biological production of CAs via AD are quite significant, especially concerning acid separation and purification, two companies have already started production of CAs via anaerobic digestion of waste: *Earth Energy Renewables* (EER) and *ChainCraft*. EER technology consists of a hybrid biological/chemical process where mixed culture anaerobic digesters naturally convert biomass to CAs, which are recovered through proprietary and patented technologies, and then chemically converted to other desired products (EER, 2019).

The company has already tested about thirty different raw materials, including glycerol, food waste, sugarcane bagasse, sugarcane molasses, cattle and chicken manure, municipal sewage sludge and cellulosic urban solid waste (Granda, 2017). They report CAs yields (C2 to C8) of about 0.65 ton acid per ton substrate, with estimated production cost at most US$ 500.00 ton^{-1} for a plant of 90 ton d^{-1}. On the other hand, conventional companies such as Celanese, BP, BASF, Eastman, OXEA, and P&G Chemical had costs ranging from US$ 400 to 2500 ton^{-1} (Granda, 2015). *ChainCraft* also develops mixed culture fermentation technologies to produce sustainable biological/chemical products by exploiting the different markets of CAs (C4 to C8) and their derivatives in close cooperation with leading companies in the chemical, food, and feed industry (ChainCraft, 2019).

The production of CAs via the AD market is still little explored, but its production potential is wide. The leading countries in the agro-industrial activities presented in this paper are China, the USA, and Brazil (Barth-Haas Group, 2017; Embrapa Cattle Milk, 2018; FAOSTAT, 2017; RFA, 2019; STATISTA, 2019). Among these countries, Brazil has the most favorable environmental conditions for anaerobic treatment and therefore has excellent potential for the implantation of biorefineries. Table 1 shows the percentage of Brazil's contribution to the agro-industrial activities explored in this review.

Table 4 brings key information on the industrial application, production system, and leading manufacturers of carboxylic acids (C2–C6). As many of these acids have antimicrobial action and are used as preservatives, the increased demand for processed foods and demand for high-quality animal feed are factors that drive the production of these commodities (Du et al., 2015; Technavio, 2018). In general, CAs are synthetically produced from petrochemical derivatives and biologically through the fermentation process of anaerobic digestion. Petroleum-based production methods supply about 90% of this CAs market demand. However, due to problems related to petroleum resources, such as risk of scarcity, high prices and severe environmental impacts, the organic production of CAs from low-cost renewable resources is receiving increasing attention, such as organic residues from agro-industrial activities (Atasoy et al., 2018; Du et al., 2015; Greses et al., 2019; Morais et al., 2019).

Besides, bio-based CAs production is more indicated for food and feed purposes, as the product is not considered a harmful or toxic ingredient by the World Health Organization (WHO), unlike chemical production (Persistence Market Research, 2019). On the other hand, for biological methods to be economically viable, the manufacturing cost and the efficiency of the systems need to be improved (Atasoy et al., 2018). Since there is plenty of raw material available with the use of AWWs and the satisfactory CAs production yields, it is clear the potentiality of the biological CAs production process from AWWs. Therefore, there is the need to invest in studies that promote the process optimization so the scale-up can have economic viability.

Table 5 brings a comparison between methane, hydrogen, and carboxylic acid platforms. It can be noted that although the CA platform showed to be the most economically advantageous, the traditional methanization becomes competitive when other variables are considered, such as the gross value-added, consolidation of the production and recovery techniques, the production scales and the possibility of installation in urban and rural environments.

5. Conclusions

The studied AWWs have excellent economic potentials for methane, hydrogen, and carboxylic acids productions, but the CA platform is more economically advantageous, especially when there is the BCCEP. However, further economic studies are needed to account for the recovery costs of these products for a better net value-added analysis, as traditional AD is simpler in terms of process control, and methane purification is cheaper. The AWWs that obtained the highest yield of mass production of CAs were swine and residual glycerol. Because of the low yields achieved, it seems that hydrogen production is the least attractive technological route.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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