Calculation of the potential production of methane and chemicals using anaerobic digestion

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Abstract

The aim of this paper is to calculate how much energy or chemicals can be potentially produced using anaerobic digestion (AD). Five feedstocks were considered: the organic fraction of municipal solid waste (OFMSW), cattle, pig and poultry manure, energy crops, agricultural residues and sewage sludge. Carbohydrates, proteins and lipids were assumed to be the biodegradable components of the feedstocks. COD (Chemical Oxygen Demand) was assumed as a basis for the calculations of methane and chemicals production. Methane production was calculated assuming that AD converts the biodegradable COD to methane with a yield of 80 % COD/COD. The potential production of chemicals, i.e. acetic, propionic, butyric and lactic acids, ethanol and hydrogen, was calculated assuming conversion yields of carbohydrates, proteins and lipids from the literature. Globally, with the assumptions done in this study, AD of the considered feedstocks can potentially satisfy 17–20 % of the total energy consumption and 33-39 % of the electrical energy requirements. Potentially, AD can generate organic acids at rates which are hundreds or thousands of times their current production rates. Ethanol and hydrogen can be produced by AD at rates which are up to 2-3 times their current production rate. The paper also discusses the main challenges to overcome in order to achieve the large potential of AD.

Keywords: biomass, anaerobic digestion, organic waste, methane, volatile fatty acids (VFAs).

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1. Introduction

Currently most of the energy and chemicals produced and consumed by mankind are generated from fossil fuels. In 2014 81 % of the world's energy supply was provided by coal, oil and natural gas.[1] Important chemicals such as organic acids (e.g. acetic, butyric and lactic acid) and hydrogen are also mainly produced from fossil fuels.[2] However, sooner or later fossil fuels will be depleted and all the required energy and chemicals will need to be generated from renewable resources. In this context, anaerobic digestion (AD) can convert biomass, a renewable resource, into methane and/or chemicals such as volatile fatty acids (VFAs), ethanol and hydrogen.[2,3] Production of these chemicals using AD would have the advantages of using biomass (often an organic waste), which is a renewable feedstock, and of using much milder reaction conditions (in terms of temperature and pressure) than traditional processes based on fossil fuels.[2] However, the use of AD for the production of chemicals such as VFAs, ethanol and hydrogen is still at the research stage or pilot scale and it has been so far hampered by the separation required to purify mixtures of diluted chemicals in water, by the need of optimising the digestion conditions to maximise the yields and by the pre-treatment requirements of lignocellulosic feedstocks.[2]

Although AD has been recognised to have a large potential in the production of energy,[4] so far very limited quantitative analysis has been reported on how much energy or chemicals could potentially be produced using this technology. In one of these studies,[5] it was estimated that over 40 billion m^3/year of biogas could be potentially produced from the AD of various sources of organic waste in India. A quantitative analysis of the amount of energy or chemicals that could be produced by AD is important because biomass,

although is a renewable feedstock, is generated at a finite rate and therefore production of renewable energy or renewable chemicals using AD is only possible if the biomass is consumed at the same rate at which it is generated.

The aim of this paper is to calculate how much energy, or as an alternative, chemicals could be potentially produced from the AD of biomass, at the current generation rates of selected feedstocks. Throughout this study, COD (Chemical Oxygen Demand) was used as a basis to calculate the potential production rates of methane or chemicals. COD is proportional to the maximum number of electrons that can be removed from an organic substance and the total COD of any given feedstock corresponds to the maximum theoretical COD of the methane or chemicals that can be produced from this feedstock.[6] Therefore, the COD is a useful tool to estimate the maximum theoretical production of methane or chemicals from organic substances.

Ultimately, this paper tries to address the question of the potential role of AD for energy or chemicals production in a fossil fuel-free world.

2. Methodology

The methodology used for the calculation of the potential methane or chemicals production is shown in Figure 1 and reported below. This methodology was applied to the global scale and to the following countries: UK, Brazil, Nigeria, India. These countries were chosen, as an example of the application of this methodology, because they were among the funders of this research (UK and Brazil) and because they represent developing countries (Nigeria and India) in different continents, however the described methodology can be applied to any countries if the required data are available.

2.1 Initial steps

The initial steps are the same for both the methane and chemicals production and involve the calculation of the feedstock generation rate, feedstock composition and conversion of the feedstock components into COD.

2.1.1 Feedstock generation rate

The feedstocks considered for AD in this study include: the organic fraction of municipal solid waste (OFMSW), animal manure, agricultural residues, sewage sludge and energy crops. These feedstocks are among the most commonly used in AD and among the most interesting for the production of chemicals in a biorefinery context.[2,4,7] MSW is the solid waste generated by cities, towns and communities. In this study, the fraction of MSW which is made of metals, glass and plastics was excluded and the remaining fraction (organics and paper) was referred to as OFMSW. The manure considered was from cattle, pig and poultry. Agricultural residues are the residues left on field after the harvest and include husks, stalks, chaff, etc. Sewage sludge are the solids produced in the biological treatment of municipal wastewaters. Energy crops are plants grown with the

specific purpose of generating energy via AD or combustion. All the considered feedstocks, except energy crops, are waste or by-products from industrial or agricultural processes or human activities. In this study, the total production of these wastes, including the volumes which are currently used for other aims (e.g. burning of agricultural residues to obtain energy, spreading manure on land as fertilizer, etc.), was considered. For each feedstock two methods (Method 1 and Method 2) for the calculation of the generation rate were used and, based on these two methods, a range for the generation rate was calculated.

For the OFMSW, in both methods the generation rate of OFMSW was calculated from equation (1):

$$OFMSW\ generation\ rate\ (dry\ matter) = \begin{pmatrix} MSW, as\ wet\ matter, generated \\ per\ capita\ per\ year\ in\ each\ country\ or\ globally \end{pmatrix} \cdot (Population\ in\ each\ country\ or\ globally) \cdot (0.46 \cdot 0.31 + 0.17 \cdot 1) \quad (1)$$

The population in each country and globally was taken in all cases from The World Bank website.[8] The coefficient 0.46·0.31 is for the organic fraction of the MSW, which was assumed to be 46% of the MSW[9] and have a dry matter content of 31 %.[10] The coefficient 0.17·1 is for the paper waste, which was assumed to be 17 % of the MSW[9] and be entirely dry. The two methods differ for the estimation of the wet MSW generated per capita per year. Method 1 used the data from Hoornweg et al., 2012,[9] while the Method 2 used data from individual studies for the different countries: UK;[11] Brazil;[12] India;[13] Nigeria;[14] global.[15]

For cattle, pig and poultry manure, the Method 1 used equation (2) where the manure generation rate per head of livestock per year[16] and the number of livestock per country or globally[17] were assumed from the literature:

$$Manure\ generation\ rate\ (dry\ matter) = (Manure\ generation\ rate, as\ dry\ matter, per\ head\ of\ livestock\ per\ year) \cdot (Number\ of\ livestock\ per\ country\ or\ globally) \quad (2)$$

Method 2 used equation (3) to estimate the manure generation rate:

$$Manure\ generation\ rate\ (dry\ matter) = (Total\ manure\ generation\ rate, as\ wet\ matter, per\ country\ or\ globally) \cdot 0.226 \quad (3)$$

In Method 2, total manure generation rate in wet basis were obtained from individual studies for the different countries: UK;[18] Brazil;[19] India;[5] Nigeria;[20] global.[21] In this method, dry matter of manure was assumed to be 22.6 % of the wet weight (average value for dairy manure) .[21]

For energy crops, in both methods the generation rate was calculated according to equation (4):

$$Energy\ crops\ generation\ rate\ (dry\ matter) = (arable\ land\ in\ each\ country\ or\ globally) \cdot 0.024 \cdot (crop\ yield) \quad (4)$$

The available arable land per country and globally was assumed from the literature[17] and the factor 0.024 accounts for the assumption that 2.4 % of the arable land area can be used for energy crop production.[22] The crop yield was assumed to be 10 t dry matter/ha/year and 20 t dry matter/ha/year in Method 1 and Method 2 respectively, which are the upper and lower ranges reported in the literature.[23]

For agricultural residues, Method 1 used equation (5):

$$Agricultural\ residues\ generation\ rate\ (dry\ matter) =$$

$$(Average\ of\ residue\ to\ production\ ratio) \cdot (total\ crops\ production\ rate) \quad (5)$$

The average of residue to production ratio[24] and the total crops production rate (considering thirteen major crops) were assumed from the literature.[17] Method 2 used the residues generation rate from individual researches: UK;[25] Brazil;[26] India;[27] Nigeria;[28] global.[29] For the global production, the value from Bentsen *et al.*[29] was divided by 0.79 to take into account that the six major crops considered in that study represent 79 % of the total production of agricultural residues.[30] For Brazil, India and Nigeria, where the values were reported as wet matter, an average moisture content of 10 % was assumed.

For the generation rate of sewage sludge, the two methods used equation (6), the only difference being the reference used for the estimation of the sewage sludge generation per capita per year. In Method 1 this variable was assumed to be 14.6 kg dry matter per capita per year,[31] while in Method 2 it was assumed to be 17.9 kg dry matter per capita per year.[32] In both cases, the population was estimated from the same reference cited above.[8]

$$Sewage\ sludge\ generation\ rate\ (dry\ matter) =$$

$$(Sewage\ sludge\ generation\ per\ capita\ per\ year) \cdot$$

$$(Population\ in\ each\ country\ and\ globally) \quad (6)$$

2.1.2 Feedstock composition

It was assumed that the only components of the feedstocks that can be converted to methane or chemicals using AD are carbohydrates (including cellulose, hemicellulose, starch and sugars), proteins and lipids. The composition of each feedstock in terms of carbohydrates, proteins and lipids was assumed according to the following references:

OFMSW;[10] Manure;[33] Energy crops;[34] Agricultural residues;[35,36] Sewage sludge.[37] Although the chemical composition of the various types of biomass may differ between countries, for the purpose of this study the same composition for each type of biomass was assumed.

2.1.3. COD of the feedstock components

In AD, in the absence of any external electron acceptor such as oxygen or nitrate, the COD in the feedstock can end up in the following products: methane, chemicals, microorganisms and undigested feedstock.[6] Therefore the yield of methane or chemical production can be easily expressed on a COD basis (i.e. as COD of the produced methane or of the produced chemicals divided by the COD of the feedstock), being 100% the maximum theoretical yield of methane or chemicals from any given feedstock when the feedstock is totally digested and in the absence of microorganisms' production. For methane production, a yield of 100 % on a COD basis corresponds to the theoretical amount of methane which can be calculated using the Buswell equation.[38]

Individual components (carbohydrates, proteins and lipids) were converted to COD basis using their theoretical COD conversion factors, which were calculated from the stoichiometry of the oxidation reactions. The general form of the oxidation reaction and the corresponding conversion factors are reported in equations (7) and (8) below:

$$C_nH_aO_bN_d + (4n + a - 2b - 3d)\ O_2 \rightarrow n\ CO_2 + (b - 2n)\ H_2O + d\ NH_3 \quad (7)$$

$$Conversion\ factor\ (g\ COD/g) = \frac{8\ (4n+a-2b-3d)}{(12n+a+15b+14b)} \quad (8)$$

The chemical composition of the organic matter considered in this study is of course dependent on many factors such as, e.g., its nature and location. In this study we assumed the following empirical formulas for COD calculations: $C_6H_{10}O_5$ for

carbohydrates, $C_5H_7O_3N$ for proteins and $C_{57}H_{104}O_6$ for lipids. Consequently, the calculated COD conversion factors were: 1.185 g COD/g carbohydrates, 1.116 g COD/g protein, 2.896 g COD/g lipids. These empirical formulas assume that carbohydrates are polymers of glucose, proteins are polymers of glutamic acid and lipids are triglycerides of oleic acid. Glucose units are the building blocks for abundant carbohydrates such as cellulose and starch, while glutamic acid and oleic acid are common amino acids[39] and fatty acids.[40] Clearly, more accurate calculations can be done by considering the empirical formulas for the particular types of carbohydrates, proteins and lipids in the various feedstocks, however this would require a more detailed chemical analysis and was not considered in this study.

2.2. Calculation of the potential methane production

2.2.1. Calculation of the total COD of the feedstocks

For the calculation of the methane production, the total COD generation rate was calculated for each feedstock by adding up the contributions of its components (carbohydrates, proteins and lipids). This is shown in Equation (9), where i = 1, 2 and 3 corresponds to carbohydrates, proteins and lipids respectively:

$$Total\ Feedstock\ COD\ generation\ rate\ (t\ COD/y) = \sum_{i=3}^{n} Feedstock\ production\ rate\ (t\ dry\ matter/y)\ \times (Composition)_i\ \times (COD\ factor)_i \quad (9)$$

The potential methane production rate from each feedstock was calculated assuming a methane yield of 80% COD/COD, i.e. 0.8 kg of methane as COD is obtained per kg of COD of the feedstock (the remaining 20 % being converted to microorganisms, or remaining undigested). The total potential methane production rate was calculated by adding up the contributions of the various feedstocks. The fraction of the total produced

methane which was originated from carbohydrates, proteins and lipids was calculated by dividing the total generation rate on a COD basis of carbohydrates, proteins and lipids, respectively, by the total feedstock COD production (given by equation (9)).

From the assumed methane yield of 0.8 COD/COD and from the assumed empirical formulas for carbohydrates, proteins and lipids, the mass fraction of each of these biomass components that is converted to methane can be calculated easily. On a mass basis, 0.24 g methane are obtained per g of carbohydrates, 0.22 g methane/g proteins and 0.58 g methane/g lipids. The higher conversion of lipids to methane on a mass basis is understandable if we consider that lipids are less oxidised than carbohydrates and proteins and therefore more energy can be obtained from their combustion than from the combustion of proteins and carbohydrates.

2.2.2 Conversion of the produced methane into energy and electricity

For the calculation of the total energy content of methane, the enthalpy of combustion of methane was assumed to be $8.90 \cdot 10^5$ J/mol (or $5.56 \cdot 10^7$ J/kg). For the calculation of the electrical energy obtainable from methane, we assumed that the total energy content of methane is converted to electricity with an efficiency of 35 %. This is the typical efficiency of energy conversion into electricity using combined heat and power (CHP) units, the most frequent devices used to convert methane energy into electricity in AD plants.

2.3. Calculation of the potential chemicals production

The potential production of chemicals was calculated starting from the calculated COD of each of the feedstock components, i.e. carbohydrates, proteins and lipids (2.1.3). The conversion yield of carbohydrates, proteins and lipids (as COD) into VFAs, ethanol and hydrogen were assumed from the following literature studies: carbohydrates,[41]

(experimental data with glucose as substrate at pH 5.5); proteins,[42] (experimental data with peptone as substrate); lipids,[43] (stoichiometry of oleate conversion). The pathways for the AD of biomass components into the chemicals considered here are reported in the literature.[2,44]

The production rate of each chemical was calculated from the generation rate of carbohydrates, proteins and lipids, converted into COD units, and multiplied by the respective conversion yield. This is shown by Equation (10), where *i* corresponds to carbohydrates, proteins or lipids and *j* to a specific chemical (such as ethanol, acetate, propionate, etc.):

$$(Chemical\ production\ (t\ COD/y))_j = \sum_{i=3}^{n} Feedstock\ production\ rate\ (t\ DM/y)\ \times$$

$$(Composition)_i \times (COD\ factor)_i \times (Yield)_{i,j} \quad (10)$$

The obtained production rates of the various chemicals were converted from tonnes COD/year to tonnes of chemical/year, using the COD conversion factors for each chemical. For each chemical, the fraction which was originated from carbohydrates, proteins and lipids was calculated by multiplying the total production of carbohydrates, proteins and lipids by the yield of the chemical and by dividing this product by the total production rate of the chemical given by equation (10).

3. Results

Table 1 shows the generation rate and composition of the considered feedstocks. For each feedstock, a range for the generation rate is reported, obtained with the two methods described in section 2.1.1. The chemical composition of the considered feedstocks is reported in terms of the biodegradable components (carbohydrates, proteins and lipids) assumed in this study. The unaccounted fraction to reach 100 % is due to other components, e.g. organic matter which was assumed to be non-biodegradable, such as lignin, and inorganic solids. The total generation rate of the considered feedstocks is in the range 8.2-9.4 Gt dry matter/year and, for most of the considered feedstocks, carbohydrates are the main components.

The data on the generation rate and composition of the various feedstocks were used to calculate the potential methane production in the considered countries and globally (Table 2). Based on the two estimates for the generation rate of each feedstock reported in Table 1, a lower and upper range for the potential methane production rate was calculated. The lower range was calculated by adding up all the lower estimations and the higher range by considering all the higher estimations. In this way the potential production of methane by AD was calculated to be in the range 1.2-1.4 Gt/year. Carbohydrates are the main methane precursor, representing 76-80 % of the biodegradable COD in the feedstocks, while 14-16% and 6-8% of the potential methane is estimated to originate from proteins and lipids, respectively. Table 2 also reports the corresponding production rate of total energy, which is in the range 68 - 79 EJ/year (assuming complete combustion of the produced methane) and the potential production rate of electrical energy, in the range 24 - 28 EJ/year.

As far as the conversion to chemicals is concerned, the conversion yields of carbohydrates into chemicals reported in Table 3 were assumed in this study. Table 4 reports the calculated potential chemicals production in the considered countries and globally. As for the methane production rate in Table 2, the chemicals production rate in Table 4 are reported as a range, calculated adding up all the lowest and all the highest estimations of the feedstock generation rates in Table 1. On a global scale, the potential production rates of acetic and butyric acids are the highest, and much higher than for the other chemicals. Carbohydrates are the main precursors for all the considered chemicals except for propionic acid. Lipids are estimated to be the origin for 21-28 % of the produced acetic acid and for 12-18 % of the produced hydrogen. This is because AD of lipids is assumed to generate only these two chemicals as intermediates (Table 3). Conversion of proteins to chemicals gives a fraction of the acetic acid (22-24 %), all the propionic acid and a small fraction of the butyric acid (5-6 %).

4. Discussion

4.1. Generation rate of the various feedstocks

Clearly the estimation of the generation rate of the feedstocks has the largest effect on the calculated potential for methane and chemicals production. Among the considered feedstocks, agricultural residues give the largest generation rates, in the region of 4.5-4.7 Gt dry matter per year on a global scale, accounting for at least half of the total generation of dry matter. The two methods considered here give very similar results for the generation of agricultural residues on a global scale. Other literature studies on the generation of agricultural residues are in general in reasonable agreement with these estimates.[30,45] A higher estimate of agricultural residues, 5.4 Gt/year, was also reported,[46] however, this study used harvest indices rather than residue to product ratios and this tends to give higher estimates.[29]

After agricultural residues, the second largest contributor to the dry matter available for AD is cow, pig and poultry manure, which is estimated to be in the range 2.7-2.9 Gt dry matter per year on a global scale. Although the two methods considered here use different approaches for the estimation of the manure generation rate, the results are in very good agreement. This indicates that the total manure generation rate can be estimated quite reliably.

As far as the global production of the OFMSW is concerned, the two estimates give significantly different values, 0.6 and 1.0 Gt/year (as dry matter). In this study the same composition and dry matter content were used, therefore the difference between the two values is due to the difference in the estimation of the total MSW according to the methods used. This difference is probably due to the difference sources used in these two

methods, however this difference has a relatively low impact on the total feedstock generation rate, since the contribution of the OFMSW to the total feedstock is lower than the contribution of manure and agricultural residues.

Energy crops, at least with the assumption that they can make up to 2.4 % of the arable land, and sewage sludge give minor, although not insignificant, contributions to the overall feedstock generation rate.

It is important to observe that the potential methane and chemicals production from AD calculated in this study only refers to the considered feedstocks and not to all the possible organic feedstocks which could be available for AD. Examples of other feedstocks for AD are other types of manure (e.g. goat and sheep manure),[47] concentrated wastewaters such as industrial wastewaters from distilleries, dairy plants, pulp and paper plants, etc., seaweed biomass,[48] forestry residues, waste oils and animal fat, olive oil waste.[49] It is also important to observe that the values reported in Table 1 refer to the total amounts of generated feedstocks, while not all these feedstocks may be collectable. The issue of collection, which is particularly important for manure, is discussed in section 4.4.

4.2 Conversion efficiency to methane and to chemicals

The values obtained for the potential methane and chemicals production depend on the assumptions about the efficiency of COD conversion to methane or to chemicals.

The maximum theoretical conversion yield of the biodegradable COD to methane is 100 % on a COD basis, however this is in practice not possible as inevitably a fraction of the feedstock COD will be converted to microorganisms.[6] The assumed 80 % COD/COD conversion of the feedstock to methane is a high yield, which was used here because the

aim of this paper is to calculate the potential methane production, i.e. the maximum possible methane production under realistic conditions. There are many references where efficiencies close to or higher than 80 % in total COD removal and in the conversion of COD to methane have been reported.[33,50-52] Very high or almost complete degradation of cellulose or of cellulosic materials under anaerobic conditions was reported by several studies, e.g.[53,54], and the topic was summarised in a recent review by this research group.[55] Even for highly lignified woody biomass without pre-treatments (apart from comminution), methane yields higher than 65 % of the theoretical value were reported.[56] High conversion of the influent COD to methane has also been reported for industrial wastewaters, e.g. model Fischer-Tropsch wastewaters (>90 % conversion of the influent COD to methane).[57] Note that these reported literature yields are based on the total COD of the feed and therefore include lignin, where present, while in our analysis we excluded lignin from the influent COD. If in these literature studies the lignin was excluded from the feed COD, their methane yield would have been higher, therefore the assumption of 80 % conversion of the feed COD (excluding lignin) to methane made in this paper is even more justifiable.

As far as the conversion of organic waste to chemicals is concerned, the yields and the distribution of the various chemicals are highly dependent on the digestion conditions e.g., temperature, pH, residence time.[2,58] Therefore, it is clear that the production rate of the various chemicals calculated in this study can be considered just as an example of the potential production of chemicals from biomass. More research is needed to completely understand the effect of the fermentation conditions on the chemicals production for the various feedstocks. Once our understanding on this matter is

developed enough, the fact that the fermentation of the same feedstock gives different chemicals depending on the operating conditions can open up interesting perspectives in terms of adjusting the fermentation conditions to produce the chemicals which are more needed by the market.

4.3 Potential and current role of AD as energy and chemicals production technology

Energy is used as electricity, heat or transportation fuel and the methane produced from AD can be used for any of these purposes. Therefore, it makes sense to compare the total energy obtainable from the anaerobically produced methane with the current total energy production in the selected countries and globally (Table 5). Globally, between 17 and 20 % of the current total energy consumption could be satisfied by the combustion of methane produced by AD. As far as the electricity generation is concerned, globally AD could potentially provide 33-39 % of the current electricity consumption. The potential contribution of AD to electricity generation is higher than its contribution to the total energy generation because electricity accounts for just approximately 18% of the total energy consumption, while it was assumed that the combustion energy of methane is converted to electricity with 35 % efficiency.

In general, these figures indicate that the potential impact and role of AD in the global energy production is very large. However, which fraction of the potential methane obtainable from AD is currently produced using this technology? While there are no reliable figures on the global methane production from AD, data from the UK, Brazil and India indicate that the current generation of methane accounts for very little fraction of the potential methane from AD. In the UK, currently AD generates approximately 0.7 Mt of

methane per year,[59] which corresponds to about 5-7 % of the maximum methane that could be potentially generated using AD in this country. In Brazil and India currently AD generates approximately 0.14 and 1.19 Mt of methane per year, respectively,[60,61] which corresponds to just 0.1% (for Brazil) and 0.6 – 1.0 % (for India) of the potential methane production calculated in this study. These figures indicate that the full potential of AD is very far from being reached, and it is farther from being reached in Brazil and India (developing countries) than in a developed country like the UK. The fact that the full potential of AD is very far from being achieved is also confirmed from the observation that the current global electrical energy generation from biogas is approximately 0.334 EJ/year (based on figures from REN21),[62] i.e. just 0.4–0.5 % of the potential electrical energy obtainable from AD according to this study (68-79 EJ/year, Table 2).

As far as the use of AD in the production of chemicals is concerned, Table 6 compares the current production of the considered chemicals on a global scale with their potential production using AD. Table 6 shows that AD can produce organic acids such as acetic, propionic, butyric and lactic acids in much larger quantities than the current global production of these substances. The potential production of acetic, propionic, butyric and lactic acids by AD is hundreds or thousands of times larger than the current production of these chemicals, which could stimulate a larger use of these chemicals and therefore a larger use of renewable feedstocks in the chemical industry. On the other hand, for ethanol and hydrogen the potential production by AD is comparable to, even though still larger than, their current production. Indeed, this study shows that AD can produce up to 2-3 times more ethanol and hydrogen than the current global production rates of these chemicals.

The use of AD to produce methane for energy purposes is alternative to its use to produce chemicals, therefore the ultimate question is whether AD should be directed towards methane or to chemicals production. The answer to this question depends on many factors, such as the availability of other technologies to produce renewable energy, e.g. wind and solar energy, the availability of other sources of methane, e.g. natural gas, the development of suitable separation technologies for the chemicals produced by AD, the environmental impact of methane and chemicals production, economics, etc. It is not the aim of this paper to provide an answer to this question, however the data in Tables 4 and 6 indicate that less than 1 % of the total feedstock available for AD would be enough to satisfy the current market requirements for many short-chain organic acids. All the remaining feedstock could be used to produce methane and still make a very large impact on the renewable energy production. An interesting third option, proposed by several researchers,[63] is a two-stage AD process, whereby the first stage is aimed at hydrogen production and the second stage at the conversion of the organic acids and the other intermediates produced in the first stage into methane. In this process, the end products of AD are hydrogen and methane. Using our calculated potential hydrogen production in Table 4, and assuming that in the two-stage process 80 % of the biodegradable COD is converted into methane and hydrogen, the COD balance indicates that the two-stage process would produce 0.11-0.13 Gt/year of hydrogen and 1.0–1.2 Gt/year of methane. In this way, we would be still be able to generate more than 2 times the amount of hydrogen currently produced and we would still generate over 80 % of the maximum methane that could be produced if AD was only aimed at methane production. These calculations show that the combined production of hydrogen and methane is a very

interesting option as it would be able to supply large amounts of hydrogen and methane without the need for the separation of the organic acids and alcohols.

4.4 Challenges and research needs

Use of AD to produce methane is an established technology, while its use to produce chemicals is still at the research stage, even though pilot scale installations for hydrogen production from MSW have been reported.[63] The research challenges that still prevent the development of AD for the production of chemicals at large scale can be summarised as follows: control of the spectrum of product distribution, achieving high product concentration in the liquid phase in order to reduce the separation costs, developing new separation processes, achieving fast digestion rates for lignocellulosic substrates. These topics have been discussed and reviewed recently and the reader is directed to these recent papers,[2,7] for an in depth analysis. It is however important to add that separation of the chemicals from the water in the liquid phase may not be needed if they are used as a mixture, e.g. for the production of biodegradable plastics such as polyhydroxyalkanoates (PHAs).[64]

In this section we will focus our discussion on the use of AD for methane production, trying to answer the following question: why is the methane production from AD so much lower than what it could be? In other words, why the full potential of AD in terms of methane and hence renewable energy generation is still so far from being reached?

There are multiple factors that contribute to the answer of this question. While, as discussed in section 4.2, there are many literature evidences indicating that the yield assumed in this study of 80% conversion to methane on a COD basis is achievable, this

yield is not necessarily easy to obtain. For a given feedstock, many factors affect the performance of anaerobic digesters, e.g. residence time, temperature, mixing, acclimation of the inoculum, and the methane yield can be significantly lower than the maximum potential yield if the digestion parameters are not optimised.[65,66] The effect of the nature of the feedstock on the methane yield is also important. Readily biodegradable waste such as food waste are typically converted to methane with higher yields than slowly biodegradable substrates such as manure or straw. For manure, the type of manure seems to have an effect of the methane yield.[33] For slowly biodegradable substrates, the contact time between the microorganisms and the substrate needs to be very long in order to measure the full methane potential. Inhibition can also be another important factor that limits the methane yield in anaerobic digesters.[67] Therefore, the operating conditions of the digesters need to be optimised depending on the nature of the feedstock to obtain the highest possible yields.

Linked to the previous point, another aspect worth considering is that there is often scarcity of data about the efficiency of feedstock conversion to methane in full scale digesters. Indeed, literature studies reporting high methane production from various types of waste are usually carried out at lab-scale[4] under optimised conditions, while the conditions at full scale might be not optimised with consequently lower methane yields. Often full-scale plants are designed without pilot- or lab-scale tests or, when lab-scale tests are carried out, they are often limited to measuring the biomethane potential (BMP) of the feedstock. BMP tests are however carried out in batch and do not necessary give indication on the residence time required at full scale to achieve the maximum methane potential. Consequently, some or many full-scale plants might not be designed with an

adequate residence time. Similarly, mixing of solid or semi-solid digesters might not be easy at full scale and this also might lead to inadequate performance. The publicly available data on the performance of full scale digesters usually reports the methane production rate and/or the electricity production and the feed demand rate. It is not possible to calculate how efficiently the digester works, i.e. which percent of the COD of the feed is converted to methane, from this data alone. It is also worth noting that in many cases, the efficiency of anaerobic digesters is reported in the literature as volume of methane per unit of organic (usually volatile) solids, e.g. as Nm^3/kg VS, rather than as percentage on a COD basis as in this study. Reporting the efficiency of digesters in units such as Nm^3/kg VS is valuable, however the use, in addition or in alternative, of percentages on a COD basis would facilitate the assessment and comparison of the efficiency of digesters among different studies and different feedstocks. Indeed, having a value for the digestion efficiency in Nm^3/kg VS does not tell how close the digester is to converting all the organic matter in the feed because the theoretical maximum (which depends on the empirical formula for the organic solids) is not known. On the other hand, an efficiency expressed as percentage on a COD basis does give this information, because the theoretical maximum is 100%.

Another issue is the collection and transportation of the waste. The generation of organic waste is often very spatially widespread with many small producers. This is the case, e.g. for MSW, especially for small communities, and for manure and agricultural residues generation by small farms. In these cases, the waste should be collected and transported to a central location where the anaerobic digester is located, and the collection and transportation costs can be significant. This has historically hindered the development of

AD. Large differences in the collection of animal manure depending on the nature of the farm have also been reported,[21] e.g. manure from beef cows was assumed not to be collected at all, while 85% of poultry manure was collected. However, despite these limitations, the role of AD in the treatment of MSW is increasing rapidly in Europe and is predicted to increase further in the coming years. The role of AD is also increasing rapidly in the treatment of farm waste, both for large and small-medium farms. As an example, an AD plant treating manure from a farm with 80,000 dairy cows is in operation in Punjab, India.[68] An important help towards the increasing diffusion of AD is the development of small-scale digesters which will be specifically valuable to isolated communities or small farms.[69]

The need to separate the biodegradable organics from other non-biodegradable solids, which is especially important for MSW, is also a problem that is limiting the diffusion of AD. For example, Satchatippavarn *et al.*[70] reported that the municipality of Bangkok, Thailand, generates over 2.7 Mt of MSW per year of which 59 % is biodegradable. However, the vast majority (over 85 %) of this waste is dumped into landfills and open dumps and only 0.4 % of it is treated by AD or composting. In this case, one of the problems is the separation of the biodegradable organic matter from other materials such as plastics. Separation at the source of biodegradable from non-biodegradable waste, widely practised in some countries, is the possible solution to this problem.

Another important problem that is limiting the use of AD is the high capital cost of the plants. To this regard, one of the challenges is how to achieve the long SRT which is often needed in anaerobic digesters with a relatively small (and therefore with a low capital cost) reactor volume. Fixed-bed or UASB reactors can provide the solution to this

challenge, since in these systems the hydraulic and solids residence times are not coupled and therefore long SRTs can be maintained with a relatively small reactor volume.[71] It is also worth observing that there has been an increase in recent years in the development and commercialisation of small scale digesters and this is likely to have a positive impact towards the reduction of capital costs.

Finally, it is important to observe that many of the types of organic waste considered in this study have other uses, which compete with their potential use for AD. E.g., the organic fraction of MSW can be converted to compost, manure can be spread on land providing large amounts of nitrogen, phosphorus and potassium, agricultural residues can be combusted to generate energy, and sewage sludge can be spread on land. All these alternative uses of organic waste have their own advantages and disadvantages, and the selection of the best possible use of the waste will be dependent on local circumstances. It is not the aim of this paper to compare AD with other technologies for waste valorisation, and studies which use economic return[66] or other methodologies for this analysis have been reported. However, it is worth observing that AD can be often used in conjunction with, rather than in alternative to, other valorisation technologies. For example, the digestate from AD processes contains most or all the mineral elements (e.g. N, P and K) in the feedstock, therefore the combination of AD and spreading the digestate on land can be seen as a way to convert the organics into energy, while still recovering and reusing the inorganic minerals in the feedstock.

In summary, the main research needs in order to achieve the full potential of AD for methane production can be deducted from the analysis of the challenges reported above and can be summarised as follows:

- Identification of the operating conditions that maximise the methane yield for the various feedstocks;
- Progress on the AD of lignocellulosic biomass;
- Optimisation and maximisation of the methane yield for full scale digesters.

5. Conclusions

Based on the estimated composition and generation rate of five biomass feedstocks, and based on the assumption of a methane yield of 80% COD/COD, AD can produce an amount of methane with an energy content equivalent to 17–20 % of the current global energy consumption. As an alternative, AD can be directed towards the production of organic acids, namely acetate, butyrate, lactate and propionate, at rates equivalent to hundreds or thousands of times their current production rates. Ethanol and hydrogen can also potentially be produced at rates up to 2-3 times higher than their current production rates. In summary, this study indicates that AD has a very high potential for the generation of energy and/or chemicals in a fossil-fuel free world.

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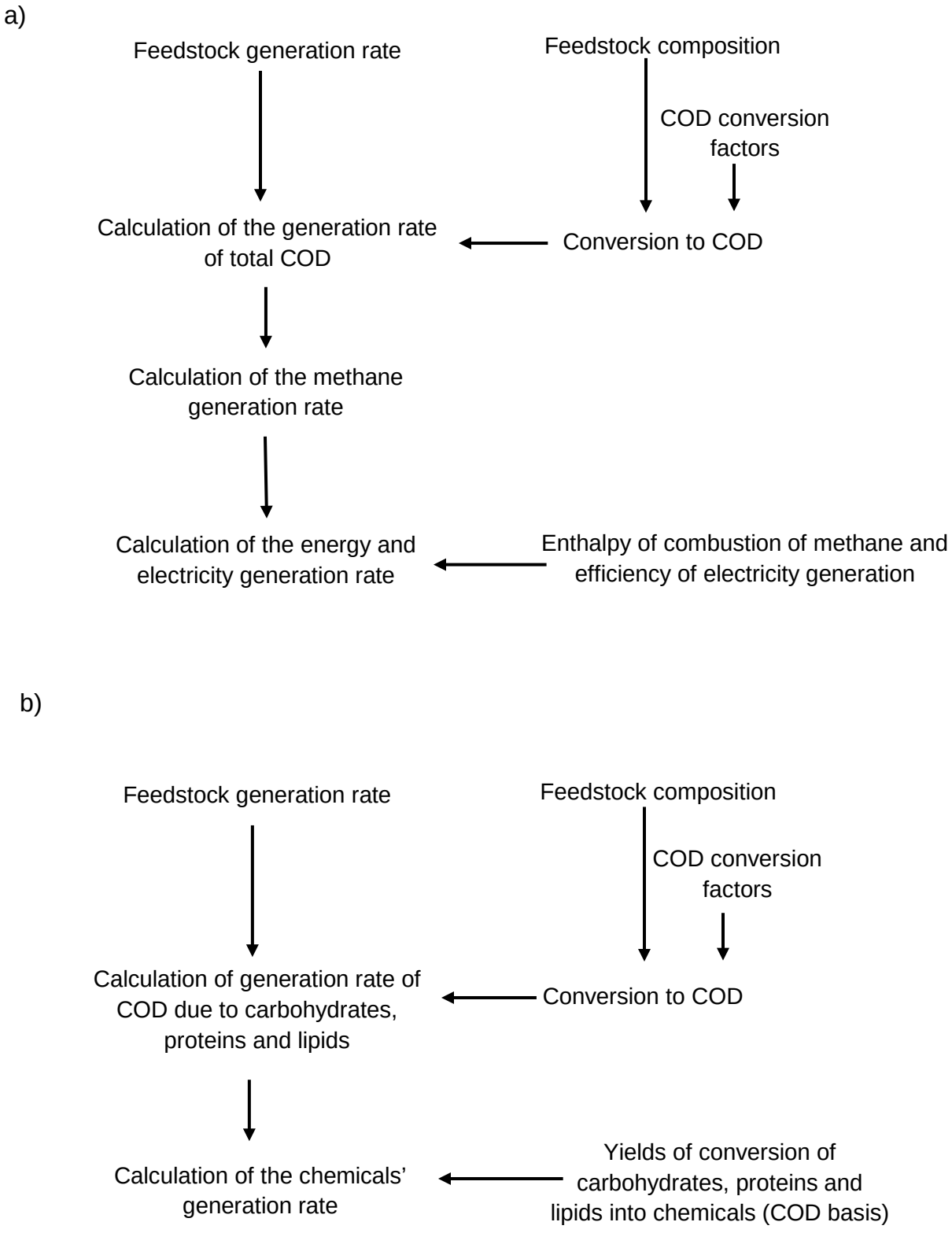

Figure 1. Scheme of the procedure used to calculate the potential methane generation rate (a) and the potential chemicals production rate (b)

Table 1. Generation rates and composition of the various feedstocks. The generation rates are given in Mt of dry matter/year. The composition is given as fraction of the total day matter. ([a] - Method 1; [b] - Method 2)

	Generation rates					Composition		
Feedstock	**UK**	**Brazil**	**India**	**Nigeria**	**Global**	**Carbohydrates**	**Proteins**	**Lipids**
OFMSW	10.0[b]-13.4[a]	24.1[b]-24.8[a]	52.1[a]-56.7[b]	12.2[a]-12.7[b]	594.0[b]-1,021[a]	0.57	0.16	0.19
Manure	18.9[b]-19.0[a]	82.9[b]-329.0[a]	150.0[b]-270.0[a]	18.8[b]-32.0[a]	2,683[b]-2,853[a]	0.56	0.14	0.062
Energy crops	1.5[a]-3.0[b]	17.4[a]-34.9[b]	37.5[a]-75.0[b]	8.4[a]-17.0[b]	335[a]-670[b]	0.66	0.081	0.019
Agricultural residues	25.0[a]-35.7[b]	315.8[a]-365.0[b]	422.4[a]-617.4[b]	42.7[a]-118[b]	4,502.8[a]-4,684.0[b]	0.70	0.038	0.020
Sewage sludge	1.0[a]-1.2[b]	3.0 [a]-3.8 [b]	19.1[a]-24.0 [b]	2.7 [a]-3.4 [b]	107.3[a]-135.0 [b]	0.27	0.42	0.13
Total	56.4-72.2	443.2-757.4	680.7-1,043.0	84.8-182.9	8,222.0-9,362.1			

Table 2. Calculated potential methane production rates. Values in brackets in the Global column represent the fraction of the total methane which comes from, left to right, carbohydrates, proteins and lipids.

	UK	Brazil	India	Nigeria	Global
Potential methane production rate (Mt/year)	10.2-13.3	77.1 – 121.7	119.4 – 178.0	15.4 – 32.0	1,222.1–1,417.4 (76-80/14-16/6-8)
Potential total energy production rate (EJ/year)	0.6 - 0.7	4.3 – 6.8	6.6 – 9.9	0.9 – 1.8	67.8 – 78.7
Potential total electricity production rate (EJ/year)	0.2 - 0.3	1.5 – 2.4	2.3 – 3.5	0.3 – 0.6	23.7 – 27.5

Table 3. Assumed yields of the various chemicals obtainable from AD. All values are in COD/COD.

Chemical	Carbohydrates	Proteins	Lipids
Acetic acid	0.13	0.30	0.67
Propionic acid	-	0.09	-
Butyric acid	0.46	0.15	-
Ethanol	0.07	-	-
Lactic acid	0.03	-	-
Hydrogen	0.14	-	0.28

Table 4. Calculated potential chemicals production rates in Mt/year. Values in brackets in the Global column represent the fraction of each chemical which comes from, left to right, carbohydrates, proteins and lipids.

Chemical	UK	Brazil	India	Nigeria	Global
Acetic acid	10.4 – 13.5	60.8 – 97.5	103.4 – 149.0	15.2 – 27.0	1,194.6 – 1,498.4 (50-56/22-24/21-28)
Propionic acid	0.5 - 0.5	2.5 - 5.8	4.5 – 7.1	0.6 – 1.1	58.8 – 69.0 (0/100/0)
Butyric acid	10.1 – 13.2	86.0 – 132.3	127.7 – 192.3	15.4 – 34.7	1,494.0 – 1,685.6 (94-95/5-6/0)
Ethanol	1.3 – 1.8	11.8 – 17.7	17.3 – 26.0	2.1 – 4.7	201.4 – 226.7 (100/0/0)
Lactic acid	1.1 - 1.4	9.2 – 13.9	13.6 – 20.4	1.6 – 3.7	157.7 – 177.5 (100/0/0)
Hydrogen	0.9 - 1.1	6.2 – 9.1	9.6 – 14.1	1.3 – 2.6	110.1 – 131.7 (82-88/0/12-18)

Table 5. Potential role of AD in the total energy production and in electrical energy production

	UK	Brazil	India	Nigeria	Global
Current total energy consumption rate (EJ/year)[72]	5.15	9.72	23.26	4.88	394.56
Fraction of the total energy that can be potentially provided by AD (%)	11 - 14	44 - 70	29 - 43	18 - 36	17 - 20
Current total electricity production rate (EJ/year)[1]	1.09	1.80	3.41	N/A	71.42
Fraction of the total electricity that can be potentially provided by AD (%)	18 - 24	83 - 131	68 - 101	N/A	33 - 39

Table 6. Comparison of the potential production rate of the chemicals considered in this study with their current production rate

	Acetic acid	Propionic acid	Butyric acid	Ethanol	Lactic acid	Hydrogen
Current production rate (Mt/year)[2,73]	7	0.4	0.08	70	0.15	50
Potential production rate by AD/current production rate	171 – 214	147 – 172	18675 – 21070	2.9 – 3.2	1051 – 1184	2.2 – 2.6