



**IEA Bioenergy**  
*Technology Collaboration Programme*

# Gasification applications in existing industrial and agricultural infrastructures for production of sustainable value-added products

Case study 2: Gasification for production of biomethanol by coupling with anaerobic digestion

IEA Bioenergy: Task 33

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Case study 2: Gasification for production of biomethanol by coupling with anaerobic digestion

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## Abstract

This section presents two case studies on methanol production from renewable feedstocks (i.e. biomass and OFMSW) via gasification integrated with anaerobic digestion.

As known methanol is an important chemical good with a large employment as-it-is, as well as a key chemical intermediate, also related to the fuel sector. To achieve the most appropriate value of the so called *Stoichiometric Number* (SN, i.e.  $(\text{H}_2-\text{CO}_2)/(\text{CO}+\text{CO}_2)$  ratio) in the gas to be converted, two pathways are adopted. Specifically, the first case describes the production of biomethanol using the producer gas from biomass gasification enriched in  $\text{H}_2$  by addition of a gaseous stream obtained via steam reforming of AD biomethane. The second case extend the approach to a methanol production entirely based on anaerobic digestion, where the producer gas is obtained by gasification of the residual digestate, thus aiming to maximize the exploitation of the feedstock processed in its whole.

## Introduction

Methanol is an important chemical good with a large employment as-it-is, as well as a key chemical intermediate and a fuel relevant for energy applications. In view of the goals about climate neutrality expected by 2050, projection for circular economy and sustainable strategies programmes, a need arises for green approaches to the production of such an important chemical. The upgraded processes should be such that they can be considered for the replacement of the more conventional ones based on the use of fossil sources and in particular on the process of steam methane reforming of natural gas.

Over the last decade, anaerobic digestion has experienced a great expansion. At EU level, as indicated by the European Biogas Association (EBA), data recently collected and assessed shows that the number of biomethane plants in Europe has doubled between 2018 and 2020, passing from 483 in 2018 to 729 [1]. According to the EBA Statistical Report 2020, there are 19 countries producing biomethane in Europe [2]. The sector is expected to further grow, and in fact by 2030, the biogas and biomethane sectors combined is expected to double their production and by 2050 quadruple. [3]

Alongside the production of biogas/biomethane, the production of anaerobic digestate is also clearly expected to increase. Some studies indicate that the reference use as agricultural fertilizer and soil improver will not be able to accommodate the entire production [4,5]. It is therefore necessary to think about possible alternatives for its use.

According to a report delivered in 2019 by TNO, the global compost production in Europe, coming from the biowaste management, was estimated at 15.8 Mton of which 4.1 Mton were digestate [6]. Digestate is often widespread in agricultural fields near the site where it is produced, unfortunately this is not always the optimal strategy as it could cause soil and water pollution, namely eutrophication, under specific conditions. A further reason for the need to evaluate other possible options of use, emerges when considering the fact that not only agricultural by-products (e.g. slurry from livestock), but also the organic fraction of municipal solid waste can be subjected to anaerobic digestion. The assessment of the risks associated with contaminants from digestate, as well as compost, used as a fertilizer and soil improver was in fact the subject of the dedicated assessment titled "Digestate and compost as organic fertilisers - Risk assessment and risk management options" (reference FC/2015/0010 - SR3 under Framework Contract ENV.A.3/FRA/2015/0010). In a final report [7] prepared for the European Commission, DG Environment, 17 substance groups were identified as potential critical contaminants in digestate and compost and based on these categories risk management options were outlined. Therefore, planning how to manage the digestate residue from AD is a crucial task, especially when spreading in agricultural land is not possible.

In anaerobic digestion usually the feedstock conversion is indeed incomplete. Quite often in fact up to 50% of the organic matter for several reasons remains unconverted [8,9], hence the fuel nature of the digestate residue and in turn the possibility of its reuse for energy purposes. In that sense, gasification is one of the available options.

In the present study biomass/biowaste gasification interconnected with the growing availability of biomethane and digestate, as a consequence of the spread of anaerobic digestion, was considered in connection to the production of green methanol (hereinafter biomethanol), i.e. methanol of renewable origin. Specifically, two case studies were considered. The first case study evaluated the production of biomethanol by enriching in hydrogen the producer gas from biomass gasification via steam reform of AD biomethane,

while the second case study evaluated a deeper integration between gasification and anaerobic digestion by considering the anaerobic digestate as a feedstock to the gasification stage.

## Integration between gasification and anaerobic digestion to methanol production: two case studies

The potential integration of biomass gasification and anaerobic digestion plants has been assessed. Such an integration in fact may be considered a useful strategy to drive towards the production of green chemicals from biomass through processes of heterogeneous catalysis. As known, gasification in general produces a gas with a composition not suitable for direct conversion into chemicals due to the low  $H_2/CO_x$  ratio. The right  $H_2/CO_x$  ratio depends on the specific targeted chemicals, but in any case, a preliminary stage of  $H_2$  enrichment is typically required. To achieve the required gas composition, the increase in  $H_2$  content can be achieved by following two methods, i.e., the endogenous and the exogenous pathways.

The anaerobic digestion process mainly produces biogas (a mixture of methanol and carbon dioxide) and digestate (the residual fraction of the biological process). In the past, biogas has been mainly used for electricity and heat generation, in order to satisfy on-site energy needs, particularly in the case of farms. Due to climate change and to the European rules on fossil exploitation, the application of anaerobic digestion for bio-methane production has received a growing attention [10,11]; to facilitate its development, it has been, and still is, supported with policies of production incentives. Upgrading systems able to convert biogas into bio-methane are currently available at commercial scale, therefore the production of bio-methane for automotive is usually preferred, especially from an economic point of view. In fact, the production of electricity from renewables (e.g. solar and wind) has made giant strides from a technological point of view, allowing to produce electricity at low cost. On the contrary, the production of alternative fuels still remains an open challenge.

The know-how developed about the anaerobic digestion process, today allows to process several feedstocks at commercial scale, such as the organic fraction of municipal solid waste. This further step forward towards waste-to-fuel concept, strongly pushed towards the installation of several plants of waste-to-methane process, thanks to the income from both municipal waste management and bio-methane sales. One of the main issues of anaerobic digestion plants is digestate management. Digestate is usually stabilized and transformed by aerobic process into compost, which may be used as agricultural soil amendment, albeit it is usually sold at very low price.

With a look at the future, the two main streams produced from anaerobic digestion plants (i.e. biogas and digestate) might be used for the production of chemicals and fuels, and gasification may play a role for this further transition towards a low-carbon economy. In this case study, several aspects of simulated gasification-anaerobic digestion integrated process are assessed and discussed. In particular, the report mainly addressed the production of methanol.

### Description of the cases

In this section the production of methanol is shortly discussed. More details are reported in the paper of Giuliano et al. [12]. The production of methanol is assessed by considering the conventional process. Methanol is a valuable substance that may be used both as a fuel and as an intermediate, as shown in Figure 1 where the ratio  $(H_2-CO_2)/(CO+CO_2)$  is the so called stoichiometric number (SN) and is quoted in molar fractions. According to the most common industrial procedures for methanol synthesis, the gaseous stream to address to the conversion reactor is characterized by an SN ratio around 2 [13-23].

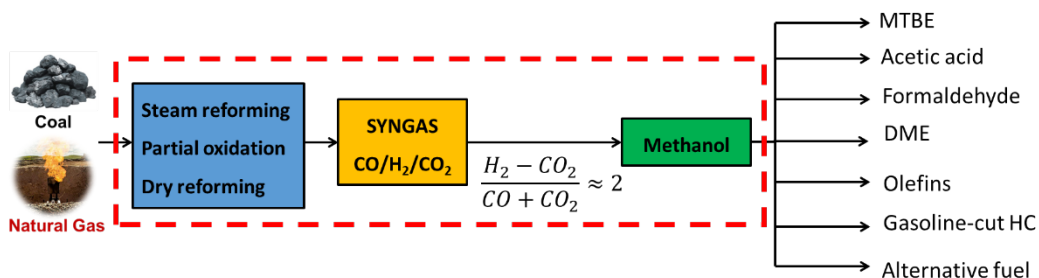


Figure 1 - Methanol production and utilization chain

Methanol is a primary raw material for the chemical industry.

According to a recent IRENA report, worldwide annual production of methanol nearly doubled over the past decade to reach about 98 Mt in 2019. [24] The conventional process is a multi-step process consisting of (i) steam reforming (or alternatives: partial oxidation, dry reforming) of natural gas (SMR) or coal for syngas production, (ii) syngas upgrading to obtain a mixture with a  $H_2/CO$  ratio suitable for the synthesis, (iii) crude methanol synthesis and (iv) methanol purification.

Concerning carbon dioxide emission, coal-based plant has the highest carbon footprint, whilst when natural gas is used, lower  $CO_2$  amount is emitted. In particular, the carbon dioxide emissions are about  $1600 \text{ kg}_{CO_2}/\text{t}_{MeOH}$  for coal-based processes and about  $900 \text{ kg}_{CO_2}/\text{t}_{MeOH}$  for natural gas-based process. [12] These emission values can strongly be reduced considering the implementation of effective carbon capture units to sequester the  $CO_2$  released in the process (e.g. blue methanol production) or by replacing the fuels of fossil origin with renewable ones, i.e. biomass or bio-waste.

In the following, two approaches based on the processes of biomass/biowaste gasification and anaerobic digestion are presented as case studies. Specifically:

Case 1: biomass gasification is coupled to a unit of bio-methane steam reforming. Such pattern is selected since likewise to SMR, steam reforming of bio-methane produces a hydrogen rich syngas, while biomass gasification usually produces a hydrogen lean syngas [25-27]. Therefore, the integration of these two processes may be useful for the production of a syngas with a composition, i.e. the ultimate SN ratio, suitable for the methanol synthesis.

Case 2: as case 1, in which biomass is substituted with digestate produced from anaerobic digestion process.

The technical aspects of this alternative are herewith discussed.

## Materials and methods

The gasification unit considered in case study 1 is based on a steam/oxygen gasification process carried out in a bubbling fluidized bed reactor of specific configuration and biomass used, described in Barisano et al. [28]. In particular, this paper reports a study about a pilot scale internally circulating bubbling fluidized bed reactor using almond shells as biomass feedstock. Briefly, biomass is gasified at atmospheric pressure and  $820\text{-}880 \text{ }^\circ\text{C}$  by using steam/ $O_2$  mixture as a gasification agent. Both char and tar present in the reactor out-stream are abated with



ceramic filter and wet scrubber, respectively.

In the case study 2, to take into account a more heterogeneous nature of the digestate residue, for its gasification a unit based on a rotary kiln reactor was considered preferable. Air was used as a gasification agent; the process was carried out at temperature in the range 800-830 and the produced gas was purified by considering cyclones and wet scrubbing. The specific configuration and digestate used were described in Freda et al. [29]. A limited number of papers are devoted to digestate gasification. Freda et al. [29] studied the effect of process parameter such as residence time and equivalence ratio on digestate gasification in a rotary kiln bench-scale plant. Rotary kiln is a well-known technology usually used for uncollected waste disposal, but that may be also used for gasification of several feedstocks. Due to the availability of experimental results, data obtained by Freda and co-workers were adopted in this study.

The gas stream finally obtained from each gasification approaches had the average composition reported in Table 1.

Table 1. Composition of the syngas stream of gasification unit (%<sub>vol</sub>, DRY)

	Feedstock	CO	H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
Case 1	Almond shell	28	32	25	10	5
Case 2	Digestate	14	12	13	5	56

Taking into account the binding arising from the SN ratio for the syngas conversion to methanol, as a base of calculation to allow a comparative approach between the two cases, an anaerobic digestion plant with a capacity of 10 t/h of organic fraction of municipal solid waste (OFMSW) is considered. Such plant may be able to produce up to 500 Nm<sup>3</sup>/h of biomethane, starting from a biogas assumed to have a CH<sub>4</sub>/CO<sub>2</sub> molar ratio of 60/40.

The process scheme of each case considered are shown in Figure 2-3. For the process simulation of these pathways the commercial software ChemCAD from *Chemstations Inc.* was used.

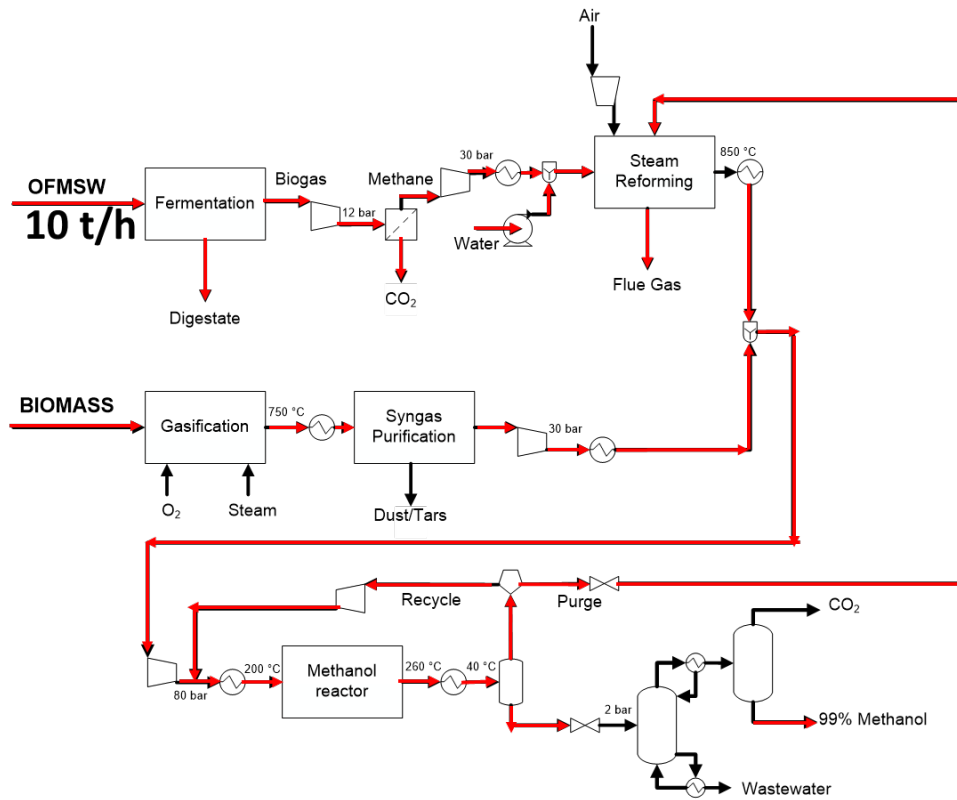


Figure 2 - Process flowsheet for Case 1.

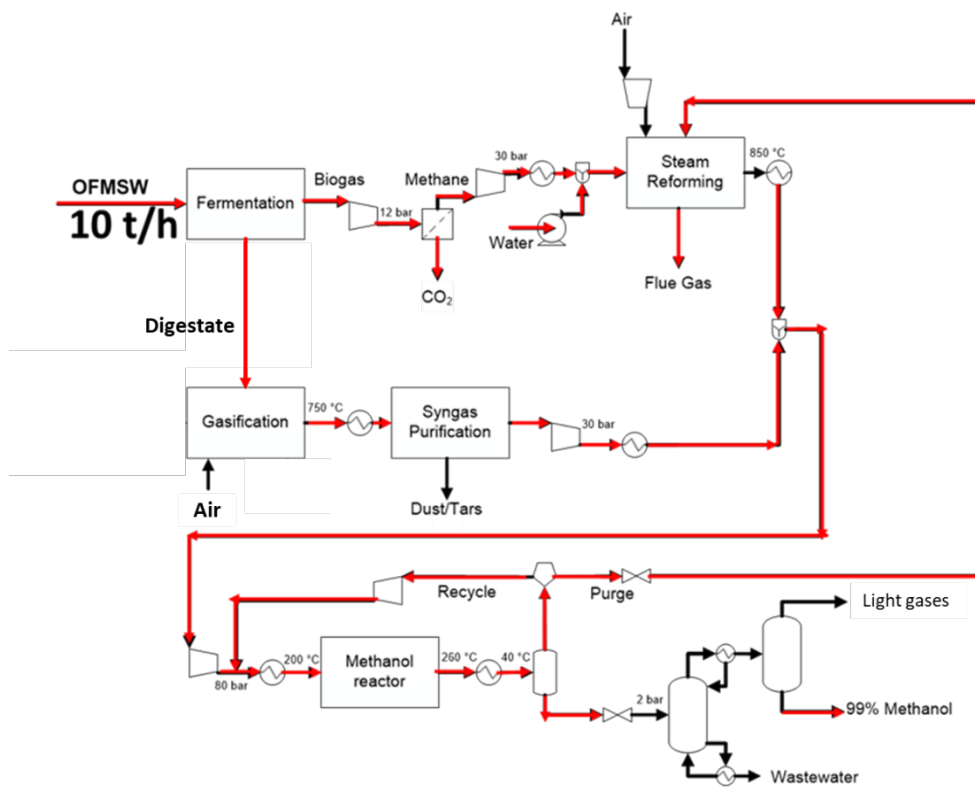


Figure 3 - Process flowsheet for Case 2.

In setting up the process modeling, the following technical aspects were assumed:

- In case study 1 where gasification is based on a process of steam/oxygen biomass gasification, the utilization of both oxygen and steam allows to obtain a quasi-autothermal process. Oxygen was assumed to be produced by conventional air separation unit;
- In case study 2 where gasification is based on gasification of the anaerobic digestate from the AD plant, the N<sub>2</sub> present in the producer gas due to the use of air as a gasifying agent was not removed until the stage of methanol recovery;
- In the simulation, it was assumed that the bio-syngas leaves the gasifier at about 750 °C and under atmospheric pressure;
- High pure bio-methane was obtained by membrane separation operating at 12 bar. This assumption is valid for already existing bio-methane plant;
- Steam reforming of bio-methane is carried out at 850 °C and 30 bar with a steam-to-methane molar ratio equals to 3.4;
- Methanol synthesis is carried out at 80 bar in an adiabatic reactor, with a reactor inlet temperature of 200 °C. The reactor was assumed to operate under equilibrium condition. As usually packed-bed reactor is used, a pressured drop of 2 bar is adopted;
- Water and other impurities (e.g. dissolved gases) are removed from methanol by distillation, to obtain a methanol stream with a purity of 99%. The unreacted syngas is re-compressed and recycled to the reactor. A purge fraction is used as fuel for the steam reformer.

An overview about the main process parameters is reported in Table 2.

Table 2. Process simulation parameters.

OFMSW flowrate (t/h)	10	MeOH reactor pressure (bar)	80
Biogas yield (t/t <sub>OFMSW</sub> )	0.5	Biomethane membrane temperature (°C)	40
Membrane biomethane recovery (%)	100	SR temperature (°C)	850
Biomethane purity (%)	100	Biomass syngas temperature (°C)	750
Steam to carbon ratio in SR (t <sub>S</sub> /t <sub>CH4</sub> )	3.4	MeOH reactor inlet temperature (°C)	200
Biomass syngas yield (t/t <sub>DRY</sub> )	1.07	Column pressure (bar)	2
Digestate syngas yield (t/t <sub>DRY</sub> )	0.99	Recycle condenser temperature (°C)	40
Biomethane membrane pressure (bar)	12	Stoichiometric ratio air/purge	2
SR pressure (bar)	30		

For each case, the environmental impact was estimated in terms of equivalent carbon dioxide (CO<sub>2</sub>eq) emission. The main items used for carbon emission calculation are summarized in Table 3.

Table 3. Equivalent CO<sub>2</sub> emission parameters.

Process item	Set-up value
Electricity (kgCO <sub>2</sub> eq/MWhe) [30]	600
Biomass feedstock (kgCO <sub>2</sub> eq/t) [31]	-1449
OFMSW (kgCO <sub>2</sub> eq/t) [32]	-1597
Digestate feedstock(kgCO <sub>2</sub> eq/t) [33]	-1821
Wastewater (kgCO <sub>2</sub> eq/t) [30]	500
Pure oxygen (kgCO <sub>2</sub> eq/t) [34]	282
Process water (kgCO <sub>2</sub> eq/t) [30]	6.5

## Results

### Case 1 - Biomass gasification coupled with Anaerobic Digestion of OFMSW for producer gas H<sub>2</sub>-enrichment

In the case 1, the biomass flowrate strongly affects the syngas composition for methanol synthesis, as well as the total and specific power consumption. The obtained results are reported in Figure 5. In particular, the methanol yield decreases from about 82% to about 62% by increasing the biomass-to-OFMSW weight ratio from 0 to 0.4. This effect is mainly related to the decrease of the (H<sub>2</sub>-CO<sub>2</sub>)/(CO+CO<sub>2</sub>) ratio. On the whole, due to the increase of syngas amount, the methanol productivity increases from 2.8 t/h to 3.5 t/h by increasing the biomass-to-OFMSW weight ratio from 0 to 0.4. Despite the increase of syngas to be compressed, the increase of the biomass flowrate causes a slight decrease of electricity demand for compression. This effect is related to the total methanol productivity. In fact, by increasing the biomass-to-OFMSW weight in the considered range, the total compression power increases from 4 MWe to about 4.8 MWe, while the specific power consumption is reduced from about 55 KWe/ton/h to about 45 kW/ton/h.

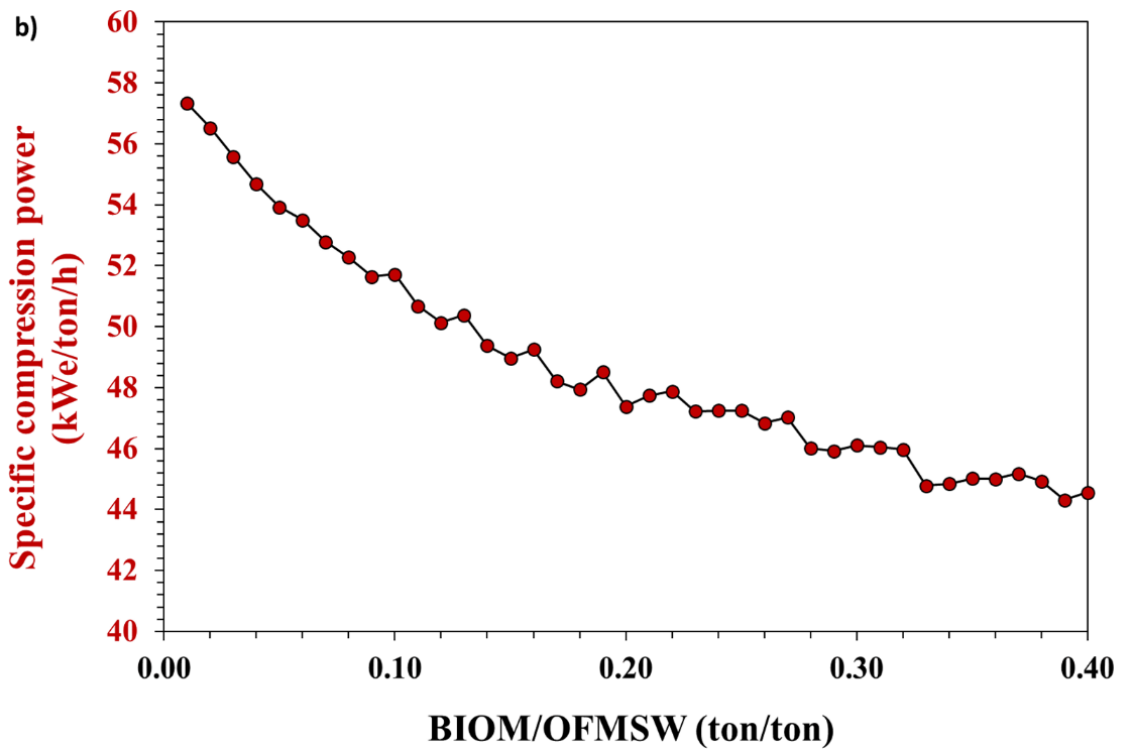
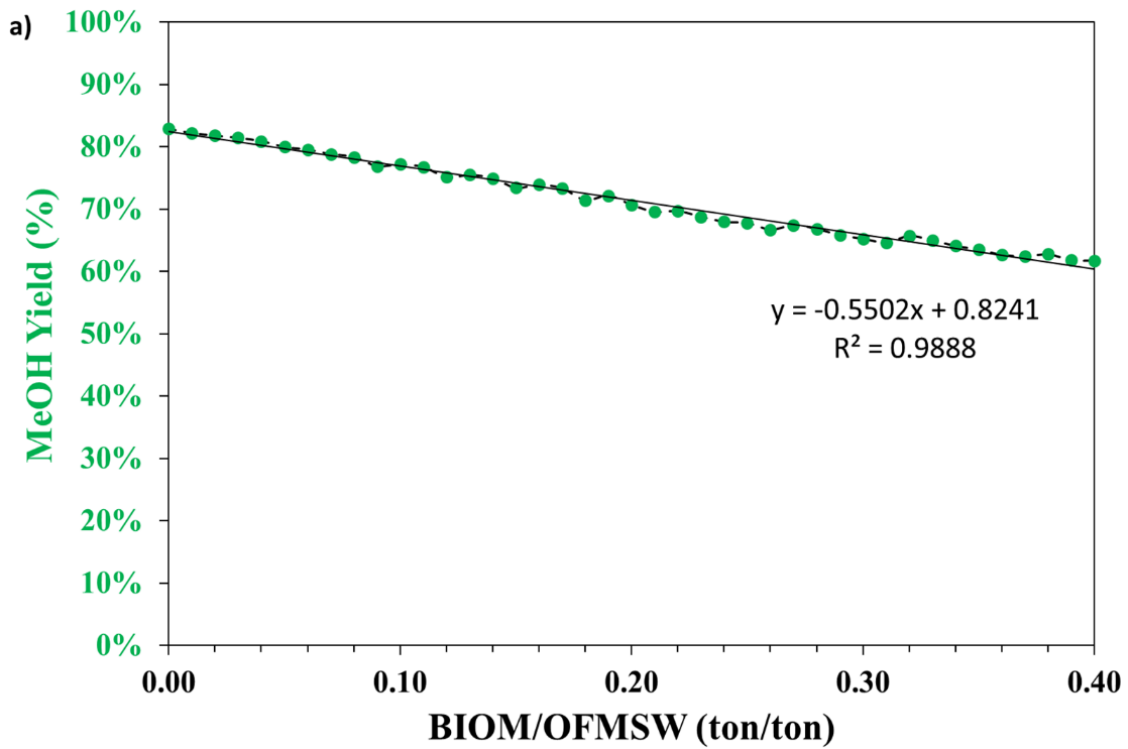


Figure 4 - Effect of biomass-to-OFMSW ratio on (a) methanol yield and (b) specific compression power consumption.

The main results, in terms of mass/energy balance and environmental impacts, are reported in Table 4.

Table 4. Main results of Case 1.

<b>Main process results</b>	
Case	1
Bio-syngas from Biomass gasification (t/h)	2
Pure oxygen to gasification (kg/h)	584
Steam to gasification (kg/h)	824
$(\text{H}_2\text{-CO}_2)/(\text{CO}+\text{CO}_2)$	2.01
MeOH production (t/h)	3.06
Purge ratio (%)	4
Electricity consumption (MWe)	4.4
Process water consumption (t/h)	6.8
<b>Environmental impacts (ktCO<sub>2</sub>eq/y)</b>	
OFMSW	-120
Digestate	60
Flue gas	18
Wastewater	18
CO <sub>2</sub> from fermentation	24
Electricity	20
Biomass	-20
Pure oxygen	2
Total	2

### Case 2 - Anaerobic Digestion of OFMSW and digestate gasification to methanol production

By considering the above mentioned aspects related to methanol production (i.e. a  $(\text{H}_2\text{-CO}_2)/(\text{CO}+\text{CO}_2)$  ratio equals to 2), the adopted integrated scheme, and the composition of digestate-derived syngas, the digestate flowrate that may be valorised by means of gasification is equals to about 3530 kg/h, dry basis. In that condition, the syngas produced from gasification may be mixed with the syngas produced by steam reforming of bio-methane with the production of a syngas suitable for methanol production.

In Table 5 the main process results are summarized.

Table 5. Main results of Case 2

<b>Main process results</b>	
Case	2
Bio-syngas from Digestate Gasification (t/h)	3.5
Air to gasification (kg/h)	3.2
(H <sub>2</sub> -CO <sub>2</sub> )/(CO+CO <sub>2</sub> )	2.1
MeOH production (t/h)	2.49
Gasification residue (t/h)	1.4
Purge ratio (%)	6.0
Electricity consumption (MWe)	2.5
Process water consumption (t/h)	5.9
<b>Environmental impacts (ktCO<sub>2</sub>eq/y)</b>	
OFMSW	-120
Digestate	18
Char	16.1
Flue gas	16.5
Wastewater	17.2
CO <sub>2</sub> from fermentation	24
Electricity	11.4
Total	-16.8

The productivity of methanol in the case 2 is slightly lower than case 1, i.e. 2.49 t/h vs 3.06 t/h. This may be associate to a different syngas composition. Similarly, the syngas composition affects the composition of purge stream and then its heating value, with an effect on purge flowrate. Indeed, purge stream is burned to produce heat for steam reforming unit. Syngas produced from digestate has a LHV lower than the syngas produced from biomass, and then a higher purge flowrate is requested for steam reformer.

The amount of electricity is lower in the case of digestate gasification. This is related to the utilization of air respect to pure oxygen, as in the case of biomass gasification.

Globally, from an environmental point of view, digestate gasification coupled with anaerobic digestion seems to be a promising way for producing methanol. Moreover, according to the simulation results, based on the biomethane available for the syngas SN ratio adjustment toward methanol requirements, the proposed approach also appears to be potentially adequate to provide the answer to the issue of digestate overproduction. In fact, of the digestate amount produced at the AD process part of it can still be kept available for the agricultural market.

Regarding the residual char, which, according to the results in Table 5, is a side product of gasification, options for valorisation need to be considered. Possible reuse will clearly depend on its chemical characteristics. Among the various possibilities, in the absence of heavy metals, the agricultural sector could also be an application for biochar, where it could potentially be used as soil enhancer [35] or readdressed back to the digester to stabilize the AD process [36-38]. A second option could be in substitution of activated carbon [39,40]. More recently, studies have been undertaken to evaluate biochars as raw materials for preparing synthetic graphite, to be further used in some types of batteries and fuel cells, and in carbon electrodes for electrochemical capacitors.[41]

The technical challenges on the integration of gasification with anaerobic digestion are discussed below.

## Gasification coupled with anaerobic digestion: challenges and perspectives

According to the summary data from the assessment carried out in the two proposed case studies, methanol production appears promising from both a mass/energy balance and environmental point of view. In fact, they can help in exploiting residual feedstocks, which otherwise would be waste requiring to be treated/disposed-off, converting them in a high-value chemical while having a low environmental impact.

The conversion yields of syngas into methanol are, among other aspects, closely linked to the degree of hydrogen enrichment, summarized in the SN parameter, and therefore to the wide availability of biomethane to subject to steam reforming, as a substitute for natural gas, to allow the implementation of the process at the size to achieve techno-economic feasibility. Thanks to the growth that is characterizing the anaerobic digestion sector, also supported by European policies on energy and the environment, the prospects for the future are favorable.

To achieve such goal two further key technical aspects need to be managed, in particular in relation to case study 2 which is the most challenging. Both aspect are related to the exploitation of digestate; these are the moisture content and the risk of ash melting.[40] The gasification processes considered, based on BFB and rotary kiln reactors, treat feedstocks with a relatively low humidity content (< 30%-wt) and producing ash with melting temperatures higher than those at which the feedstock conversion is typically conducted (800-850 °C).

Drying can be an energy demand process [43], however it has to be considered that this treatment is also required for the digestate itself when considering possibility for its wide commercialization and use other than on-site spreading [44]. A reduction of the moisture content below 20%-wt can indeed be achieved via waste heat at the AD site, combustion of off-gas stream from the biogas upgrading to biomethane, and/or in combination with solar technologies [45].

Concerning the ash melting, this risk will actually depend from the specific characteristics of the produced ash that therefore need to be well characterized in its temperature behavior. The use of such digestate can still be evaluated considering gasification at a temperature lower than the most common ones. Gasification at  $T < 800$  °C leads to reductions in conversion efficiencies, so if the ash melting occurs at particularly low  $T$  (< 700 °C) it will be necessary to evaluate the opportunity to reuse the digestate in a mixture with matrices with ash less subject to melting or in an ash melting process.

## Conclusion

Gasification coupled to anaerobic digestion can be a promising approach to produce methanol of renewable origin. Based on the two case studies herein presented, the mass and energy balances are both favorable.

In particular, the second case study, in which the integration between the two processes is the strongest one, proposing the use of anaerobic digestate as feedstock for gasification, is



the most promising in perspective. In fact, it provides a possible alternative use of the solid residue from AD, whose availability is expected to exceed the capacity of use as agricultural soil improver when produced from fermentable agricultural residue or avoid accumulation as waste when the material produced does not reach the specifications for commercial uses.

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