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Waste-to-Methanol: direct CO_2 emissions assessment for the methanol production from municipal waste-derived syngas

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The valorization of municipal waste represents one of the major opportunities for the next future. In particular, the Organic Fraction of Municipal Solid Waste (OFMSW) can be used in anaerobic digesters to produce biogas/biomethane. Furthermore, a fraction of Municipal Solid Waste (e.g. non-recyclable plastics, paper cardboard, etc.) can be converted to Refuse Derived Fuel (RDF). Both biogas/biomethane and RDF may be further converted in syngas (a mixture of H_2, CO and CO_2) by using several technologies, such as steam reforming for the former, and gasification for the latter. Syngas may be used as fuel in CHP plants or for the production of chemical intermediates and fuel. The digestate derived from anaerobic digestion, as well as CO_2 from biogas, can be used as nutrients source to grow microalgae, which are feedstock suitable for supercritical water gasification (SWG). In this paper, an integrated process is proposed, by coupling an anaerobic digestion plant for biomethane production with (i) high-temperature gasification of RDF and (ii) SWG of algae grown up with digestate and CO_2 from biogas. The biomethane is assumed to be converted in syngas by steam reforming. Considering its importance for the chemical industry chain, methanol is considered as a target product. Methanol synthesis is assessed in terms of mass and energy balances and direct CO_2 emissions. The results show that high-temperature endothermic processes require the use of purge gas as a fuel in a burner to sustain itself. The lowest direct CO_2 emission value per kg of methanol produced is obtained in the case of high use of RDF, minimum recycling of CO_2 to algae production and minimum purge ratio.

1. Introduction

The carbon content present in scraps and waste represents an important opportunity for the transition to the Low Carbon Economy. Municipal Solid Waste (MSW) represents the largest amount of produced waste of a country. Therefore, the valorization of MSW is attracting growing attention from both the research and industry sectors. In this regard, the plant capacity is a crucial aspect to be considered. In fact, the plant size should properly be designed in order to have an optimum between investment costs (which are higher for smaller plants) and raw materials supply (that may be a problem for large size plants) (Galanopoulos et al., 2020).

1.1 Literature survey and open challenges

In this framework, the integration of different technologies and processes for the valorization of raw materials may be a strategy to improve the valorization rate of MSW (Giuliano et al., 2019a). Several process technologies can be used to valorize wastes. Gasification, anaerobic digestion, sugar-based plants, chemical looping, microalgae cultivation are some examples of green processes recently proposed in the circular economy framework. In particular, the organic fraction of municipal solid waste (OFMSW) is currently used to produce biogas (a mixture of methane and carbon dioxide) via anaerobic digestion (Pellegrini et al., 2015). Biogas can be then upgraded, e.g. by membrane-based separation systems, to produce bio-methane with CO_2 as a side-product. Bio-methane can be used in the automotive sectors, as well as to produce syngas for the subsequent synthesis of hydrogen, methanol and other fuels or chemicals. Other non-recyclable fractions of MSW (e.g. plastics, paper cardboard, and so on) can be converted to Refuse Derived Fuel (RDF) which may be considered a feedstock suitable for thermal gasification to produce syngas (Lombardelli et al., 2017). Both the processes show some drawbacks. A large amount of CO_2 is usually emitted from anaerobic digesters, while a syngas with a low H/C ratio is obtained from thermal gasification (Sofia et al., 2013). Nevertheless, some strategies may be useful to address such challenges. Syngas may be upgraded to a higher H/C ratio by water-gas shift and carbon capture, while carbon dioxide, coming from anaerobic digestion process and/or carbon capture units, may be used as C-source in photobioreactors producing algae. The latter are in turn feedstock suitable for supercritical water gasification to produce additional syngas (Nurdiawati et al., 2018). Integration of these process technologies may lead to an integrated system for syngas production with very low direct CO_2 emissions. One of the more valuable compounds produced from syngas is methanol, as well for its potential derivates (Bonura et al., 2020). Nurdiawati et al. (2019) studied the conversion of the microalgae into methanol through dual-stage chemical looping and efficient process integration with maximum energy recovery: a conversion process of microalgae into methanol by utilizing CO_2 generated within the process and, thus, with negative-carbon emission. Lombardelli et al. (2017) studied the valorization of Municipal Solid Waste through the gasification of RDF and anaerobic digestion of OFMSW to produce electricity and thermal energy, comparing these processes with the traditional landfill disposal option. To efficiently produce methanol a syngas should have a composition with R ratio, equal to $(H_2 – CO_2)/(CO + CO_2)$ on mole basis, greater than 2 (Bozzano and Manenti, 2016). In general, the first assessment of the environmental impact of new integrated processes aims at estimating the direct CO_2 emissions. Next, it is necessary to evaluate the indirect emissions and, thus, the overall CO_2 emissions, also considering the CO_2 equivalent emissions (Castelo Branco et al., 2013).

1.2 Aim of the work

In this work, an original process flowsheet is proposed to evaluate the direct CO_2 emissions for the production of methanol from both OFMSW and RDF. The integration of anaerobic digestion, RDF/algae gasification, algae photosynthesis with CO_2 and digestate, steam reforming, methanol synthesis is assessed in terms of mass and energy balances. A sensitivity analysis on the main process parameters is performed in order to find the optimal configuration minimizing the direct CO_2 emission per unit of mass of produced methanol.

2. Process simulation methods

2.1 Process flowsheet description

Figure 1 shows the block diagram of the integrated process considered in this work. The OFMSW (Migliori et al., 2019) and RDF (Borgogna et al., 2019) are considered as primary raw materials of the process. OFMSW is fed to an anaerobic digestion process, producing biogas and digestate, while RDF is fed to a gasification unit for producing syngas Digestate is used as a source of nutrients for the cultivation of microalgae (Chakinala et al., 2010). The biogas is purified by membrane technologies, obtaining pure CO_2 and bio-CH_4. The CO_2 from biogas is sent to the microalgae photobioreactors. Bio-CH_4 stream may be (red line in Figure 1):

1. completely sent to a Steam Reforming (SR) unit to obtain H_2-rich syngas;
2. completely used as fuel in the gasification process of RDF (Borgogna et al., 2019);
3. partially used in the steam reformer (50%) and in the RDF fueled gasifier (50%).

RDF is gasified by means of a High Temperature (HT) gasifier (Iaquaniello et al., 2017) in order to obtain high-quality syngas, albeit with an R ratio not suitable for direct methanol synthesis (i.e. R <1). The technology uses CH_4 to sustain and stabilize the gasification in CH4/RDF ratio equal to 11% wt. After a gas cleaning, RDF-derived syngas is obtained. Digestate and CO_2 are used as a source of nutrients and as a source of carbon respectively in the photosynthesis process for microalgae growth. The pure carbon dioxide derived from biogas or carbon capture units can be (red line in Figure 1):

1. completely used in algae photobioreactors;
2. completely released into the atmosphere (green line in Figure 1);
3. partially sent to the photobioreactor and partially released into the atmosphere.

Supercritical water gasification (SWG) carried out at 240 bar and 600 °C is considered for algae gasification for syngas production (Chakinala et al., 2010). As above mentioned, the synthesis of methanol requires syngas with an R ratio greater than 2. The compositions of syngas obtained from gasification (either thermal or with supercritical water) usually do not allow the attainment of this R value, therefore, a conditioning section to partially convert the CO to CO_2 and H_2 by water gas shift (WGS) reaction and a CO_2 capture section (Chi et al., 2020) are added. By properly balancing these two parameters (CO conversion and CO_2 capture) it is possible to obtain the required R value. After methanol purification, the unreacted syngas is separated and recycled, with a properly chosen purge stream. The purge stream may be valorized through a burner to obtain high-temperature thermal energy. The purge ratio, defined as the flowrate of purge with respect to the total unreacted syngas, is a degree of freedom. In this case, only three values (10%, 55% and 100%) are assumed as possible (red line in Figure 1). The flue gas produced by the purge combustion is considered as a stream with direct CO_2 emissions (green line in Figure 1). Finally, pure methanol is obtained by distillation.

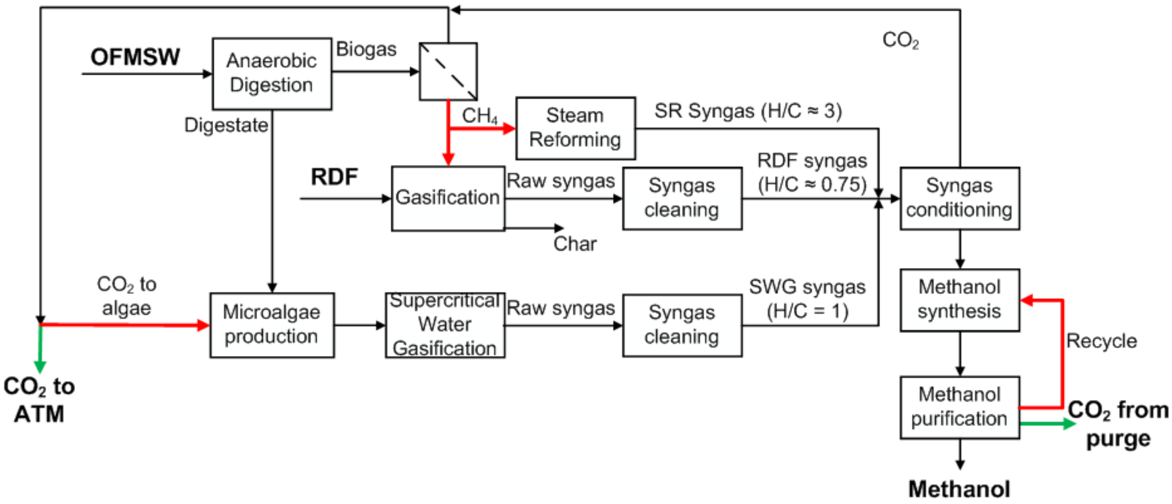

Figure 1: Process block flow diagram of the proposed process integration. Red lines are referred to the process degree of freedom. Green lines are referred to the CO_2 direct emission streams.

2.2 Process simulation assumptions

Process simulations, carried out by means Aspen Plus® V11, are based on several process assumptions. The size of the proposed integrated plant is based on the OFMSW flowrate, which is set at 10 t/h (75'000 t/y). This value corresponds to 10 % of organic waste produced by a large city (e.g. Rome) (D'Adamo et al., 2021). The biogas/syngas yields obtained from solid feedstocks and their composition are set according to literature data. In particular, the yield to syngas in the gasifier and the syngas composition were assumed from Borgogna et al. (2019) fixing only one feedstock kind as RDF and only one gas composition with experimental results. The process conditions (i.e. temperature and pressure of each unit), influencing the energy analysis and chemical equilibria, are set as equal to the optimal process conditions estimated in the reference literature. Table 1 summarizes all the process conditions and assumptions considered in this paper. In particular, the mass ratios of syngas and methane with respect to the RDF are essential to estimate the methane consumption in the gasifier and the yields to syngas and methanol. The digestate is considered to contain the amount of carbon estimated by Freda et al. (2019). The carbon present in the digestate is considered a carbon source for the microalgae, so even in the absence of CO_2 sent to the photobioreactor (100% released into the atmosphere), the production of SWG-syngas is always considered. The flowrate of RDF is limited by the quantity of CH_4 obtained from the biogas, so the RDF can achieve a maximum value when all the bio-methane is used for RDF gasification. Methane is used in the gasifier to perform a high-temperature gasification to obtain a tar-lean syngas. Table 2 reports the compositions of the three main syngas streams, based on literature data. In particular, the *R* ratio is greater than 2 only for the SR-syngas (equal to 3), while in the case of RDF and algae-gasification *R* less than 1 is assumed.

2.3 Direct CO_2 emission assessment

In order to obtain the optimum values of the three main degrees of freedom (percentage of gasified RDF, CO_2 to algae and purge ratio of unreacted syngas after the methanol reactor) of the considered process flowsheet, the evaluation of direct CO_2 emissions per unit of mass of produced methanol is carried-out for each case considered in this paper. As described, however, two of the main units considered in this work, such as SR and SWG, require heat transfer at high temperatures, i.e. 850 °C and 600 °C, respectively. As a result, in order to properly estimate the direct emissions, it is necessary to evaluate a heat integration of high-temperature energy flows. In particular, the heat required by the SR (Q_{SR}) and SWG (Q_{SWG}) must be equal to or less than the high-temperature heat obtainable by combustion of the purge stream (Q_{BURN}). The efficiency of the syngas burner was considered about 1 in this case (Dion et al., 2013). If the difference $Q_{HT} = (Q_{SR} + Q_{SWG}) - Q_{BURN} > 0$, the proposed integrated process is not able to fully satisfy the heat demand of the high-temperature reactors, and additional fuel supply, e.g. fossil natural gas, is required.

Table 1: Summary of main process simulation parameters

	Units	Value	Reference
OFMSW	t/h	10	(Giuliano et al., 2019b)
Yield to biogas	%wt	50	(Migliori et al., 2019)
CH_4 in biogas	%mol	60	(Migliori et al., 2019)
CH_4 recovery	%	100	(Giuliano et al., 2020a)
SR pressure	Bar	30	(Giuliano et al., 2019b)
H_2O/CH_4 ratio	/	3	-
SR temperature	°C	850	(Giuliano et al., 2019b)
WGS pressure	Bar	30	-
WGS temperature	°C	400	-
SWG pressure	Bar	240	(Chakinala et al., 2010)
SWG temperature	°C	600	(Chakinala et al., 2010)
Syngas/RDF	%wt	125	(Borgogna et al., 2019)
CH_4/RDF	%wt	11	(Borgogna et al., 2019)
O_2/RDF	%wt	45	(Borgogna et al., 2019)
MeOH synthesis pressure	Bar	80	(Giuliano et al., 2020b)

3. Results

Figure 2 reports the results obtained from the process simulations in terms of additional high-temperature heat (Q_{HT}) and the CO_2 emission (EM_{TOT}) in terms of kg of emitted CO_2 per kg of produced methanol, as a function of (i) the CO_2 used in photobioreactors, (ii) the purge ratio from methanol purification section, and (iii) the bio-methane usage level in RDF-gasifier. In particular, RDF flowrate is directly related to the bio-methane flowrate to the gasifier, for the reasons above mentioned. In the graph of Figure 2a only the points with Q_{HT} less than zero indicate that the process integration may be considered with no additional/external heat flows. These points are represented by 55% and 100% purge ratios and a maximum possible flow rate of RDF (yellow and green triangles). In these cases, for any value of "CO_2 to algae" the calorific value of the purge is higher than the heat necessary for the SWG process alone. The SR process is not present, because with maximum RDF flowrate all the bio-methane is sent to the gasifier. The Q_{HT} value is negative but it increases with the increase of "CO_2 to algae". Three other points are at $Q_{HT} < 0$, all for “CO_2 to algae” equal to 0%. Two of which (green and yellow diamonds) for RDF at 50% and only one point relating to purge ratio equal to 10% and RDF 100% (blue triangle). The direct CO_2 emissions grow as the amount of RDF used increases (i.e. as the bio-methane flowrate to the gasifier increases), as purge ratio increases and "CO_2 to algae" decreases. The methanol production increases strongly when RDF flowrate increases and weakly when "CO_2 to algae" decreases, decreasing strongly as a function of purge ratio. This is because RDF offers material to be converted to methanol, while CO_2 recovery via algae does not increase effectively the methanol yield as the R ratio of SWG-syngas is low, so the recovered CO_2 is then largely sequestered via carbon capture. Additionally, the higher is the purge ratio lower is the carbon atoms available to be converted to methanol. From these analyses, the CO_2 emissions can be estimated, and results are reported in Figure 2b, which shows that the lower specific emission values are obtained for lower purge ratio values. The increase of RDF flowrate causes an increase in methanol production, but with a higher specific direct CO_2 emission (EM_{TOT}).

Table 2: Syngas compositions considered in this work

%mol	RDF syngas (Borgogna et al., 2019)	SR syngas (Giuliano et al., 2019b)	SWG syngas (Chakinala et al., 2010)
CO_2	11.4	5.6	27.8
CO	38.1	8.2	3.1
H_2	37.1	47.1	46.1
CH_4	0.5	4.3	18.1
N_2	3.8	-	-
H_2O	8.6	35.0	-
C_2H_6	-	-	4.9
$(H_2 - CO_2)/(CO + CO_2)$	0.5	3.0	0.6

Conversely, with a higher RDF flowrate (i.e. higher bio-methane flowrate to the RDF gasifier) the purge LHV is higher, with a positive effect on available high-temperature heat. The increase in CO_2 usage rate in algae photobioreactors involves a decrease in the specific CO_2 emission function EM_{TOT}, albeit with a significant increase in the heat necessary for the SWG process. However, since low purge ratios cannot make the high-temperature energy balance sustainable, they must, therefore, be discarded with the exception of the point corresponding to CO_2-to-algae = 0%, purge ratio = 10% and maximum RDF flowrate (i.e. all the bio-methane used in RDF gasifier). This is the optimal combination for the proposed integrated process. Among the other thermally sustainable solutions, the conditions indicated by yellow triangles in Figure 2 are better than the other options, thanks to the balance between the the heat of the purge combustion and the lower heat demand due to the absence of SR.

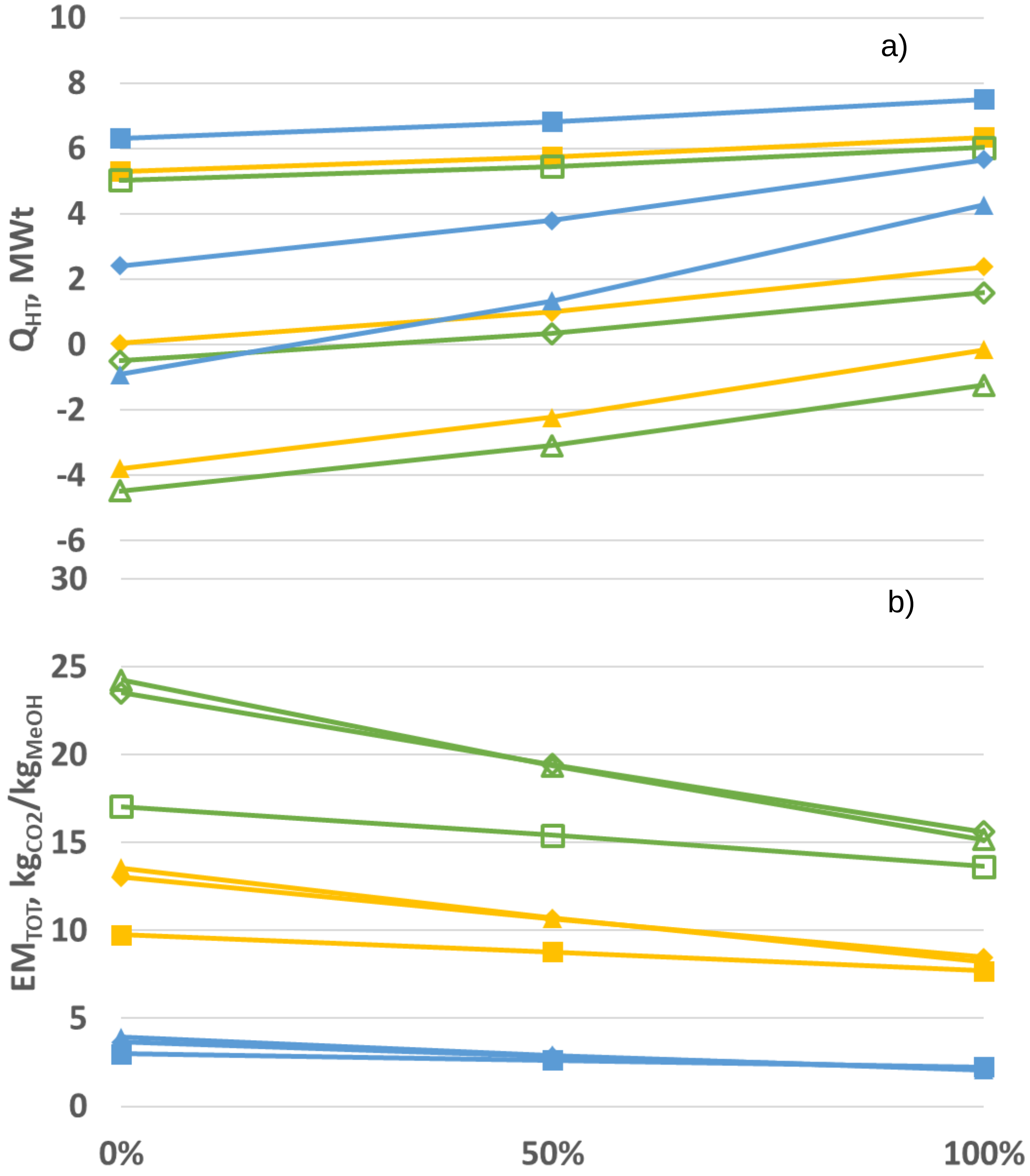

Figure 2: a) Heat duty required at a temperature higher than 600°C; b) total direct CO_2 emissions per kg of produced methanol with respect to the CO_2 to algae percentage. Colors correspond to different purge ratio values: blue, 10%; yellow, 55%; green, 100%. Symbols correspond to different percentages of used RDF with respect to the maximum allowed by methane: square, 0%; diamond, 50%; triangle, 100%.

4. Conclusions

In this work, an integrated waste-to-methanol process is proposed and evaluated from an environmental point of view. The attention was focused on the direct CO_2 emissions from a methanol production plant using both OFMSW and RDF as primary feedstock. The syngas used for the synthesis of methanol is obtained by mixing three syngas streams: derived from (i) the steam reforming of biomethane obtained from the anaerobic digestion of OFMSW, (ii) the gasification of RDF and (iii) the supercritical water gasification of microalgae grown using the carbon dioxide obtained from both biogas and CO_2 capture units and digestate as a source of nutrients. Process simulation data show that it is not always possible to thermally sustain the high-temperature endothermic processes (SR and SWG) through the heat released by the combustion of the purge gas deriving from the methanol purification unit, i.e. unreacted syngas. Further analysis of the resulting energetically sustainable cases suggested that the optimal solution is achieved combining the following conditions: minimum use of CO_2 as a substrate for microalgae (set to zero), minimum purge ratio (set to 10%) and maximum syngas flow rate from RDF (corresponding to the elimination of SR). Further work will be addressed to carry out a deeper analysis of the energy balance in order to allow a higher recycle of captured CO_2, by combining SWG and more efficient conversion to methanol.

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