Research Paper

Energy and environmental assessment of solid recovered fuels valorisation: Waste-to-Chemicals options vs co-combustion in cement plants

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ABSTRACT

The increasing interest in Waste-to-Chemical (WtC) technologies operating with Solid Recovered Fuels (SRF) from non-recyclable plastic streams requires a quantitative analysis on the actual convenience of this alternative valorization pathway.

This study assesses SRF in selected WtC technologies for hydrogen and methanol production and compares it with the well-established practice of co-combustion in the cement industry. Two case studies are considered: the first one represents the current scenario where SRF is used in co-combustion for cement production meanwhile the chemical is produced by steam reforming; in the second scenario, the cement plant is fed with pet-coke only, leaving SRF as a feedstock for WtC.

WtC performance assessment has been carried out in Aspen Plus®, whereas cement production and steam reforming have been characterized based on literature information.

The two scenarios have been assessed for two SRF qualities (different LHV and biogenic content) calculating primary energy and fossil CO_2 emissions.

The results show that SRF from plastic waste as a feedstock in WtC is less effective than its utilization in cement plant: when WtC technology for hydrogen production is adopted, additional 9.1% (SRF-1) and 8.6% (SRF-2) of energy consumption is estimated and 25.8% (SRF-1) and 24.1% (SRF-2) additional fossil CO_2 is emitted with respect to the corresponding conventional cases (i.e., chemical from steam reforming and SRF burnt in the cement kiln). When considering methanol production, WtC technology requires 6.2% (SRF-1) and 5.6% (SRF-2) increase of primary energy and 30.2% (SRF-1) and 28.4% (SRF-2) additional fossil CO_2 against the conventional cases.

1. Introduction

Plastic waste recycling covers an important role in the European directives fostering a circular economy model aiming at 55 %$_{w/w}$ recycling of plastic contained in packaging waste by 2030 (The European Parliament, 2018b) and at a maximum limit of urban waste to landfill equal to 10 % by 2035 (The European Parliament, 2018a). Improving recycling systems could lead to progressive reduction of fossil fuels consumption and it represents one of the European strategies to reach carbon neutrality within 2050 (The European Parliament, 2021). Plastics recycling may envisage four general categories (Rahimi and García, 2017; Solis and Silveira, 2020): *primary* or closed-loop recycling; *secondary* or mechanical recycling; *tertiary* or chemical recycling; *quaternary* recycling or energy recovery.

In the year 2020 about 29.5 million tonnes of plastic post-consumer waste have been collected in the 27 European countries, in Norway, in Switzerland and in the United Kingdom (Plastics Europe, 2021); 42 % of this amount has been destined to energy recovery, 34.6 % has been directed to recycling facilities, 23.4 % has been sent to landfill and the remaining 0.2 % of the total plastic waste being used for chemical recycling.

With the purpose of decreasing plastic waste for landfill disposal, in case of limited contaminations and reduced content of chlorine, non-recyclable plastic material can be employed together with non-hazardous and non-recyclable waste streams such as paper, tire and biomass after sorting of Municipal Solid Waste (MSW) or industrial waste (Nasrullah et al., 2014; Grosso et al., 2016) to produce high quality Solid Recovered Fuel (SRF) meeting the specification

requirements of UNI EN 21640 from the European committee for Standardization based on several indicators (e.g., net calorific value, mercury content, chlorine content). SRFs are commonly used for energy recovery in waste incineration or co-incineration plants (Beckmann et al., 2012; Iacovidou et al., 2018), partially replacing fossil fuels; moreover, meanwhile the use of biogenic fractions reduces fossil CO_2 emissions from fuel combustion, the addition of non-recyclable plastic waste in SRF enhances LHV of the blend, improving its chemical properties (Ferronato et al., 2024).

A sector that nowadays widely adopts SRF partially replacing conventional fossil fuels is the cement industry (Federbeton Confindustria, 2023). The clinker production process attains high temperature, high residence time of gases and oxidative conditions in the kiln, making waste combustion viable due to decomposition of organic compounds, and typically lower emissions of dioxins, furans and volatile organic compounds than other waste combustion systems (World Business Council for Sustainable Development ((WBCSD) − Cement Sustainability Initiative (CSI), 2014). As reported by the Italian techno-economic association of cement − AITEC (AITEC, 2021), the application of alternative fuels such as SRF in cement plants is a well-established practice, with European rates of substitution with alternative fuels above 50 % in 2020, and peaks above 70 % in Austria and Poland; additionally, SRF application for clinker production is part of the decarbonization strategy considered by this hard-to-abate sector. On the other hand, high-quality SRF (i.e., high LHV) may be potentially employed in Waste-to-Chemical (WtC) processes increasing their energy efficiency (Borgogna et al., 2019), thus potentially reducing SRF availability for co-combustion in the cement sector. With reference to this scenario, the preferred route for SRF application in cement versus its use in WtC needs to be assessed evaluating energy and environmental impacts of the two different pathways.

Chemical recycling implies chemical decomposition of plastic polymers into monomers or the conversion into liquid or gaseous raw material generating a variety of fuels or chemical products. This recycling technique has seen limited applications at full scale (van der Hulst et al., 2022), but it is currently being evaluated to process mixed plastics and waste which cannot be mechanically recycled. WtC technologies commonly involve pyrolysis or gasification, the latter being employed in several pilot plant facilities (Waldheim, 2018; Solis and Silveira, 2020; Lee et al., 2021; Quicker et al., 2022; Wang et al., 2023). Waste gasification leads to the production of a syngas with relevant fractions of H_2, CO, CO_2 and CH_4 (Arena, 2012) that may be suitable for the synthesis of valuable chemicals such as methanol and hydrogen. The main challenge of plastic gasification is given by tar formation causing relevant operational problems and leading to lower process efficiency; to overcome this issue, operations with high temperatures is recommended (Ponzio et al., 2006). Compared to combustion, waste gasification can reduce the formation of dioxins, furans and NO_x (Consonni and Viganò, 2012) and sulfur compounds can be removed more easily through syngas treatment (Simbeck et al., 1993), avoiding the release of SO_x in atmosphere. Moreover, high pressure gasification allows easier removal of carbon dioxide through physical absorption systems (Simbeck et al., 1993).

Among the existing gasification-based technologies, waste-to-hydrogen and waste-to-methanol processes have achieved higher technological maturity (Waldheim, 2018), thus being assessed by the literature for several feedstocks: Borgogna et al. (2022) have performed a techno-economic evaluation on the production of H_2 from municipal solid waste detailing the performance of the gasification step operating with oxygen and methane. Rudra and Tesfagaber (2019) have evaluated the performance of a combined system processing municipal solid waste for hydrogen production from gasification and integration with district heating. Hydrogen production from municipal solid waste has been also assessed by Qi et al. (2023), who have studied the chemical looping gasification with $CuFe_2O_4$ for hydrogen production. Rosha and Ibrahim (2023) have evaluated hydrogen production via municipal solid waste gasification with subsequent amine-based carbon dioxide removal.

Biomass to methanol processes have been assessed by several authors (Clausen et al., 2010; Giuliano, Freda and Catizzone, 2020; Bobadilla et al., 2023; Lombardelli et al., 2024). Leveraging on gasification processes, waste-to-methanol technologies have been addressed by Borgogna et al. (2019) studying a system operating with refuse derived fuel gasified with oxygen and methane. Ali et al. (2023) have investigated the conversion of municipal waste (i.e., plastic waste, food waste and their blend) into methanol via steam gasification adding CaO for CO_2 capture to achieve proper syngas composition (i.e., module) for methanol production. Sun et al. (2022) have also investigated methanol production from municipal solid waste based on gasification and including carbon capture; among the different process configurations analyzed by Sun, the presence of either water–gas shift or solid oxide electrolysis to adjust H/C ratio. Prifti et al. (2023) have investigated the conversion of plastic waste to methanol through gasification at 850 °C working with steam and oxygen.

Despite their potential role as emerging solutions for selected waste material recycling, a scarcity of studies assessing the performance of gasification based WtC technologies for hydrogen and methanol production with SRF is recorded from the literature. Based on extensive modelling activity developed in Aspen Plus® environment (AspenTech, 2024), the present study delivers the design and performance characterization of two WtC options for hydrogen and methanol production based on high-temperature two-stage gasification with two different SRFs generated from residues of plastic sorting (known as "Plasmix" in Italy) (Cossu et al., 2017) with and without biogenic content, encompassing publicly available information at pilot scale. Moreover, the results of the work offer an unprecedented systemic vision on the convenience between the possible implications of SRF utilization in chemical recycling for chemical production, versus its conventional use for co-combustion in cement plants. The comparative analysis delivers a quantitative evaluation on energy and environmental indicators such as primary energy consumption and CO_2 emissions. The work paves the ground for a complete life cycle assessment which shall rely on future availability of experimental data for higher results accuracy.

2. Materials and methods

2.1. Approach and methodology

The assessment of the two alternative applications of plastic waste material in (i) the cement sector or in (ii) chemical recycling relies on the production of different amounts of the same useful outcomes, such as clinker and chemical product (hydrogen or methanol), investigating the impact of the process in terms of primary energy consumptions, electric consumption, fossil CO_2 emissions (direct and indirect).

To this purpose, each scenario requires the evaluation of two cases, such as "Case A" and "Case B".

Case A, which represents the current and established industrial practice, considers SRF dedicated to co-combustion in cement plants and the consolidated steam reforming technology as a conventional generation of the chemical (hydrogen, methanol).

Indeed, in Case A, mass and energy balances and the evaluation of CO_2 emissions are carried out on a system in which the cement kiln is fed with a combination of pet coke and SRF so that the contribution of the alternative fuel constitutes 50 % of the total energy demand of the cement plant, whereas the chemical (hydrogen or methanol) is produced by steam reforming technology (Kalamaras and Efstathiou, 2013; Bertau et al., 2014).

On the other hand, Case B is meant to describe an alternative and less developed option for SRF utilization. In particular, in Case B SRF is processed in the Waste-to-Chemicals technology producing hydrogen or methanol. Therefore, the cement kiln is totally fed with fossil fuel (i.e., pet coke), since SRF is no longer available for co-combustion.

Primary energy consumption, electric consumption and fossil CO_2 emissions are considered as figures of merit to compare and assess

energy and environmental impacts of Case A and Case B. The two scenarios (i) production of clinker + hydrogen and (ii) production of clinker + methanol, have been calculated for both qualities of SRF.

During the assessment, all Cases B consider a common reference of a cement plant fed with 100 % pet coke. Starting from the energy demand of this reference plant, an increase of 10 % of the thermal duty is assumed for co-combustion of SRF in cement plants of all Cases A.

Two different solid recovered fuels are analyzed, namely SRF-1 and SRF-2, representative of two typical alternative fuels with and without biogenic fraction respectively.

To ensure a coherent analysis, for each scenario, the same amount and the same type of SRF are used alternatively either as fuel for the cement plant (Case A) or as a feedstock for the WtC process (Case B).

Generating the same quantity of final products, i.e., same amount of clinker and same amount of hydrogen/methanol, the different energy demand and fossil CO_2 emissions deriving from the two cases of each single scenario can provide and insight on the convenience on gasification vs. conventional co-combustion applications of SRF.

2.2. Concept of the comparative analysis

The adopted methodology of the comparative analysis is described in the following steps. For the sake of clarity, a graphical representation has been provided in the Supplementary Material (§ S1).

STEP 1: The reference cement plant produces 1 tonne of clinker consuming 3.23 GJ_{LHV} of pet coke emitting 0.33 tonnes of fossil CO_2 from combustion (Romano et al., 2014). The specific indicators and parameters selected for the reference cement plant (Cases B) refer to (Romano et al., 2014).

STEP 2: The same amount of clinker (1 tonne) is produced in the corresponding cement plant analyzed in Case A, in which the energy demand is satisfied by co-combustion of pet coke and SRF. The quantity of SRF has been calculated to satisfy 50 % of the total energy demand of the cement plant, in line with European average of thermal substitution range (Cembureau - The European Cement Association, 2022, 2024; Federbeton Confindustria, 2023); as mentioned in §2.1, an increase of 10 % of the specific thermal energy requirement with respect to the reference cement plant is assumed. Hence, the total thermal duty of cement plant to produce 1 tonne of clinker for Case A is roughly 3.55 GJ_{LHV}, half deriving from SRF and half from pet coke: 1.78 GJ_{LHV} comes from 0.05 tonnes of pet coke and 1.78 GJ_{LHV} derives from a certain quantity of SRF, that depends on its LHV. If the considered SRF contains a certain amount of biomass, a fraction of the CO_2 emissions of the cement plant will be biogenic; instead, in all Cases A the combustion of the pet coke will generate 0.18 tonnes of fossil CO_2.

STEP 3: The same amount of SRF taken as input for the cement plant of Case A (step 2) is adopted to produce the chemical (hydrogen or methanol) in the Waste-to-Chemicals technology from Case B (step 3). Based on the WtC process energy conversion efficiency described in §4 for hydrogen and methanol production, the amount of chemical generated by the WtC technology from the given SRF quantity has been calculated, as well as the associated CO_2 emissions (direct emissions from the WtC process and indirect emissions from its electric consumption). Moreover, in the scenario considering methanol production, the direct CO_2 emissions are calculated starting from the total carbon content (fossil and biogenic) in the considered SRF, assuming that all the carbon contained in the produced methanol is fossil.

STEP 4: The same quantity of chemical obtained from WtC in Step 3 is now produced within the framework of Case A by a conventional technology such as steam reforming. Conversion efficiencies, reported in Table 1, allow the calculation of the required mass flow rate of natural gas.

For hydrogen production, the CO_2 emissions of steam reforming process are evaluated as the product between the amount of consumed natural gas and its emission factor. For methanol production, the CO_2 emissions derive from the difference between the carbon contained in

Table 1

General assumptions useful for comparative analysis. Net specific electric consumption of steam reforming is assumed to be zero as the process is self-sustaining (i.e., it produces the electricity that it consumes).

Pet coke			
Lower Heating Value [MJ/kg]	34.17		
Emission factor [$kgCO_2$/kg Pet coke]	3.48		
Natural gas (NG)			
Molar composition [mol/mol]	CH_4	C_2H_6	N_2
	0.90	0.06	0.04
Molecular mass [kg/kmol]	17.36		
Lower Heating Value [MJ/kg]	46.50		
Emission factor [$kgCO_2$/kg NG]	2.585		
Hydrogen production			
Lower Heating Value [MJ/kg]	120.00		
Energy conversion efficiency of steam reforming [GJ_{H2}/GJ_{NG}]	0.75 (Consonni and Viganò, 2005)		
Net specific electric consumption of steam reforming [MWhel/t H_2]	0.00 (Consonni and Viganò, 2005)		
Methanol production			
Molecular mass [kg/kmol]	32.04		
Lower Heating Value [MJ/kg]	19.91		
Energy conversion efficiency of steam reforming [GJ_{MeOH}/GJ_{NG}]	0.66 (Collodi et al., 2017)		
Net specific electric consumption of steam reforming [MWhel/t MeOH]	0.09 (Collodi et al., 2017)		

the inlet natural gas and the carbon remaining within the produced methanol.

Once the chemical product to be generated and the type of SRF to be considered as inlet material have been defined, it is possible to compare total primary energy, electric consumptions and fossil CO_2 emissions for Cases A and B of the considered scenario.

It is important to highlight that CO_2 emissions related to raw mill calcination, electric consumptions and indirect CO_2 emissions of cement plants are not represented in the comparison because they are considered the same for all the Cases A and Cases B, thus they don't affect the comparative analysis. The electric consumptions of cement plants are, however, taken into account.

2.3. Relevant assumptions

Table 1 reports the information on the pet coke fed to cement plants, on the natural gas fed to steam reforming, on the energy yields and on the electric consumptions assumed for steam reforming process to produce hydrogen and methanol.

The CO_2 emissions related to the calcination reaction in the cement plant are considered constant for all scenarios, hence not included in the comparative analysis.

Specific CO_2 emissions from conventional steam reforming processes for hydrogen and methanol production reported in §4.1 and §4.3 have been calculated based on the respective energy efficiencies from Table 1 (i.e., 75 % $GJ_{H_2}/GJ_{NG_{LHV}}$ (Consonni and Viganò, 2005) and 66 % $GJ_{MeOH}/GJ_{NG_{LHV}}$ (Collodi et al., 2017)).

In Cases A, an increase of 10 % of the specific thermal energy duty with respect to the reference cement plant is assumed to represent the input thermal duty increment due to co-combustion (Genon and Brizio, 2008).

The total specific electric consumption of cement plants is considered equal to 57.70 kWh/t clinker also for Cases A, neglecting the possible extra electric consumption resulting from co-combustion.

The indirect CO_2 emissions from electric consumption are considered equal to 268.6 $kgCO_2$/MWhel (ISPRA, 2020).

2.4. Reference Solid Recovered Fuels (SRFs).

Plasmix can be made up of two different residual streams deriving

from plastic waste mechanical treatments: the so-called Undersieve from sieving operations and the residues from sorting operations, also known as "End-of-line" or "End-of-belt" (Cossu et al., 2017). Each Plasmix stream has its own characteristics which depend on the specific plastic sorting manufacturing facility.

The properties of the solid recovered fuels SRF-1 and SRF-2 considered in this study have been assumed from publicly available information on commercial "Plasmix" (Petriglieri, 2014). SRF-1 is representative of a typical composition of solid recovered fuel with higher organic fraction and produced from a Plasmix obtained as a mixture of Undersieve and End-of-line fractions; SRF-2 is generated from a Plasmix stream richer in plastic content and obtained by the End-of-line fraction only.

Properties of the two alternative fuels are reported in Table 2. The amount of biomass in the dry ash-free material is calculated according to Fellner and coworkers (Fellner et al., 2007). SRF-1 is characterized by a moderate LHV (24.63 MJ/kg), by a relevant ash content (13.39 % on dry basis) and by low biogenic CO_2 emissions (14.89 %). Instead, SRF-2 is featured by a considerable LHV (33.69 MJ/kg), but all carbon dioxide resulting from its combustion is fossil, since it is assumed that the biomass content in this fuel is zero.

3. WtC process design and simulation

Process design and performance of the WtC technologies for hydrogen and methanol synthesis are respectively reported in §4.1 and §4.3 meanwhile details on design, process simulation and performance validation have been reported in the Supplementary Material.

WtC technologies selected for hydrogen and methanol have been simulated with Aspen Plus® to close mass and energy balance for the different scenarios, allowing the calculation of yield indicators (e.g., energy efficiency and specific electric consumption) needed for the comparative analysis.

The WtC process to produce hydrogen encompasses a two-stage gasification technology (Waldheim, 2018; Lee et al., 2021) (10 bar, 1350 °C in the second stage), a syngas cleaning step, a two stages-Water Gas Swift (WGS) unit (Chein and Yu, 2017) and a Pressure Swing Adsorption (PSA) system at 20 bar (Consonni and Viganò, 2005; Du

Table 2
Main features of the two SRFs considered in the study. Percentage of moisture and fixed carbon are assumed and the volatile matter percentage are calculated as a difference.

	SRF-1: Undersieve and End-of-line fractions	SRF-2: End-of-line fraction only
Proximate analysis (wt%, as received)		
Moisture	10.00 (assumed)	5.00 (assumed)
Fixed carbon	7.57 (assumed)	7.57 (assumed)
Volatile matter	70.38	86.91
Ash	12.05	0.52
Ultimate analysis (wt%, dry basis)		
C	61.80	77.50
H	7.60	11.90
O	15.60	5.20
N	0.01	4.02
S	0.28	0.06
Cl	1.33	0.77
Ash	13.39	0.55
Fuel properties		
LHV [MJ/kg]	24.63	33.69
LHV [MJ/kg dry]	27.64	35.59
% Biomass in DAF	22.70	0.00
% Biogenic CO_2 emissions	14.89	0.00
Emission factor [kg CO_2/kg SRF]	2.04	2.70

et al., 2021) to generate pure hydrogen compressed up to 60 bar. The WtC process for methanol production considers a two-stage gasification (5 bar, 1200 °C in the second stage) (Lee et al., 2021), a syngas cleaning step, one stage WGS reactor (inlet temperature equal to 350 °C and 20 bar), an Acid Gas Removal (AGR) system (37.5 bar) to remove sulfur compounds and CO_2 (Gatti et al., 2014) achieving the desired syngas molar module for methanol synthesis (2.1 mol/mol) (Dieterich et al., 2020), a methanol reactor (Lombardelli, et al., 2022; Lombardelli, et al., 2022; Rinaldi et al., 2023) (250 °C, 60 bar) and a methanol purification step with two flash stages and a distillation column (Ghosh et al., 2019).

Mass and energy balance for the conventional cement plant (Romano et al., 2014) and steam reforming technologies for chemical production (Consonni and Viganò, 2005; Collodi et al., 2017) have been taken from the literature.

4. Results and discussion

Results of the simulations of the WtC technology for hydrogen production with the two different SRF considered in this study are reported in this section, showing process flow diagram and key energy and performance indicators obtained as an output of the modelling work. Based on this information, the comparative analysis for the first scenario (clinker and hydrogen production) has been performed, calculating energy consumption and fossil CO_2 emissions.

The same approach has been adopted to characterize the scenario envisaging clinker and methanol production.

4.1. Performance assessment of the WtC technology for hydrogen production from simulations

Fig. 1 represents the process flow diagram of the WtC technology for hydrogen production used to simulate the performance of the WtC technology fed with the two considered SRFs. The stream tables of the simulations and the description of the main components showed in Fig. 1 are reported in the Supplementary Material.

As shown in Fig. 1, the process is considered autothermal as it is assumed that the necessary steam for gasification and for shift reaction is generated within the process itself, by means of thermal waste recovery (i.e., heat exchanger network, mainly for water pre-heating) and by heat extraction from gasification. This heat extraction causes a partial oxidation of the syngas necessary for steam production, with consequent reduction of the hydrogen and carbon monoxide content, hence a decrease of the final produced hydrogen yield. Moreover, the heat of the hot syngas exiting the gasification process (1350 °C) is not exploited as the syngas stream is directly conveyed to the water quench without a heat recovery. Hence, the possibility to extract heat from the hot syngas may allow production of part of the required steam, resulting in beneficial effects on process efficiency. A possible improvement in the efficiency of the simulations can derive from an alternative way of generating the steam needed for the entire process.

Table 3 summarizes the most relevant mass flow rates of the process fed with SRF-1 and SRF-2. It also indicates the specific parameters on the consumptions, emissions and hydrogen production. Details on process simulation results have been included in the supplementary material.

The results show that higher carbon and hydrogen content in the inlet material, hence a higher LHV, improve gasification process performance, generating a syngas with higher content of hydrogen and carbon monoxide. The high presence of carbon monoxide in the syngas can increase hydrogen conversion through water gas shift reaction, raising hydrogen production yield. Results highlight that a feedstock with a higher LHV is associated to a superior specific hydrogen production (0.13 kg H_2/kg $_{SRF-2}$ versus 0.09 kg H_2/kg $_{SRF-1}$): SRF-2 utilization in the selected WtC technology results in a 40 % mass yield increase compared to the case when SRF-1 is employed. Considering LHV$_{SRF-2}$ is ∼ 37 % higher than LHV$_{SRF-1}$, only a moderate increase in energy efficiency is recorded. As reported in Table 3, higher specific
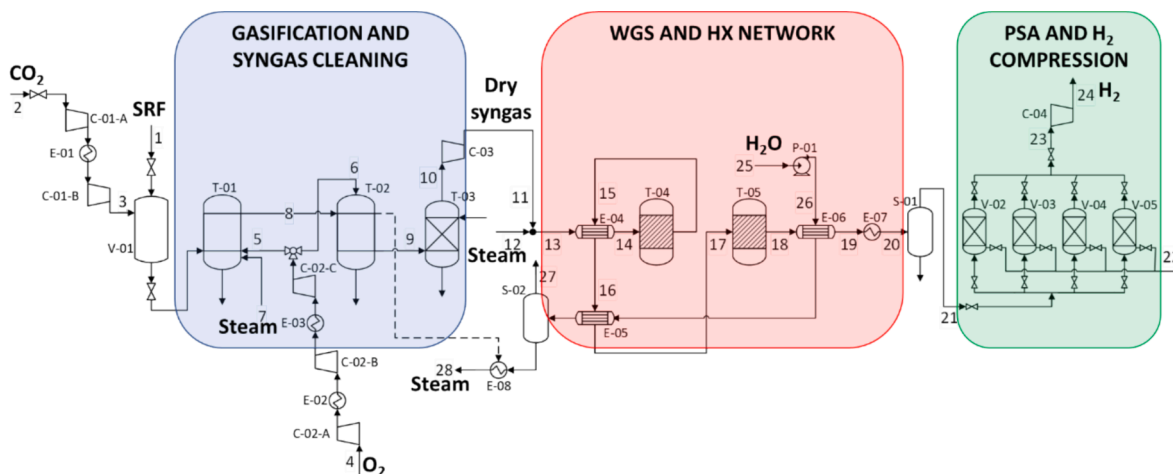
Fig. 1. Process flow diagram of the WtC process for hydrogen production.

Table 3
Performances of the WtC technology for hydrogen production using SRF-1 and SRF-2.

Hydrogen production simulations		SRF-1	SRF-2	
Mass balance				
ID	Stream	Value	Value	Unit
1	Dry SRF	5.42	5.42	t/h
2	CO_2 lock-hopper	0.33	0.33	t/h
4	O_2 gasification	6.00	9.00	t/h
5	O_2 first stage	3.03	5.44	t/h
6	O_2 second stage	2.98	3.56	t/h
	Steam	12.36	14.45	t/h
7	Gasification	2.62	2.30	t/h
12	WGS	9.75	12.15	t/h
10	Clean syngas	9.54	12.01	t/h
24	Produced H_2	0.54	0.71	t/h
Energy duty				
ID	Description	Value	Value	Unit
	Electric power	2'901	4'144	kWel
C-01	CO_2 compressor	19	19	kWel
C-02	O_2 compressor	413	620	kWel
C-03	Syngas compressor	320	419	kWel
C-04	H_2 compressor	315	417	kWel
P-01	Water pump	13	15	kWel
–	From thermal duty	319	404	kWel
–	Air Separation Unit (ASU)	1'501	2'250	kWel
Specific indicators				
Indicator		Value	Value	Unit
Specific O_2 consumption		1.11	1.66	kg O_2 gasif/kg dry SRF
Specific steam consumption		2.28	2.67	kg steam TOT/kg dry SRF
Gasification		0.48	0.42	kg steam gasif/kg dry SRF
WGS		1.80	2.24	kg steam WGS/kg dry SRF
Specific H_2 production		0.10	0.13	kg H_2/kg dry SRF
		0.09	0.13	kg H_2/kg SRF
Specific electric consumption		5.38	5.80	MWhel/t H_2
Specific CO_2 emission (fossil)		19.70	21.83	kg CO_2/kg H_2
Energy efficiency		0.44	0.45	GJ H_2/GJ SRF

steam consumption for hydrogen production is required when SRF-2 is used, due to the higher carbon content of the alternative fuel. Since steam is generated internally to the process, the higher steam requirement causes a reduction of hydrogen and carbon monoxide in the syngas, hence limiting the energy efficiency (0.45 GJ H_2/GJ $_{SRF-2}$ versus 0.44 GJ H_2/GJ $_{SRF-1}$).

The utilization of a high-quality inlet material (i.e., higher LHV) results in a considerably lower value of energy efficiency of the WtC technology with respect to the energy efficiency of the benchmark hydrogen production technology based on steam reforming (0.75 GJ H_2 / GJ Natural Gas) (Consonni and Viganò, 2005; Nnabuife et al., 2023).

Feeding WtC with higher LHV inlet waste material brings to a higher electric specific consumption (5.80 MWhel/t H_2 with respect to 5.38 MWhel/t H_2). This can be attributed to the higher specific oxygen consumption, that results in higher electric consumptions for oxygen compressors and for the air separation unit assumed to consume 250 kWhel per tonne of O_2 at 99.5 % of molar purity. This specific electric consumption for oxygen production is in line with what is reported in

(Zhang et al., 2014) for large-scale O_2 production plants.

Specific fossil CO_2 emissions from steam reforming process have been calculated and compared against the specific fossil emissions for H_2 production with WtC fed with both SRF-1 and SRF-2: the conventional process of steam reforming is estimated to generate 8.90 kg CO_2 FOSSIL/kg H_2 and this data is in line with literature values in the range of 8.89–9 kg CO_2 FOSSIL/kg H_2 (without considering CO_2 capture system) (Sun et al., 2019; Zapantis and Zhang, 2020). The results of the simulations bring to 19.70 kg CO_2 FOSSIL/kg H_2 using SRF-1 and to 21.83 kg CO_2 FOSSIL/kg H_2 with the use of SRF-2, including the contribution of the indirect emissions deriving from electric consumption. The larger emissions of WtC technology are mainly due to the lower specific production (hence, energy efficiencies – GJ H_2/GJ SRF) of the innovative process. A higher specific fossil CO_2 emission is estimated with the use of SRF-2, because of the lack of biomass within this SRF and because of the slight increase of indirect CO_2 emissions, caused by the increase of specific electric consumption.

4.2. Comparative analysis for hydrogen and clinker production

Fig. 2 summarizes the main results of the comparative analysis for the two scenarios of hydrogen and clinker production with SRF-1 and SRF-2 in terms of thermal and electric energy demands and fossil CO_2 emissions. Addition information on results have been reported in the Supplementary Material (§ S6.1). The energy demand is broken down into the different contributions (natural gas, SRF, pet coke) with electric energy reported apart. For the two Cases A, the thermal energy demand accounts for natural gas for hydrogen production and from SRF and pet coke for clinker production, and electric energy is consumed by the cement plant. For Cases B, the thermal energy demand accounts for the contribution from pet coke (clinker production) and from the alternative fuel in the WtC process (hydrogen generation), with electric consumption for the cement plant and for the WtC technology reported separately.

From the results, Cases B are characterized by a higher energy consumption than the corresponding Cases A. Indeed, Case B with SRF-1 requires an additional 9.1 % of primary energy (i.e., higher primary energy consumption) than Case A to guarantee the same production; similar consideration when using SRF-2, for which the extra primary energy consumption of Case B compared to Case A is equal to roughly 8.6 %.

The higher consumption of Cases B is mainly due to the lower efficiency of the WtC technology with respect to the conventional technology; thus, WtC requires a higher energy demand to generate the same amount of hydrogen with respect to the corresponding technology (steam reforming) from Case A. Despite the utilization of a high-LHV SRF, only a slight increase in the energy efficiency of the WtC process is recorded, with the conventional technology being associated to better performances.

In addition to energy demand, a similar comparative analysis is performed also for the fossil CO_2 emissions (see Fig. 2), where the different contributions of fossil emissions are highlighted. Both scenarios adopting WtC technology for hydrogen production show a higher generation of fossil emissions. Therefore, Cases B present higher
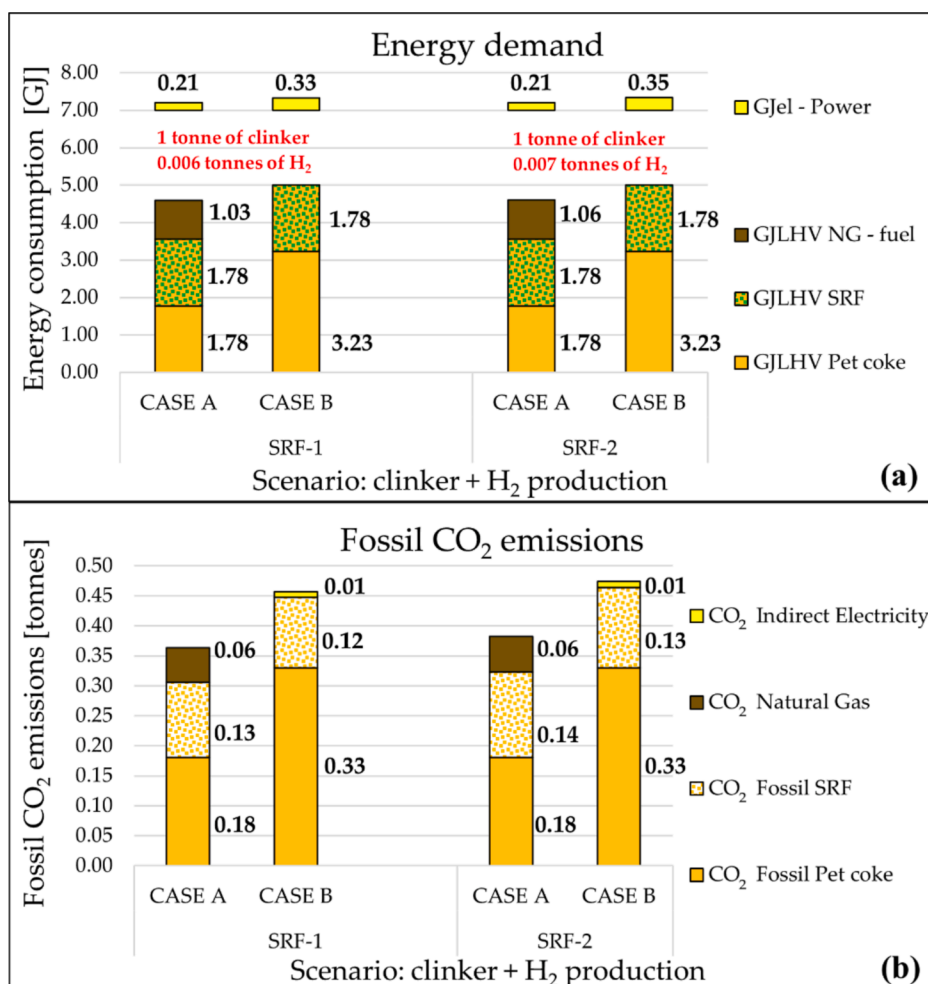

Fig. 2. Main results of the two scenarios of hydrogen and clinker production. (a) Comparison of energy demand. (b) Comparison of fossil CO_2 emissions.

emissions than corresponding Cases A. More specifically, when SRF-1 is investigated, Case B shows additional 25.8 % of fossil CO_2 emissions than the corresponding Case A, meanwhile with SRF-2, the extra fossil CO_2 emissions are equal to 24.1 %. This is mainly caused by the higher specific emissions of the WtC technology with respect to the steam reforming process. In addition, for the scenario in which SRF-1 is used, the cement plant of Case B does not benefit from a partial substitution of pet coke fossil emissions with the biogenic emissions of the biomass part contained in SRF, as the cement plants in Cases B use pet coke only.

4.3. Performance assessment of WtC technology for methanol production from simulations

The process flow diagram of the WtC technology for methanol synthesis with both SRFs is represented in Fig. 3. The related stream tables associated to the two simulations and the description of the main components showed in Fig. 3 are reported in Supplementary Material.

The main flow streams and indicators representative of methanol production, consumptions and CO_2 emissions of the WtC process with SRF-1 and SRF-2 are reported in Table 4.

The quality of the feedstock influences the final methanol yield depending on the feedstock calorific value, hence affecting syngas composition and process yield, as verified in (Borgogna et al., 2019) for different feedstocks with different LHVs. Feedstock material with higher LHV is associated to higher mass yield of the process (0.75 kg MeOH/kg $_{SRF-2}$ versus 0.53 kg MeOH/kg $_{SRF-1}$), and a slightly higher energy efficiency (0.44 GJ MeOH/GJ $_{SRF-2}$ versus 0.43 GJ MeOH/GJ $_{SRF-1}$); however, the conventional steam reforming process reaches better energy performances (0.66 GJ MeOH/GJ Natural Gas). SRF-2 utilization in the selected WtC technology results in a 40 % mass yield increase compared to the case when SRF-1 is employed. Considering LHV_{SRF-2} is ~ 37 % higher than LHV_{SRF-1}, only a moderate increase in energy efficiency is recorded.

The higher nitrogen content in SRF-2 requires a higher purge to reduce inert quantity in the methanol reactor, reducing energy efficiency. Moreover, the adopted process configuration features direct quench of the syngas produced in the gasifier following the gasification process with no heat recovery. The possibility of heat recovery from syngas exiting the second stage at 1200 °C can contribute to steam production decreasing oxidation of syngas carbon monoxide and hydrogen content during gasification. Together with the optimization of the purge flow rate hence of the steam produced from the boiler, these can have beneficial effects on methanol production yield.

The evaluated specific electric consumptions of the two simulations

are quite similar: 1.23 MWhel/t MeOH using SRF-1 and 1.24 MWhel/t MeOH with SRF-2.

For what concerns specific fossil CO_2 emissions, the conventional technology of steam reforming is considered to generate 0.33 kg CO_2 $_{FOSSIL}$/kg MeOH, including indirect electric consumption emissions. This value is in line with the range reported in (NETL, 2013). In the simulations of the WtC process, specific emissions calculated when SRF-1 is employed are equal to 2.21 kg CO_2 $_{FOSSIL}$/kg MeOH. The use of SRF-2 generates 2.58 kg CO_2 $_{FOSSIL}$/kg MeOH, also accounting for indirect emissions.

Despite the better specific production, the utilization of waste material with higher LHV generates higher specific fossil emissions because of its zero biogenic content. Hence, the conventional technology produces lower specific fossil emissions than WtC technology.

4.4. Comparative analysis for methanol and clinker production

The main numerical results of the comparative analysis for methanol and clinker production with SRF-1 and SRF-2 are reported in Fig. 4, specifying primary energy and electric consumptions and fossil CO_2 emissions. Detailed information on results have been reported in the Supplementary Material (§ S6.2). The considerations on energy demand and on fossil CO_2 emissions for the two scenarios of methanol and clinker production are in line with the reported considerations for hydrogen and clinker generation. For the two Cases A, thermal energy demand accounts for natural gas for methanol synthesis and from SRF and pet coke for clinker generation, meanwhile electric energy is consumed by the cement plant and by the steam reforming technology. In Cases B, the thermal energy demand accounts for pet coke for clinker production and alternative fuel in WtC process for methanol generation, with an electric consumption for the cement plant and for the WtC technology reported separately.

Fig. 4 highlights the higher energy demand for Cases B with respect to the corresponding Cases A in order to generate the same amount of final products: with SRF-1, Case B consumes 6.2 % more primary energy than Cases A and the extra consumption for Case B with SRF-2 is 5.6 %. The WtC technology presents a lower efficiency than the conventional technology and, thus, it requires a higher energy demand to generate the same amount of methanol. The utilization of the SRF with a higher LHV causes only a slight increase in WtC energy efficiency, with steam reforming technology achieving better performances.

A similar comparative analysis is also considered for fossil CO_2 emissions. The emissions deriving from calcination of the raw meal and from electric consumption of cement plants are not reported because
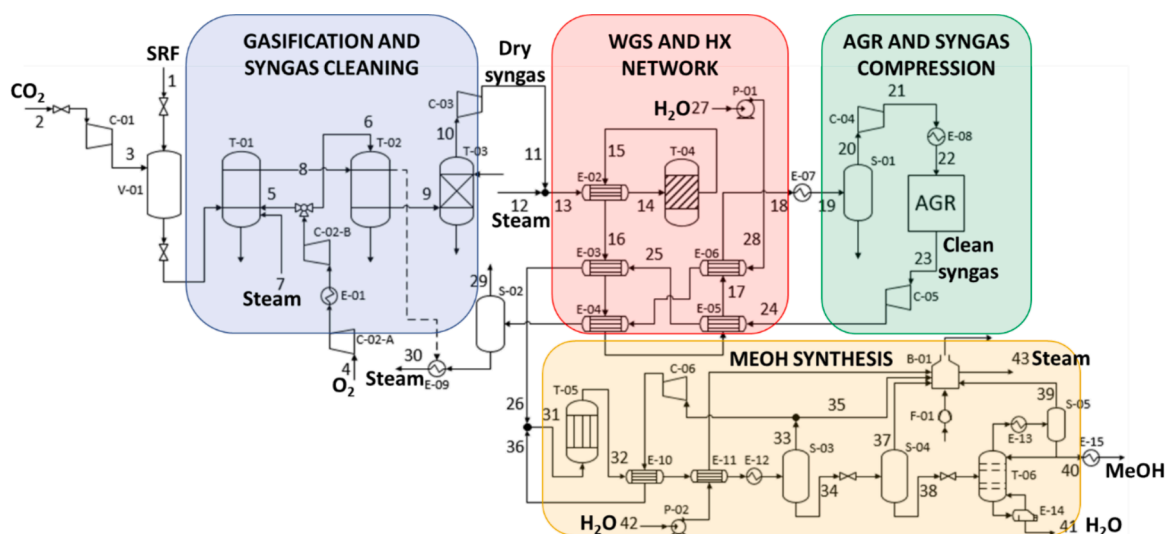

Fig. 3. Process flow diagram of the WtC process for methanol production.

Table 4
Performances of the WtC technology for methanol production using SRF-1 and SRF-2.

Methanol production simulations		SRF-1	SRF-2	
Mass balance				
ID	Stream	Value	Value	Unit
1	SRF	15.97	15.13	t/h
2	CO_2 lock-hopper	0.60	0.57	t/h
4	O_2 gasification	15.59	21.60	t/h
5	O_2 first stage	10.43	15.31	t/h
6	O_2 second stage	5.16	6.29	t/h
	Steam	13.75	15.42	t/h
7	Gasification	6.37	8.69	t/h
12	WGS	5.97	6.43	t/h
–	AGR	1.41	0.30	t/h
10	Dry syngas	25.70	32.21	t/h
	Produced MeOH	8.52	11.28	t/h
Energy duty				
ID	Description	Value	Value	Unit
	Electric power	10'515	13'996	kWel
C-01	CO_2 compressor	3	3	kWel
C-02	O_2 compressor	749	1'037	kWel
C-03	Syngas compressor	1'868	2'603	kWel
C-04	Inlet AGR compressor	746	1'019	kWel
C-05	Shifted gas compressor	510	758	kWel
C-06	Recycle gas compressor	340	338	kWel
F-01	Boiler air fan	15	69	kWel
P-01	Water pump heat exchanger	11	10	kWel
P-02	Water pump boiler	3	7	kWel
–	AGR auxiliaries (pumps, compressors)	1'525	1'705	kWel
–	Air Separation Unit (ASU)	3'897	5'399	kWel
–	From thermal duty	846	1'048	kWel
Specific indicators				
Indicator		Value	Value	Unit
Specific O_2 consumption		0.98	1.43	kg O_2 gasif /kg SRF
Specific steam consumption		0.86	1.02	kg steam TOT/kg SRF
Gasification		0.40	0.57	kg steam gasif/kg SRF
WGS		0.37	0.43	kg steam WGS/kg SRF
AGR		0.09	0.02	kg steam AGR/kg SRF
Specific MeOH production		0.53	0.75	kg MeOH/kg SRF
Specific electric consumption		1.23	1.24	MWhel/t MeOH
Specific CO_2 emission (fossil)		2.21	2.58	kg CO_2/kg MeOH
Energy efficiency		0.43	0.44	GJ MeOH/GJ SRF

they are assumed to be constant for all the scenarios.

Cases A (SRFs in co-combustion for cement production and methanol from steam reforming) generate lower fossil emissions than corresponding Cases B (SRFs for methanol production). Indeed, using SRF-1, Case B generates 30.2 % more fossil CO_2 emissions than Case A and with SRF-2 the extra emissions of Case B are 28.4 % compared to corresponding Case A. Cases B are characterized by a higher specific emission factor of the WtC process than the conventional technology and this is the main cause of the higher fossil CO_2 emissions of Cases B. Moreover, when SRF-1 is used, the cement plant of Case B does not benefit from a partial substitution of fossil emissions as the cement plants are fed with pet coke only.

5. Conclusions and recommendations

The present work investigates chemical recycling technologies based on gasification to treat solid recovered fuel composed of residual fractions from plastic sorting. A comparison between waste-to-chemical processes with SRF utilization and the well consolidated co-combustion in cement plant has been carried out to evaluate whether the alternative waste treatment pathway can provide a sustainable solution in terms of energy efficiency and environmental impact (i.e., fossil CO_2 emissions). In the analysis, two different types of SRF have been considered (with and without biogenic carbon) and fed to two different WtC technologies for hydrogen and methanol production simulated in

Aspen Plus®.

For the two SRFs, two different cases have been compared: Case A and Case B. Case A is representative of the state-of-the-art pathway, with SRF used for co-combustion in cement plants, and hydrogen or methanol produced with conventional steam reforming technology. Case B has been defined to describe the alternative application of the SRF in the WtC process for chemical synthesis, meanwhile clinker is produced by a cement plant fed with pet coke only.

WtC technologies for production of both hydrogen and methanol show a mass yield (kg$_{chemical}$/kg$_{SRF}$) which is ~ 40 % higher when fed with SRF-2 characterized by no biogenic content and higher LHV (+37 % with respect to LHV$_{SRF-1}$). On the other hand, limited beneficial effects on the energy efficiency have been recorded when using fossil SRF in WtC, highlighting the relevance of steam production impacts on the energy performance.

All the investigated scenarios report Cases B showing higher energy consumptions and higher fossil CO_2 emissions than the corresponding Cases A, mainly due to the lower specific yields and higher specific emissions of the WtC processes with respect to the conventional technology for hydrogen and methanol production based on steam reforming. When WtC technology is used (Cases B), additional 9.1 % (SRF-1) and 8.6 % (SRF-2) of energy consumption is estimated and 25.8 % (SRF-1) and 24.1 % (SRF-2) additional fossil CO_2 is emitted with respect to the corresponding conventional cases (i.e., chemical from steam reforming and SRF burnt in the cement kiln) to produce clinker and hydrogen. For
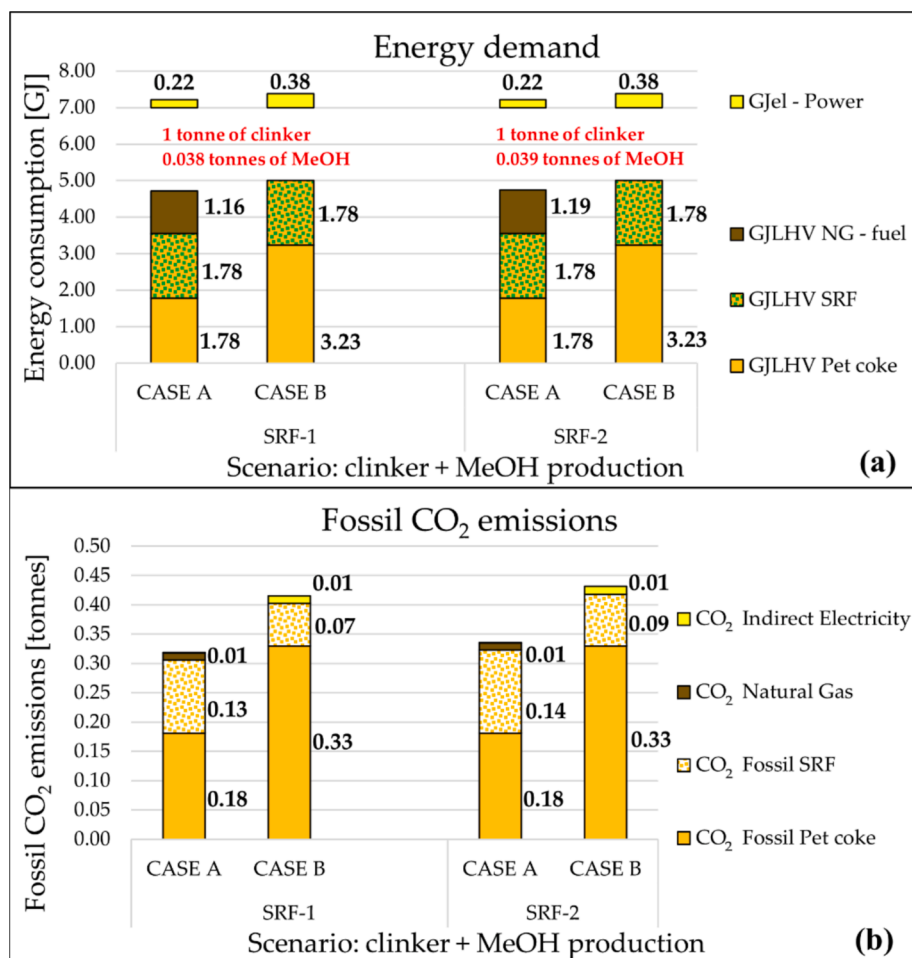
Fig. 4. Main results of the two scenarios for methanol and clinker production. (a) Comparison of energy demand. (b) Comparison of fossil CO_2 emissions.

methanol and clinker production, scenarios using the WtC technology record 6.2 % (SRF-1) and 5.6 % (SRF-2) increase of primary energy and 30.2 % (SRF-1) and 28.4 % (SRF-2) additional fossil CO_2 against the conventional cases.

In conclusion, co-combustion of solid recovered fuels in cement plant is nowadays a well-established strategy to reduce consumption of fossil fuels and to decrease fossil CO_2 emissions associated to clinker production, thanks to the partial biogenic content and to the lower CO_2 emission factor of the alternative fuels.

Since WtC processes usually require high quality waste as input material to increase their mass yields, this may compete with mixed plastics utilization in the cement sector, which is needed to stabilize the inlet SRF material employed in the co-combustion processes. Therefore, SRF stabilization allows to burn low-quality waste fractions, hence finding a valuable fate with respect to landfill disposal. If mixed plastics will no longer be available to cement plants, co-combustion could lose its role in the non-recyclable waste treatment, also hindering one of the decarbonization strategies of this "hard-to-abate" sector leveraging on the SRF biogenic content.

On the other hand, WtC technologies offer the possibility to generate valuable products starting from non-recyclable waste, avoiding consumption of fossil fuels towards circular economy. Given the scarce amount of publicly available information, further investigation is required to thoroughly assess WtC performance, addressing future work to maximize energy recovery from steam production. Moreover, recording experimental data at relevant scale is necessary to validate simulation results, paving the ground for a thorough Life Cycle Assessment (LCA). Even if the results of this study provide relevant insight on

the sustainability of the studied technologies within the proposed framework, additional tools (Aghbashlo et al., 2022; Soltanian et al., 2022) can be applied to comprehensively assess the environmental outcomes of WtC adoption.

CRediT authorship contribution statement

A. Conversano: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization. **D. Sogni:** Writing – original draft, Validation, Software, Investigation, Formal analysis, Data curation. **G. Lombardelli:** Writing – original draft, Validation, Software, Methodology, Investigation, Data curation. **D. Di Bona:** Writing – review & editing, Visualization, Supervision, Project administration, Investigation, Formal analysis, Conceptualization. **F. Viganò:** Writing – review & editing, Visualization, Validation, Supervision, Investigation, Data curation, Conceptualization. **S. Consonni:** Writing – review & editing, Visualization, Supervision, Project administration, Methodology, Investigation, Conceptualization.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2024.10.006.

Data availability

Research data and detailed process simulations results reported in the supplementary material

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