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Combined Oxidation-Gasification system for waste treatment with supercritical water: LCA and performance analysis.

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Abstract: In this study the environmental performance of a first of a kind integrated process based on supercritical water gasification and supercritical water oxidation, was evaluated using Life Cycle Assessment (LCA). The process was applied to the treatment of carbon black and used oil as model waste. Mass and energy balances were performed using Aspen Plus, and the environmental assessment was carried out through SimaPro. For the analysis was chosen a "From cradle to grave" approach, considering impact categories like climate change, ozone depletion, human toxicity, particulate matter, land use, resource depletion and others relevant indicators. The environmental profile of SCW-GcO process was compared to other technologies for treatment of dangerous wastes, solvent mixture and exhaust mineral oils by using Ecoinvent database. It is shown that SCW-GcO allows reducing impacts in different category and obtaining a favorable positive life cycle energy balance, achieving a good environmental performance.

Keywords: Supercritical water, oxidation, gasification, Life Cycle Assessment, waste, carbon black.

1. Introduction

The enhancement of people's living levels increases the volume of organic waste that is produced worldwide. Waste landfilling is an unsuitable method that leads to unacceptable occupation of land, polluted soil and water and air pollution. New generation incinerators have reached a noticeable level of air pollution control, but some major drawbacks do continue to exist. On average, the efficacy of an incinerator to reduce the solid mass of waste is only 70%. Despite the low concentration of armful pollutant at the stack (dioxins, fine particulate and NOx), the total amount of pollutants emitted in the atmosphere is huge and it increases year by year.

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In an influential report, the National Academy of Science expressed substantial degree of concern for the effects of incremental burden of emissions from multiple incinerators on a region, which can expose a very broad population to pollutants such as dioxin and some metals that are recognized as persistent, widespread and potent [1].

Air pollution, disease extension and social problems should encourage research towards new technologies that are able to overcome drawbacks of landfilling and incineration. Supercritical water based processes could be one of such technologies, if some technical problems were solved.

Supercritical water based processes were developed since the ’70s of the last century to exploit the extraordinary properties that water exhibits above its critical point (22.1 MPa and 374°C): a drastic decrease in pH, dielectric constant, ionic product, viscosity and thermal conductivity [2]. At these conditions SCW essentially acts as a non-polar fluid with solvation properties resembling those of low-polarity organic fluids and is able to dissolve organic matter breaking down molecules.

Properties of supercritical water have been exploited for the treatment of organic matter through two main processes: supercritical water gasification (SCWG) and supercritical water oxidation (SCWO). The main idea of SCWG is to benefit from the special properties of SCW as solvent and reaction partner for fast hydrolysis of organic matter and consequent production of pressurized gases (mainly H_2, CH_4, CO and CO_2). High solubility of the intermediates in the reaction medium significantly inhibits tar and char formation that are one of the main drawback of conventional gasification. Indeed, the reactive species originating from organic matter are solvated in water and consequently the reaction rate of polymerization to unwanted products like tar and char is reduced. Altogether, this leads to high gas yields at relatively low temperatures [3].

SCWG has been mainly studied for the valorization of biomasses such as ligneous-cellulosic materials, sewage sludge, wastes from agro-food industry, and microalgae [4]. However, until now this technology has not found an industrial scale operating application

The main drawbacks of SCWG are:

1. Conversion of organics to gas is complete only in very limited cases. For instance, when the organic concentration is low (say <5%wt), when reactor temperature is very high (T>700 °C), when special catalysts are used, or when in the organic matter the C/O mole ratio is low [5].
2. SCWG needs a high amount of heat to bring water to operating conditions. This heat increases when the organic concentration is kept low [6].
3. The amount of organic matter that is not converted to gas remains dissolved in liquid water after depressurization of the effluent stream. This polluted water has a very high organic content (TOC range of 2000-11000 mg/l) that must be treated as a special waste [7].

In the case of SCWO, an oxidant (air or pure O_2) is added to the reaction medium in order to totally oxidase organic matter that is dissolved in water. Product gas is mainly composed of CO_2 and excess O_2 [8]. Thanks to the relatively low temperature of the process (T<800 °C), when compared to conventional incineration, NOx and dioxins are not produced [9]. Acid substances such as HCl, H_2SO_3 and H_3PO_4 remain dissolved in liquid water after the cooling of the reaction phase, and so do not pollute the effluent gas [10].

SCWO is able to convert organic matters with yields in the order of 99.9% in a short residence time

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(30 to 180 s). The reaction is exothermic and a large part of the heat produced from the reaction can be recovered in properly designed heat exchangers downstream of the reactor [11]. Because oxidation transforms all organic matter into CO_2, organic matter, when treated through SCWO, is not exploited as a source of valuable gas and organic liquids. For this reason, SCWO is properly employed as a final stage of the treatment of wastes at the end of their life cycle. Another special application is that of very dangerous wastes that require a reaction environment having a high content of water. Some examples of special wastes treated through SCWO are: explosive matter [12], polychlorinated biphenyls (PCBs), sewage sludge, spent catalysts, and chemical weapons [13] [14].

Up to know, little work regarding the combination of the two technologies has been developed.

In a study by Qian et al. [15] a combined process for the treatment of sewage sludge is proposed. The aim of the process is to reduce the oxidant consumption in SCWO, using SCWG as a pretreatment of sewage sludge. No heat integration between the two reactors has been considered.

In our vision, SCWO and SCWG reactors can be coupled in a manner that allows a continuous exchange of matters and heat between the two reactors. In this way advantages of both SCWG and SCWO can be valorized and their drawbacks can be overcome.

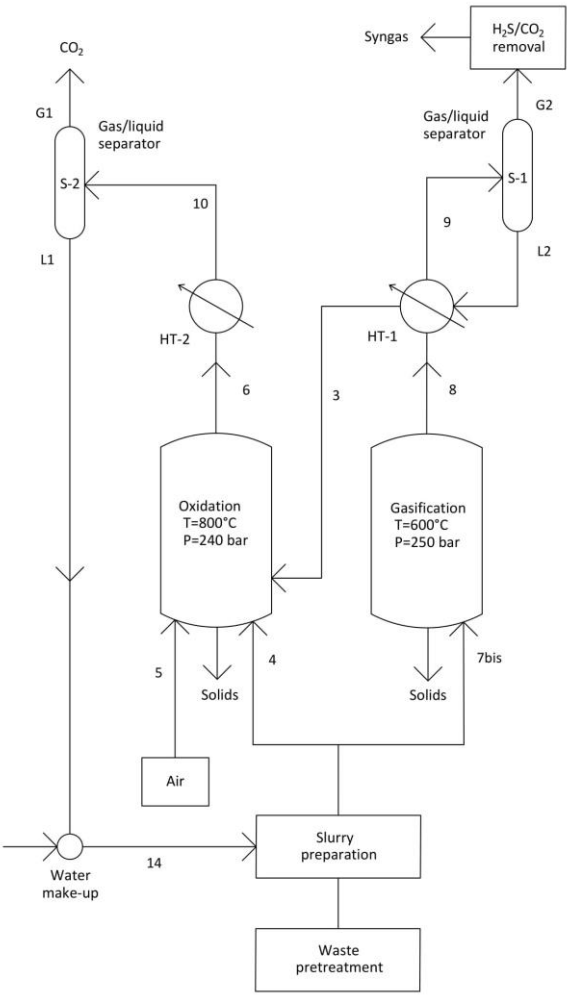
2. A new process design

This work proposes a first of a kind integrated process that allows an efficient use of these two technologies through a combined reactor that is able to maximize the performance of both SCWG and SCWO. The Supercritical Water Gasification combined Oxidation (SCW-GcO) concept is illustrated pictorially in figure 1 where main input and output streams are reported.

In principle, the primary feedstock could be any organic matter in solid or liquid state. In the case of municipal solid waste (MSW) the pre-treatment could be a pyrolysis unit that transforms the waste in an oily stream and a carbonaceous stream. Because for a given gasifier the admissible range of feedstock properties is narrow [16], feedstock at the gasifier could be preferably an organic waste at liquid state such as a mixture of solvents, chemicals and oil from chemical and process industry. On the contrary, oxidation can support much more change of feedstock composition and can also accept solids suspended in water.

The waste at liquid state mixed with water, is at first sent to the SCWG reactor (stream 1) where it is

Figure 1. Pictorial scheme of the SCW-GcO process



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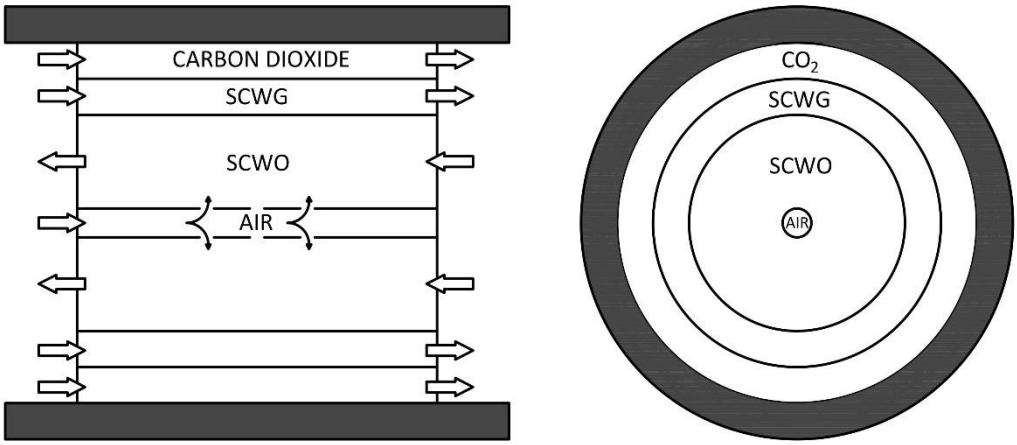
partially converted to a gasification reactor effluent (stream 2), which after cooling and gas-liquid separation (S-1) gives rise to a hydrogen-rich syngas stream (stream 3) and a liquid water/oil mixture ("oil" being partially gasified organic matter, whose amount depends on the gasification yield) (stream 4). After heating in a high-pressure heat exchanger (HT-2), it is continuously fed to the oxidation reactor where all organic carbon is completely converted to CO_2 (conversion yield >99.9%) (stream 5), producing the heat necessary to sustain gasification. The oxidation reactor is fed with compressed air and a secondary charge of waste (solid and/or liquid organic feedstock) (stream 6) that have the role to sustain the oxidation reaction. The H_2 rich syngas (stream 3) is treated to strip CO_2 and possible traces of polluting gas (H_2S).

This process arrangement allows overcoming two drawbacks of gasification:

1. Since supercritical water gasification does not reach 100% efficiency (typical efficiency are between 60-90% depending on the feedstock), the liquid residue of gasification that is an harmful waste can be destroyed in the integrated oxidation section.

2. the SCWO generates the heat that is necessary to sustain the endothermic gasification with an improvement of the heat balance of the process.

Figure 2. Internal design of the Supercritical Water Gasification combined Oxidation



The main feature of the combined plant is that the two reactors (gasification and oxidation) are fully integrated from a chemical and thermal point of view as shown in figure 2.

The outside wall of the reactor is made of stainless steel resistant to high operating pressures. The internal volume is separated in three concentric chambers by means of septa made in titanium to stand up to corrosion. The differential pressure between the chambers is regulated at few bars, in order to use thin septa. The central volume is used for oxidation, where air must is supplied as feed for the reaction. To ensure that air reacts exclusively in the central part of the reactor, to avoid the formation of hot spots, it is introduced into a cylinder with three lateral holes in the reaction zone. Adjoining area is where gasification occurs, without oxygen. The third chamber, in contact with reactor wall, is crossed by carbon dioxide or other gas, which acts as cooling fluid and inert fluid that protect the wall from corrosion. The reactor is also a heat exchanger with countercurrent flows, where hot oxidation products preheat the cold gasification input current.

This technology has been patented [17].

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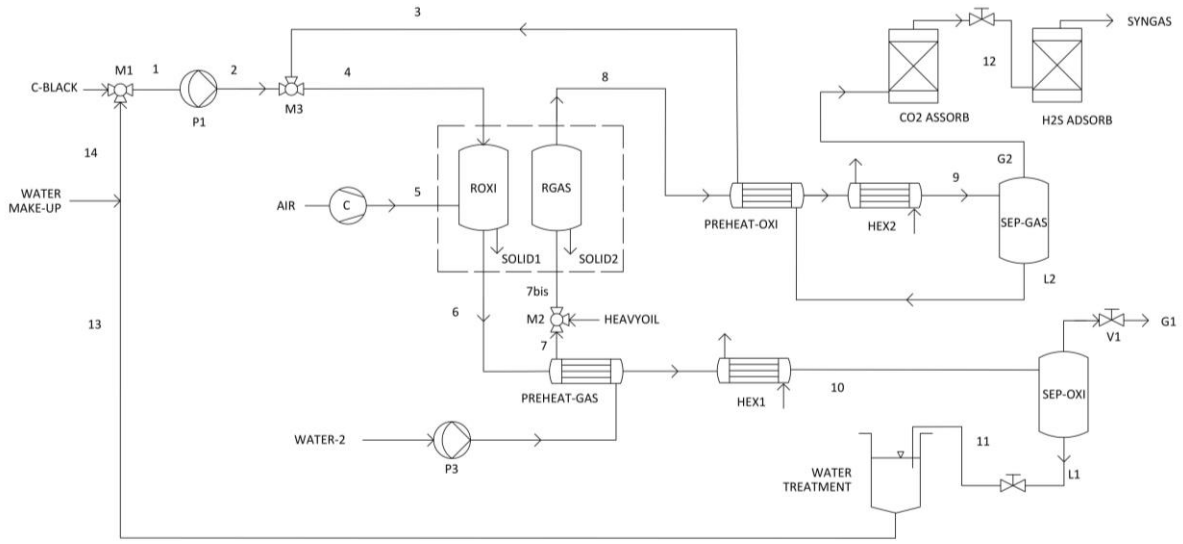
3. Model and Simulation

In the following paragraph a base process scheme of SCW-GcO with a nominal capacity of 100 kg/h is presented and discussed. The process has been simulated using AspenPlus™ package. The conceptual process design is described in figure 3 where a flowsheet is reported.

Figure 3. Flowsheet of SCW-GcO process



Organic matter could be any kind of waste matter in solid or liquid state. As an input of the simulation we selected heavy oil for gasification and carbon black for oxidation which properties are reported in table 1.

Table 1. Characterization of main input flow

HEAVY OIL	
HHV *[MJ/kg]*	43.39
Composition	
Heavy-oil has been simulated as a mixture of 36 compounds including alkanes such as hexane, cycloalkanes, aromatics such as benzene and thiophene	

CARBON BLACK	
HHV *[MJ/kg]*	37.77
Composition *[%weight]*	
C	15.9%
PYRENE	15.7%
FLUANTHE	15.7%
ANTHRACE	13.8%
PHENANTR	13.8%
NAPTHALE	12.4%
CARBAZOL	6.1%
DINITROP	3.3%
DMETDBTI	1.2%
METDBTIO	1.1%
DIBENTIO	1.0%

The process consists of:

1. Mixing unit (M1) where organic matter (C-black) is mixed with water at the desired concentration and pumped up to 25 MPa by means of pump P1. The concentration of the organic must be carefully selected on the basis of two constrains: a) the capacity of the pump to effectively prime the slurry at high pressure; b) the heating value of the organic matter must be sufficient to sustain gasification.

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2. Mixing unit M3 where C-black slurry (stream 2) is mixed with stream 3 that is a water slurry that contains the un-gasified products that comes from the gasification section.

3. PREHEAT-OX where stream 3 prior to enter in the oxidation reactor is pre-heated by hot gasification products (8).

4. SCW Oxidation reactor (ROX) fed with hot water slurry (4) formed in M3 and compressed air (5) through compressor C.

5. The supercritical water gasification reactor (RGAS) is fed with a water slurry formed by mixing in M2 hot water (7) and heavy-oil. Water is fed by pump P3 and, prior to enter in RGAS, is pre-heated in a heat exchanger (PREHEAT-GAS) by oxidation product (6).

6. After cooling in the heat exchangers PREHEAT-GAS and HEX1, the oxidation products are separated in SEP-OX where two phases are obtained. A gas phase G1, which is made mainly by carbon dioxide, nitrogen and unreacted oxygen. A liquid phase L1, which is made mainly of water and acid products formed during oxidation.

7. The gasification products (8) are extracted from the reactor, cooled in PREHEAT-OX and HEX2 and finally separated in SEP-GAS where a gas phase (G2) and a liquid phase (L2) are formed. G2 is a syngas composed of H_2, CH_4, CO, CO_2 and traces of other light hydrocarbons. If sulphur would be present in the organic fed, H_2S will form during gasification. In this case, a H_2S removal unit (H2S-ADSORB) would be necessary to purify the product gas. It is forerun by CO2-ASSORB unit, which is necessary to remove CO_2 from syngas.

8. Streams solid1 and solid2 are ashes and salts that eventually precipitate in the reactors and must be removed.

Although simulation were performed at various temperature and feed concentrations, we report here a description corresponding to only one set of operating conditions whit the gasification temperature set at 600 °C and oxidation temperature at 800°C.

The input of the plant is made up of four streams: pure water at 16 kg/h (PERCOLAT), pure water at 14.17 kg/h (WATER), carbon black at 4.0 kg/h (C-BLACK); pyrolysis oil at 4.72 kg/h (HEAVYOIL); air at 60 kg/h (AIR). The simulated output steams are: G1 (CO2-OUT) gaseous products of oxidation after separation from liquid phase, L1 (ACIDWTR) aqueous products of oxidation containing sulfuric and chloridric acid, SOLID1 ash formed in the OXIDATOR, SOLID2 ash formed in the GASIFIER, CH4-OUT The main product stream, RESIDUE CO2 and H2S obtained after gas cleaning.

Table 2. Operative conditions of SCW-GcO process streams

STREAM	**T** *[C°]*	**P** *[bar]*	**FLOW RATE** *[kg/h]*
C-Black	25	1	4
1	25	250	20
2	268	250	10.1
3	141	250	30.1
4	135.11	250	30.71
6	307.55	250	90.71
8	359.84	250	18.9
9	100	250	8.18
Water2	25	1	14.17
Heavy-Oil	25	1	4.72
G1	60	250	59.5
L1	60	250	31.21
G2	100	250	8.19
SYNGAS	59.96	1.9	3.3
AIR	25	250	60
PERCOLAT	25	1	16

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3.1 Gasifier model

The gasification section is modelled by applying a RGibbs block, which predict the final product composition based on the principle of minimizing the total Gibbs free energy. The expected species specified in the Gibbs block consist of major gas constituents (CO, H_2, CO_2, CH_4), light hydrocarbons (C_2H_4 and C_2H_6), inorganic species (HCl, H_2S, N_2, NH_3, COS and HCN) and tar components (C_6H_6, C_7H_8 and $C_{10}H_8$ and higher hydrocarbons). The design residence time of the gasifier has been set at 120 s.

The Gasification Efficiency, defined as

$$\mathbf{GE}, \% = \frac{\mathbf{Gas\ Mass\ Flow\ Rate\ Out}}{\mathbf{Mass\ Flow\ Rate\ In}} \times \mathbf{100} \quad (1)$$

is 43.3%. It expresses the mass of as produced in the gasification chamber with respect to the amout of organic matter fed to the reactor. The flow rate and gas compositions of produced gas are reported in table 4. These value refers to stream G2 at the exit of the separator. The liquid stream L2 is mainly composed of water (98%), carbon dioxide (1.55%), methane (0.18%), hydrogen sulfide (0.18%) and traces of hydrogen, carbon monoxide, ethane.

Table 3. Compositions and flow rates of gas produced from gasification section of the SCW-GcO plan

	Molar flow rate *[mol/h]*	**GAS OUT composition** *[mol%]*
H_2	58.2	6%
CO	6	1%
CO_2	105.2	11%
H_2S	6.27	1%
SO_2	6.37E-08	0%
CH_4	217.65	23%
C_2H_6	0.057	0%
Water	570.26	59%
Total molar flow	963.64	100%

For what concerns oxidation section, the efficiency is expressed as % of TOC removal from the inlet stream of organic matter.

$$\mathbf{TOC_{removal}}, \% = \left(\mathbf{1} - \frac{\mathbf{TOC_{effluent}}}{\mathbf{TOC_{feed}}}\right) \times \mathbf{100} \quad (2)$$

where TOC is the total organic carbon (mg/L). The effluent is the stream L1 at the exit of the oxidation separator. The feed is the stream 4 (figure 3). In our case study, the TOC has been calculated as 99.3%, which is a value coherent with that measured experimentally, that typically are above 99%.

The stream G1, at the exit of the oxidation separator, is mainly composed by: N_2 (83.05%), CO_2 (15.7%), Ar (0.9%), H_2O (0.3%) and O_2 (0.01%); which allows a direct discharge to atmosphere without further post-treatments.

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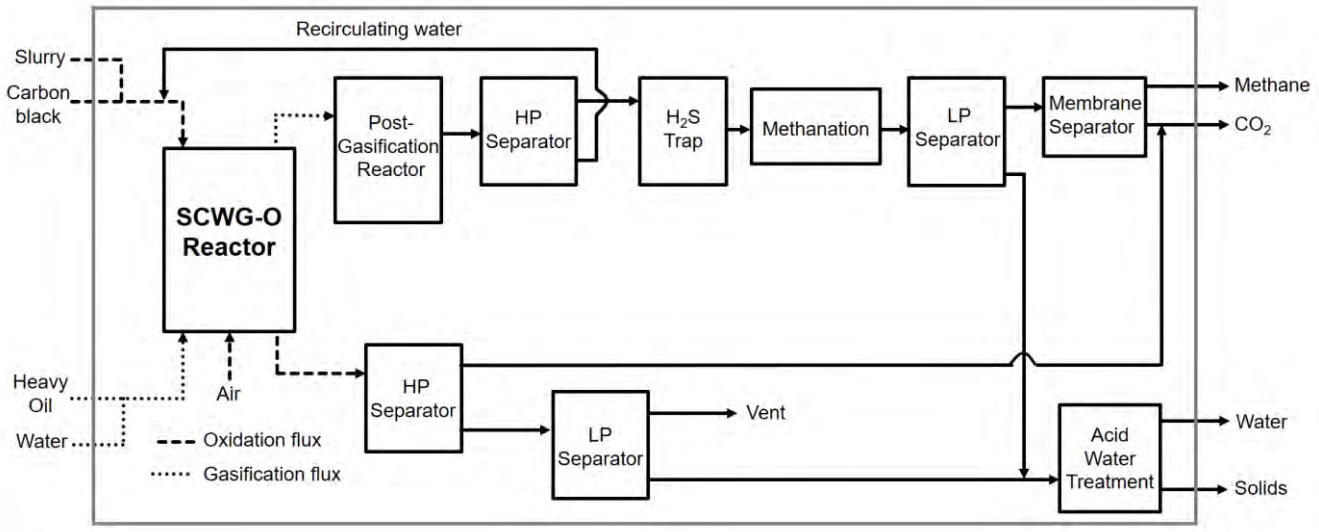
3.2 Life Cycle Assessment

The goals of this analysis is the evaluation of energy-environmental performance and the identification of the hot spots of the SCW-GcO process. The functional unit referred to throughout the LCA is a ton of treated waste (carbon black, heavy oil and leachate inputs). Analysis is carried out according to a "cradle to gate" approach: from the extraction of raw materials to the production of methane deriving from the treatment of waste. The supply chain of the waste to be treated has been neglected, such as leachate, carbon black, heavy oil and the plant start-up phase. Looking entire useful life, considered in ten years, in terms of environmental impact the start-up phase is negligible. The end-of-life and disposal phases of the plant were also not taken into consideration. In fact, since the object of study is a pilot system in the construction phase, the results obtained, referred to this phase, would be characterized by a high uncertainty and would therefore be unreliable. Two cases were examined:

- in the first (*Case 1*) the co-production of methane will not consider;
- in the second (*Case 2*) the avoided impact associated with this valuable product will be quantified.

For avoided impact mean that the methane produced decreases the consumption of natural gas, from fossil sources, used for feeding the users connected to the distribution network. This benefit associated with the production of methane is appreciated exclusively during use. During production this has not any influence on energy consumption and the environmental impacts assessed. The functional unit (FU) of reference for LCA is 1 ton of treated waste: carbon black, heavy oil and leachate. System boundaries (SB) determine the process units to be included within the evaluated system. The system boundaries set for the LCA of SCW-GcO are shown in Figure 4. In *Case 2* boundaries are extended to power plant for electricity production using methane.

Figure 4. Life-cycle flowchart of the overall system



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4. Results

Before analyze environmental impact, energy consumptions were examined. These concern production phase and working phase of the pilot plant. About production of components, reactors required highest energy consumption (Fig. 5). They are non-commercial components custom made for the pilot plant.

Figure 5. Primary energy for the production of components

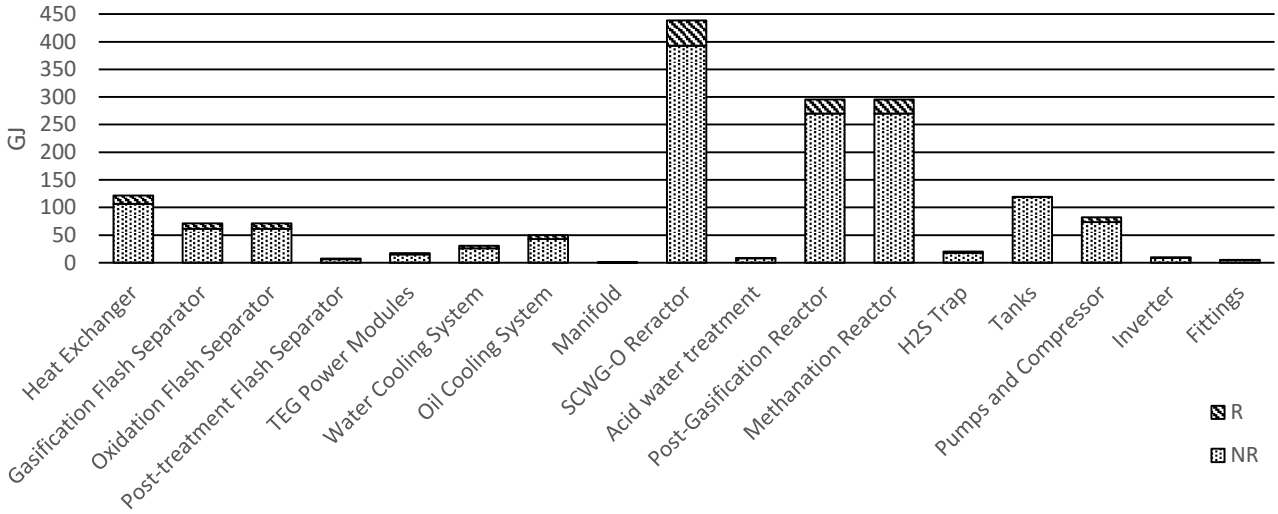


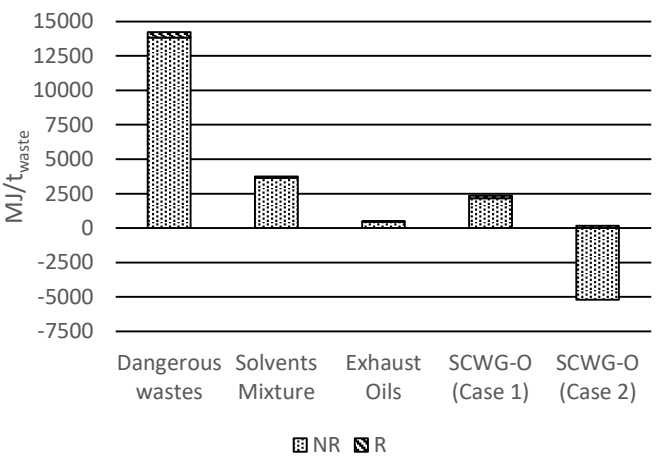
Table 4. Output streams description (Ecoinvent v3.5 database)

Output stream	LHV [MJ/kg]	EE [MJ/kg]	TE [MJ/kg]	Residues [kg/kg$_{waste}$]
Dangerous Wastes	17	17,11	1,27	0,07563
Solvents Mixture	21,7	17,11	1,27	0,07563
Exhaust Oils	34,7	25,82	2,44	0,01143

Novel process was compared with typical hazardous waste incinerators (HWI) for the treatment of dangerous wastes, solvents mixture and exhaust oils (Table 4). Plant has wet flue gas scrubber and low-dust SCR DeNO$_x$ facility. Gross thermal efficiency 74,4% and gross electric efficiency 10%.

As show in Figure 6, *Case 2* has negative consumption due to methane recovery and use for electric energy production. It is clear that this case is the most suitable to replace old system for the treatment of hazardous waste, that's been taken into consideration for the environmental impacts analysis. Figures 7-9 summarize the main results of LCA with all impact categories considered by SimaPro software and its databases: Climate change (CC), Ozone depletion (OD), Human toxicity with cancer effects (HT-C), Human toxicity without cancer effects (HT-NC), Particulate matter (PM), Ionizing radiation HH (IR-HH), Ionizing radiation E (IR-E), Photochemical ozone formation (POF), Acidification (AC), Terrestrial eutrophication

Figure 6. Energy consumption in working phase



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(TE), Freshwater eutrophication (FE), Marine eutrophication (ME), Freshwater ecotoxicity (FE), Land use (LU), Water resource depletion (WRD), Mineral, fossil & renewable resource depletion (MFRD).

In particular, regarding incineration of Dangerous Wastes, SCW-GcO process has less impacts in every category as show in Figure 7. About incineration of Solvents Mixture (Fig. 8), combined process has higher impacts in AC due to a greater production of acid water and in WRD due to an higher consumption of water for the dilution of inputs. Comparison in Figure 9 between SCW-GcO and incineration of Exhaust Oils show as there is not a best process between they. Only in two categories impacts are comparable, in other cases one process is better than other. The choice must be made evaluating the importance of each category. As shown previously, energy consumption is favored in combined system.

Figure 8. Impacts comparison between Dangerous waste incineration and SCW-GcO

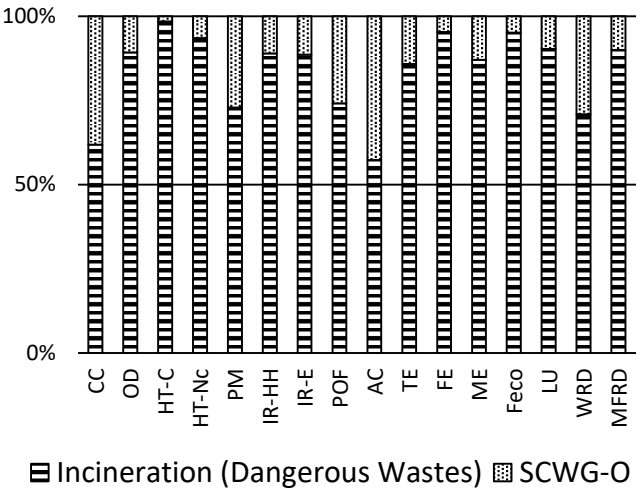


Figure 7. Impacts comparison between Exhaust oil incineration and SCW-GcO

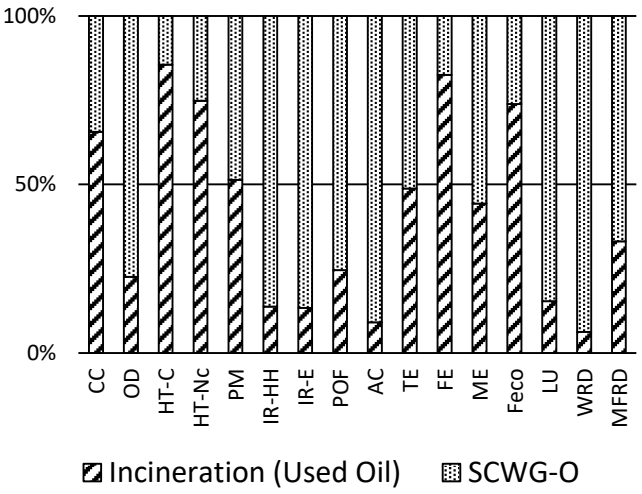
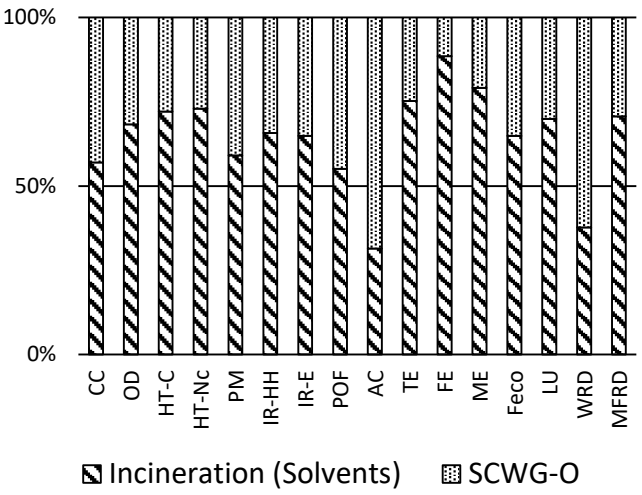


Figure 9. Impacts comparison between Solvents incineration and SCW-GcO



5. Conclusion

The main goal of the current study was to determine if the innovative process can be a viable alternative to classic incineration treatment of hazardous wastes. Analysis has shown that in most of the cases SCW-GcO is the best option for minor environmental impact and in all cases has a less energy consumption to clearly of methane produced use.

SCW-GcO is a new process that has been designed and simulated in the framework of research program Moterg-Bio, financed by the Italian Minister of Industrial Development (MISE). This work was supported by Archimede Solar Energy S.r.l., Italy, and financed by the Italian Minister of Industrial Development (MISE). SCW-GcO has been patented: international patent request number PCT/IB2016/052044.

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