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Approach for Smart Use of Wastes and Biofuels

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ABSTRACT

The urgent need to reduce greenhouse gas emissions by gradually abandoning fossil fuel sources is required due to climate-changing emergencies. Employing as much as possible renewable energy, in any form and any field, together with a reduction of per capita energy need, can reduce this tendency and contrast the catastrophic consequence of our planet temperature increasing. In this scenario, biofuels production, together with reuse and recycling represent a correct strategy to contrast environmental degradation. Biofuel has been the subject of great interest over the past decade. Their development from the first to the fourth generation has led to significant improvements in the production cycles and extended the interest in new resources. The availability of different choices could permit to use always the best solution to maximize the result.

In this paper, the different biofuel generations are presented with the aim of highlighting strengths and weaknesses to identify a smart approach to energy conversion and land utilization. Even today the first-generation biofuels are the most widespread, while second-generation gives a small contribution, with a low replacement share of fossil fuels. Land use and competition with other human necessities are the most relevant constraints in this evaluation. In general, the production of gaseous fuels requires less energy than liquid for both the first as well as second-generation technologies. When considering gaseous options, biomethane should be preferred for convenient energy balance in the productive process and when biogas cannot be directly employed. Moreover, biomethane gives the possibility to be added to the existing gas network. The new third and fourth-generation technologies could allow a considerable efficiency increase while reducing the problem of the biofuel productive chain.

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1. Introduction

The increasingly evident effects of climate change require rapid and decisive action to limit its harmfulness, given the continuous increase in CO₂ concentration in the atmosphere (today about 420 ppm). The European community set some objectives in the past aimed at the reduction of greenhouse gas (GHG) emissions by 2020 [1, 2]. The objectives were: renewable sources at 20% of the total energy consumption, energy saving of 20% to reduce primary sources consumption, and a minimum share of 10% of biofuels in transport. All these goals were overall achieved, even if not uniformly in the countries involved, [3]. However, the meet of this first important milestone was facilitated by the availability of renewable sources that were easier to access, also being energy and economically most convenient to exploit. The challenge, on the other hand, is more difficult with the new objectives of the European Green Deal for 2050, which set a very ambitious goal of eliminating net GHG emissions by 2050 [4]. The achievement of these objectives will require a total and progressive reorganization of the production system, supported by considerable economic efforts, in addition to the exploitation of renewable resources that are more difficult to access. All the sectors should be involved to reconsider the exploitation of resources in a global way avoiding any form of waste. To this end, a strong contribution to reducing the demand for energy and materials should come from the development of circular economies and the widespread use of secondary raw materials (i.e. materials or products no longer usable for the initial purpose) that will be part of a new system instead of becoming waste. In the transport sector, especially land-based ones, total decarbonisation focuses heavily on progressive electrification through renewable sources. However, the use of biofuels, as well as in fixed plants to produce electricity, will also be significant for powering vehicles with endothermic engines or fuel cells. The coexistence of biofuel vehicles with electric ones would allow a lower demand for batteries. This strategy could limit the exploitation of raw materials for their production, which would seem not globally sustainable, in the light of current knowledge. Moreover, biofuels could be indispensable for decarbonising sectors that are difficult to electrify, such as naval or air and land over long distances. In any case, the complexity and extent of the problem will require an approach with multiple solutions. Therefore, there will not be a single energy system, but many diversified ones to reduce GHG emissions, even at a local level. This procedure could favour the most efficient production technologies that minimize competition with other primary needs of local ecosystems.

Knowledge and technologies for biofuel production have greatly improved over the past decade. Today it is possible to have a much broader scenario ranging from first and second-generation biofuels up to the third and fourth generation together with electro-fuels. Currently, the most extensive production still concerns first-generation biofuels, while the use of second, third, and fourth-generation ones remains limited. However, the prospects, especially for the third and fourth-generation ones, are very encouraging, thanks to the possibility of obtaining environmental benefits on the territory. Furthermore, the use of microorganisms capable of exploiting wastewater for their growth can reduce the requirement of land and water, which remain available for other needs. For example, biodiesel consumption in Europe in recent years reached a share of about 6% in 2019, including both conventional biodiesel (derived from food biomass, 4.6%) and advanced biodiesel (for a total of 1%) [5]. Most of the advanced fuels derive from waste animal fats and vegetables, while only 0.2% derive from agroforestry raw materials and cellulose, thus not including edible parts. The goal of achieving GHG neutrality by 2050 should boost the development of biofuels in the coming years. For example, from a review study on transport fuels future scenarios, it is clear that biofuels and even more advanced biofuels are expected to contribute to more than 17% by 2050 [6].

This paper aims to analyse the various possible options for the production of biofuels, identifying the most sustainable paths together with strengths and weaknesses. This approach is justified as biofuels have a limited conversion efficiency (lower than 1% for I and II generation feedstock), being a form of solar energy storage. Therefore, less sustainable paths should be discouraged, considering the gap compared to other forms of renewable energy with higher efficiency (10% - 20% of photovoltaic solar panels), even if much more expensive.

2. General Considerations about Energy Use

Figure **1** shows the general scheme for setting the problem of the use of waste and biomass. Any technological process should be optimised through energy necessity reduction, employing pathway production improvement,

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and good reuse. This approach, together with the increasing capability to use renewable sources, could lead to significatively fossil fuel dependence reduction. About renewable sources, the paths that allow direct conversion into mechanical or electrical energy are separated from the production of biomass, which must undergo subsequent conversions. However, biofuel production, particularly hydrogen, is a way for green electricity storage when produced more than the needs.





When reuse is not possible, the goods should not be considered waste, but a renewable source, if it is possible to recover part of their energy content. The best solution for recovering is recycling, which allows saving the energy used to obtain original crude material minus the energy involved in the recycling process. Analysing in more detail the possible pathways of waste treatment: 50% would return to reuse/recycling; 30% is organic material to be sent for biofuel production (biogas and waste vegetable oil) or composting; 10% can be used for energy purposes; the remaining 10% destined for landfills or used as inert material in particular sectors (i.e., in civil engineering, foundations, roadways, etc.), Figure **2**. Both composting and biofuels production eliminate the problem of CH₄ emissions from organic waste landfilling. CH₄ has a greenhouse effect about 28 times higher than CO₂ on a 100-year basis [7], while the combustion of this gas produces an amount of CO₂ equal to about 3 times by weight. Therefore, the CO₂ equivalent saving of combustion compared to landfilling is approximately 10 times. Furthermore, the combustion of this gas in substitution of gasoline and diesel oil leads to a further reduction of CO₂ emissions of about 25%, with the same efficiency.

For non-recyclable wastes, thermochemical or biological processes can be considered to recover only heat content. Agricultural and forest residues are within this last category (not recyclable wastes). In particular, with thermochemical or biological processes it is possible to not only produce biofuels from wastes but also any kind of biomass. In the case of biomass from dedicated energy crops, it is necessary to take into consideration the energy required for land treatment and cultivation.

The use of wastes and biomass in thermochemical and biological processes to obtain biofuels, electrical energy or heat, leads to a reduction of the greenhouse effect, thanks to a better CO_2 balance [8]. Net heat recovered is at zero CO_2 emission because the CO_2 produced during combustion is just the same trapped during vegetable growing. The net heat is the biofuel energy content minus the energy used for the fuel production process.



Figure 2: Routes of use of waste for recycling and energy purposes.

The main issue of wastes and biomass use is to find the best efficiency transformation processes to obtain the highest fossil fuel substitution to give the lowest impact on pollution, human health, and land-use competition.

3. Energy and Biofuels Production from Waste and Biomass

Biomass can be used in different ways for the production of energy or fuels, with effects on the demand for resources. They range from dedicated crops, which could compete with land use for other primary human or environmental needs, to those that only use wastes from other production processes. Among the crops dedicated to the production of fuels, microalgae should be highlighted, because they require very low quantities of land or pure water, being cultivated with water, often not usable for other human activities, or even with wastewater.



Figure 3: Paths of production of fuels of different kinds and electro-fuels.

Figure **3** shows a general outline to identify the production paths of the various biofuel generations, as well as of electro-fuels. These last are considered to be produced using electricity, obtained entirely from renewable sources and not usable directly.

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The highest conversion efficiency lies with direct energy production through burning or pyrolysis/gasification due to fewer steps to go from biomass to energy without the necessary processes to refine and purify the biofuel. Liquid and gaseous fuel from pyrolysis and gasification of solid wastes and biomass can give the highest efficiency when utilised in combined cycles (gas and steam turbine) together with the lowest emissions. This last target is possible thanks to better control of combustion temperature and air index with liquid or gaseous fuel than direct incineration of solid wastes and biomass. In Figure 4, the net electrical efficiencies and combined heat and power (CHP) overall efficiencies for thermal use of waste or biomass of some plants are shown. The vertical black lines (variation bars) indicate data dispersion, principally depending on plant size. Data [9-13] are referred to as typical plants. Anaerobic fermentation, which is a part of the production process for first-generation gaseous fuels, is more suitable to produce biogas from the organic fraction of municipal solid waste (MSW), then used in a sparkignition (SI) or dual fuel diesel-gas engine coupled to an electrical generator, due to relatively low size plant. In this case, efficiency is calculated starting from the wet organic fraction of MSW and it is about 20% for electrical net efficiency, which can rise to about 40% in a CHP plant. The efficiency values are calculated on the base of net plant energy output and so considering the fraction of the energy required for digester operation. Therefore, biogas allows the capture of CH₄, which spontaneously forms from the decomposition of organic material, contributing to GHG emission reduction into the atmosphere, deriving from the transfer of organic material to landfills. Incineration of conventional refused derived fuel (RDF) usually follows the Rankine cycle. The efficiency shown in figure (25% and 75% respectively of electric and CHP production) does not include the energy used to produce RDF. The third technology is referred to big plants regarding wood biomass residues gasification to produce syngas for a combined cycle plant. In this case, the efficiencies are calculated starting from the energy content of the wood collected to the plant and include the energy used to gasify the solid feedstocks. For this reason, electric and CHP efficiency (35% and 75%) are lower than typical fossil natural gas combined cycle plants (typically about 60% as electric efficiency and almost 90% as CHP overall efficiency).



Figure 4: Net electrical and CHP efficiency of some plants for thermal use of waste or biomass.

When direct energy production from waste and biomass is not possible or convenient, biofuels production can be an alternative. The main biofuels are bioethanol, biodiesel, biomethane and, in lower quantity, biohydrogen. Even if they permit a lower global efficiency than direct energy production, they allow a practical way to extract, store and deliver biomass energy content.

Future development programs towards a sustainable economy foresee the use of biofuels derived mainly from biomass. However, although biomass is renewable, the low conversion efficiency to biofuels may not allow for the total replacement of fossil fuels. Therefore, it is crucial to select biofuels that allow recovery of the maximum biomass energy content to have a competitive sustainability pathway because different production processes do

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not involve the same efficiency. This kind of approach certainly applies to first-generation biofuels, but also the second-generation ones, for the wide diffusion of data that allows defining the average production efficiency. For the III and IV generations, similar evaluation criteria could be used, which consider the production efficiencies as a function of the fuel produced and the microorganisms used in the processes. However, biofuels from algae have fewer limitations than I and II generation biofuels for large-scale production, being the land-use competition issue less relevant. Therefore, the choice of the optimal fuel to be privileged is also less relevant, while it is more important to analyse the advantages and disadvantages of widespread use. Instead, in the case of electro-fuels, it is essential to evaluate their use as renewable electricity storage compared to other options.

3.1. First Generation Biofuels

In the case of first-generation biofuels, production should be oriented in a less energy-intensive way and with less use of land, selecting the most sustainable path. This aspect is very important, due to the high competition with land use for food production. In Table **1** the main first-generation biofuels are shown.

Biofuel	Biomass Feedstock (Dedicated Crops)	Production Process
Bioethanol	Sugar/starch crops (sugar beets/canes, cereals)	- Hydrolysis - Fermentation
Biodiesel	Oil crops (rape, sunflower, palm)	Cold pressing/extractionTransesterification
Biomethane	Sugar/cellulosic crops (maize, grass)	 Anaerobic fermentation Upgrading (CO₂ removal)

Table 1: Main first-generation biofuels.

In Table **2**, some parameters to compare the energetic performance of first-generation biofuels from dedicated energy crops are reported, [14, 15]. The energy balance values are the highest found in the literature.

	Bioethanol	Biodiesel	Biomethane
Average crop yields	From wheat: 2600 l/ha From sugar beets: (EU) 5500 l/ha From sugar cane: (Brazil) 6500 l/ha	From rape: 1200÷1500 l/ha From sunflower: 1000÷1200 l/ha	From maize: 3000÷3600 kg/ha 4300÷5000 Nm³/ha with ρ=0.7 kg/Nm³
Lower heating value, [MJ/kg]	21	33	49
Gross biofuel energy, [GJ/ha]	60÷110 (EU)	30÷50	140÷180
Car mileage, [km/ha]	20000÷40000 (7 km/l)	20000÷30000 (20 km/l)	60000÷70000 (20 km/kg)
Energy balance	2:1	3:1	3:1
Main byproducts	Lignin	Glycerine	Fertilizer

When biofuels are produced starting from dedicated crops, an energy balance is necessary. A fraction of the biofuel energy content is employed in plant cultivation and production process, considering also byproducts. The energy balance permits the comparison of the total outputs (biofuel and correspondent byproducts) with the total input energy (fuels, fertilizers, etc.). In Europe, bioethanol has the lowest energy balance, therefore, its production could not be convenient, while almost the same values for biomethane and biodiesel have been found. Focusing on biofuel gross energy per hectare (GJ/ha), biomethane shows the best performance, 2-3 times the energy of

biodiesel per hectare, and therefore permits higher energy production with the lowest impact on land use (at the same energy balance). Moreover, biomethane could be injected into the existing natural gas network. The production of biogas, instead of biomethane, would be even more convenient since the upgrade phase for CO₂ separation is not necessary. The fuel produced would be usable in fixed heat and power plants. On the other hand, biogas is not suitable for transport means due to storage problems. At the same time, it could not be convenient to inject in the NG grid due to larger volumes to treat for the presence of inert species. This last aspect would be less relevant in the case of use in a local area if the quantities introduced would not significantly alter the composition of the gas network.

3.2. Second Generation Biofuels

In the case of second-generation biofuels, production could be oriented in a less energy-intensive way and with less land use. This aspect is less binding than first-generation biofuels, as it is possible to use all parts of the plant. However, the optimization of the process, with the choice of the most sustainable path, remains crucial for the need to exploit the complexity and cost of the production plant, which are high due to the use of synthesis and catalysis processes.

In Table **3** the main second-generation biofuels are shown.

Table 5. Main Second-generation biorders from lightcendosic materia	Table 3:	Main second-generation	biofuels from lignocellulosic material
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Biofuel	Production Process
Cellulosic ethanol (bioethanol)	- Advanced hydrolysis - Fermentation
Synthetic diesel oil (biodiesel)	 Gasification from biomass to syngas: generally, an H₂, CO, CO₂, N₂, H₂O, O₂ and CH₄ mixtures Synthesis (gas to liquid, (GTL) from CO and H₂ to liquid) Fuel conditioning (separator, hydrocraker)
Synthetic natural gas (SNG, biomethane)	 Gasification Methanation (from CO and H₂ to CH₄) Fuel conditioning (H₂O, CO₂ removal)
Synthetic hydrogen (biohydrogen)	 Gasification CO water-gas shift (from CO and H₂O to H₂) Fuel conditioning (purification)

In Figure **5**, the indicative values (technologies under development) of second-generation biofuels production processes are reported, [16-18].

Cellulosic ethanol efficiency does not include the energy contained in lignin, which is a byproduct of the process. For synthetic diesel oil, some authors [19] report a production efficiency similar to synthetic natural gas (SNG) when a co-production of SNG and synthetic diesel oil is made. However, SNG shows the highest production efficiency, while synthetic hydrogen has only slightly lower efficiency, and so it can be considered as a good option for H₂ production with renewable sources.

3.3. Third and Fourth Generation Biofuels

Competition with other primary human needs (food production), including the consumption of fresh water, can be significantly reduced with the development of technologies for the production of third-generation biofuels. The production of biofuels always passes through the treatment of biomass but is obtained by the cultivation and





harvesting of microalgae. Microalgae are characterized by rapid growth and high biomass production. Algae can also be used as raw materials for the production of various goods with a high economic value, whose byproduct (the oil extracted) is a raw material for biodiesel production [20]. For this reason, in the medium-long term, the production of biodiesel from microalgae, in addition to being sustainable, could become an economically viable solution. The advantage consists in limited use of land and sources of fresh water and low competition with food production, through the exploitation of strains of specific microorganisms, for example, lipid-rich in the case of biodiesel. The production of algal biofuels depends mainly on the selected algae species and their properties. Some microalgae are able to transform nutrients contained in water and sunlight and CO₂ into fats with high efficiency [21]. In addition to biodiesel, obtained through transesterification of lipids or fats, it is possible to produce other biofuels. For instance, biogas could be produced through anaerobic digestion of the entire algal biomass or residues of lipid extraction, or bioethanol, and biobutanol, from the fermentation of algal carbohydrates by microbes or yeasts [22].

The diffusion of microbial technology for the production of biofuels is complex due to many factors concerning the assessment of the life cycle of microalgae and the technical-economic feasibility. It is a type of technology that is not yet economically sustainable due to the low ratio of solar energy to that stored in biofuel production. The cultivation of algae can be carried out in open systems or closed and controlled systems (photobioreactors). In the photobioreactors, it is possible to control the consumption of carbon dioxide (of non-atmospheric origin) and algae growth achieving average biomass productivity ranging between 20-50 g/m2 per day [23], depending on solar radiation. Moreover, there are potentials up to 650 g/m2 per day [24], based on the type of photobioreactor and the required energy input. These high productivity values refer to plants with a lower impact on land use, but with a worse energy balance. The collection takes place through systems such as centrifugation, filtration or gravity sedimentation.

Generation IV biofuels aim to increase production yield compared to generation III microalgae. For this purpose, genetically modified microalgae, which use renewable, cheap and widely spread raw materials, are involved to improve the production of biofuels. Moreover, one of the goals is to overcome the photosynthesis limit of the low conversion efficiency into biomass (about 1%), with the development of microorganisms capable of producing biofuels directly. Unlike the case of genetic modifications aimed at increasing biomass yield, this other treatment can result in the direct conversion of carbon into biofuel already inside the cell. This technology is based on the genetic modification of some bacteria to obtain different biofuels, such as H2, ethanol, butanol, or biogas [25]. The post-processing of these microorganism only concerns the purification and concentration of the biofuel. The direct conversion of CO₂ into biofuels using sunlight exploits particular cyanobacteria, which are quicker to engineer than more complex organisms, with the possibility of achieving conversion efficiencies of sunlight into biomass/biofuel close to 10% [26]. Since these are genetically modified organisms, all the material that can cause the risk of gene transfer must be reclaimed during the entire production process. Therefore, the

residual fraction undergoes treatments for material recovery downstream of the biofuel extraction processes (through simple purification or gasification, liquefaction, anaerobic fermentation, etc.) while the remaining part is made safe for disposal. The disposal of residues is another relevant aspect. The byproducts obtained from the energy extraction phase and the residual water from the collection process must undergo appropriate mitigation practices [27]. These aspects could affect production costs in a not negligible way.

Ultimately, the advantages of using III and IV generation microalgae, compared to biomass used in I and II generation technologies, are:

- High lipid content (over 50% in some species);
- Low land demand;
- High growth rate of biomass;
- Possibility of feeding with the nutrients contained in urban wastewater, providing a valid and economical tool for the treatment of polluted waters.

The disadvantages associated with the cultivation of microalgae are mainly given by:

- High production costs;
- Difficulty in cultivating a single species with the required characteristics;
- For the IV generation, treatment of potentially genetically modified residues.

3.4. Electro Biofuels

The production of I, II, III and IV generation biofuels uses biomass as feedstock for various treatment, or the action of particular bacteria, to replace the use of fossil fuels to contain the increase of CO₂ in the atmosphere. A different way of reducing the concentration of CO₂ in the atmosphere, combined with the production of fuels, is offered by electro-fuels. For their production, it is proposed to use electricity, if in excess, which cannot be used directly or for the efficient recharging of batteries, especially in the transport sector. For this reason, electro-fuels allow the storage of renewable electricity in the form of biofuels. Electro-fuels are mainly produced using the electrolysis of water to obtain hydrogen. Once the H₂ has been produced, it can be used directly as an energy source or used for the production of other carbon-based fuels through synthesis processes and specific catalysts, depending on the fuel to be produced. In this case, in addition to electricity and H₂, carbon dioxide is also needed, which can be taken from both the ambient air and the exhaust gases of the heating systems [28]. The passage through electrolysis determines a lower overall efficiency of electro-fuels compared, for instance, to battery electric vehicles, which would use electricity directly. Therefore, the use of electric fuels should be privileged only when direct use of electricity is not possible (for instance, heavy road transport over long distances, sea and air transport).

Some new technologies based on microbial electrosynthesis are under development. They exploit the ability of some engineered microorganisms to directly capture electrons emitted by electrodes immersed in water [29]. In this way, it could be possible to increase production efficiency by reducing the steps required to switch from electricity to biofuel, increasing the sustainability of electro-fuels and their maximum contribution to the replacement of fossil fuels.

Ultimately, the advantages of using electro-fuels compared to biomass used in I, II, III and IV generation technologies are:

- Use of land or water similar to that of IV generation algae;
- Possibility of using electro-fuel production together with CO₂ sequestration techniques in thermal plants powered by fossil fuels. However, long-term CO₂ storage could zero plant CO₂ emissions, while

electro-fuel production would realize a not-closed CO₂ cycle, which only contributes to lowering the CO₂ emission from the fossil source;

- Possibility of using atmospheric CO₂, to create a closed cycle, with relative energy balance similar to what is done with biomass biofuels;
- Possibility of storing electricity surplus without the aid of rare or not widespread and expensive/impacting materials, such as those used in batteries, nor with the complexity of use and maintenance of batteries and charging systems (infrastructures).

On the contrary, the main disadvantages can be summarized in:

- Low global efficiencies due to the two-step process: use of electricity to produce chemical energy (contained in the fuel) which must then be converted back into energy, with the efficiency of thermal cycles;
- Low availability of electric surplus expected in the future. Indeed, for optimizing the use and distribution networks, the electricity surplus is expected to be reduced to the minimum;
- Higher energy cost compared to battery storage (which offers a high-efficiency conversion from electric to electric).

CONCLUSIONS

A smart approach aimed at reducing both wastes and per capita energy demand should focus not only on improving the efficiency of production processes but also on effective operative methods. These last should encourage the reduction of component production, the reuse of goods, and material recycling, together with energy recovery and renewable sources. Among them, biofuels with a positive energy balance used to reduce the demand for fossil fuels, regardless of the sector in which they are used, lead to a reduction in CO₂ emissions. However, it should be taken into account that the conversion efficiency of solar energy into biomass is limited to about 1% by photosynthesis. This results in a problem of large land use for the I and II generation biofuels, partly limited by the III and IV generation thanks to the use of algae that can grow in aquatic environments. Therefore, the maximum benefit would be from those biofuels which require the minimum energy in the production phase with respect to the heat content of the fuel.

In this study, gaseous biofuels produced through the first and second-generation technologies (biogas/biomethane or syngas/SNG) turned out to be the most convenient energetic solution. In particular, biogas and syngas are efficient solutions for thermal and electrical energy production in power plants, while biomethane or SNG could be the most sustainable solution in the transport sector and natural gas network injection. Furthermore, biofuels from wastes are always an optimal choice, as they allow both to recover energy and reduce the problem of disposal itself.

Algae, used in III and IV generation biofuels, have a low level of competition with other uses, reducing the problem of the most convenient type of fuel to produce. Instead, a clear improvement could be provided by biofuels produced directly from particular bacteria, which could bring the solar energy conversion efficiency to biofuels up to values of about 10%.

Biofuels from waste, algae, agricultural/forest biomass and bacteria can also be accompanied by electro-fuels from electric surplus from sources with reduced CO₂ emissions. However, this solution should be limited due to low global efficiencies for the double energy conversion involved in the production and utilization: from electrical to chemical and from chemical to mechanical. Instead, electro-fuels for electricity storage do not require rare and expensive to be extracted materials, with an advantage over batteries.

GLOSSARY

CHP	Combined heat and power	NG	Natural gas
GHG	Greenhouse gas	RDF	Refused derived fuel
GTL	Gas to liquid	SI	Spark ignition
MSW	Municipal solid waste	SNG	Synthetic natural gas

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