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BIOFUELS FROM ABANDONED MINES: A STARTING POINT FOR FUTURE DEVELOPMENTS

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ABSTRACT. Abandoned mines and quarries represent sites with the request of restoration due to their pollution. On the other hand, biofuels represent a response to the present request of sustainable energy, in order to reduce the CO_2 emission, in transportation, but also in energy production and domestic use. However, biofuels production seldom requires lands for the biomass cultivation. In this paper, the use of the dismissed mines and quarries is suggested for the cultivation of algae, as biomass production. To support this approach, a theoretical numerical evaluation of a typical dismissed quarry is developed in order to highlight the feasibility of the approach itself.

Since 1850, global thermal measurements have been carried out, and the analysis of their data has highlighted that the last decades have been the hottest ones (Trifirò 2019); moreover, previsions point out a continuous increase of the global mean temperature, of the order of 2–4°C before the end of the century. Anthropogenic contribution to this global warming has considered extremely likely. But, even if we consider the possibility that human activities don't make a contribution to whether and climate changes, pollution represents an unquestionable cause of the decrease of the quality of life, due to its health consequences (Sertorio 1990; Kleidon 2009; Barman *et al.* 2010; Kleidon 2010a,b; Volk and Pauluis 2010; Kleidon 2012; Lucia and Sciubba 2013; Cohen *et al.* 2017; Contiero *et al.* 2019; Lucia *et al.* 2021). Consequently, some changes towards sustainability have to be introduced in human activities.

In 2017, the UN IPCC Conference in Marrakesh has suggested to contain the increase in temperature up to 2°C (Trifirò 2019). The goal to limit the global warming well below to 2°C above the pre-industrial levels was set with the Paris Agreement, a legally binding international treaty on climate change. The scientific input into the Paris Agreement was provided by the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. The aim is to limit the temperature increase to 1.5°C above the pre-industrial levels (IPCC 2018). So, the goal 13 of Sustainable Development Goals (climate action) can be considered a key factor on the framework of Sustainable Development. Thus, an improvement in the technologies results fundamental for power generation and transportation, for industrial production and also in agriculture.

Indeed, actual society uses fossil fuel as the main source of energy, with two related consequences (Rittmann 2008): (i) the risk of geopolitical turmoil and (ii) the continuous increase of greenhouse gasses emissions. Consequently, biofuels have been considered as a possible response to the previous problems; indeed, they represent possible alternative resources (Chum and Overend 2001; Nigam and Singh 2011; Catalán-Martínez *et al.* 2018), with three main characteristics (Lang *et al.* 2001; Lee and Lavoie 2013):

- easy availability: they can be obtained by different biomasses;
- technical and environmental feasibility: the biofuels can be obtained by using biomasses, produced by photosynthesis living systems that, during their life consume the same amount of CO_2 emitted in the biofuels combustion;
- economic competitivity: each country is able to produce locally the row materials for biofuel production.

But, in relation to the competition with edible crops, the loss of biodiversity, the land-use changes and water depletion (Lucia and Grisolia 2018; Chowdhury and Loganathan 2019; Correa *et al.* 2019), the ethical responsibility, their energy and costs requirements (Carriquiry *et al.* 2011), biofuels must be obtained by considering sustainable processes. In this context, the technical potential of macro-algae and micro-algae, for biomass production and, greenhouse gases abatement can represent a possible response to sustainable energy production. Indeed, biofuel production from these water resources is becoming an interesting topic of research, in particular with possible waste water treatment or polluted natural resources, but also in relation to co-production of high value products for an economic development (Wellinger 2009). Today, algal biodiesel production represents an important economic sector for its application in the transportation of people and goods, by trucks, ships and boats, while biomethane represents an important production for domestic and power generation uses.

Around one hundred thousand species of algae are believed to live on the Earth, but only about twenty species of them are involved in industrial and economical processes (Wellinger 2009). Macro-algae produce a great amount of biomass, evaluated in of $7-30$ t ha^{-1}yr^{-1}, but their major problems are related to the off-shore growth (Buck and Buchholz 2004). On the contrary, micro-algae live both in marine and in freshwater environments. They present a photosynthetic mechanism similar to ground plants, but their simple cellular structure, together with their aqueous environment, allows them to obtain a more efficient light energy conversion into biomass (Wellinger 2009; Grisolia *et al.* 2020).

Old and abandoned mines and quarries could represent an ideal location for algae culture, because:

- there is often water, but polluted, so it is not useful for human use;
- mines are circumscribed places, so, invasive species could not escape from the site;
- in underground mines, algae can live by using LED light, and the temperature remains constant, too;
- mines are inexpensive, so, companies can use them for new economic activities, with the social consequence of employment creation;
- algae support land reclamation, because they sequester metals from previous mining activities.

TABLE 1. Range temperature growth of some microalgal and cyanobacteria strains presented in literature.

Strain	Range of temperature [°C]	Reference
Ankistrodesmus falcatus	5.0 – 35.0	(Talbot *et al.* 1991)
Arthrospira maxima	16.0 – 33.3	(Singhal and Kumar 2017)
Arthrospira platensis (*Spirulina*)	15.3 – 33.3	(Delrue *et al.* 2017)
Asterionella formosa	−7.3 – 29.8	(Ras *et al.* 2013)
Botryococcus braunii	5.0 – 45.0	(Yoshimura *et al.* 2013)
Chaetomorpha valida	17.0 – 32.0	(Singh and Singh 2015)
Chlorella minutissima	10.0 – 35.0	(Aleya *et al.* 2011)
Chlorella pyrenoidosa	5.2 – 45.8	(Ras *et al.* 2013)
Chlorella sorokiniana	13.0 – 45.0	(Huesemann *et al.* 2016)
Chlorella vulgaris	4.0 – 28.0	(Allaguvatova *et al.* 2019)
Cryptomonas marssonii	−2.4 – 30.0	(Ras *et al.* 2013)
Euglena gracilis	13.3 – 32.0	(Buetow 1962)
Haematococcus pluvialis	14.0 – 28.0	(Evens *et al.* 2008)
Oscillatoria aghardhii	5.0 – 35.0	(Talbot *et al.* 1991)
Scenedesmus acutus	15.0 – 40.0	(El-Sheekh *et al.* 2017)
Scenedesmus sp.	−3.1 – 32.7	(Ras *et al.* 2013)
Tetradesmus obliquus	25.0 – 40.0	(Nazidir *et al.* 2018)

In this short communication we wish to highlight the possibility to exploit old and abandoned mines and quarries in order to cultivate and produce biofuels and other useful co-products. So, we develop a preliminary quantitative evaluation of the biomethane and ammonia production from microalgal biomass grown in a typical dismissed quarry in the Alessandria district (Piedmont, Italy), starting from the data collected during a study (Pompeo 2015) at the Politecnico di Torino. The characteristics reported in the study (Pompeo 2015) can be summarised as follows:

- flooded area, named lake: 17 ha;
- maximum lake depth: 26 m;
- walkable area: 15 ha;
- water temperature range in the lake: 5-15°C.

Usually, the depth considered as exploitable, for the microalgal growth in open ponds, is about 30×10^{-2} m (James and Boriah 2010; Eustance *et al.* 2015). Moreover, the temperature is a crucial factor to select the proper microalgal strain that can grow in the environment conditions considered (Blanchard *et al.* 1996; Finenko *et al.* 2003; Serra-Maia *et al.* 2016; Lucia and Grisolia 2021). There exists an optimum temperature for each species: it usually varies in the range $15-30$°C (Kumar *et al.* 2010). At lower temperatures, a limit in the cell growth can occur (Tiong-Kai-Ru *et al.* 2020). The range temperatures in which particular microalgal strains have been exposed to verify their growth are shown in Table 1(Buetow 1962; Talbot *et al.* 1991; Evens *et al.* 2008; Aleya *et al.* 2011; Ras *et al.* 2013; Yoshimura *et al.* 2013; Singh and Singh 2015; Huesemann *et al.* 2016; El-Sheekh *et al.* 2017; Nazidir *et al.* 2018; Allaguvatova *et al.* 2019).

Now, in order to determine the theoretical methane and ammonium yields of the anaerobic digestion, it is necessary to known the composition of the examined organic matter (Angelidaki and Sanders 2004). The maximum potential yields can be obtained by considering a theoretical approach, which does not consider the requirements to cell maintenance and anabolism) from the following reaction (Sialve *et al.* 2009):

$$C_aH_bO_cN_d + \left[\frac{4a+3d-b-2c}{4}\right] H_2O \longrightarrow \left[\frac{4a-3d+b-2c}{8}\right] CH_4 + \\ + \left[\frac{4a+2c+3d-b}{8}\right] CO_2 + d\ NH_3 \tag{1}$$

The specific theoretical methane yield $[L_{CH_4} g_{TS}^{-1}]$ (TMY) can be evaluated as follows (Sialve *et al.* 2009; Heaven *et al.* 2011):

$$TMY = \frac{\tilde{V}_{CH_4}}{8}\ \frac{4a+b-2c-3d}{12a+b+16c+14d} \tag{2}$$

being $\tilde{V}_{CH_4}$ the normal volume of CH_4. From the Equation (1), it can be estimated the ammonium production yield TAY [mg g_{TS}^{-1}] (Sialve *et al.* 2009):

$$TAY = \frac{17\cdot 10^3 \cdot d}{12a+b+16c+14d} \tag{3}$$

Moreover, when the composition of the organic matter considered is known, it is possible to estimate the biomethane higher calorific value obtainable from the biomass, by using the Du Long equation (Heaven *et al.* 2011), expressed in [MJ kg_{TS}^{-1}]:

$$HHV = \frac{1}{100}\cdot\Big(34.1\ C + 102\ H - 9.85\ O + 6.3\ N + 19.1\ S\Big) \tag{4}$$

where C, H, O, N and S are respectively the carbon, hydrogen, oxygen, nitrogen and sulphur biomass percentage content in the microorganism. Thus, in order to show a set of preliminary data on the theoretical methane yield and ammonium production, that can be obtained from some microalgae and cyanobacteria strains, we have considered an average composition and some biomass productivity values from literature data, as reviewed by Li *et al.* (2019). Following the theoretical approach suggested by Sialve *et al.* (2009) and Heaven *et al.* (2011), we have obtained the theoretical methane yield and the ammonium production, considering the following mean microalgal composition, as reported by Angelidaki and Sanders (2004):

- proteins: $C_{2.5}H_{3.5}O_{1.0}N_{0.5}$;
- carbohydrates: $C_{6.0}H_{10.0}O_{5.0}$;
- lipids: $C_{57.0}H_{104.0}O_{6.0}$.

In Table 2, the theoretical methane yield and ammonium production for the main components (proteins, carbohydrates and lipids) are summarised, calculated by using the Equations (2) and (3), by referring to the above reported mean chemical composition. By considering the average value of the percentage composition in proteins, carbohydrates and lipids given by Li *et al.* (2019) for some microalgal and cyanobacteria strains, it is possible to calculate their specific theoretical methane yield and the ammonium production, as shown in Table 3. Moreover, following Nwoba *et al.* (2018), the mean value of biomass productivity given

TABLE 2. Theoretical methane yield (TMY) and ammonium production (TAY), calculated by using Equation (2) and Equation (3), with the average mean proteins, carbohydrates and lipids given in (Angelidaki and Sanders 2004)

	Proteins	Carbohydrates	Lipids
TMY $\left[L_{CH_4}\ g_{TS}^{-1}\right]$	0.496	0.415	1.015
TAY $\left[mg\ g_{TS}^{-1}\right]$	150	–	–

by Li *et al.* (2019) has subsequently been divided by a factor of 2.1, in order to consider the differences between the culture systems adopted. This value has been obtained by comparing the same strain microalgal growth in a photobioreactor with open ponds (Nwoba *et al.* 2018). So, the productivity of the same culture in a photoreactor results 2.1 times higher than the one on open ponds. The latter presents a reduced productivity due to the external environmental conditions.

TABLE 3. Mean biomass productivity (P), average theoretical methane yield (TMY), ammonia production (TMY) and higher calorific value (HHV), calculated by using the average percentage composition values for some microalgal and cyanobacteria strains presented in Ref. (Li *et al.* 2019).

Strain	P [g L^{-1} d^{-1}]	TMY [L_{CH_4} g_{TS}^{-1}]	TAY [mg g_{TS}^{-1}]	HHV [MJ kg^{-1}]
Arthrospira maxima	0.23	0.451	81.04	18.72
Arthrospira platensis	2.18	0.420	61.62	17.13
Botryococcus braunii	0.02	0.368	27.22	14.37
Chlamydomonas rheinhardii	1.41	0.521	59.39	20.81
Chlorella sp.	1.26	0.625	67.43	24.78
Chlorella pyrenoidosa	0.525	0.576	72.63	23.21
Chlorella vulgaris	0.11	0.644	67.43	25.47
Haematococcus pluvialis	0.055	0.553	59.39	22.12
Isochrysis galbana	0.915	0.443	33.41	17.31
Scenedesmus obliquus	0.039	0.559	41.94	21.74

Now, following the literature results, in relation to our quarry, we consider that the microalgae are cultivated in the first 15 cm of depth. Moreover, we consider that we can harvest them leaving at least the 50% of them, in order to allow them to continue their reproduction. Under these hypotheses, it is possible to evaluate, the annual energy data, for each strain, as summarised in Table 4.[1]

In relation to the last data available for the methane energy consumption of the Alessandria district, which is reported to be 599471 GJ yr^{-1}, the annual energy values for each

[1]All the calculations performed to obtain the numerical values provided in Tables 2, 3 and 4 are available in a supplementary spreadsheet file at https://cab.unime.it/journals/index.php/AAPP/rt/suppFiles/AAPP.992SC1/0.

TABLE 4. Mean theoretical annual energy obtainable from the quarry lake for the different algal strains, considering the hypotheses introduced.

Strain	Annual energy [GJ yr^{-1}]
Arthrospira maxima	9540
Arthrospira platensis	82757
Botryococcus braunii	637
Chlamydomonas rheinhardii	65037
Chlorella sp.	69196
Chlorella pyrenoidosa	26998
Chlorella vulgaris	6208
Haematococcus pluvialis	2696
Isochrysis galbana	35106
Scenedesmus obliquus	1879

strain (Table 4) is considered as a possible supply source for the Alessandria district consumption. Consequently, we can highlight that the use of the quarry lake for the biomethane production from microorganisms could represent a sustainable supply, in order to reduce the consumption of fossil fuels. Indeed, human life is related to a clean and healthy water, air, and environment, because humans need water to drink, water to grow food, unpolluted air to breathe, etc. Recently, the growing pollution due to human activities has been pointed out. Today, we are in a crossroad, and we must intervene in order to obtain a mitigation of the increase of the global mean temperature and a reduction of pollutants and greenhouse gasses emissions. A possible contribution to sustainable activities can be obtained by using biofuels, with particular regards to biodiesel for heavy transportation, and biomethane for energy production and domestic uses.

In this paper, we suggest the use of the dismissed mines and quarries to produce biofuels for energy and domestic uses. In particular, we have taken in consideration a typical dismissed mine in Piedmont, in order to develop a theoretical quantitative evaluation of biomethane and ammonia production from microorganisms biomass and the annual energy obtainable from them. It have been registered 378 dismisses mines and quarries only in Piedmont (Agenzia per la Protezione dell'Ambiente e dei Servizi Tecnici 2006). Consequently, in relation to our previous theoretical evaluations and the great number of quarries and mines present in Italy, it could be interesting to develop studies to design future possible exploitation of this solution to obtain biofuels in a sustainable way, recovering dismissed places which can not be used in an alternative way.

Biofuels represent an economic opportunity with important environmental consequences (Lucia 2016; Lucia and Grisolia 2017, 2019), in relation to the reduction of climate emissions from the transport and energy sector (Prajapati *et al.* 2014). Biofuels are mainly produced from land based crops, with negative consequences on the agriculture. This effect is the well known "Indirect Land Use Change" (Paitan and Verburg 2019). In order to reduce this effect, it is important to produce biofuels in different ways (Alaswad *et al.* 2015; Duran *et al.* 2018; Bittencourt-Sydney *et al.* 2019; Zabed *et al.* 2019). In this paper, we have suggested the use of the dismissed mines, in order to upgrade them towards new sustainable economic activities, with social and ecological consequences for the districts where they are located.

Indeed, the dismissed mines represent polluted areas, often abandoned, without activities, with the request of restoration. Brown *et al.* (2016a,b) have investigated the possibility to use reclaimed surface mines in order to cultivate switchgrass to produce lignocellulosic biomass for biofuels production. Shang *et al.* (2010) have studied the opportunity of exploiting the wasted water of mining industry coming from dewatering, for on-site microalgae cultivation in raceways, for biodiesel production. If we consider dismissed mines as a new opportunity for the sustainable development, we can produce biomethane, biofuels and other chemical substances, with possible markets. In this way, these sites represent a new opportunity of economy for their district. Moreover, new activities require new workers. In this way, also social benefits can be obtained by these sites. Thus, exploiting the abandoned mines to cultivate and produce biofuels by micro-organisms, such as microalgae, is a viable way to give a new lease of life to abandoned places, dispersed in our territories. Moreover, microalgae represent a possible pathway to obtain biomass feedstock, in order to produce biofuels (Zuorro *et al.* 2021). This can be linked to different characteristics of microalgae:

(1) they can provide a continuous biomass supply, due to the non seasonality of their harvesting (Schenk *et al.* 2008);
(2) they can be harvested in all kinds of water: seawater, freshwater or wastewater, that can result in a fewer freshwater consumption for their harvesting and the possibility to use areas not otherwise exploitable (Mata *et al.* 2010; Phukan *et al.* 2011);
(3) they have a short doubling time during their exponential growth, usually less than 3.5 h (Chisti 2007);
(4) they present a great potential yield per unit of cultivated area, if compared to land-based crops, presenting a biofuel yield 10–10^2 times greater (Demirbas 2010).

This short communication represents a starting proposal for the development of future improvements of this topic. Our aim is to highlight the use of dismissed lands, in this case quarries, for energy purposes. In this way, it is possible to give a second life to dismissed and abandoned places, moving towards an implementation of a local circular economy. Further investigations must be carried on in order to determine the suitable microalgal or cyanobacteria strain that can be grown in the quarry and that can be anaerobically digested.

Authors' contributions

Conceptualization, U.L and G.G..; methodology, U.L. and G.G.; software, G.G.; validation, U.L., D.F. and G.G.; formal analysis, U.L., G.G.; investigation, U.L., G.G.; resources, U.L., D.F.; data curation, U.L. and G.G.; writing-original draft preparation, U.L., D.F. and G.G.; writing—review and editing, U.L., D.F. and G.G.; visualization, G.G.; supervision, U.L., D.F.; project administration, U.L., D.F.; funding acquisition, U.L., D.F. All authors have read and agreed to the published version of the manuscript.

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