BIODIESEL PRODUCTION FROM MICROALGAE BY FIXATION OF CO_2 WHICH CREATES GREENHOUSE EFFECT IN ATMOSPHERE: REVİEW

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Abstract: Fossil fuels, which make up 80% of the world's energy, are the main source of carbon dioxide emissions. Diesel engines in particular cause more than 30 million tons of CO_2 emissions per year in traffic, so we need to meet our fossil combustion needs with biofuels, renewable energy that will reduce greenhouse gas emissions. Microalgae make photosynthesis using CO_2 and sunlight and accumulate lipids in their biochemical structures. These lipids can be converted to biodiesel by the transesterification process. Microalgal biodiesel does not increase the greenhouse effect because it makes CO_2 fixation and accelerates the carbon cycle. In diesel engines, it reduces carbon monoxide emission by 48%, unburned hydrocarbon rate by 67%, CO_2 emission by 80%, and aromatic hydrocarbons with carcinogenic effect by 75-90% and does not generate SO_2 emission since it does not contain sulfur. It reduces the negative effects on ozone layer by 50% compared to diesel fuel. Wastewater and flue gas can be supplied to the system during production and resources can be treated. The nutrients such as N, P in the wastewater can be treated by microalgae and CO_2 can be absorbed through the microalgae in the flue gases of the factories and emissions can be reduced. Biogas, bioethanol, protein, carbohydrate, pigment, fertilizer and animal feed can be obtained from the biomass remaining after production. Over 95% of biodiesel production is made from vegetable raw materials. However, microalgae grow faster than vegetable raw material, realize 1.8 kg CO_2 absorption per 1 kg biomass, do not need clean water, arable land, and do not compete with food crops such as soy, sunflower. For these reasons, microalgal biodiesel, which has a reducing effect on waste disposal and global warming, should be used in diesel engines. In this study, *Chlorella vulgaris* with high oil content and high carbon dioxide biofixation rate were investigated in biodiesel production.

Keywords: Renewable Energy, CO_2, Microalgae, Biodiesel, Wastewater Treatment, *Chlorella vulgaris*

1. INTRODUCTION AND THEORETICAL FRAMEWORK

World energy consumption is increasing rapidly and will continue to increase due to a population growth of approximately 1% per year. Fluctuations in oil prices have further exacerbated the situation and further reduced oil supply due to political pressure. The impacts of climate change and the devastating consequences of the oil crisis and other fossil fuels are expected to be felt at the beginning of 2030-2050, and the need for alternative fuels is therefore increasing. Renewable and alternative energy sources such as solar, wind, hydropower and biofuels need to be researched and developed. Solar, wind and hydroenergy can be used to generate electricity, but liquid biofuels are the only alternative to liquid transport fuel. Liquid biofuels are classified into three main groups based on their raw materials, processing or production technologies. First generation liquid biofuels - bioethanol and biodiesel - are produced from corn, sugar cane, wheat and various vegetable oils, but have been criticized for their competitiveness with food crops for production, the use of arable land and the need for clean water, and the demand in the market is decreasing day by day. . Second generation liquid biofuels are produced from sources such as corn cob waste, palm kernel, lingo-cellulosic waste, non-edible vegetable seed oils, waste edible oils, waste vegetable oils and animal oils. Although the use of such raw material resources in production overcomes the problems faced by first generation liquid biofuels, consistent supply of raw materials becomes difficult. This difficulty leads to the development of third generation liquid biofuels (biobutanol and microalgal biofuels). Biobutanol is a promising gasoline alternative to microalgal biofuel (Nagarajan, Chou, Cao, Wu & Zhou, 2013).

Production of third generation biofuel (biodiesel) from microalgae has several advantages over vegetable raw material:

• Unlike terrestrial oily plants, microalgae do not require arable land and clean water use and do not compete with food crops.

• Compared to plants, microalgae can double themselves in just one hour and be harvested daily. They produce 10 times more oil than vegetable raw materials.

• Microalgae can grow in waste water and provide biological removal of nutrients such as N, P.

• Biolological fixation of CO_2 by photosynthesis can be achieved by providing flue gas to microalgae culture media, thus avoiding flue gas emissions in the atmosphere.

• Microalgae can tolerate harsh weather conditions, while plant growth and the energy of terrestrial plant oil depend on seasonal conditions, sunlight and all other weather conditions.

• When used in diesel engines, microalgal biodiesel reduces carbon monoxide emission by 48%, unburned hydrocarbon rate by 67%, CO_2 emission by 80%, and aromatic hydrocarbons with carcinogenic effect by 75-90% and does not generate SO_2 emission since it does not contain sulfur. It reduces the negative effects on ozone layer by 50% compared to diesel fuel.

• Microalgal biodiesel achieves a bi-directional emission reduction because it provides a high rate of CO_2 biofixation while producing and also produces less CO_2 emissions when the product is used in diesel engines.

• Microalgal biodiesel does not increase the greenhouse effect because it fixes CO_2 and accelerates the carbon cycle. It dissolves in 99% nature and complies with EN and ASTM standards.

1.1 Biochemical Structure of Microalgae

Microalgae are single-cell photosynthetic organisms. The biochemical composition of microalgae consists of four basic groups: proteins, carbohydrates, nucleic acids and lipids in varying proportions depending on the type of microalgae. The most energy-rich compound is lipid (37.6 kJ g^{-1}) followed by proteins (16.7 kJ g^{-1}) and carbohydrates (15.7 kJ g^{-1}) (Sajjadi, Chen, Raman & Ibrahim, 2018). Microalgae breeding has been developed especially for providing food supplement and animal feed due to its biochemical structure. During the energy crisis of the 1970s, the US National Renewable Energy Laboratory (US NREL, formerly SERI) Water Species Program (ASP) began to use microalgae biofuels as alternative energy sources (Sheehan, Dunahay, Benemann & Roessler, 1998). Microalgae are mainly planted as biofuel feedstock and are preferred in biofuel production for reasons such as high oil efficiency, no need for arable land compared to crop competitors, no competition with food crops and no need for clean water. On the contrary, it can perform biological treatment of wastewater by using wastewater in the feeding processes of microalgae, and it can also provide the absorption of greenhouse gases that cause pollution in the atmosphere by CO_2 fixation.

1.2. Biodiesel Production and Transesterification from Microalgae Species

The amount of oil obtained by microalgae photosynthesis varies between 5.87 L / m^2 and 13.69 L / m^2, which corresponds to 10-23 times more than terrestrial oil producing plants (Demirbas, 2011). However, when the physicochemical characterization of microalgal oils is examined, it is seen that the mass is 0.85–0.89 g / cm^3 and the viscosity is 3.8–4.4 mm^2 / s (Pankaj, Suseela & Toppo, 2011).

Chlorella vulgaris microalgae species have the highest lipid content and biomass productivity. The oil content of *Chlorella vulgaris* species is 10.0-60.0% dry weight biomass, oil productivity is 11.2-40.0 mg / L day, the volumetric productivity of the biomass is 0.02-0.20 g / L day, the spatial productivity is 0.57-0.95 g / m^2 day and the most suitable for biodiesel production It is considered to be productive species (Elcik and Çakmakcı, 2017). Fatty acid methyl esters (FAME) (biodiesel) and glycerol (by-products) are formed as a result of the reaction of triglycerides and methanol in biodiesel production from microalgae species. By-product glycerol can be separated from biodiesel by phase separation. These conversion reactions are called transesterification and are based on the chemical reaction of methanol and glycerol using catalyst. In the transesterification process, ethanol, propanol, butanol can be used instead of methanol. As catalyst, basic catalyst (potassium hydroxide, sodium hydroxide and sodium methoxide), acid catalyst (hydrochloric acid, sulfuric acid, sulfonic acid phosphoric acid), enzymatic catalyst containing lipases and inorganic heterogeneous catalyst (solid phase catalyst) are used. Microalgae based biodiesel production generally consists of extraction of oils from microalgae, removal of excess solvent and production of biodiesel catalyzed by homogeneous or heterogeneous catalyst.

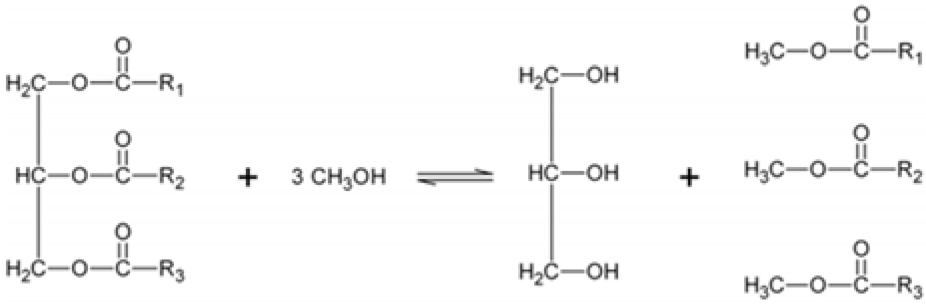

Figure 1. Transesterification (Babcock, Clausen, Popp & Schulte, 2008)

1.3 Performing CO_2 Fixation with Microalgae

The increased concentration of carbon dioxide in the atmosphere is a major source of global warming that can have devastating consequences for the environment and climate. As of 2019, the amount of CO_2 in the atmosphere has reached a record level of 410.96 ppm. One of the main reasons for this increase is the flue gases of thermal power plants and factories, while the other is internal combustion diesel vehicles originating from fossil fuels in traffic and these sources create a high rate of air pollution. Therefore, it is necessary to reduce the CO_2 content of the flue gases and the emissions of diesel vehicle exhausts. Biological fixation of CO_2 can be carried out by plants or photosynthetic microorganisms. Microalgae are the most effective single-celled organisms in CO_2 fixation due to their growth rates and higher photosynthetic yields compared to terrestrial plants. Microalgae perform photosynthesis 50 times faster than plants, perform CO_2 fixation, accelerate the carbon cycle, and produce O_2 pain. In the meantime, microalgal biomass accumulates a significant amount of lipids, carbohydrates, proteins and other valuable compounds, such as pigments and vitamins, which can be used as bioactive substances in the biochemical structure. (biohydrogen or methane) (Anjos, Fernandes, Vicente, Teixeira & Dragone, 2013). Microalgal biomass plays an important role in the purification of flue gases from factory or thermal power plants. The microalgal organism releases oxygen in the dark phase of photosynthesis by using CO_2 within it, thereby reducing CO_2 emissions. Then, microalgal biodiesel can be produced from algae biomass obtained by a chemical process called transesterification. Previous studies include simulated flue gases (Lee, Lee, Shin, Park & Kim, 2000), flue gases from municipal waste incineration plants (Douskova et al., 2009) and flue gases emitted from coal-fired power plants (McGinn et al., 2011). showed that microalgae can be used successfully. In addition, microalgae species with high CO_2 fixation ability can minimize the significant costs of flue gas treatment processes. In this respect, *Chlorella* species are considered important candidates for CO_2 fixation. Ho, Chen, Lee & Chang (2011) showed that the CO_2 fixation rate of *Chlorella vulgaris* species was between 0.73 and 1.79 g L-1 day-1. In addition, CO_2 fixation by *Chlorella vulgaris* was found to be unaffected by volatile organic compounds present in the air stream (Keffer and Kleinheinz, 2002). The amount of CO_2 fixed by microalgae can be found from the basic photosynthesis reaction as in the equation. In this context, 1 kg dry microalgae mass performs 1.83 kg CO_2 biofixation.

$4\ CO_2$ + nutrients + H_2O + light $\rightarrow 4CO_{0.48}H_{1.83}N_{0.11}\ P_{0.01} + 3(1/2)O_2$

4 mole CO_2 : 4 mole microalgae biomass(4 x 44.0095 g mol^{-1} CO_2 = 4 x23.385 g mol−1 biyokütle)

CO_2 fixation rate=1.882 x (biyokütle) g day^{-1} (Hariz, Takriff, Ba-Abbad, Yasin & Hakim, 2018)

1.4 Biological Treatment of Waste Water with Microalgae

Today, although the strategic importance of fresh water is greater than ever, issues related to sustainable water management are being discussed in almost every scientific, social or political agenda all over the world. Freshwater resources are under serious quantitative and qualitative threat. Increased pollution, industrialization and rapid economic development pose serious risks to the availability and quality of water resources in many parts of the world. For this reason, production systems should use clean water at the lowest level and treat wastewater generated after production processes. Water can be saved by using treatment water in agricultural land or various industries. Conventional biological treatment processes include: (a) variable efficiency depending on the component to be disposed of; (b) the cost of operating costs; (c) secondary contamination of chemical processes (eutraphication); and (d) loss of valuable potential nutrients (N, P) (Abdel-Raouf, Al-Homaidan & Ibraheem, 2012). Microalgae cultures offer a cost-effective approach to removing nutrients from waste water (tertiary waste water treatment-biological treatment). They have high capacity for inorganic nutrient intake and can grow in open pond systems as in waste water treatment plants. Microalgae can meet the inorganic nitrogen and phosphorus they need to grow from waste water during biological treatment. In the meantime, they are treated by absorbing heavy metals such as Fe, Zn in the waste water. In their study, Lau, Tam & Wong (1996) examined the wastewater treatment ability of microalgae. In the study, *Chlorella vulgaris* type microalgae removed 86% of inorganic nitrogen and 78% of inorganic phosphorus in waste water. Colak and Kaya (1988), 50.2% nitrogen and 85.7% phosphorus removal from industrial waste water has realized. Microalgal biodiesel is obtained from microalgae oils by transesterification process and has similar properties as petro-diesel. In addition, microalgal biodiesel is more suitable than bioethanol in vehicles because no significant engine modifications are required.

1.5 Microalgal Biorefinery System

Following the biodiesel production process from microalgae, different conversion processes are carried out from microalgal biomass to carbohydrates, proteins, lipids, polyunsaturated fatty acids, pigments, antioxidants, vitamins, nutraceuticals, recycled fibers and bio-active substances, bio-fertilizers, biohydrogen, biotane, biotane, biodiesel, bioethanol and biopolymers). Since the harvested microalgae biomass is rich in protein, pigment, 3-3 fatty acids, vitamin C, vitamin B12 and minerals, it can be used as animal and fish feed or as agricultural soil regulator. *Chlorella sp.* it can be used as a nutrient for fish and animals for easy digestibility and contains 40–52% high protein and 35–50% digestible protein compared to plant-derived proteins. At the same time, liquid / gaseous fuels and biochar can be produced by thermochemical transformations from biomass. In the absence of oxygen, biochar, bio-oil and bio-gas can be produced by pyrolysis at a temperature between 200 and 750 ° C. On the other hand, bioethanol can be obtained by fermentation process and biogas can be obtained by anaerobic digestion. Raw material can be supplied to the food, pharmaceutical and cosmetic industries through the extraction of carbohydrates, proteins, pigments and antioxidants from waste biomass. The development of a holistic approach to waste water and CO_2 use with microalgal sowing is becoming a sustainable alternative to holistic waste management and resource recovery. The microalgal bio-refinery with process integration is able to provide an existing bioeconomic system to produce high-value multiple products at the same time (Mohan et al., 2019).

1.6 Life Cycle Assessment of Microalgal Biodiesel Production (LCA)

Life-cycle assessment is the technique of assessing the environmental impacts associated with all stages of a product's life, from raw material extraction to material processing, production, distribution, use, repair and maintenance, and disposal or recycling. The major differences between the published LCAs on microalgal biodiesel production are mainly due to differences in microalgae cultivation, the use of harvesting and processing technologies, the lack of supportive engineering and economic analysis, and the use of LCA methodologies that generally do not comply with those currently used to regulate greenhouse gas emissions. The current LCA for microalgal oil production is based on a detailed engineering design and economic analysis of large scale microalgal biodiesel production using open pond systems. In advanced biofuels, it has been calculated that the LCA of microalgal biodiesel will reduce greenhouse gas emissions by 70%. Greenhouse gas emissions are estimated to be 28.50 g CO_2e / MJ for microalgal biodiesel and 85 g CO_2e / MJe for refined fossil diesel in Europe. Soybean biodiesel has lower greenhouse gas emissions, 21.25 g CO_2e / MJ, but as agricultural land requires, this figure increases to 83.25 g CO_2e / MJ, reaching the fossil diesel fuel level (Woertz et al., 2014).

2. AIM

The aim of this study is to investigate the reduction of the emission values of the flue gases of factory and thermal power plants by fixing the CO_2, which is the greenhouse gas that creates global warming effect by microalgae, to investigate the microalgal biological treatment with N, P removal by providing domestic or industrial wastewater to the microalgal biodiesel, microalgal biodiesel. The aim of this study is to investigate the exhaust emission values by using in engines and to evaluate the life cycle of microalgal biodiesel production process together with microalgal biorefinery system.

3. SCOPE

This paper presents the negative effects of fossil fuels on environment, comparison of biofuels in terms of raw material source, reduction of emission values by microalgae of CO_2 causing global warming, biological role of microalgae in biological treatment of wastewater, biochemical production of *Chlorella Vulgaris* and the life cycle evaluation of the designed biorefinery systems.

4. RESULTS AND CONCLUSION

In this study, the treatment of CO_2 and waste water in microalgal biofuel production was investigated and the life cycle evaluation of different biofuels and raw materials from biomass was investigated. *Chlorella vulgaris*, which has a high oil content, is of great importance in the production of biofuels from microalgal biomass. In terms of environmental benefits, it is possible to fix 0.73 to 1.79 $gL^{-1}day^{-1}$ CO_2 from such flue gases and to remove 86% nitrogen and 78% inorganic phosphorus from wastewater, and to weigh about 10-60% dry biomass for biodiesel production. oil. The current LCA for microalgal oil production is based on a detailed engineering design and economic analysis of large scale microalgal biodiesel production using open pond systems. In advanced biofuels, it has been calculated that the LCA of microalgal biodiesel will reduce greenhouse gas emissions by 70%. Greenhouse gas emissions were estimated to be 28.50 g CO_2e / MJ for microalgal biodiesel. In the future, the use of microalgal biofuels will become more important if fossil fuel reserves are depleted and their environmental impacts become risky for living.

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