Biodiesel and Its Importance as an Alternative Energy Source for the Fuel Crisis

CHAPTER 15

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Abstract Upsurging of the population throughout the world has given a negative effect on daily energy consumption. Fossil fuel reserves are decreasing gradually due to the energy demand and the need of finding alternatives is growing. Biodiesel is such an alternative that derived from crops and animals. It is also contributing to the green environment as it does not emit carbon dioxides, carbon monoxides, hydrocarbons and particulate matter comparative to petroleum diesel. There are several types of oils and fats that are used in deriving biodiesel such as edible oil and non-edible oils. Palm oil, jatropha oil, soybean oil, castor oil, algae and animal fats are some of the feedstocks used in producing biodiesel. Waste cooking oil is an economical alternative for the sources of biodiesel. The triglycerides of oils and fats are used to produce alcohols and esters which could be result from catalytic or non-catalytic reactions. Biodiesel is composed of mono-alkyl esters of long-chain fatty acids and is synthesized mainly by pyrolysis, microemulsion and transesterification. The transesterification is the most common and widely used method of manufacturing biodiesel. Acid catalyzed transesterification, alkali catalyzed transesterification, enzyme catalyzed transesterification and non-catalytic esterification are broadly used in the transesterification process. Properties, such as, cetane number, cloud and pour point, density and viscosity have an enormous impact on the quality of biodiesel. This chapter provides an overview of the manufacturing process and characteristics of biodiesel.

Keywords: Alternatives, Biodiesel, Edible and non-edible oils, Transesterification

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Introduction

Energy is the most indispensable resource for existence. With the industrial upheaval in the 18th and 19th centuries, energy has become a vital factor for the human beings. Transportation has become a key important sector in energy consumption. It plays a crucial role in the world's economy and the development of any country. The demand for the primary energy supply is fulfilled with fossil fuels such as natural gases, petroleum and coal. By the end of 2050, global energy consumption will increase by 50%, due to the population growth and development of new technologies (Shahid and Jamal, 2011). During the past years, transportation has an enormous growth due to the upsurge of number of vehicles used all over the world. Hence, many statistical estimations have pointed out a rise in energy consumption by 1.8% each year (Atabani *et al.*, 2012). The largest energy consumption is from the industrial and transportation sector. Transportation is responsible for 30% of the energy consumption around the world, of which more than 80% is due to the road transportation. Currently, transportation is responsible for nearly 60% of the oil demand, having 97% of the energy consumption from oils and very little volume of natural gases (Atabani *et al.*, 2012).

With high energy consumption, large amount of carbon dioxide (CO_2) is released to the atmosphere over the years, thereby increasing the environmental pollution and global climate change. The major contributor for the release of these air pollutants are vehicle engines. Despite of pollution caused from ozone and smog, diesel exhaust also contains, carbon monoxides, oxides of nitrogen, hydrocarbon toxic contaminants and diesel particulate matter (Chincholkar *et al.*, 2005). Hresearchers are prompt to find alternative sources to cater to the increasing demand of energy and reduce environmental pollution. Biodiesel is an excellent alternative, as it contains numerous advantages, such as, biodegradable, contains low amount of sulfur and aromatic compounds, sustainable, non-toxic and efficient. It is a very economical and promising source of alternative fuel, as it reduces the reliance of imported petroleum fuels. Biodiesel has an incredible potential for its usage of versatile feedstocks and decisive characteristics (Lyu *et al.*, 2021). In developing countries including South Asian countries, such as Sri Lanka and India, high amount of energy is needed in order to provide a standard living. Sri Lanka, due to economical imbalance and inflation is experiencing a massive fuel crisis for the past few months. Therefore, to overcome the ill-effect of economic crises and global warming, biodiesel would be an excellent alternative.

Biodiesel

Biodiesel is a green alternative for diesel derived from fossil fuels. It is environmentally friendly, low toxic and has non-emission of hydrocarbons. Biodiesel is chemically classified as a combination of mono-alkyl esters of fatty acids and long chain fatty acids (Zhang *et al*., 2016). Palmitic oil, soyabean oil, stearic oil, rapeseed oil, palm oil, canola oil and sunflower oil are some of the organic oils used in producing biodiesel. Other than that, catalysts are also used in manufacturing biodiesel. Biodiesel is defined according to ASTM D 6751 (American Society for Testing and Materials), as a fuel composed of mono-alkyl esters of long chain fatty acids of natural oils and fats (Zhang *et al.*, 2003). Oils and fats are mainly composed of triglycerides containing long chain fatty acids bound with a glycerol backbone (Fukuda *et al*., 2001). Oils and fats cannot be used directly as a fuel because of free fatty acid (FFA), acid composition, gum formation due to oxidation and polymerization, high viscosity and carbon deposits. The major problems associated with the substitution of triglycerides as diesel are high viscosity, poly unsaturated character and low volatility (Mishra and Goswami, 2018). There are three main processes to overcome these drawbacks, such as transesterification, pyrolysis and micro-emulsion. Among those processes, the most commonly used method is transesterification. Triglycerides react with short chain monohydric alcohols in the presence of a catalyst such as acid catalysts, alkali catalysts and enzyme at high temperatures in order to obtain fatty-acid alkali esters (FAAE) and glycerol (Fukuda *et al*., 2001). Transesterification is one of the most efficient and cost-effective methods that can be used in producing biodiesel.

Having a similar viscosity as petro-diesel, biodiesel is observed as amber-yellow liquid. Biodiesel manufacturing is a costly procedure compared to petro-diesel, which seems to be the major drawback. Operational weaknesses of biodiesel are low engine power, small engine power and difficulty of prolong storing due to degradation. Higher cloud and pour point, lower energy capacity, low speed, high emission of nitrogen oxides are some of the physical drawbacks that biodiesel possesses (Graboski and McCormick, 1998).

Feedstock of Biodiesel

Sources of biodiesel can be ranged from oils and fats to algae, microalgae and fungi. Most of the feedstocks are from plant-based oils and animal fats. However, waste cooking oil and non-edible vegetable oils are also highly economical sources of raw materials that can be used in manufacturing biodiesel in large scale. Edible oils are produced from vegetable sources mostly used for human consumption. It does not need any chemical process for the oil extraction. It is economically expensive to produce biodiesel from edible oils due to high demand and limited supply (Bhuiya *et al.*, 2014). The most common edible oil feedstocks are palm oil, sunflower oil, rapeseed oil, soybean oil and peanut oil. Palm oil is one of the most important oils to produce biodiesel due to its high productivity. Usually, 1.25 L of palm oil could produce 1 L of biodiesel (Ishola *et al.*, 2020). Due to its many health benefits, soybean oil is highly beneficial and used for human consumption. To produce 1 L of biodiesel, 1.3 L of soybean oil is needed. Soybean oils are mostly harvested in USA, Brazil and East Asia (Colombo *et al.*, 2019). Another highly productive oil is rapeseed or canola oil which is mainly harvested in Europe and Canada. Rapeseed oil produces 1 L of biodiesel from 1.1 L of oil (Qiu *et al.*, 2011).

Non-edible oils are mainly applied for industrial use such as for soaps, detergents and the paint industry. Mostly used non-edible oils are jojoba oil, animal tallow castor, jatropha oil and waste cooking oil (Atabani *et al.*, 2013). Although, non-edible oil is economically preferable in producing biodiesel, the yield is low compared to edible oils. This happens due to higher amount of FFAs contained in non-edible oils. Hence, FFAs content should be lowered before it is used in manufacturing biodiesel (El-Gharbawy *et al.*, 2021). Jatropha is cultivated in elevated temperatures like in Egypt and is also the main source of feedstock in Asian and African countries as well. Jatropha seeds have nearly 30-35% of oil. Hence, the seeds could be used to produce a considerable amount of biodiesel (Juan *et al.*, 2011). Castor oil is another non-edible vegetable oil, which is highly viscous but biodiesel made from castor oil has extremely low pour and cloud points. Therefore, it is preferable in winter conditions (Keera *et al*., 2018). Waste cooking oil is a very promising alternative to produce biodiesel as it has a very low price. Other than that, it is renewable, easy to assemble, widely available and also reduces the need of land for crop cultivation. Waste cooking oil contains a higher amount of FFAs, which hinders the reaction of transesterification and produces significantly low yield (Degfie *et al.*, 2019). Biodiesel production through algae is highly economical and easy process as it contains 20-80% of oil which is converted to fuel (Tharusha and Ratnatilleke, 2021). Some of the algae species such as Ulothrix, Euglena and Tribonema are highly productive in producing biodiesel (Khan *et al.*, 2017). Cyanobacteria and microalgae are considered as the latest feedstock for gaining biodiesel. Modifying of these microorganisms genetically, cultivating them to attain different fuel characteristics are seems to be very much productive.

Fatty Acid Composition of Crop Edible and Non-edible Oils and Its Contribution to Biodiesel Production.

Fatty acid is an important aspect in any sources of biodiesel production. The fatty acid content of a source/crop is highly dependent on the quality and the geographical conditions of which it is cultivated. Some of the available fatty acids contain in oils are palmitic acid, oleic acid, linoleic acid, stearic acid, myristic acid, lauric acid (Hellier *et al*., 2015; Alves *et al.*, 2019). These fatty acids and alcohols in oils may have a considerable influence on the properties of biodiesel such as cetane number, melting point, cloud point, cold flow, lubricity and viscosity. The impact in these properties is affected by individual unsaturated fat methyl ester in biodiesel. These properties also enhance with an upsurge of chain length and diminishes with the increase of unsaturation. Even though, the upsurge of the degree of unsaturation helps increment of the behavior of biodiesel at low temperatures, certainly there are obstacles such as lowering of cetane number and deprived oxidation stability (Hellier *et al*., 2015).

Biodiesel Production Technologies

In order to produce biodiesel, oil extraction is an essential step in which seeds and kernels are used. Mechanical extraction, enzymatic extraction and solvent extraction are the three main methods of extracting oils (Aransiola *et al.*, 2019). The most conventional method of extracting oils is mechanical extraction. In this method, 60-80% yield can be extracted from seeds (Subroto *et al.*, 2015). Solvent extraction is another technique, which the oils are extracted with the use of a liquid solvent (Razal *et al.*, 2012). Soxhlet extraction, hot water extraction and ultrasonication are used in solvent extraction methods (Luque-Garcia and Castro, 2004). Enzymatic oil extraction is one of the most promising methods of extracting oils (Solanki *et al.*, 2020). There are many obstacles in processing vegetable oils or any other oils to get the approximate values of biodiesel such as low volatility, higher viscosity and polyunsaturated conditions (Balat and Öz, 2008). Hence, to overcome these hindrances and produce biodiesel, Three main methods are used; (i) pyrolysis, (ii) microemulsion and (iii) transesterification (Mishra and Goswami, 2018).

(i). Pyrolysis

Pyrolysis is also known as thermal cracking or decomposition of organic matters or change in chemical composition in the presence of a catalyst due to the application of thermal energy and in the absence of air (Higman *et al.*, 1973). Vegetable oils, animal fats and natural fatty acids are used as substrates for pyrolysis technique. The biodiesel produced through pyrolysis is considered as suitable for use in diesel engines for its properties such as lower viscosity, pour and flash point. The pyrolyzed vegetable oils contains a lower cetane number, acceptable levels of sulfur and water content (Parawira, 2010). Alkanes, alkadines, alkenes, carboxylic acids and aromatics are produced due to the thermal cracking process (Hsu, 2012). There are three types of pyrolysis namely slow pyrolysis, fast pyrolysis and flash pyrolysis. These types of pyrolysis differ from one another by the rate of heating, particle size, processing temperature and residence time. During pyrolysis, thermal cracking or degradation of organic matter of the feedstocks occurs at temperatures of 300 – 500 °C and ends at 700 - 800 °C. Under these temperatures, breakdown of long-chain carbon, oxygens and hydrogens into smaller molecules occurs (Patel *et al*., 2020).

(ii). Microemulsion

Microemulsions are known as colloidal dispersion of optically isotropic fluid having dimensions of not more than 1-150 nm (Zare *et al*., 2020). It is a transparent and a stable colloidal dispersion and is formed from two immiscible liquid and ionic amphipathic. Microemulsions are made from solvents like ethanol, methanol, butanol and hexanol. These types of microemulsions are excellent in owning maximum viscosity necessities, which is significant in biodiesels. They also can improve the spray characteristics of biodiesel by vaporizing all the low boiling components of the micelles (Schwab *et al*., 1987).

(ii). Transesterification

Transesterification is considered as the most promising, common and frequently used method of synthesizing biodiesel. Triglycerides react with alcohols, therefore it is also known as "alcoholysis". The process involves few reversible and consecutive steps (Fabiano *et al.*, 2012). Transesterification is a stepwise reaction which comprises of 1 mole of triglyceride to produce 3 moles of fatty acids. Glycerol is the main by-product of biodiesel synthesis which is used in many industries including pharmaceutical and cosmetics. There are two different methods used in transesterification namely, catalyzed transesterification and non-catalytic transesterification (Fukuda *et al.*, 2001). Three equations below (Eq.1-3) indicate the conventional steps of biodiesel manufacturing (Perez *et al.*, 2014). The block diagram of biodiesel manufacturing plant is shown in Fig. 1 (Walpita *et al.*, 2012).

$$TRIGLYCERIDE\ (TG) + ROH \leftrightarrow DIGLYCERIDES\ (DG) + RCOOR1 \quad (1)$$
$$DIGLYCERIDES + ROH \leftrightarrow MONOGLYCERIDES\ (MG) + RCOOR2 \quad (2)$$
$$MONOGLYCERIDES + ROH \leftrightarrow GLYCEROL + RCOOR3 \quad (3)$$

Catalytic method is the most prominently used transesterification method as it has a higher yield. The use of catalyst is very much vital as it upsurge the rate of reaction, because solubility rate of alcohols is somewhat lower. Catalysts such as, alkali catalyst, acid catalyst and enzyme catalysts increase the rate of alcohol solubilizing with oils and fats (Juan *et al.*, 2011; Thangaraj *et al.*, 2018). Alkaline catalytic transesterification is known as the most promising, fastest, economical, productive and the most evanescent method of producing biodiesel. Catalysts such as NaOH, KOH, K_2CO_3, $KOCH_3$, NaOCH and NaMeO are used increasing the rate of biodiesel synthesis. NaOH and KOH are most commonly used catalysts as they are cost effective (Trejo-Zárraga *et al.*, 2018). However, in order to use these alkaline catalysts, the FFA content of the oils should be lower than 0.5%. Beyond these limits, soap formation will occur and the yield will decrease. Though, use of alkaline catalysts is best to uses, various obstacles are also found, for example, glycerol recovery is difficult, alkaline wastewater should be treated prior to dumping, catalysts should be removed and it is energy intensive (Nasreen, 2018). Strong acids like H_2SO_4, HCl, H_3PO_4, ferric sulphate and sulphonic acids are the main types of catalysts used in acid catalyzed transesterification. Compared to alkaline catalytic transesterification, acid catalysts are more tolerant to FFAs and water. It gives an excellent yield but the process is time consuming. However, acid catalyzed transesterification is widely used all over the world for its excellent conversion efficiencies, tremendous yield, and low energy use (Thiruvengadaravi *et al.*, 2012). Enzymatic catalytic esterification known as a trouble-free process to produce biodiesel. Lipase enzymes are used as the catalyst for the triglyceride and alcohol reactions. It conveys the best tolerance for the FFA content in oil feedstocks. Furthermore, it also has a tendency to react with long-chain alcohols compared to short-chain alcohols. Hence, reaction with ethanol is much likened than to methanol. With the use of enzyme catalysts, recovery of glycerol and eradication of soap and catalysts are no longer needed. Even though, enzyme catalytic process is much trouble-free and easy to handle and it is uneconomical (Szczęsna Antczak *et al.*, 2009). Non-catalytic transesterification includes supercritical methanol transesterification. This method involves high temperature and pressures. It is very efficient in time and uses low energy for producing biodiesel. Hence, it is also an environmental-friendly process. Nevertheless, supercritical methanol transesterification is highly expensive and has a higher methanol consumption compared to catalytic transesterification (Demirbas, 2008).

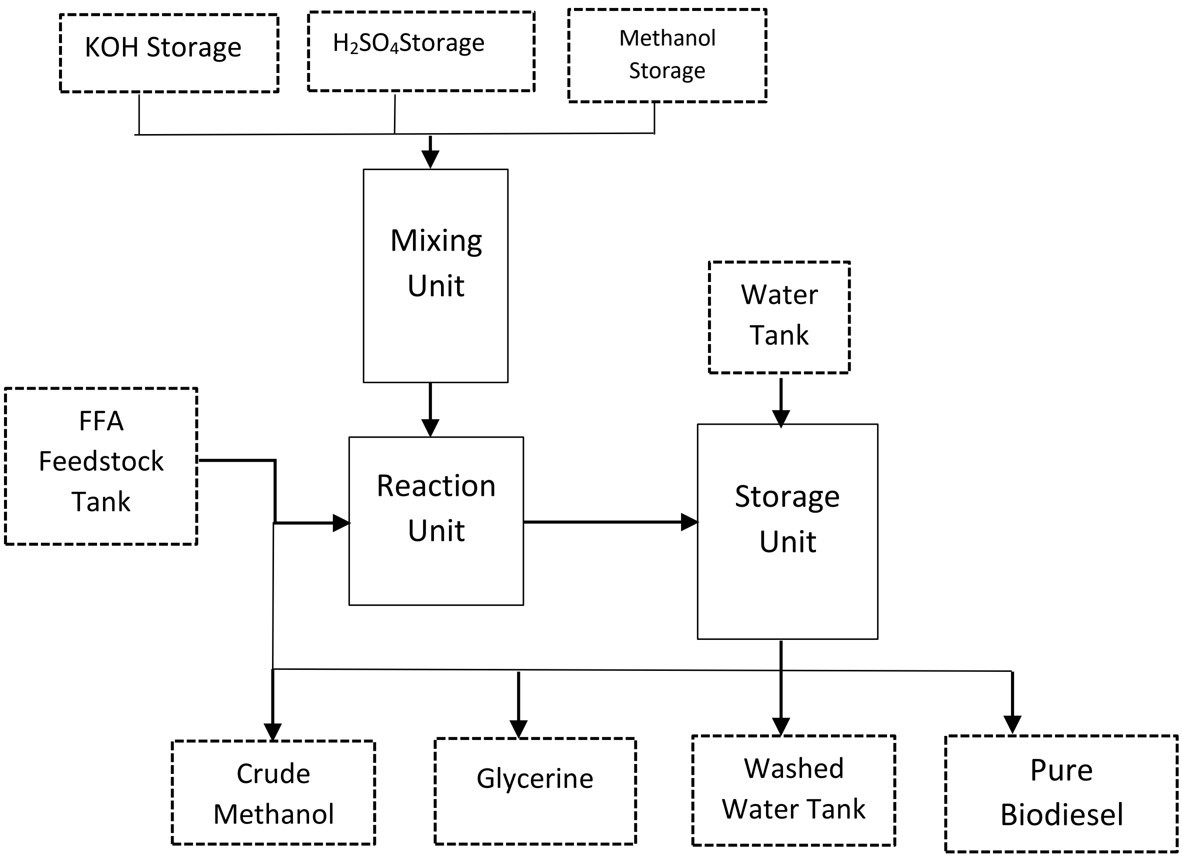

Figure 1. Block diagram of a biodiesel plant

Characterization of Biodiesel

The characterization of the properties such as density, flash point, cetane number, pour point and cloud point, viscosity, oxidation stability and calorific value interpret the quality of the fuel. Density of any fuel is directly link with the engine performance. It also has an effect on cetane number, viscosity and combustion quality. When the density increases, the size of the fuel droplets increases and the rate of emission will upsurge as density is also relates with output of engine. Furthermore, the efficiency of the atomization expands with lower density. Density of biodiesel is measured with ASTM standards D1298 (Pratas *et al.*, 2011). Flash point is known as the temperature which the fuel will ignite. It indicates the flammability of the fuel. Generally, the flash point of biodiesel is much higher compared to petroleum diesel as it has a flash point of 150 °C, which is considered to be safe to handle, store and transport (Gülüm and Bilgin, 2015). Cetane number determines ability of auto ignition. Higher the cetane number gives the quicker ignition, indicating rapid startup of the engines and smooth and noiseless running. Biodiesel has the highest cetane number comparable to convectional diesel. The cetane number is directly proportional to saturation and fatty acid chain length. Higher the fatty acid chain lengths and saturation could result in higher cetane number (Sivaramakrishnan and Ravikumar, 2012). Pour point and cloud point are very significant properties of fuels to evaluate their performance at low temperatures. During winter weather conditions, solidification of fuel may block and damage the engines due to poor lubrication. Biodiesel has cloud and pour point higher than the petroleum diesel. Hence, a blend of biodiesel and normal convectional diesel will be a better substitute during the winter and cold conditions (Kannan *et al*., 2018; Ogami *et al.*, 2018).

Viscosity is another highly significant parameter for biodiesel as it relates with the combustion of the engine. It indicates the ability of a liquid to flow and affects the fluidity of the fuel (Tesfa *et al.*, 2010). Due to the larger molecular structure, biodiesel has a viscosity much higher than the normal convection diesel. Hence, at low temperature weather conditions, the viscosity of biodiesel becomes much thicker. Greater viscosity deteriorates the combustion quality and increase the emission (Ramírez Verduzco, 2013). Oxidation stability of biodiesel is a measure of its reactivity with air and oxidation. The presence of unsaturated fatty acids and double bonds makes the biodiesel more prone to react with atmospheric oxygen. Hence, antioxidants are needed in preventing the oxidation. Due to the molecular structure of biodiesel, it has lower oxidation stability comparative to diesel derived from fossil fuels (Pullen and Saeed, 2012). Calorific value is a vital property determining the quality of biodiesel. The output of an engine is dependent on the calorific value. The greater the value gives higher the heat in combustion, thereby enlightening the performance of the combustion. Biodiesel contain much lower calorific value than petroleum diesel (Ozcanli *et al*., 2013).

Biodiesel as an Alternative Energy for Fuel Crisis

The Sri Lankan fuel and economic crises hit the nation in the month of June 2022, making long queues for days. Sri Lanka is currently experiencing the worst economic crises, upsurging of the dollar rates day by day, which put the government in a place that they could no longer afford the high demand. Hence, it pushes Sri Lanka to think about new alternative methods to beat up the high demand and the upsurging of prices. Biodiesel is one simple option at least could give a partial solution to fulfil the energy demand. The main feedstocks for biodiesel are plant seeds. Seeds like, Kithul, Avocado, Mee, Domba, Rubber seed, Endaru, Palmyra, Mango, Tamarind, Kaneru, Jack seed, Rambutan, sugarcane are the most abundant plants that grow within the country. Other than that, algae and bacteria such as, cyanobacteria, also possess high yields when producing biodiesel. Sri Lanka is well-known as a tourist kingdom.

Hence, it also possesses huge number of hotels and restaurants, where they throw out the waste cooking oils, which is also known to be an economical and cost-effective method of synthesizing biodiesel. Waste cooking oil also can be found in every house residing in Sri Lanka. Hence, it will be a source of income for everyone, during this economic crisis.

Conclusions and Future Prospects

Energy has become the major requirement to maintain a better behavioral and living standards of the world. Due to the increase in population, the fossil fuel derivatives are being finite and the need of alternative energy sources is upsurging. Transportation sector is one of the largest energy consumers in the world. Petroleum diesel has many disadvantages including the environmental damage caused from the emission of gases such as CO_2, carbon monoxide and sand particulate matter. Hence, scientists and researchers around the world are motived to investigate new sources of alternative and renewable energy. Biodiesel is the most attractive and commonly used alternative to the petroleum diesel, possessing enormous environmental and natural benefits. Oils derived from crops such as palm, soybean, jatropha, sunflower and animal fats are the main sources of feedstocks used to produce biodiesel. Other than that, waste cooking oil from hotels and restaurants and oils derived from algae are some of the economical feedstocks for manufacturing biodiesel. Hence, the selection of best feedstock that could produce higher yield with minimum cost is vital. The technologies such as thermal cracking (pyrolysis), microemulsion and transesterification are used in manufacturing biodiesel. Transesterification is the most commonly used method. Characterization of properties of biodiesel are essential to maintain the quality of biodiesel. Those include density, flash point, cetane number, pour point and cloud point, viscosity, oxidation stability and calorific value. At the current state, biodiesel is economically less productive and much investigations are needed to make it competitive compared to the convectional diesel. Providing funds to continue research and financial aid for those who are capable of manufacturing biodiesel will be worthwhile.

Conflict of Interest

Authors have declared that no competing interests exist.

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