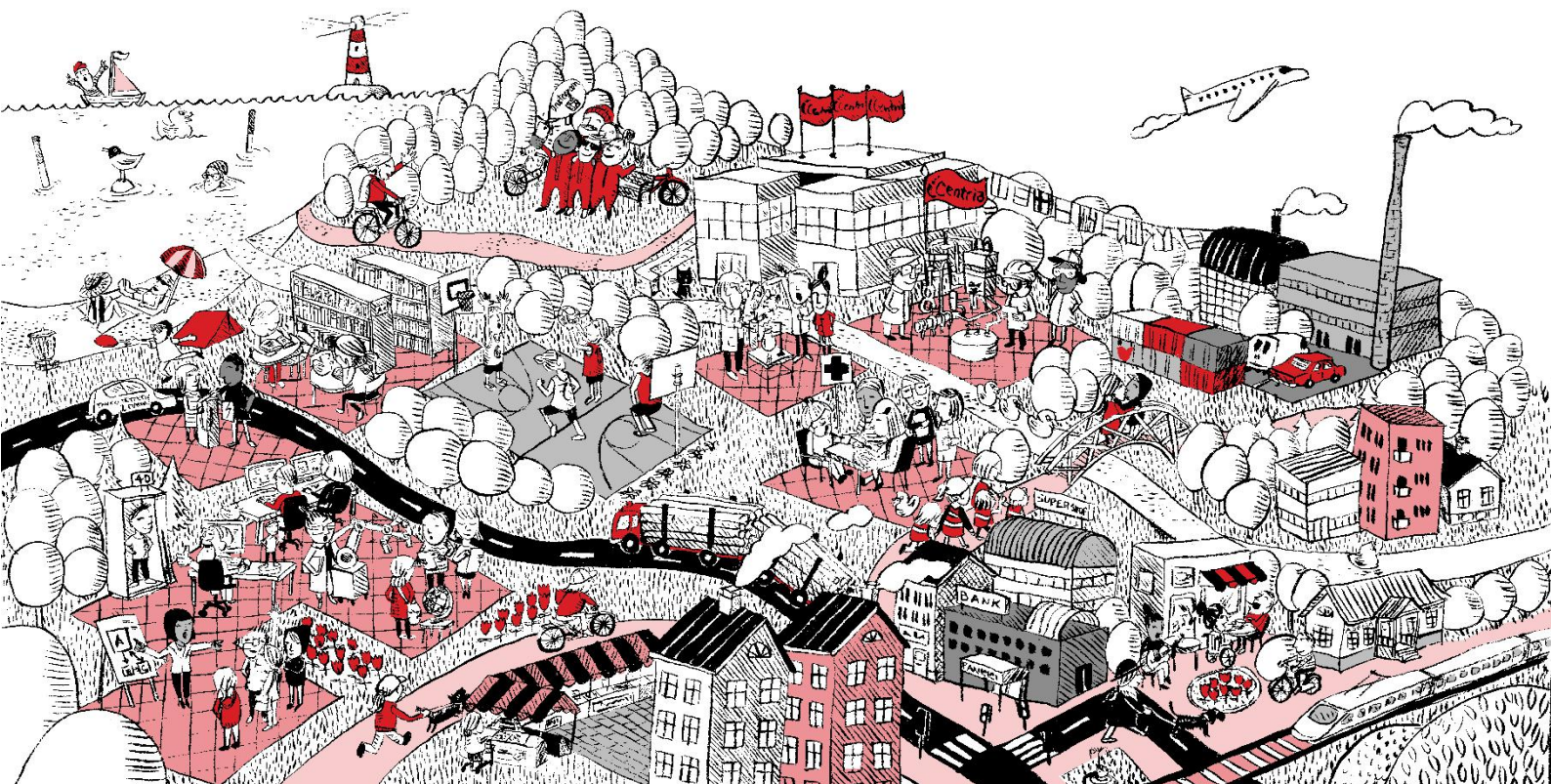


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**BIODIESEL PREPARATION BY INDUSTRIAL
TRANSESTERIFICATION AND ITS IMPACT ON THE
ENVIRONMENT**

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ABSTRACT

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Name of thesis BIODIESEL PREPARATION BY INDUSTRIAL TRANSESTERIFICATION AND ITS IMPACT ON THE ENVIRONMENT		
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<p>At present, the dual problems caused by the shortage of non-renewable resources of fossil fuels and the negative impact of fossil fuels on the ecological environment are becoming increasingly serious, making the development and application of renewable energy an important part of the energy strategies of countries around the world. Biodiesel is a typical renewable and clean fuel, which is produced from some natural and renewable raw materials (vegetable oil, waste oil and microbial grease). Biodiesel is easy to burn, non-toxic and biodegradable. Compared with petroleum-based regular diesel, biodiesel has high cetane number, low aromatic content, better low-temperature startability and low greenhouse gas emissions. It has received considerable attention in controlling pollution caused by petroleum combustion. Among the methods for preparing biodiesel, transesterification is the most commonly used technique. The aim of this thesis work was to further investigate the application of transesterification technology in industrial production and its impact on the environment.</p> <p>Heterogeneous catalysts are more promising than homogeneous catalysts because they can be easily separated from the product and reused in several cycles, thus reducing the overall production cost. Immobilization of lipases on nanocatalysts increases their activity and surface area and has the advantage of easy catalyst recovery and multi-cycle reuse, at the same time enzyme stability can be improved by immobilization. Liquid lipase formulations for biodiesel production are growing rapidly because they have better miscibility with the reactants, reduce mass transfer limitations and increase reaction rates. Selection of the right catalyst is a key factor in biodiesel synthesis. Heterogeneous catalysts and lipase catalysts are excellent choices.</p>		

<p>Key words Biodiesel, Heterogeneous catalytic, Homogeneous catalytic, Life Cycle Analysis, Transesterification</p>

CONCEPT DEFINITIONS

List of abbreviation

OPEC	Organization of Petroleum Exporting Countries
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Assessment

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CONCEPT DEFINITIONS
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1 INTRODUCTION

According to the Organization of the Petroleum Exporting Countries (OPEC) Monthly Oil Market Report (OPEC 2021), published in December 2021, total global oil demand reached an average of 96.5 million barrels per day in 2021 and is expected to reach an average of 100.6 million barrels per day in 2022. The report notes that total global oil demand is expected to continue to recover and will far exceed pre-pandemic levels, primarily given the world's COVID-19 control measures and their potential impact on transportation fuel demand, as well as the worsening of the global outbreak due to the emergence of Omicron sub variant. Researchers predict that world oil consumption will increase to an average of 118 million barrels per day by 2030, and at this rate, global crude oil reserves will be depleted by 2060. (OPEC 2021.) At the same time, large-scale climate change such as global warming is more than ever a major issue often highlighted by the international community due to the rapid accumulation of greenhouse gases such as carbon dioxide from anthropogenic activities (e.g., burning fossil fuels to meet energy demand). The rate of sea ice melting and sea-level rise due to global warming is currently occurring in the Earth's ecology. According to the United Nations Intergovernmental Panel on Climate Change (IPCC), about one million species could become extinct if the global average temperature rise breaches the 1.5 °C minimum edges. (IPCC 2018.)

At present, the dual problems caused by the shortage of non-renewable resources of fossil fuels and the negative impact of fossil fuels on the ecological environment are becoming increasingly serious, making the development and application of renewable energy an important part of the energy strategies of countries around the world. Renewable energy will minimize the dependence on fossil fuels to offset the effects of climate change while enabling a transition to more sustainable energy sources. Biodiesel is an environmentally friendly renewable energy source, which meets the energy demand and conforms to the concept of sustainable development and circular economy. Therefore, the research and application of biodiesel have received increasing attention and have become an important part of the energy strategy of many countries. (Borugadda & Goud 2012.)

Biodiesel is a typical renewable and clean fuel produced from several natural and renewable feedstocks (vegetable oil, waste oil and microbial grease). Biodiesel can be an excellent alternative to fossil fuels, either as a direct substitute for petroleum-based diesel or as a blend with fossil diesel in any ratio and to create a stable blended biodiesel system. (Kamaraj, Rao & Balakrishna 2021.) Compared to petroleum-based regular diesel, biodiesel has a high cetane number, low aromatic content,

easy to be burn, better low-temperature start-up, and lower greenhouse gas emissions, and is non-toxic, biodegradable, and has received considerable attention in controlling pollution caused by petroleum combustion. (Badawy, Mansour, Daabo, Aziz, Othman, Barsoum, Basouni, Hussien, Ghareeb, Hamza, Wang, Wang & Fadhil 2021.)

Several common techniques have been established for the preparation of biodiesel, including direct or blended-use, microemulsion, thermal cracking, and transesterification. Among these methods, transesterification is the most commonly used technique because it has advantages over other production methods, such as the ability to use a variety of abundant feedstocks, the ability to improve fuel properties by reducing fuel viscosity, and higher cost-effectiveness and conversion efficiency. (Ramli, Farooq, Naeem, Khan, Hummayun, Iqbal, Ahmed & Shah 2017.) The catalysts used in transesterification are classified as chemical (acid or base) catalysts and biocatalysts. Chemically catalyzed transesterification has been adopted for industrial production due to its higher yield and superior capacity. However, there are significant challenges associated with transesterification in terms of industrial production processes, including difficulties in product recovery and catalyst reusability. The advent of multi-phase catalytic transesterification and enzyme-catalyzed transesterification has effectively addressed these issues and reduced the overall process cost. (Mishra & Goswami 2018.)

The purpose of this thesis is to investigate the application of transesterification technology in industrial production and its impact on the environment. This thesis studied the basic principle of biodiesel preparation by transesterification, analyzed the application of continuous two-stage transesterification process in industrial production of biodiesel, discussed the transformative role of four new biodiesel production equipment in the industrial production process of biodiesel, and gave an outlook on the application prospect of industrial production of transesterification technology through the analysis of the impact of industrial production of biodiesel on the environment.

2 PRODUCTION OF BIODIESEL

The main raw materials for biodiesel production are fresh or waste vegetable oils and animal fats. The simple and easily available raw materials give biodiesel a renewable nature, let it independent from non-renewable petroleum resources. Biodiesel can be obtained through various chemical processes, among which transesterification is the preferred and most straightforward preparation method for biodiesel production. (Mishra & Goswami 2018.)

2.1 Mechanism of transesterification

Transesterification is a method of reaction between oil and alcohol to obtain the main product biodiesel (fatty acid methyl ester) and by-product glycerol, and the use of a catalyst can effectively accelerate the reaction process. The reactants of the transesterification method are usually triglycerides from raw fats and oils, and the alcohol of choice uses methanol (or ethanol). Triglycerides are converted to diglycerides in the reaction, followed by the conversion of diglycerides to monoglycerides and monoglycerides to glycerol, and methanol gets one methyl ester molecule from each glyceride in each conversion step to produce fatty acid methyl esters. (Thangaraj, Solomon, Muniyandi, Ranganathan & Lin 2019.) The basic principle of the transesterification method is the reaction of triglycerides with methanol to form fatty acid methyl esters and glycerol is shown in Figure 1.

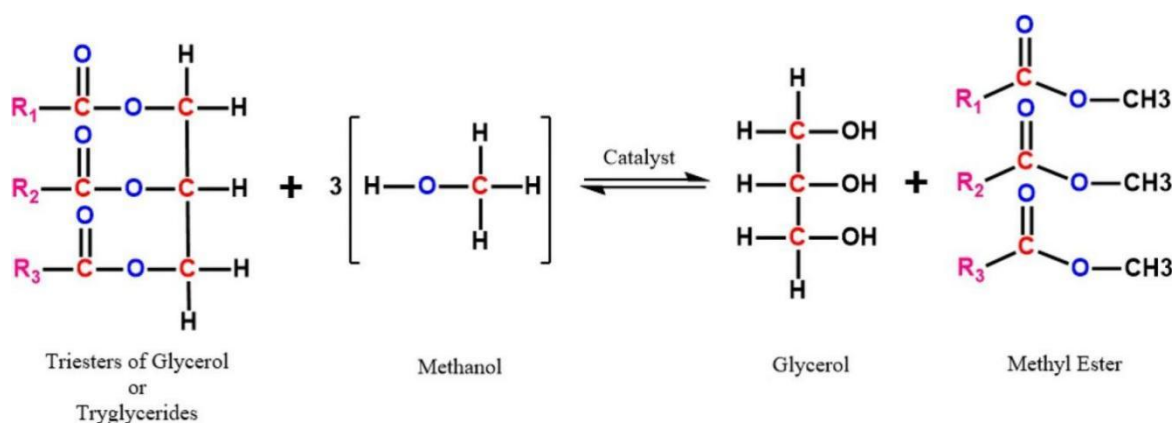


Figure 1: Fundamentals of the transesterification method (Bharti, Chalia, Thakur, Sridhara, Thakur & Sharma 2021)

The main reactants of the transesterification method are triglycerides present in animal fats and vegetable oils. Triglycerides are mainly divided into saturated and unsaturated types. In saturated triglycerides, all vacant sites in the chemical structure are occupied by hydrogen atoms bonded to carbon atoms. Saturated triglycerides are a type of fat molecule, are solid at standard pressure and temperature, and exhibit a high melting point. In unsaturated triglycerides, there are fewer vacancies for hydrogen atoms bonded to carbon atoms due to the presence of double bonds in the chemical structure. Under standard pressure and temperature conditions, they are usually liquid and exhibit a lower melting point than fats. Alcohols consist of hydroxyl groups, while organic acids consist of carboxyl groups. When alcohol reacts with an organic acid, the hydroxyl group and the carboxyl group combine, and the resulting substance removes the water molecule inside and finally forms an ester. (Hayyan, Hashim, Mirghani, Hayyan & Nashef 2014.)

The main components of the feedstock oil for industrial production of biodiesel are triglycerides, free fatty acids and water. When the oil contains a large amount of free fatty acids and water, a series of reactions such as saponification and hydrolysis will occur and the feedstock oil will not be converted to biodiesel, but a large amount of soap will be generated, which will inhibit the separation of biodiesel, glycerol and rinse water, generating more effluent and reducing the efficiency of the catalyst. (Mohadesi, Aghel, Maleki & Ansari 2019.) Various factors that affect the yield of biodiesel in transesterification reactions include reaction time, temperature, pressure, catalyst type and concentration, feedstock oil type, and the molar ratio of the alcohol-oil blend (Mishra & Goswami 2018).

The transesterification reaction is divided into catalytic and non-catalytic processes using various feedstock oils and different solvents. Catalysts used for biodiesel production are classified into two types: homogeneous and heterogeneous catalysts. If the catalyst is in the same phase as the reactants in the transesterification, it is a homogeneous catalytic transesterification. Correspondingly, if the catalyst and the reactants are not in the same phase, the process is called heterogeneous catalytic transesterification. Another special type of catalysis is being investigated, which is the use of biological enzyme catalysis that is ecologically beneficial. (Singh, Arora & Singh 2021.) In industrial production, transesterification techniques using catalysts are widely used, but problems arise in the production process of this method, such as the recovery of the substances participating in the reaction and the purification of the final product, which makes the production process more complicated and also makes the production cost increase. Therefore, non-catalytic transesterification technology has

been studied, and the emergence of supercritical method and co-solvent method has effectively solved the difficulties caused by catalysts to some extent. (Mathew, Raina, Narisetty, Kumar, Saran, Pugazhendi, Sindhu, Pandey & Binod 2021.) Based on the research (Mandari & Devarai 2021), according to the characteristics of the reaction process, the transesterification method can be divided into acid-base homogeneous catalytic transesterification, heterogeneous catalytic transesterification, and biocatalytic transesterification, which use catalysts, and supercritical method and co-solvent transesterification, which do not use catalysts.

2.1.1 Acid-base homogeneous catalytic transesterification method

The conventional method used for biodiesel production is to utilize a homogeneous catalyst. Homogeneous catalysts are catalysts that exist in the same phase as the reactants. Because acids and bases are more common and less costly, homogeneous bases or homogeneous acids are often used as catalysts for transesterification techniques in industrial production. Acid-base homogeneous catalytic transesterification methods use catalysts including acids, bases, and their combined applications. (Mandari & Devarai 2021.)

Biodiesel production usually uses homogeneous base catalysts such as hydroxide, and sodium or potassium carbonate. The commonly used bases catalyst in homogeneous catalytic transesterification is sodium hydroxide or potassium hydroxide which dosage is 0.4 %~2.0 % of oil mass. Homogeneous base catalysts are usually used in industry for the following reasons: firstly, mild reaction conditions; secondly, high conversion yield can be achieved in a short time; thirdly, higher catalytic activity; and fourthly, easy to obtain, which can bring good economic benefits. (Elsheikh, Man, Bustam, Akhtar, Yusup & Muhammad 2014.) The limitation of this method is that it is sensitive to the purity of the reactants, the content of free fatty acids, and the water content of the sample, and therefore, side reactions such as saponification and hydrolysis need to be kept to a minimum. (Mohadesi, Aghel, Maleki & Ansari 2019.)

Another method for the preparation of biodiesel is the use of acid catalysts. Usually, the preferred acid catalysts are sulfuric acid, hydrochloric acid, or sulfonic acid. One advantage of homogeneous acid-catalyzed transesterification reactions over homogeneous base catalysis is that they are not sensitive to the amount of free fatty acids in the feedstock, but homogeneous acid-catalyzed transesterification reactions are particularly sensitive to water content. When vegetable oil and methanol are subjected to

a transesterification reaction, the yield of esters will decrease when the water content of the reaction mixture is 0.1 %. When the water content reaches 5 %, the reaction is almost completely inhibited. The disadvantages of homogeneous acid-catalyzed transesterification reaction are easy corrosion of equipment, more waste generated by neutralization reaction, which is not an easy recovery, generation of secondary products, high reaction temperature, long reaction time, slow reaction rate, weak catalytic activity, and complex process. (Oglio, Sousa, Campos, Vasconcelos, Silva, Ribeiro, Rodrigues & Kuhnen 2015.)

Acid-base complex catalysis converts fatty acids to fatty acid methyl esters in the presence of an acid catalyst, followed by the conversion of triglycerides to fatty acid methyl esters in the presence of a base catalyst. Acid-base complex catalysis avoids the deactivation of the base catalyst caused by fatty acids and water and can make the full use of free fatty acids. The method will be used in two steps to produce biodiesel. In the first step, since the feedstock oil has a high content of free fatty acids, this step of the process must use an acid catalyst to reduce the free fatty acid content to 0.5 %-1 %. In the second step, a transesterification reaction is performed with a base catalyst to increase the yield of biodiesel. In the study, a maximum biodiesel yield of 98.26 % was achieved in the first step using 1 % sulfuric acid to reduce the free fatty acid content, followed by the use of potassium hydroxide as a catalyst in the second step. (Mohadesi et al. 2019.)

The acid-base complex catalyzed transesterification method has mild reaction conditions and can increase the biodiesel yield. However, the extraction of catalyst in two stages requires additional separation steps and subsequent treatments such as neutralization and acid-base separation after the reaction, resulting in long process flow, relatively high reaction time, increased production cost, and environmental pollution problems such as wastewater and waste residue discharge. (Talebian-Kiakalaieh & Amin 2015.)

2.1.2 Heterogeneous catalytic transesterification method

In addition to the acid-base homogeneous catalytic method, the heterogeneous catalytic method is also widely used and more maturely developed. Most of the heterogeneous catalysts use solid acids and solid bases, which can avoid the problem of difficult separation of liquid acids and bases and the discharge of wastewater and sludge. (Vitiello, Taddeo, Russo, Turco, Buonerba, Grassi, Serio, & Tesser 2021.) The use of a solid base catalyst in a reaction system allows for easier separation of the

catalyst from the products of transesterification than the use of a solid acid catalyst, and the solid base catalyst is more active near the boiling point of methanol. (Antunes, Veloso & Henriques 2008.) This means that compared to solid acids, solid bases have higher reactivity, simplify the process of catalyst separation and recovery, and shorten the reaction time, enabling continuous production and reducing production costs (Faba, Ferrero, Dias & Eimer 2019).

Unlike homogeneous catalysts and reaction mixtures that react in the same phase, heterogeneous catalysts are not in the same phase as the reaction mixture. Because it is within a different phase, the heterogeneous catalyst has the advantage of being easily separated and recoverable for reuse. Transesterification with heterogeneous catalysts means that several steps of washing, purification of biodiesel, and recovery of catalyst are reduced, thus ensuring higher efficiency, profitability, and lower production costs. In addition, the heterogeneous catalytic transesterification method is also characterized by its ability to be applied to extreme reaction conditions, as it can participate in the reaction and play its catalytic role at reaction temperatures up to several hundred degrees Celsius. (Ramli et al. 2017.)

heterogeneous solid base catalysts are usually base or basic oxides with large surface areas, such as basic zeolites, basic earth metal oxides, and hydrotalcite. Calcium oxide is widely used as a solid base catalyst with many advantages such as long catalytic life, high activity, low solubility in methanol, and mild reaction conditions required. (Faba, Ferrero, Dias & Eimer 2019.)

Although multiphase solid acid catalysts have low activity, they are still used in many industrial processes. The use of solid acid catalysts offers the following advantages: insensitivity to free fatty acid content, elimination of the purification step for biodiesel, easy separation of the catalyst from the reaction product, and reduced corrosion problems. Due to their sufficient acid strength, heterogeneous solid acid catalysts such as zirconium sulfate and zirconium tungstate have been used to catalyze transesterification for biodiesel production. (Vitiello, Taddeo, Russo, Turco, Buonerba, Grassi, Serio, & Tesser 2021.)

2.1.3 Biocatalytic transesterification method

Biocatalysts are mainly natural lipases, which have been shown to catalyze transesterification reactions. Enzymatic biocatalysts are divided into extracellular lipases and intracellular lipases, both of which

can be immobilized. The advantage of immobilization is its ease of regeneration from the reaction mixture and its ability to improve the utilization of this system. There are several methods to immobilize lipases, including adsorption, covalent binding, retention, encapsulation, and cross-linking. Adsorption remains the most widely used method for the immobilization of lipases. (Zhao, Qi, Yuan, Du & Liu 2015.)

The biological enzyme method has the advantages of a small amount of alcohol, few by-products, no pollutant emission, high stability, reusable, and the reaction process is less affected by free fatty acids and water in the raw material. However, the low carbon alcohols are toxic to the enzyme during the reaction process, the lipase is easily inactivated, the reaction time is long, the reaction yield is low, and the lipase is expensive, which is not suitable for large-scale industrial production. However, due to the irreplaceable environmental friendliness of enzymatic reactions and the development of genetic engineering technology, efforts have been made to modify lipases by bioengineering methods to obtain lipases with higher catalytic activity and better tolerance to the organic environment. (Quayson, Amoah, Hama, Kondo & Ogino 2020.)

2.1.4 Supercritical transesterification method

Supercritical transesterification is a method to prepare biodiesel by transesterification reaction without catalyst in the supercritical state of methanol. The basic principle of supercriticality is that when the temperature of a substance exceeds its critical temperature, the gaseous state and liquid state will be indistinguishable, and the substance will be in a flow state where it will not coalesce under any pressure. Due to the poor mutual solubility of methanol and oil, the reaction system is in two phases, and the transesterification reaction can only be carried out at the interface of the two phases, so the mass transfer is limited, and therefore the reaction rate is low. However, in the supercritical state, methanol and fats and oils are homogeneous, and the rate constant of homogeneous reaction is large, so the reaction time is short; in addition, no catalyst is used in the reaction, so the subsequent process is simpler, no waste liquid is discharged, and the cost is greatly reduced. (Rathnam, Modak & Madras 2020.)

The supercritical transesterification method can commendably solve the problem of difficult separation of reaction products and catalysts, therefore, it has received wide attention. Free fatty acids affect the occurrence of the transesterification reaction. The free fatty acid content of the raw material

determines the quality of the raw material, and a higher free fatty acid content means a lower quality of the raw material. Supercritical transesterification method requires lower quality of raw materials and can convert both free fatty acids and oils with high water content into biodiesel, which improves the yield to a certain extent. Supercritical fluid can be used as a co-solvent for oils and methanol, which greatly increases the reaction rate. The reaction process has no saponification reaction, and the separation and purification process of the products is simple. The disadvantage is that the reaction needs to be carried out at high temperatures and pressure, and the energy consumption is relatively high. (Bernal, Lozano, Verdugo, Burguete, Sánchez-Gómez, López, Pucheault, Vaultier & Luis 2012.)

2.1.5 Co-solvent transesterification method

The presence of the co-solvent overcomes the low reaction rate caused by the very low solubility of alcohols in the triglyceride phase. The rate of conversion of oils and fats to esters is also very slow due to the low solubility of methanol in oils and fats. One way to overcome these problems is to add a co-solvent that is soluble in both methanol and fats and oils. (Zhao 2020.) Tetrahydrofuran is an excellent co-solvent and was chosen because it has a very similar boiling point to methanol while the system requires a fairly low reaction temperature. The use of a co-solvent such as a tetrahydrofuran can significantly accelerate the rate of the transesterification reaction (Huang, Xiao, Yang & Guo 2021). The outstanding advantage of the co-solvent method is that only a short reaction time with co-solvent is required at room temperature and pressure, and no catalyst residue is present in either the biodiesel or glycerol phases (Zhao 2020).

2.2 Industrial production process of biodiesel

Based on the principle of biodiesel preparation by transesterification, biodiesel has gradually moved from laboratory preparation to industrial production. The wide variety of feedstocks, different reaction and separation conditions, and different types of catalysts make the industrial production of biodiesel a complex system. The traditional process for preparing biodiesel is batch production. (Biodiesel Technical Notes 2017.) Batch production is a series of processing activities in which raw materials are processed in a prescribed sequence of steps to produce a limited amount of product at the end of the sequence, and then the raw materials are added again and the sequence is repeated to produce the next batch of product. (Vidhya 2017.) Batch production of biodiesel is mainly applied in small plants, and

this production mode is simple in process and flexible in operation, but the time consumed in production is long. (Biodiesel Technical Notes 2017.) In order to reduce the production time, some factories produce continuously by optimizing their equipment. The continuous process will be constant and simultaneous in all aspects of the production operation, with uninterrupted production and output products. This process is easy to automate and control, and the quality and yield of the products are stable, in which the new biodiesel production plant gives scope to a significant role. (Sansawang, Chimmanee & Butsing 2016.)

2.2.1 Feedstock for biofuel production

The feedstock is the key to the production of biodiesel, and the cost of feedstock accounts for more than 70% of the total cost in the preparation of biodiesel, therefore, large-scale, cheap and energy-usable oil resources are the key to biodiesel industrialization (Günay, Türker & Tapan, 2019). At present, the development of the biodiesel industry varies among different countries internationally. The European Union mainly uses rapeseed oil as raw material to produce biodiesel and is the largest biodiesel producing region in the world, the United States mainly uses soybean oil as raw material to produce biodiesel, the Philippines uses coconut oil and Malaysia uses palm oil as raw material. (Yusoff, Zulkifli, Sukiman, Chyuan, Hassan, Hasnul, Zulkifli, Abbas & Zakaria 2020.)

The feedstock for biodiesel production is not only vegetable oil, but also waste oil and microbial grease. The advantages of vegetable oil feedstock are high oil content, easy seed harvesting, storage, transportation and processing procedures, and the disadvantages are limited cultivation due to the arable land area. The advantage of animal oil in waste oil raw materials is not affected by the arable land area, its raw materials are abundant and cheaper, wide sources and huge production, the disadvantage is that compared to vegetable oil impurities are more, the source is scattered, while collection requires a lot of human and material resources. The advantage of waste oil raw materials is the wide range of sources and huge reserves, which can effectively solve the problem of waste oil pollution. The disadvantage of this is that there are various impurities in the oil and grease, and the pretreatment process is complicated. The advantage of microbial oil and grease raw materials is that the supply of raw materials is sufficient, does not occupy arable land and freshwater resources, and can be managed and produced on a large scale. The disadvantage of this is that there are many kinds of microorganisms, the research is more difficult and the cost of oil production is larger. (Abbas, Hussain, Iqbal, Nadeem, Qasim, Hina & Hafeez 2016.)

2.2.2 Continuous two-stage transesterification process

The continuous two-stage transesterification process to produce biodiesel is the most mature process technology developed so far, and most of the biodiesel manufacturers in production have chosen this method. In this method, methanol and catalyst are mixed first, and then it is reacted with oil and grease raw materials in a certain ratio into the first stage transesterification reactor, and the resulting mixture is separated of glycerol. The resulting product is fed into the second stage reactor, supplemented with methanol and catalyst and then continue the reaction, and the glycerol is separated after the reaction, and the obtained product is washed and dehydrated to get the finished biodiesel. (Gerpen 2019.)

The continuous two-stage transesterification process requires a number of attention in the actual production. First, pretreatment is needed before starting the preparation. If the raw material contains a large amount of free fatty acids, special treatment is needed. When the free fatty acid content is higher than 5 %, an acid catalyst (e.g. sulfuric acid) needs to be used to react with the free fatty acid to form methyl ester. This will reduce the free fatty acid content and avoid the impact of the saponification reaction on the experiment to the maximum extent. Secondly, glycerol must be separated at the end of the reaction in the primary transesterification reactor. This is because the transesterification reaction is reversible and the methyl ester may recombine with glycerol to form glycerol monoesters. Due to the low solubility of glycerol in the ester, this separation usually occurs very quickly and can be accomplished with a settling tank or centrifuge. Finally, the purpose of the water wash step is to remove any remaining catalyst, soap, salt, methanol, and free glycerol from the biodiesel. Neutralization before washing reduces the amount of water required and minimizes the potential for emulsion formation when wash water is added to the biodiesel. After the washing process, any remaining water is removed from the biodiesel by a vacuum flash process. (Gerpen 2019.)

The most typical application of a continuous two-stage transesterification process is at Lurgi in Germany, where the production process involves intensive mixing of methanol with oil in the presence of a catalyst, followed by separation of the lighter methyl ester phase from the heavier glycerol by gravity. The feedstock oil, methanol, and catalyst are mixed in reactor number one and made to separate into two phases at the end of the reaction. The lighter fatty acid methyl ester and oil are mixed and reacted with other methanol and catalyst in reactor number two, and then separated by gravity. The lighter phase is washed with water, which removes residual glycerol or methanol dissolved in the ester

phase, and then vacuums dried to give biodiesel. The heavier glycerol from reactor number two containing excess methanol and catalyst is recycled to the front end of reactor number one. The glycerol leaving reactor one, which still contains excess methanol, is recovered by distillation in a methanol recovery column and sent back to reactor one. Wash water from the aqueous scrubber column is used in the methanol recovery column. Thus, the entire methanol is consumed in the production of methyl ester. The heavier fractions from the methanol recovery column are processed in a glycerol water evaporation column to recover crude glycerol as a by-product. This can be further refined by distillation, bleaching (if required), and vacuum drying. (Luna, Calero, Sancho, Luna, Posadillo, Bautista, Romero, Berbel & Verdugo 2013.) The flow chart for the production of biodiesel at Lurgi is shown in Figure 2.

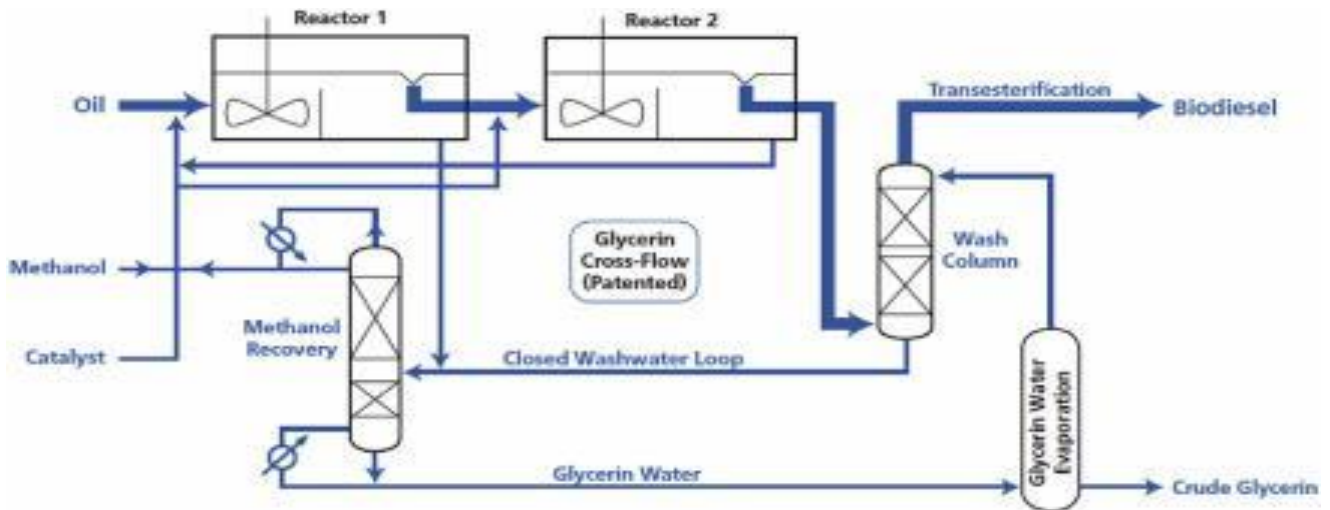


Figure 2: Flowchart of biodiesel production at Lurgi (Luna et al. 2013)

In Lurgi's process, the reaction in the second reactor stage maximizes the biodiesel yield and quality, while, at the same time, forming the recovery and recycling of methanol. The closed wash cycle system achieves wastewater reduction. The separation by gravity process eliminates the need for centrifuges and reduces costs. (Luna et al. 2013.)

2.2.3 Innovative biodiesel production process

Nowadays, as the drawbacks of batch processes long reaction times are becoming apparent, and as industrial production equipment continues to be optimized, more plants are moving towards

continuous production. The continuous process has led to gradual automation of the process and a steady increase in the quality and yield of the products. The continuous process still operates on the principle of the transesterification method, which is based on the batch process and optimizes the process chain by replacing it with new equipment. The key to the continuous process is the continuous reaction equipment, and the new devices are now mainly pipeline reactors, fixed bed reactors, microreactors and catalytic membrane reactors (Gupta, Agarwal & Dalai 2020). The design of the reactor and the optimization of the process conditions have led to a great improvement in the yield of biodiesel, which provides a good development idea to achieve high-efficiency production of biodiesel (Tran, Chang & Lee 2017).

The tube continuous transesterification technology for biodiesel preparation generally uses homogeneous catalysts, which are simple in construction, easy to operate, and of high practical value. Poor mutual solubility of methanol and grease, the transesterification reaction can only occur at the contact interface between them, so the mixing of the two in the tubular reactor can greatly affect the reaction rate of the transesterification process. To increase the degree of mixing, the tube reactor is usually spirally distributed inside the tube to increase the turbulence intensity of the fluid inside the tube, and the flow rate must be able to make the material completely in the turbulent state when choosing the circulation pump, otherwise, it will affect the rate of the transesterification reaction. (Santacesaria, Turco, Tortorelli, Russo, Serio & Tesser 2012.)

A fixed bed reactor is a reactor in which fluid is reacted through a bed level formed by stationary solid material. The surface of solid material can provide a contact surface for reactants, when the solid catalyst is used as bed filler, which will lead that the catalyst concentration per unit volume is high and the reaction rate is fast. With the appropriate solid catalyst, a high yield of biodiesel can be achieved at a suitable molar ratio of alcohol to oil, air velocity, reaction time, and pressure. (Xiao, Gao, Xiao, Fu & Niu 2012.)

Microreactors generally refer to micron or millimeter size reactors with the continuous fluid operation. Because of the small channel size of the reactor, the specific surface area inside the reactor can be significantly increased to enhance the mass and heat transfer process, which can effectively reduce the reaction time and control the reaction temperature. At the same time, its operation is simple and the yield can be adjusted by increasing or decreasing the number of reaction channels, which has potential advantages in practical applications. Microreactors have also been successfully applied to the continuous preparation of biodiesel by changing the inner diameter of the microreactor, designing the

internal shape and components, and using suitable co-solvents and catalysts. Due to the small characteristic size of the microreactor, the liquid flow in it is generally considered to be laminar, in which the mixing process relies mainly on diffusion rather than turbulence. Since grease and methanol are immiscible liquids, transesterification reactions in microreactors are generally carried out in two ways to enhance the contact between the two to improve the conversion. Firstly, a co-solvent is used to convert the non-homogeneous system of grease and methanol into a homogeneous system, thus removing the effect of interfacial mass transfer. Secondly, the microreactor configuration is designed to form very thin flow layers or small size microdroplets to enhance mass transfer. (Tiwari, Rajesh & Yadav 2018.)

The catalytic membrane reactor couples catalytic reactions with membrane technology and performs reactor design and optimization. The main advantage is that intermediate processes can be omitted, resulting in a significant reduction in operating costs and equipment consumption. Compared with conventional reactors that separate the catalytic reaction from the separation process, catalytic membrane reactors can overcome the deficiencies of non-homogeneous catalysts through membrane material design and catalyst loading capacity regulation. And the reactor can be combined with membrane separation technology to selectively remove reaction products, improve the reaction conversion rate, while simplifying the production process, energy saving and environmental protection. Therefore, catalytic membrane technology has been widely appreciated and gradually become one of the frontier research fields for biodiesel preparation today. (Ma, Lv, Du, Han, Lu & Ding 2017.)

3 EFFECT OF BIODIESEL TECHNOLOGY ON THE ENVIRONMENT

At present, the world is facing the crisis of fossil fuel depletion due to the expanding energy demand and the drastic consumption of non-renewable resources such as fossil fuels, while the negative impact of fossil fuel combustion on the ecological environment is becoming increasingly serious. Excessive use of fossil fuels has led to global environmental degradation effects such as the greenhouse effect, acid rain, ozone depletion, and climate change. In the current context, the search for alternative fuels has become important as they will play a pivotal role in areas related to sustainable development, energy conservation, efficiency, and environmental harmony. (Borugadda & Goud 2012.)

Biodiesel is a renewable liquid fuel that can be used in any diesel engine without prior modification and has been more appealing due to its environmental benefits. It reduces exhaust emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitro polycyclic aromatic hydrocarbons, and particulate matter compared to conventional petroleum diesel engines. It is chemically different from petroleum diesel and assumes quality risks depending on the raw material, physical properties, and production process. In terms of sulfur content, aromatic content, and biodegradability, biodiesel is a better alternative to conventional diesel fuel. In addition, the key factor that makes biodiesel an attractive alternative to diesel is that it can be derived from renewable resources and has good environmental benefits. Biodiesel is much less polluting than petroleum diesel and consequently emits much less of almost all pollutants, and blending biodiesel into petroleum diesel can help reduce emissions. (Blasio 2019.)

In biodiesel production, life cycle analysis is important to quantify the amount of energy and raw materials consumed and the emissions released at each production stage. Taking palm oil biodiesel production as an example, the life cycle analysis of the biodiesel production process can be divided into three stages, including the agricultural production stage, the industrial production stage, and the consumer application stage. (Yusoff, Zulkifli, Sukiman, Chyuan, Hassan, Hasnul, Zulkifli, Abbas & Zakaria, 2020) The agricultural production stage includes the planting, harvesting, transportation, and storage of oilseed crops. The industrial production phase involves the pretreatment of oil feedstock and the production of biodiesel by transesterification. The consumer application phase includes storage, distribution and transportation to gas stations, and final combustion of biodiesel. (Bello, Ranganathan & Brennan 2017.) The life cycle analysis diagram of biodiesel production is shown in Figure 3.

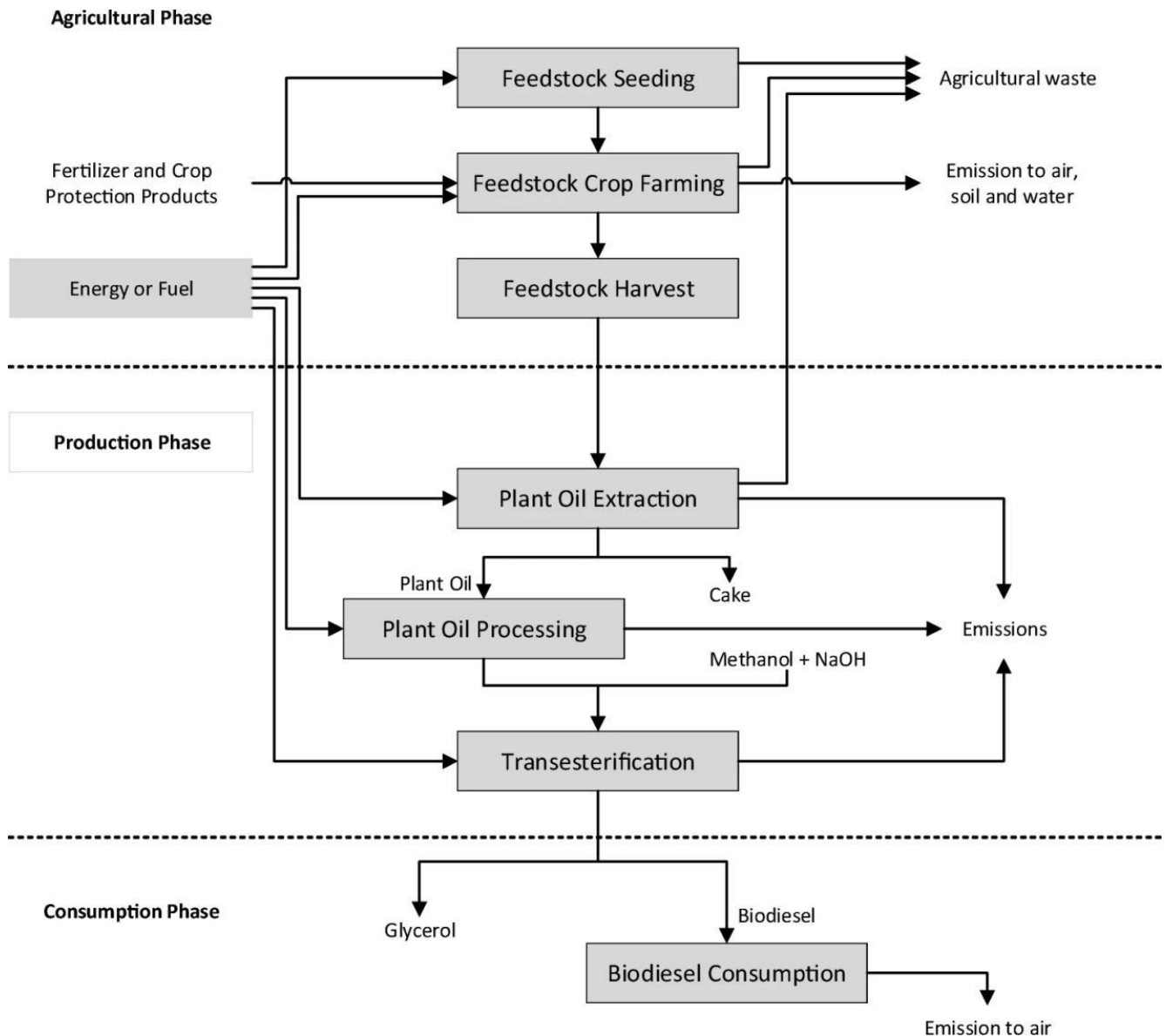


Figure 3: Life cycle analysis diagram of biodiesel production (Yusoff, Zulkifli, Sukiman, Chyuan, Hassan, Hasnul, Zulkifli, Abbas & Zakaria, 2020)

3.1 Environmental impact of the feedstock phase

Various feedstocks are used for biodiesel production, providing environmental benefits according to their requirements for agriculture, transportation, and some other conditions. A comprehensive LCA of biodiesel from different feedstocks (soybean, Jatropha, microalgae) was conducted and the environmental performance was compared with that of conventional fossil fuels. Compared to

conventional diesel, biodiesel performs better in terms of global warming potential, ozone layer depletion and abiotic depletion, mainly due to the absorption of carbon dioxide and solar energy from the environment through photosynthesis during agricultural production when vegetable oil is chosen as the raw material. However, the poor performance in terms of acidification, eutrophication, photochemical oxidation and toxicity is a result of the fertilizers, chemicals. required in the cultivation and harvesting of agricultural production. (Hoque & Gee 2013.)

In another study, the environmental performance of second-generation biodiesel was compared with waste oil-based biodiesel which had a less environmental impact on all damage categories (climate change, human health, and ecosystem quality). The disadvantage of jatropha-based biodiesel in terms of environmental performance was attributed to the fertilizer, chemical, water, and land requirements for biomass cultivation and harvesting. However, waste edible oil-based biodiesel exhibits serious environmental impacts on impaired categories of resources including mineral extraction and non-renewable energy demand. The total environmental burden is reduced by 74 % when using waste vegetable oil as feedstock compared to jatropha oil. (Li, Ahmed, Watson & You 2020.) From the above reserach, it can be concluded that waste oil is the most important encouraged feedstock in biodiesel production.

3.2 Environmental impact of the production phase

In addition to comparing different potential feedstocks, LCA was also performed from the perspective of comparing different technological pathways for biodiesel production. Methanol is used as a feedstock in all substitution processes, significantly contributing to the depletion of abiotic resources as methanol is synthesized from fossil resources. Compared to methanol, ethanol may be the preferred choice due to its renewable source. In other words, ethanol is responsible for absorbing large amounts of carbon monoxide, significantly reducing the greenhouse gas effect of the manufacturing system. (Jambulingam, Srinivasan, Palani, Munir, Saeed & Mohanam, 2020) In addition to this, the non-catalytic (supercritical conditions) route using co-solvents is a relatively more environmentally friendly process. This is because no catalyst is used and that vapor consumption is lower compared to other processes (Rathnam, Modak & Madras 2020).

At the same time, the acid-catalyzed route usually has the highest environmental impact, mainly due to the high energy distribution associated with the methanol recovery operation. Supercritical non-

catalytic processes can reduce acidification by 75.4 %, abiotic resources by 31.3 %, marine aquatic ecotoxicity by 79.3 %, and global warming by 49.6 % compared to base-catalyzed processes (Bernal, Lozano, Verdugo, Burguete, Gómez, López, Pucheault, Vaultier & Luis, 2012). When comparing the environmental impact of base catalysts (potassium hydroxide and sodium hydroxide), sodium hydroxide exhibits a greater environmental impact on ecosystem quality and human health. This can be explained by the fact that sodium hydroxide is an environmentally hazardous substance compared to potassium hydroxide. In addition, sodium hydroxide produces water-soluble salts upon neutralization and precipitates potassium hydroxide by reacting with sulfuric acid to potassium sulfate, and the salt precipitation reduces overall water use and polluted water discharge to the environment. (Singh & Olsen 2012.)

3.3 Environmental impact of the application phase

Biodiesel LCA in its application phase is mainly focused on automotive fuel. Compared to fossil diesel automotive engines, biodiesel engines reduce the exhaust emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter. In terms of sulfur content, aromatic content and biodegradability, biodiesel is a better alternative to fossil diesel fuel. Biodiesel can be blended into fossil diesel fuel, which helps to reduce exhaust emissions. (Singh & Olsen 2012.) Because the performance of vehicle engines does not change with the combustion of fuels produced by different technological routes, the emission performance and ignition behavior of biodiesel become important indicators when comparing it with conventional diesel fuels. (Mayo & Boehman 2015.)

To investigate the emission performance of biodiesel fuels, the effect of atmospheric oxygen concentration on the physical and chemical ignition behavior of biodiesel and diesel fuel blends was studied using a light diesel injector equipped with an accessible constant volume combustion chamber. Compared to fossil diesel, biodiesel contains less sulfur and aromatics, despite its slightly lower calorific value. Biodiesel is an oxygenated fuel, which contributes to adequate combustion of the fuel and reduces hydrocarbon and soot content. The emission of nitrogen oxides from biodiesel combustion is significantly lower than that of fossil diesel, mainly because the cetane number of biodiesel is higher than that of fossil diesel, which makes the ignition delay period of the fuel shorter, the premixed combustion exothermic peak lower, the engine cylinder temperature lower, and the emission of nitrogen oxides from combustion lower. The carbon soot emissions of biodiesel are reduced compared

to fossil diesel. Physical and chemical ignition delays were analyzed in the study by detecting the excited formaldehyde and hydroxide chemiluminescence using an optical filter and photomultiplier tube system. While biodiesel has a slightly longer physical ignition delay due to the extended atomization and evaporation process, its chemical ignition delay is much shorter than that of diesel, which is attributed to the long-chain hydrocarbon fuel structure and the availability of fuel oxygen. (Mayo & Boehman 2015.)

4 APPLICATION PROSPECTS OF BIODIESEL TECHNOLOGY

Biodiesel has been a hot topic of research on new sustainable energy sources in recent years. Interest in and development of biofuels has increased dramatically in recent years in response to the need to create a sustainable energy supply and combat climate change. The commercial and environmental sustainability of the biodiesel industry is still being debated. Research to make biodiesel production more cost-effective and environmentally benign is progressing rapidly. (Salaheldeen, Mariod, Aroua, Rahman, Soudagar & Fattah 2021.) Many countries such as Indonesia, Canada, Brazil, Argentina, Chile, China, and India are implementing mandatory policies to blend biodiesel with traditional fossil fuels. Feedstock availability and the cost-effectiveness of the biofuel production process are among the key factors driving interest in any given generation of biofuels. In the future, biodiesel demand will increase significantly due to government requirements to shift to renewable energy sources, rising crude oil prices, and increased environmental pollution. (Nguyen, Nguyen, Su, Ong, Juan & Wu 2021.)

The selection of suitable feedstock oil is a key factor in the production of cost-effective biodiesel. The selected feedstock oil should not compete with food crops. The use of feedstock oils (e.g., non-edible oils, jatropha oil, and animal fats) for biodiesel production is currently being studied extensively because these oils do not compete with human food. In particular, Jatropha plants can grow well on poor and infertile soils and can withstand all types of climates. Jatropha seeds also contain a high oil content of up to 50 %. (Villalobos, Yarce, Delgado, Ojeda & Tuirán 2020.) Currently, microalgae are explored as a substitute for vegetable oils. Microalgae also absorb carbon monoxide and contribute to the reduction of greenhouse gases. Oil-bearing microalgae have received much attention as a new source of feedstock for biodiesel production. In the future, research should focus on microalgal lipid feedstocks as potential feedstocks for biodiesel production. (Lebeuf, Mazaud & Rataj 2021.)

In biodiesel production, heterogeneous catalysts and immobilized enzyme catalysts are superior to conventional homogeneous catalysts. Transesterification of lipids and methanol with suitable catalysts is a widely accepted method for biodiesel production. Homogeneous catalysts have been developed on an industrial scale because they offer faster reaction rates and higher yields. However, they also have various disadvantages such as additional neutralization steps, cumbersome purification processes, wastewater generation, and non-recoverability of the catalyst. In contrast, the use of heterogeneous catalysts, such as waste biomass-based catalysts and nanocatalysts, is rapidly increasing. Heterogeneous catalysts are more promising than homogeneous catalysts because they can be easily

separated from the product and reused in several cycles, thus reducing the overall production cost. Heterogeneous catalysts show the potential to overcome the challenges of homogeneous catalysts and replace them on an industrial scale. (Ingle, Philippini, Martiniano, Silva & Chandel 2020.) Immobilization of lipases on nanocatalysts increases their activity and surface area and has the advantage of easy catalyst recovery and multi-cycle reuse, by which the stability of the enzyme can be improved. Liquid lipase formulations for biodiesel production are growing rapidly because they have better miscibility with the reactants, while reduce mass transfer limitations and increase reaction rates. However, the use of lipases for biodiesel production on an industrial scale is still a challenge to overcome due to their high cost. (Quayson, Amoah, Hama, Kondo & Ogino 2020.)

5 CONCLUSION

Growing energy demand and the need to reduce dependence on fossil fuels are expanding the market for biodiesel. Through the study of transesterification technology of biodiesel and its environmental impact analysis, the competitiveness of biodiesel development is highly dependent on industrial feedstock and production capacity. When choosing industrial feedstock for biodiesel preparation, waste oil and grease feedstock is significantly better than vegetable oil and grease feedstock in terms of cost and environmental friendliness. Microalgal lipid feedstocks, which are alternatives to vegetable oil and grease feedstocks, can also be used as potential feedstocks. Studies on biodiesel production capacity have shown that the involvement of catalysts in the transesterification method reduces the activation energy of the reaction and accelerates the process to provide better biodiesel yields in a shorter time. Depending on the type of catalyst, reaction parameters and reaction output vary considerably, and the selection of the right catalyst is a key factor in biodiesel synthesis. Multiphase catalysts and lipase catalysts are excellent choices. In the industrial production of biodiesel, in addition to the choice of catalyst, the production method also determines the quality and yield of the product. With the continuous optimization of reactor equipment as well as process conditions, continuous process has started to gradually replace batch process, in which new biodiesel production equipment such as pipeline reactor, fixed bed reactor, micro reactor and catalytic membrane reactor play a very important role. In the application stage, both the automobile engines mixed with biodiesel and fossil diesel and the automobile engines directly using biodiesel have effectively reduced the emission of harmful gases, and the use of biodiesel has created great environmental and social benefits.

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