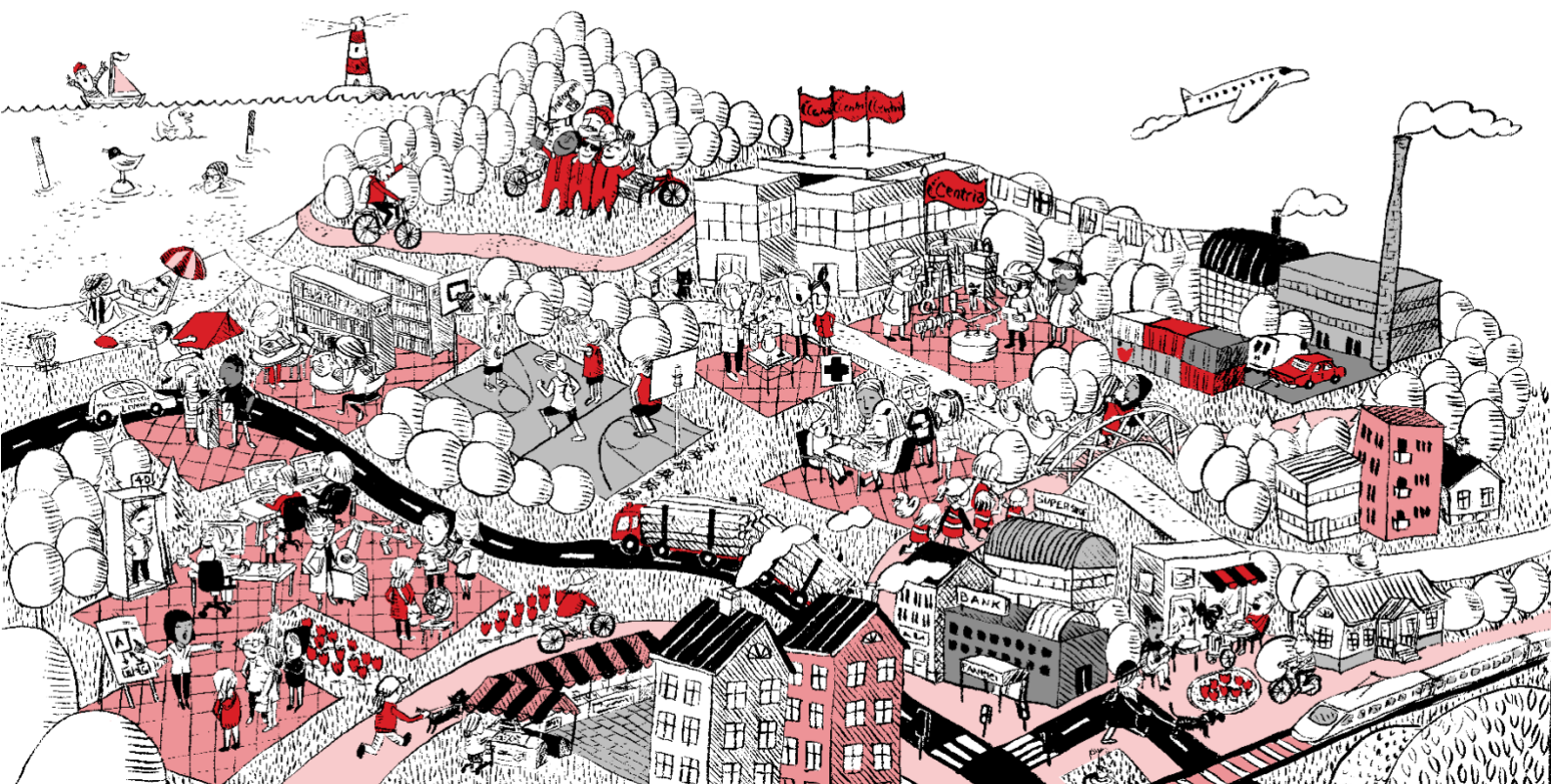


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**EXTRACTION AND TRANSFORMATION OF MICROALGAL OIL  
TO BIODIESEL**

**Thesis  
CENTRIA UNIVERSITY OF APPLIED SCIENCES  
Degree Programme  
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## ABSTRACT

<b>Centria University of Applied Sciences</b>	<b>Date</b> August 2021	<b>Author</b> Haoran Xia
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<p>Biodiesel is one of the fastest growing renewable sources of low nitrogen and sulfur content while releasing less pollutants during the combustion process. Microalgae are widely distributed in the world with high fat content, high proliferation rate and high energy conversion efficiency as an important raw material for biodiesel production. However, due to its high production cost and low cost, microalgae biodiesel is still in the primary stage of development. In this study, from the perspective of solving the existing problems of low yield, the production methods of biodiesel raw materials, low yield and low energy consumption of microalgae biooil were studied, from the screening of microalgae to the methods encountered in the preparation of biodiesel.</p> <p>The selection of carbon sulfonate nanosheets in solid acid catalysis was discussed. Solid acid catalyst is one of the commonly used catalysts for the synthesis of biodiesel. Compared with homogeneous acid catalyst, it has the advantages of easy separation, small volume, corrosion resistance and recoverability. It also eliminates the consideration of the acid value of the reactants and has a wider applicability than the base catalyst. However, the current solid acid catalyst has low activity and requires higher reaction temperature.</p>		
<p><b>Key words</b> Biodiesel, Microalgae, Nanosheets, Solid acid catalysts</p>		

## CONCEPT DEFINITIONS

### List of abbreviation

2D                      Two dimensions

### List of units

nm                      Nanometer

mmol/g                Millimole per gram

m<sup>2</sup>/g                    Square meters per gram

**ABSTRACT**  
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## 1 INTRODUCTION

Energy is the driving force of economic development, and the energy crisis means the crisis of global economic development. According to the 2017 World Energy Statistical Report recently released by British Petroleum Company, (Petroleum, B. 2017) the global proven oil reserves are 1.7067 trillion barrels, which can meet the global production needs for 50.6 years. Natural gas and coal reserves would cover only 52.5 and 153 years of global production. As the world energy crisis and environmental problems become more prominent, it is imperative to develop clean and renewable energy. The United States, Japan and other energy exporting countries have realized the importance of energy security and actively develop renewable energy. (Shen, Poovaiah, Ziebell, Tschaplinski, Pattathil, Gjersing & Dixon 2013.)

Worldwide, the traditional raw materials for biodiesel production mainly include soybean oil, rapeseed oil and sunflower oil. In addition, there are other oily plants such as oil palm, coptis wood, jatropha, as well as animal fat and waste cooking oil. However, these raw materials are not sustainable in producing biodiesel. At present, about 3% of biodiesel is produced from animal and vegetable oils, and the additional animal and vegetable oils needed for biodiesel will cause problems for the world's food supply. (Steriti, Rossi, Concas & Cao 2014.) Microalgae is the most promising and future raw material for biodiesel production, which has the characteristics of wide distribution, fast growth, high oil content and strong environmental adaptability. Compared with other oil crops, microalgae only needs cultivation area to produce biodiesel. Meanwhile, microalgae cultivation can be used in non-cultivated land of tidal flat or derelict lands. Microalgae can also be transformed to produce biodiesel and other related metabolic products. At the same time, the massive burning of fossil energy and the emission of sulfur dioxide, carbon dioxide and other gases are the main sources of acid rain and greenhouse effect. Therefore, looking for clean and renewable energy that can replace fossil fuels is one of the important problems that human society urgently needs to solve at present. (Postma, Miron, Olivieri, Barbosa, Wijffels & Eppink 2015.)

Walling breaking and crude oil extraction from microalgae are the key and difficult points in microalgae biodiesel production technology. How to extract oil from microalgae cells with low energy consumption and high efficiency is of great significance to reduce the cost of biodiesel and to market biodiesel technology. (Gerken, Donohoe & Knoshaug 2013.)

At present, the traditional industrial method of biodiesel production is mainly homogeneous catalytic method. Homogeneous catalytic method to liquid acid (such as hydrochloric acid, sulfuric acid, phosphoric acid) or liquid alkali (such as sodium hydroxide, potassium hydroxide, sodium methoxide) as the catalyst. (Knothe, Krahl & Van Gerpen 2015.) Although homogeneous catalysts have high efficiency, they are highly corrosive to equipment, resulting in a large amount of wastewater produced during product separation and purification processes, and serious environmental pollution. (Le, Nishimura & Ebitani 2019) In recent years, efforts have been made to develop reusable heterogeneous catalysts and new methods for biodiesel production. Therefore, hope to find the catalyst that can improve the production efficiency in the process of biodiesel preparation and provide the basis for the efficient industrial production of biodiesel by microalgae.

The objective of this study is to find a catalyst that can improve the production efficiency of biodiesel from microalgae, reduce production cost, save energy consumption, and effectively control the discharge of a large amount of waste liquid in the production process. Furthermore in the future there is an opportunity to produce on a commercial scale.

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## **2 SEED SELECTION AND ADVANTAGES OF MICROALGAE INTO BIODIESEL**

Algae have existed on Earth for about 3.5 billion years, with some 23,000 species, and are the earliest prokaryotes capable of photosynthesis. Algae are simple and diverse in structure. The spherical cells are the most common type. Algae perform photosynthesis because algae contain chloroplasts, which make the conversion of light energy possible and self-sufficient. Algae also have many uses, playing an important role in food, agriculture, medicine, aquaculture, and as a food source for everything from whales to insects. In terms of biomass energy, algae can reduce combustion emissions such as carbon dioxide, sulfur oxides of nitrogen oxides. Algae can remove heavy metals, ammonium salts and phosphates that pollute water sources and play the role of purifying lakes. (Milne, Evans & Nagle 1990.) They advantages include wide distribution range, fast growth rate and high lipid content. Like lipid crops, algae can produce biomass energy through photosynthesis. Microalgae cells can be cultured on a large scale, then collected and dried. The oil is extracted with hexane or benzene as a solvent, and then converted into biodiesel by esterification reaction. The remaining microalgae can also be used for a variety of purposes, such as animal feed, pyrolysis, or liquefaction to produce biomass oil. Therefore, the research on the preparation of biodiesel from microalgae has become an important topic for the development of bioenergy industry. Biomass energy is an energy that stores chemical energy in biomass as a carrier. The specific process is as follows: biomass absorbs carbon dioxide from the air and converts it into biomass energy through photosynthesis. The carbon dioxide generated after the combustion of biomass energy is released back into the air, in other words, carbon cycle is realized, and it is regarded as renewable energy. (Modiba, Enweremadu & Rutto 2015.)

In conclusion, microalgae are environmentally friendly raw materials, which are beneficial but harmless to the environment. Microalgae can be used for a variety of purposes, such as the preparation of vitamins, carotenoids, eicosapentaenoic acid, docosahexaenoic acid and other medicine and health products, as well as other unsaturated fatty acids and biodiesel, and the remaining dried algae can also be used as feed. Microalgae are in big demand for energy applications, such as biodiesel or jet fuel. So for future renewable energy, meager biofuel has great potential, offering a possible solution to the problem of limited natural resources. (Rodolfi, Chini, Zittelli, Bassi, Padovani, Biondi, Bonini & Tredici 2009.)



## **2.1 Oil-rich microalgae and microalgae lipids**

Thousands of species of algae have been discovered, but some algae are better suited to biofuels than others. The characteristics of a species should take into account the climate in which algae grow. According to the Aquatic Species Project and other algae production researchers, the characteristics required for algae species to produce biofuels are lipids, growth and efficiency, pollution and harvesting. (Jones & Mayfield 2012.)

Based on the above criteria, many microalgae species have been identified as suitable feedstocks for biofuel production. Microalgae of each species produce different proportions of lipids, carbohydrates, and proteins. Because most of the natural oil produced by microalgae comes in the form of triglycerides, which is suitable for oil production of biodiesel, microalgae are focused on the algae-biofuel field. To obtain better economic benefit, it is necessary to increase the lipid content in microalgae. Fortunately, many microalgae could control their metabolism by simple manipulation of the chemical composition of their culture medium, resulting in a high-fat production capacity. Some algae, under good growing conditions, can double their biomass in 24 hours. Therefore, the characteristics of fast growth, high oil content and easy harvesting should be taken into consideration when selecting microalgae varieties for cultivation. The two most important species, one from prokaryotic cyanobacteria and the other from *Microcystis aeruginosa*. (Schneider 2006.)

## **2.2 Prominent advantage of biodiesel production from microalgae**

Biofuels can be divided into three generations according to their different raw materials. The first generation of biofuels mainly includes ethanol made from corn, potatoes, etc., and biodiesel made from soybean oil. The first generation of biofuels is characterized by using food crops as raw materials, and the preparation technology has been mature and commercialized. In order to overcome the inherent defects of the first generation of biofuels, the second generation of biofuels using non-food crops as raw materials came into being, which refers to ethanol made from lignocellulose and biodiesel made from palm oil and leprosy oil. (Samorì, Barreiro, Vet, Pezolesi, Brillman, Galletti & Tagliavini 2013.) Although non-food crops do not compete with people for food, they do occupy land for food crops. The loss of land for food crops will eventually lead to tight food supplies and higher prices. At the same time,

the yield of non-food crops is relatively low, and the cost is relatively high. Due to the influence of seasons and growth cycle, biooil cannot be provided stably for a long time. In order to meet the demand of biofuel for social and economic development and avoid the situation of competing with people for food and land, the third-generation biofuel with microalgae and microorganisms as raw materials has become a hot spot in international research. (Halim, Harun, Danquah & Webley 2012.)

Microalgae is an ideal biofuel raw material due to its fast growth and high oil content. Compared with traditional biofuel, microalgae have great advantages. The quantum efficiency of ordinary terrestrial plants in converting solar energy into biomass energy is less than 1 %. while the quantum efficiency of microalgae cells is as high as 2-10 %. (Samorì et al.2013.) As a result, the growth rate of microalgae is extremely fast, and the biomass increase can reach 1-3 times per day. In addition, microalgae have strong growth adaptability and can grow and multiply in various water environments. The growth cycle of microalgae can be as short as 5-7 days, much less than the months or even years required for the growth of ordinary land plants. Under the irradiation of light, microalgae cells transform nutrients such as carbon dioxide and water into different organic products by metabolism and store them, thus realizing the conversion of solar energy to biomass energy. (Minowa, Yokoyama, Kishimoto & Okakura 1995.)

### **3 MICROALGAE WALL BREAKING AND SOXHLET EXTRACTION**

The extraction efficiency of oil from microalgae was not only related to the content of bio-oil but also related to the total oil content in microalgae. The oil composition and content of microalgae are the decisive factors of whether they can be used as biodiesel feedstock. The oil content and composition of microalgae are closely related to algae species, growth cycle and culture mode. Therefore, it is of great significance to establish a rapid and accurate lipid determination method for the detection of microalgae lipid extraction effect. (Fan, Huang, Wang & Li 2012.)

Conventional methods for oil content detection include organic solvent differential weight method. For example, chloroform methanol is used for extraction, and the solvent contained in microalgae is steamed and weighed. The difference between the dry weight of the cells before and after the microalgae is the extracted oil content. The fluorescent dye Nile red method is also one of the methods for quantitative determination of the mass percentage of microalgae oil. In addition, infrared spectroscopy technology has been proposed for the detection of microalgae lipids, which can detect carbohydrate and protein content at the same time. (Prabakaran & Ravindran 2011.)

#### **3.1 Microalgae cells break walls**

One of the main problems in the process of biodiesel production from microalgae by chemical conversion is how to extract oil from microalgae biomass efficiently. (Schenk, Thomas-Hall, Stephens, Marx, Mussnug, Posten & Hankamer 2008.) Microalgae biomass generally still contains about 80% water after mechanical dehydration, and evaporation of this water fraction consumes enormous energy. In order to reduce the energy consumption of biodiesel produced from algae, scholars have proposed a number of production processes to extract oil directly from algae in recent years. When oil was directly extracted from wet algae, water prevented the contact between oil and organic extractant, and the tough and dense cell wall of microalgae prevented the diffusion of oil into extractant, leading to low oil extraction rate. In order to improve the efficiency of oil extraction directly from wet algal biomass, researchers have proposed a number of methods to destroy the cell wall of microalgae. (Lee, Lewis & Ashman 2012.)

According to the different principles of microalgae wall breaking, the wall breaking methods can be divided into mechanical method and non-mechanical method. The classification of the above methods is shown in Figure 1. Non-mechanical methods mainly include chemical methods and enzymatic methods. (Postma, Miron, Olivieri, Barbosa, Wijffels & Eppink 2015.) Chemical method refers to the use of reagents such as sodium hydroxide, sulfuric acid, nitric acid, and hydrogen peroxide to destroy the cell wall of microalgae. Chemical method can effectively destroy the cell wall of microalgae and has lower energy consumption compared with physical method. However, this method requires the use of a large number of chemical reagents, and the subsequent treatment is more complex than physical method. (Halim et al. 2012.) At the same time, the introduced chemical reagents may react with oils and other substances, which will deteriorate the quality of microalgae oils and reduce the oil extraction rate. Enzymatic hydrolysis means that the cell wall of microalgae is hydrolyzed by biological enzymes, and finally the wall is broken. Enzymatic hydrolysis method has the advantages like mild reaction conditions, low energy consumption, good wall breaking effect, clean and pollution-free. (Gerken, Donohoe & Knoshaug 2013.) However, the cost of biological enzymes is high, the reaction process is slow, and it takes a long time to achieve microalgae cell wall breaking. Mechanical methods mainly include ball milling method, high-speed homogenizing method, high pressure homogenizing method, microwave method, ultrasonic method, steam thermal method and other wall breaking methods. Physical method can effectively destroy microalgae cell wall without adding additional reagents, with simple technological process and no subsequent treatment after wall breaking. Therefore, it is a hot research topic at present. (Halim, Rupasinghe, Tull & Webley 2013.)

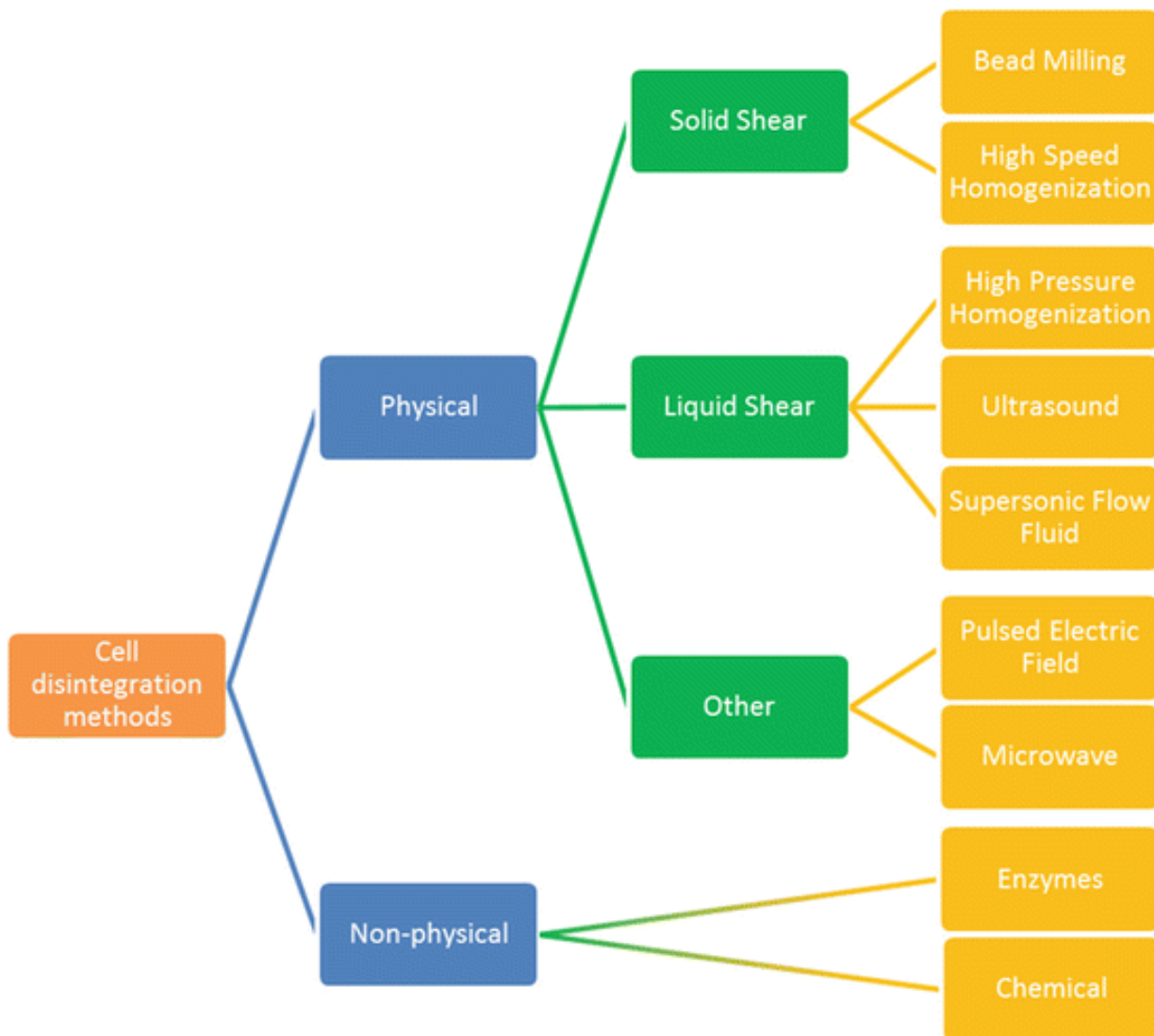


Figure 1. Wall-breaking method of microalgae (Lee, Lewis & Ashman 2012)

### 3.1.1 Ball-breaking method

Ball milling means that the grinding balls made of stainless steel, ceramics and glass are rubbed with microalgae cells in the cavity driven by the stirring rotor, and the cell walls of microalgae are destroyed through friction and impact (as shown in Figure 2). (Postma et al. 2015.) Under the optimum conditions, the microalgae cell wall can be destroyed effectively after a single treatment by ball milling method, which has the advantages of large processing capacity, controllable average temperature, simple operation, and easy industrialization. However, the energy consumption of ball milling is too high, and the local high temperature generated during ball milling may lead to the decomposition of organic components of microalgae. (Doucha & Lívanský 2008.)

Material by hollow shaft ball mill feed end into the cylinder body, when the ball mill cylinder rotation, grinding medium because of inertia and centrifugal force effect, the effect of friction, making it attached to the cylinder liner was taken away by cylinder, when was brought to a certain height, be cast down by its own gravity, the whereabouts of the grinding medium like projectile of cylinder body of the material to break. The material is uniformly entered into the first bin of the mill by the feeding device through the spiral of the feeding hollow shaft. The bin has stepped lining board or corrugated lining board, inside which are steel balls of various specifications. The centrifugal force generated by the rotation of the cylinder will bring the steel ball to a certain height and then fall, which will have a pounding and grinding effect on the material. After the material reaches rough grinding in the first warehouse, it enters the second warehouse through the single-layer compartment plate, which is inlaid with flat lining plate and contains steel balls to further grind the material. (Halim et al. 2013.)

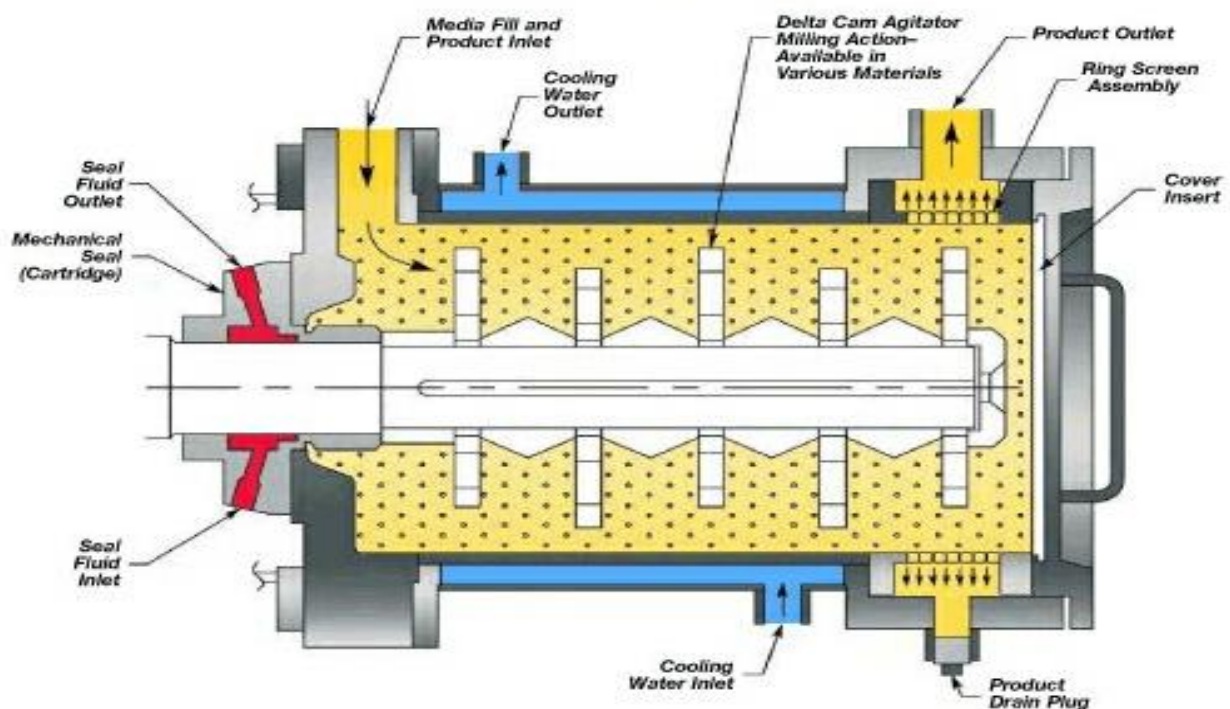


Figure 2. Internal structure of microalgae wall breaking equipment by ball milling. (Postma et al. 2015)

### 3.1.2 High pressure homogeneous wall breaking method

The high-pressure homogeneous wall breaking method destroys the cell wall of microalgae using the cavitation generated by high pressure fluid impact and its shear force. As shown in Figure 3, when the high-pressure microalgal fluid passes through the valve quickly, it will impact with the ring. Meanwhile, due to the sharp change in liquid pressure, hydraulic cavitation will occur, and the holes generated by hydraulic cavitation will generate enormous shear force and impact force during crushing, resulting in the fragmentation of microalgal cells. (Spiden, Yap, Hill, Kentish, Scales & Martin 2013.) The main factors affecting the effect of high-pressure homogenization are liquid pressure and biomass concentration of algal fluid. The high-pressure homogenization method is easy to be industrialized, but it can only treat the microalgae liquid with low biomass concentration, which leads to the complicated subsequent treatment process and high cost. (Spiden et al. 2013.)

High pressure homogenizer adopts high pressure reciprocating pump as power transmission and material conveying structure to transport materials to the working valve (first level homogenizing valve and second level emulsifying valve). When the material has not yet passed the working valve, the spool and seat of the first level homogenizing valve and the second level emulsifying valve are closely attached together under the action of force. When the material passes through the working valve, the spool and the valve seat are forced to open a slit by the material, and the pressure and balance force are generated respectively. The material is homogeneous at the valve, and the pressure drops. With the sudden release of pressure, the spool, the seat and the impact ring, which are three small areas, have similar strong cavitation and explosion effect. Furthermore with the material through the gap between the valve core and seat ring shear effect and impact impact tell impact effect, through strong combination, so that particles can be ultrafine. The function of the secondary emulsifying valve is mainly to make the refined particles more evenly distributed. (Gerken, Donohoe & Knoshaug 2013.)

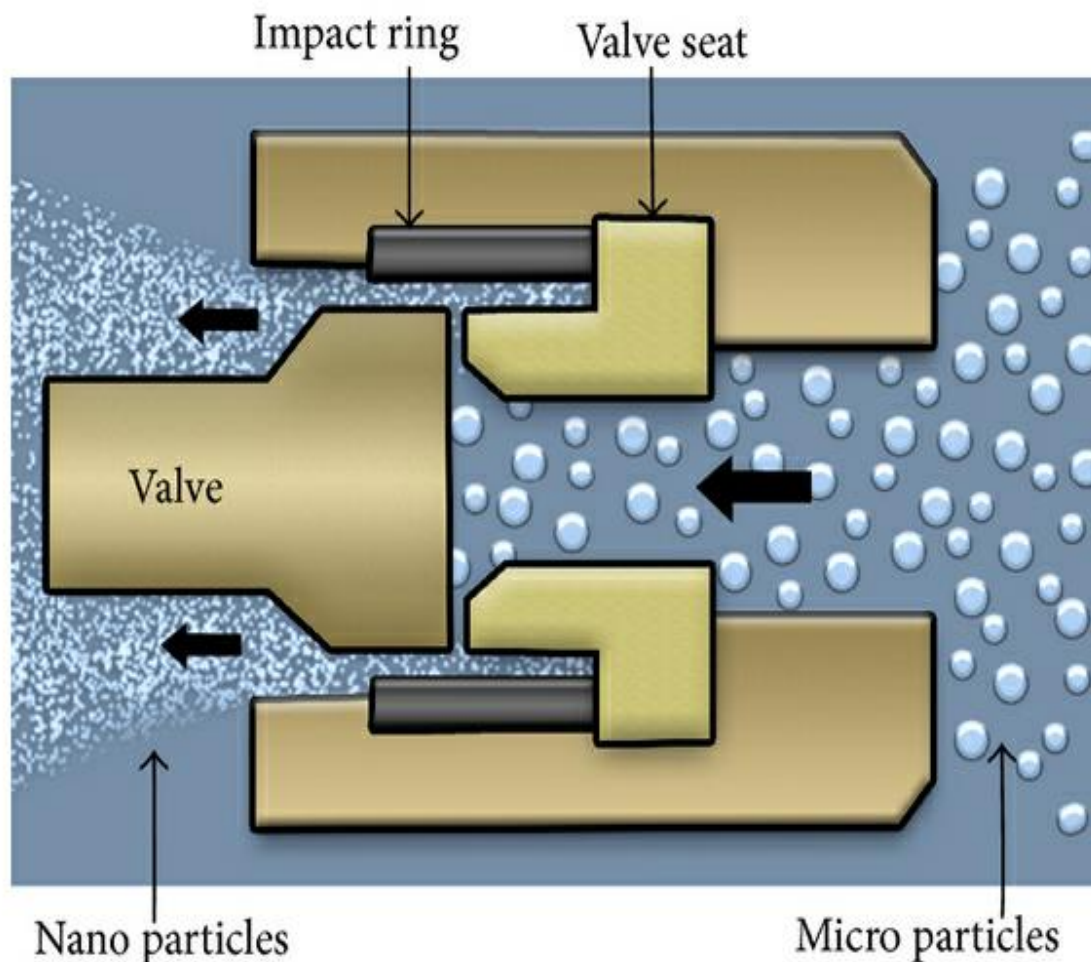


Figure 3. High pressure homogeneous wall breaker. (Doucha & Lívanský 2008)

### 3.2 Soxhlet extraction of microalgae oil

This part is mainly about the research of Soxhlet extraction. Using the principle of solvent reflux and siphon, the solid material can be extracted by pure solvent every time, so the extraction efficiency is higher. When the solvent is heated and boils, the steam rises through the guide pipe and is condensed into the liquid drops into the extractor. When the liquid level exceeds the highest point of the siphon, the phenomenon of siphon occurs and the solution flows back into the flask, so that the solvent soluble part of the material can be extracted. (Samorì, Barreiro, Vet, Pezzolesi, Brilman, Galletti & Tagliavini 2013.) According to the similar phase solution principle, the oil can dissolve in some organic solvents (such as petroleum acid) and combined with the low boiling point of organic solvents, the oil components in microalgae cells were repeatedly extracted by means of repeated reflux evaporation and steaming.



Because the extraction solvent is determined according to the polarity of substances, in the process of Soxhlet extraction, lipids such as phospholipids, lipid soluble cellulose and free fatty acids will be extracted together with the oil. In the whole extraction process, the solvent is recycled many times, and the energy consumption is high, but the extraction is more sufficient, and the extraction time is long. (Samori et al. 2013.)

### 3.2.1 Soxhlet extractor model

The structure of Soxhlet extractor is shown in the Figure 4 below. The whole Soxhlet extractor is composed of parts, in which the lower part is a spherical extraction bottle, the middle part is a suction pipe connected with a siphon and a vapor outlet pipe, the upper part is a reflux condenser with a grinding mouth. The spherical condensing pipe is selected to increase the condensing area. (Lee & Han 2015.)

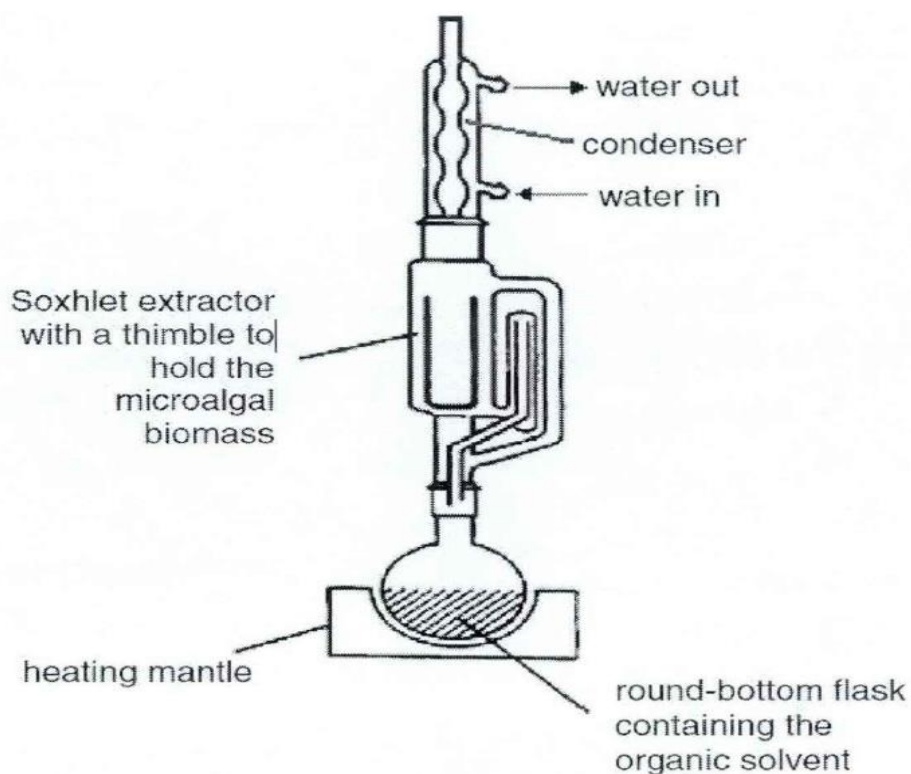


Figure 4. The Soxhlet apparatus. (Lee & Han 2015)

### 3.2.2 Soxhlet extraction steps and procedures

Weigh the mixture of wet algal mud or dry algal powder and deionized water, place it in a beaker and put it in an ultrasonic cell crusher with the ultrasonic probe at the middle and lower part of the liquid height. Turn on the ultrasonic equipment, and set the ultrasonic frequency, ultrasonic time and clearance time. The mass was recorded as the treated sample, mixed with petroleum ether, and placed together in a three-mouth flask. The three-mouth flask is placed in the water bath environment, and the speed of the strong blender is set. Set the centrifugation speed, filtrate, and separate the algal cells from the petroleum acid solvent.(Gerken, Donohoe & Knoshaug 2013.)

The pretreated algal powder was added with anhydrous Korean chloride powder and placed together in the filter paper barrel. A hollow "filter paper seedling" was sandwiched in the center of the filter paper barrel to make the sample between the two, so as to overcome the defect that the fat of the sample in the center of the filter paper barrel was not easy to be extracted clean.(Gerken et al. 2013.)

Install the extractor and place it in the middle of the water bath, then place the filter paper cylinder containing the mixture of microalgae and anhydrous chlorinated powder in the extractor tube, and inject the separated petroleum ether solvent at the same time, then add the unextracted petroleum acid above the height of the siphon, and the petroleum ether solution added should be about the height of the siphon. An anhydrous Korean chloride drying pipe is connected at the end of the condensing pipe to prevent moisture from entering the extraction pipe and affecting the experiment. Open the inlet valve of the condensing pipe and heat it for extraction. Control the heating temperature, too high temperature will cause the oxidation of oil components. (Lee et al. 2015.)

To detect whether the oil in the mixture has been completely extracted, take a clean glass slide, take out a trace solution from the extraction tube, drop a drop on the glass slide, wait for the solvent to evaporate naturally, and observe whether there is oil trace. If there are obvious oil marks nearby, the extraction is not sufficient. Otherwise, the extraction can be considered complete. After the extraction, the filter paper cylinder containing the mixture was taken out with tweezers, the solvent was heated and refluxed for several times, the grease remaining on the wall of the extraction tube was washed out, and the extraction solvent was recovered. (Lee, Yoo, Jun, Ahn & Oh 2010.)

#### 4 PREPARATION OF BIODIESEL

At present, the production of biodiesel is mainly made use of cool reaction or cool exchange reaction. In order to improve the reaction rate in the reaction process, different kinds of catalysts have been developed and applied to the production process. The catalysts used in biodiesel production can be divided into enzyme catalysts, base catalysts and acid catalysts. (Furukawa, Uehara & Yamasaki 2010.)

The chemical reactions in the preparation of biodiesel include the esterification of higher fatty acids with methanol and the transesterification of fatty acid glycerides with methanol. The esterification reaction is relatively simple. Under the catalyzed action of carbon-based solid acid catalyst, the advanced fatty acid is first attacked by proton, the first generation of carbonium ion and methanol is nucleophilic, the tetrahedral intermediate product is unstable. Then a rearrangement reaction occurs, dehydration occurs, and the protons are transferred to the sulfonic group on the surface of the carbon-based solid acid for esterification. The specific reaction is shown in Figure 5. The chemical equation of the transesterification reaction is shown in Figure 5. Transesterification reaction is a complex reaction of esterification. First, the active carbonyl group of protic triglyceride accepts hydroxyl ion under the catalysis of solid acid to form carbon tetrahedral intermediate. Because the intermediate is unstable and rearranges the reaction, the diglyceride continues to be transesterified with methanol in the same manner. Until it converts to one molecule of glycerol and three molecules of fatty acid methyl ester. (Pua, Fang, Zakaria, Guo & Chia 2011.)

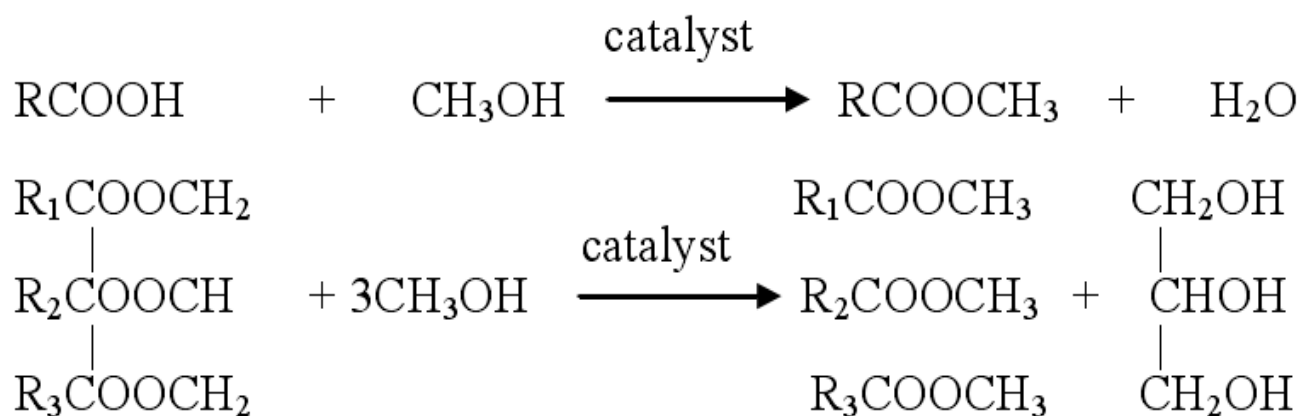


Figure 5. Esterification and transesterification reaction equations. (Pua et al.2011)

## **4.1 Homogeneous catalyst**

Homogeneous catalysis refers to the catalytic reaction system in which the catalyst is indistinguishable from the reaction medium and forms a homogeneous phase with other components in the medium. Homogeneous catalysis is often used in liquid phase reactions. In the catalytic reaction of the material, whether the reaction raw materials or catalysts, they are dissolved in the reaction medium, and in independent molecular form and dispersed. In the preparation of biodiesel, the use of homogeneous catalysts can be divided into two categories, homogeneous acid catalysts and homogeneous base catalysts. (Ehimen, Sun & Carrington 2010.)

### **4.1.1 Homogeneous acid catalysis**

Hydrochloric acid, sulfuric acid, phosphoric acid and organic sulfonic acid are all common homogeneous acid catalysts. (Lee et al. 2013) Most of these homogeneous acid catalysts have a low price, a wide range of sources and a wide range of applications. However, in industrial use, they have high requirements for equipment, and the waste liquid treatment after the reaction also brings a high cost to enterprises. (Furukawa, Uehara & Yamasaki 2010.)

When using homogeneous acid catalyst to prepare biodiesel, it can also catalyze the cooling of free fatty acid, resulting in waste of catalyst and loss of catalytic efficiency. Although the free fatty acids in the raw materials have little influence on the catalytic effect of acidic catalysts, they will increase the amount of catalysts, increase the cost and aggravate the environmental pollution. (Ahmad, Rashid, Patuzzi, Baratieri & Taufiq-Yap 2018) The reaction rate of homogeneous acid catalyst is much slower than that of homogeneous base catalyst, so higher molar ratio of alcohol to oil, reaction temperature and catalyst dosage are needed in the reaction to meet the expected production requirements. At the same time, the equipment in the preparation process also needs special materials, which increases the maintenance cost of the reaction equipment. (Li, X.C., Wang & Zheng 2019.)

### **4.1.2 Homogeneous base catalyst**

At present, homogenous alkali catalyst is the most widely used in the industry for the preparation of biodiesel. However, the reaction of alkaline substances with free fatty acids and water in the raw material

will reduce the catalytic efficiency of the catalyst, or even deactivate the catalyst. (Wang, Lyu, Sima, Cui, Li, Zhang & Gan 2019.) It also makes it difficult to separate the products after the reaction is over.

A homogeneous base catalyst is an alkaline substance similar to sodium hydroxide. Homogeneous base catalyst is only used in the process of high catalytic efficiency, fast reaction speed and low requirements on equipment advantages. Although the common homogeneous base catalyst has many advantages, it has disadvantages such as easy deactivation during storage, high demand on feedstock oil, and easy saponification during reaction, which will affect the quality of biodiesel and even cause pollution to the environment. (Geng, Yu, Wang & Zhu 2012.)

## **4.2 Solid catalyst**

At present, homogeneous catalyst is favored by enterprises in the industrial production of biodiesel, but the final product is difficult to separate, requires a large amount of water for washing, and is easy to cause corrosion to equipment, especially pollution to the ecological environment. (Kawashima, Aihara, Kobayashi, Kyotani & Tomita 2000.) This makes the enterprises in the treatment of pollution will spend more money, is not conducive to the long-term development of enterprises. Therefore, in order to solve this problem, the solid catalyst with easy separation, high catalytic efficiency and good reusability came into being. Moreover, due to the support of the catalyst, it can support a variety of catalytic active substances, can adapt to more complex feedstock oil, and is easy to separate, high reuse, which has attracted the attention of many researchers. (Kawashima et al. 2000.)

### **4.2.1 Solid acid catalyst**

It is not affected by fatty acids, and can use waste oil to improve the utilization rate of raw materials. Besides, it is easy to separate after transesterification reaction, and will not produce waste acid, so as to reduce the corrosion degree of equipment, reduce the production cost and be environmentally friendly. The solid acid catalysts commonly used are mostly solid superacids, supported solid acids, inorganic salts and metal oxides, as well as modified molecular sieves. (Li, Qin, Lai & Fang 2014.)

The solid acid catalyst has good oil tolerance, which makes the solid acid catalyst able to adapt to a variety of raw materials, and because the catalyst and the reactants are in different two phases, it is easy

to achieve the separation of the catalyst, and the reuse rate is greatly increased. However, solid acid catalyst is not widely used in industry, because the reaction speed of solid acid catalyst is lower than that of basic catalyst, and the reaction system catalyzed by solid acid requires higher molar ratio of alcohol to oil and higher temperature, which will generate higher energy consumption and increase the production cost. (Ma, Wan, Chen, Xu, J & Xue 2018.)

#### **4.2.2 Solid base catalyst**

Solid base catalyst is a commonly used catalyst in the small test stage and has been widely studied. Compared with solid acid catalysts, its catalytic reaction speed is fast and the amount of raw materials is small. Solid base catalysts have high catalytic activity, good reaction selectivity, a wide range of sources, and good reusable performance after the end of the reaction. (Aili, Xiaomin, Tianbao, Xuguang & Bingshe 2007.) However, there are also evident shortcomings, such as the complex preparation process of solid base catalyst, high storage requirements, and long-term exposure to air, which can easily lead to the decline of activity. The quality of the reaction raw materials is highly required, especially sensitive to the content of free fatty acids. If the acid value of the raw oil is too high, it will easily lead to the occurrence of saponification reaction, which will have a great impact on the catalytic reaction. Therefore, the solid base catalyst is still mainly used in the pilot stage, and has not been used in industry on a large scale. Current solid base catalysts mainly include alkaline earth metal oxides, ion exchange resins, hydrotalcite, hydrotalcite-like solid bases, and supported solid bases, etc. (Aili et al. 2007.)

## **5 SULFONIC CARBON-BASED SOLID ACID**

Sulfonic acid carbon-based solid acid is based on carbon material as carrier, which has some acid groups on its surface through chemical modification, and has acid active center. According to the structure classification, the sulfonic carbon-based solid acids can be divided into ordinary sulfonic carbon-based solid acids, porous sulfonic carbon-based solid acids and ordered mesoporous sulfonic carbon-based solid acids. (Okamura, Takagaki, Toda, Kondo, Domen, Tatsumi & Hayashi 2006.)

### **5.1 Preparation of sulfonic carbon-based solid acids**

There are many reports on the research of carbon-based solid acids of sulfonic acid type. Previously, researchers usually used sawdust, glucose, starch, sucrose, cellulose as raw materials under certain conditions to prepare sulfonic acid type carbon-based solid acid catalyst. The methods of sulfonic acid type carbon-based solid acid catalyst include direct carbonation sulfonation and carbonation followed sulfonation. (Suganuma et al. 2008.)

#### **5.1.1 Direct carbonation sulfonation**

Direct carbonization sulfonation method refers to the carbonization and sulfonation of carbon source and sulfonating agent reaction at the same time, one step to complete the carbonization and sulfonation to obtain the macroporous structure of common sulfonic acid carbon-based solid catalyst. Using glucose as raw material, in the presence of light ethyl sulfonic acid and acrylic acid, a one-step mild hydrothermal carbonization reaction was carried out at 180°C for 4 hours to obtain a highly sulfonated carbonaceous sphere with a diameter of 100-500 nm, and its acidity could reach 2.10 mmol/g. (Lee et al. 2013.) Took distillers' grains as raw material and carried out carbonization and sulfonation simultaneously with concentrated sulfuric acid. Preparation of sulfonic acid with carbon-based solid acid catalyst. The optimal concentration of sulfuric acid, preparation temperature and time of sulfonating agent were determined by response surface methodology. Its acidity can reach 1.73 mmol/g. The method of preparation of sulfonic acid type carbon-based solid acid catalyst small specific surface area, pore distribution, is widespread even low activity deactivation. (Ma et al.2018.)

### 5.1.2 Carbonation followed sulfonation

First carbonization and then sulfonation method refers to carbonization of carbon source or mesoporous carbon material first, and then sulfonation, introducing sulfonic acid group on the carbon surface to obtain sulfonic acid type carbon-based solid acid catalyst. In this method, the sulfonic acid group is covalently linked with the aromatic carbon atom, and the stability is good. Thanh et al used wood chips as raw materials, processed with phosphoric acid and then carbonized to produce porous biochar, and then sulfonated with sulfuric acid to prepare porous carbonic sulfonic acid type solid acid promoter. (Thanh, Long, Dien, Phuong, Hoang, Minh, Phuong & Hue 2020.) The sulfonic acid carbon-based solid acid catalyst prepared by this method has large specific surface area, high catalytic activity and good stability. The carbon materials commonly used in the preparation of sulfonic acid type carbon-based solid acid catalyst include activated carbon, carbon nanotubes, mesoporous carbon and ordered mesoporous carbon. (Bala, Misra & Chidambaram 2014.)

### 5.2 Functionalization of sulfonic acid groups in carbon materials

Ordered mesoporous sulfonic acid carbon-based solid acid is synthesized by chemical modification by branching the acid active group onto the surface of carbon materials. The main methods of ordered mesoporous sulfonated carbon-based solid acids include sulfonation with concentrated sulfuric acid and reduction sulfonation with diazo sulfonate. (Wang, Liu, Waje, Bozhilov & Feng 2007.) Sulfonation of concentrated sulfuric acid mainly refers to the mixing of carbon materials and concentrated sulfuric acid in a certain proportion, and then stirring for a certain time at a certain temperature. In 2004, sulfonated carbon-based solid acid was synthesized for the first time. They carbonized and sulfonated tea at the same time in the presence of concentrated sulfuric acid in a nitrogen atmosphere of 250 degrees. The surface area of the solid acid obtained was  $24 \text{ m}^2/\text{g}$ , and the concentration of sulfonic acid was  $4.9 \text{ mmol/g}$ . The catalytic activity of solid acid is much higher than that of sulfuric acid. (Figueiredo & Pereira 2010.)

In addition to the use of concentrated sulfuric acid, other methods have been developed to sulfonate carbon materials to obtain carbon-based solid acid catalysts, such as diazosulfonate reduction. Diazo sulfonate reduction method refers to the diazo salt of amino benzene sulfonate (with hydrophilic groups) on the surface of carbon materials for group modification, the principle is that the diazo - carbon bond



fracture will form free radicals, and then its covalent bond with the surface of carbon materials. (Aili et al. 2007.)

### **5.3 Carbon sulfonate nanosheets**

Carbon materials are cheap and easy to obtain, with large specific surface area and good chemical stability in strong acid-base environment, and have always been widely used as carriers in catalyst research. In particular, 2D nanosheets of carbon materials have extremely high specific surface. It has been reported that carbon nanosheets with a thickness of 5~8 nm and an aspect ratio of 6000~10000 have been successfully prepared. (Milne Evans & Nagle 1990.) If the sulfonic acid group is loaded in the form of covalent bond in the carbon nanotubes, it has good stability and is not easy to be separated in the reaction. This allows it not only to have the high volume, high catalytic activity and selective, corrosion resistant equipment of traditional solid catalyst. It has good thermal stability and can be recycled. (Atchudan, Joo & Pandurangan 2013.)

A new method for the synthesis of 2D carbon nanosheets was studied. Gelatin was used as the carbon source, doped with B and N elements to form 2D carbon nanosheets, and then sulfonic acid was loaded on them. The effects of temperature and time on the acid content and the catalytic performance of biodiesel were studied. The reaction conditions (reaction temperature, alcohol-oil ratio) and the reusability of the catalyst were also investigated. (Abdollahi-Alibeik & Shabani 2014.)

#### **5.3.1 The reaction mechanism**

Acid catalyzed transesterification is a reaction catalyzed by protic acid. As shown in Figure 6. First, the triglyceride combines with a hydrogen ion to form an intermediate, and the electrons are offset. The carbonyl carbon lacks electrons and has nucleophilic addition with the alcohol, which is then decomposed into another alcohol and ester after rearrangement. So acid strength has a significant effect on the reaction. (Saravanan, Tyagi & Bajaj 2016.)

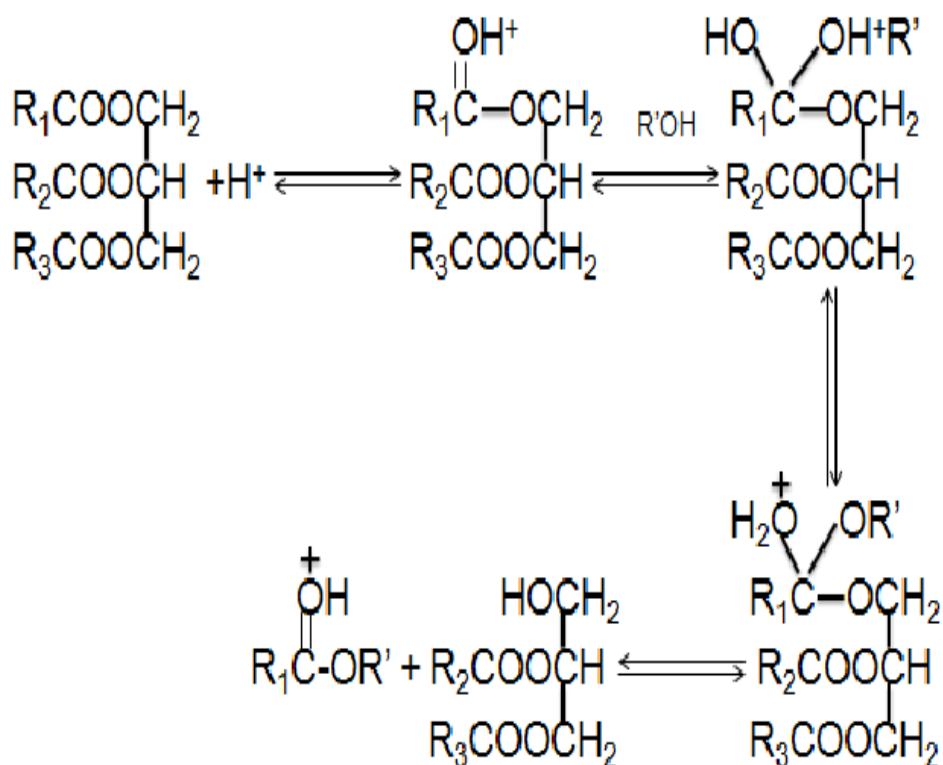


Figure 6. Reaction mechanism of proton acid catalyzed transesterification. (Saravanan et al. 2016)

### 5.3.2 Preparation mechanism of carbon sulfonate nanosheets catalyst

Formation mechanism of carbon sulfonate nanosheets. First, the boric acid is dehydrated and recrystallized. Due to the inherent lamellar structure, the accumulated lamellar structure is formed, and the gelatin molecules are evenly dispersed among the lamellar and exist in the lamellar form. At this time, the lamellar thin place can reach 100~200 nm. After sintering at 9000 degrees, the gelatin is carbothermal reduced to form nano-scale carbon organic molecules, which exist mainly in sheet form. Boric acid breaks down into boron trioxide and water vapor. Boron is heterozygous to the carbon in the skeleton and acts as a binder to nitrogen. After impregnation and forging with sulfuric acid, 2D carbon nanosheets with sulfonic acid groups were finally formed. (Chisti, Y. 2007.)

## **6 PROSPECT OF BIODIESEL PRODUCTION FROM MICROALGAE**

Biodiesel is a hot topic of sustainable new energy research in recent years. As a new generation of raw materials, microalgae have the advantages of large oil content and sustainable regeneration. Microalgae biofuels have the potential to replace fossil fuels because they are inherently efficient at converting solar energy into chemical energy, and microalgae have a much higher potential yield of the oil needed to produce biofuels than land crops. (Rodolfi, Chini Zittelli, Bassi, Padovani, Biondi, Bonini & Tredici, 2009.)

The preparation technology of microalgae bioenergy is feasible, but the research progress of microalgae bioenergy is slow due to the high cost. In order to reduce the production cost of microalgae bioenergy, future research should focus on the following aspects: screening algae species that accumulate oil in step with biomass growth, screening filamentous algae and other algae species that are resistant to protozoa predation and easy to harvest. The metabolic pathway of microalgae was modified by genetic engineering technology to improve its oil yield. The photobioreactor is designed to be more easily divided into space, easy to scale up, easy to operate and high efficiency. To develop the full price development technology of microalgae, maximize the value of microalgae, and then reduce the production cost of microalgae bioenergy. The development of microalgae bioenergy not only needs to make progress in algal seed selection, improvement, cultivation, harvesting, extraction, transformation and other technical research, but also needs to combine with the development of intermediate products in the production process of microalgae bioenergy, which is expected to achieve breakthrough progress. (Lee, Yoo, Jun, Ahn & Oh 2010.)

## 7 CONCLUSION

This thesis mainly study since the following four aspects. Microalgae wall breaking, microalgae oil extraction, microalgae oil preparation biocatalyst, alginic acid catalyst. The mechanical wall-breaking extraction method acts on the dry algal powder, which is to impose mechanical force on the microalgal cells to forcibly destroy the cell structure and accelerate the release of intracellular substances, so as to achieve the purpose of rapid oil extraction. The enhanced extraction process is completed by means of collision, impact, grinding, shearing and dispersing the algal powder.

Soxhlet oil extraction method is based on the similar phase solution principle of the oil can dissolve in some organic solvents, and combined with the low melting boiling point of organic solvents, repeated reflux evaporation and distillation methods are used to extract the oil components in microalgae cells. In addition to solid catalysts, acid catalysts also have liquid catalysts. Compared with the liquid acid catalyst, the solid acid catalyst has several advantages, such as easy separation from the product, easy continuous processing, non-toxic and environmentally friendly, and not easy to corrode equipment. Although conventional solid acid catalyst overcomes the disadvantage of liquid acid, it also has the problem of low catalytic activity.

Through the study of carbon nanosheets, this solid acid catalyst can solve a series of problems such as equipment corrosion, environmental pollution, difficult to reuse and post-treatment caused by using homogeneous catalyst. The specific surface area of carbon sulfonate nanosheets was larger and the reaction sites were more, which improved the catalytic activity of the catalyst.

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