The advancement on the preparation of biodiesel using rapeseed oil as material

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Abstract

Compared with other plant origin oils like vegetable oil or tree borne oil seeds, rapeseed oil has an ideal and optimum composition of fatty acids regarding to engine technology for the production of high-quality biodiesel. Transesterification is the most important procedure for the preparation of biodiesel. The catalyst of transesterification from rapeseed oil to biodiesel was reviewed in this paper including the liquid acid and base catalysts, solid acid and base catalysts, lipase catalyst and nano catalyst. Catalyzing the transesterification by nano solid base will be a promising research area for the production of biodiesel.

Key words: rapeseed oil, biodiesel, transesterifiction, catalyst

Introduction

In recent years, the world has been confronted with energy crisis due to the depletion of resources and the increasing environmental problems. The situation has led to the search for an alternative fuel, which should be not only sustainable but also environment friendly. One possible alternative to fossil fuel is the use of plant origin oils like vegetable oils and tree borne oil seeds (Zhao et al., 2006). Rapeseed oil has an ideal and optimum composition of fatty acids regarding to engine technology for the production of high-quality biodiesel. In the process for the preparation of biodiesel using rapeseed oil as material, the key technology is the transesterification of triglycerides to fatty acid alkyl esters and glycerol. The catalyst of transesterification from rapeseed oil to biodiesel was reviewed in this paper including the liquid acid and base catalysts, solid acid and base catalysts, lipase catalyst and nano catalyst. (Karmee & Chadha, 2005; Shah et al., 2006; Zhu et al., 2006).

Rapeseed oil-the important material for product biodiesel

In 1898, Rudolph Diesel first demonstrated his compression ignition engine at the World's Exhibition in Paris, in which peanut oil was used as the original biodiesel. However, it is difficult for the vegetable oil (e.g. pure rapeseed oil) to be applied directly as a cheap and convenient alternative in conventional Diesel, because some technical problems existed such as high density, viscosity, poor filtration and low volatility. So it needs some sort of modification before vegetable oil is used as substitute of conventional fuels.

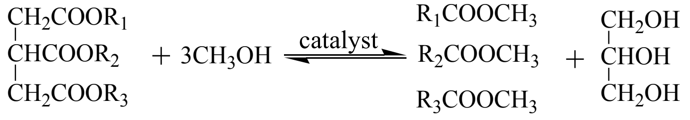
Rapeseed oil is a very important source not only of the edible-oil technology but also of biodiesel technology. It has an ideal and optimum composition of fatty acids with regard to engine technology for the production of high-quality biodiesel. And the by-product, rape meal and rapeseed cake, is a high quality protein feed ingredient which can be used instead of soy meal, particularly in cattle rations. Therefore rapeseed oil is a superior oil stock for biodiesel production in most of European countries, partly because rapeseed produces more oil per unit of land area compared to other oil sources, such as soy beans (Xie et al., 2007). However, rapeseed biodiesel costs more than standard diesel fuel in the costs of growing, crushing and refining rapeseed biodiesel. Prices of rapeseed oil are of fairly high levels at present because of the increasing demand on rapeseed oil for this purpose, although world production is growing rapidly, with FAO reporting that 36 million tonnes of rapeseed was produced in the 2003-2004 season, and 46 million tonnes in 2004-2005 season.

Some high-performance rapeseed varieties have been developed to resolve the resource problem in China. The new rapeseed variety was called double-zero type, which is low in glucosinolates (bitter principals) and practically free of erucic acid. In China, double-zero rapeseed was produced in large volumes since the mid 1990s. Rapeseed production is primarily concentrated in the Yangtzi valley region. In particular, some universities in China, such as Huazhong Agricultural University, have developed high-performance rapeseed varieties. These research groups have established a novel technique of molecule labeling method to assisting the selection of oilseed rape, which is applied in the utilization of oilseed rape breeding, and built up several breeding varieties of Hybrid Brassica napus L oilseed rape(Quijada et al., 2006; Qian, W. et al., 2006). This will largely enhance the efficiency of breeding and the yield of oilseed rape. Rapeseed "oil cake" is also used as fertilizer in China, which may be used for ornamentals, such as Bonsai (Ozcimen & Karaosmanoglu, 2004). Thus it is promising for the preparation of biodiesel using rapeseed oil as material in China.

Biodiesel Preparation

The rapeseed oils contain free fatty acids, phospholipids, sterols, water, odourants and other impurities, which cannot be used as fuel directly. To solve these problems, the rapeseed oil requires slightly chemical modification, such as transesterification, pyrolysis and emulsification. Transesterification is the most important procedure for the preparation of biodiesel using rapeseed oil as material. The reaction of transesterification and corresponding catalysts are the focus in below.

Rapeseed oil comprised of 98% triglycerides and small amounts of mono-and diglycerides (Arzamendi et al., 2006). Triglycerides are esters of three molecules of fatty acids and one of glycerol containing substantial amounts of oxygen in their structure. The fatty acids vary in their carbon chain length and in the number of double bonds (Jeong et al., 2004). In the process of transesterification, the first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule per mole of glyceride at each step (Dossin et al., 2006). The overall chemical reaction process is as follows:



Scheme.1 Transesterification of triglycerides

Up to now, the catalysts in transesterification of triglycerides include the liquid acid and base catalysts, solid acid and base catalysts, lipase catalysts and nano solid base catalysts as the novel one recently, which are described as follows.

1. The liquid acid and base catalyst

In the acid-catalyzed process, sulfonic acid and hydrochloric acid are often used as catalysts. However, the reaction time is very long (48-96h) even at reflux of methanol, and a high molar ratio of methanol to rapeseed oil is needed (30-150:1 mol/%). Several comprehensive studies have been reported based on the base catalyzed transesterification (Lopez et al., 2005). Also known as methanolysis, this reaction is commonly carried out in the presence of homogeneous base or acid catalysts. Potassium hydroxide, sodium hydroxide, and their carbonates, as well as potassium and sodium alkoxides such as $NaOCH_3$, are usually used as base catalysts for this reaction. The base catalysts are better than acid catalysts, due to the higher catalytic activity and less corrosive, which are most often used commercially. However, in the conventional homogeneous manner, removal of the base catalysts after reaction is a major problem because it wills product large amount waste water.

2. Solid acid catalyst

Strong liquid acid catalysts react slower and need higher reaction temperatures. Nonetheless, acid-catalyzed processes could produce biodiesel from low-cost feedstocks, lowering production costs. Thus solid acid catalysts have been developed to replace liquid acids. The corrosion and environmental problems associated with them could be avoided and product purification protocols reduced, significantly simplifying biodiesel production and reducing cost using solid acid catalysts. Sulfated zirconia (SO_4/ZrO_2) and sulfated tin oxide (SO_4^{2-}/SnO_2) have been shown to have applicability for several acid-catalyzed reactions (Lotero et al., 2005). Jitputti, Kitiyanan et al. catalyzed transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. In the case of SO_4^{2-}/ZrO_2, only 1 wt.% of this acidic solid was needed to catalyze the reaction, resulting in fatty acid methyl esters content higher than 90% (Jitputti, Kitiyanan et al., 2006). However, research dealing with the use of solid acid catalysts for biodiesel synthesis has been limited due to pessimistic expectations about reaction rates and unfavorable side reactions.

3. Solid base catalyst

Some solid base catalysts have been reported include hydrotalcite, alkaline-earth metals, carbamidine. Liu Xuejun et al. catalyzed the transesterification of soybean oil to biodiesel using SrO as a solid base (Liu, He et al., in press). And the same reaction catalyzed by potassium oxide loaded on alumina (Xie et al., 2006).There are many advantages to product biodiesel using solid base catalyst, such as vulnerable separated, easily realized automatic production, successive and repeatedly employed. But the reaction proceeded at a relatively slow rate in most of the experiments using heterogeneous catalysts. The reaction mixture constitutes a three-phase system, oil/methanol/catalyst, in which the reaction is inhibited because of the presence of heterogeneous catalysts.

4. Lipase-catalyzed transesterification

Recent studies (Turkan & Kalay, 2006) showed that biodiesel could also be produced enzymatically by lipase-catalyzed transesterification. In conventional chemical process for biodiesel production, alkali or acid is usually adopted as the catalyst. However, there are several problems associated with chemical processes such as difficulty in glycerol recovery, excessive energy cost, and the need for removal of catalyst from the product and so on. Enzymatic methods can solve these problems which allow mild reaction conditions and no chemical waste is produced. However it hasn't been reported that the technology of industrialization of lipase-catalyzed transesterification, because its price is very expensive and the catalytic efficiency of mono-lipase is very low.

5. Nano solid base catalyst

Nano solid catalyst particles have many advantages compared with general solid catalysts. For example, Nano solid catalysts have very small diameter, and large superficial area. These properties maybe solve the problem in application of general solid base, such as small reaction surface and strong resistance of transmitter. Recently, most researches about catalysts in transesterification concentrate in solid base. However nano solid base catalyst is applied in other reactions. In a word, very few researches were reported about nano solid base catalyst in the transesterification of biodiesel preparation. VenkatReddy, C. R. et al. reported that Soybean Oil and Poultry Fat to Biodiesel Catalyzed by Nanocrystalline Calcium Oxides. With their most active catalyst, deactivation was observed after eight cycles with soybean oil and after three cycles with poultry fat

(VenkatReddy, Oshel et al., 2006).

A novel nano-solid-base catalyst was prepared by our Lab, recently, which has been successfully applied to prepare biodiesel from rapeseed oil. The effects of varied factors on catalyst preparation have been analyzed by uniform design. More environmental friendly ant high efficiency catalysts will be researched in further work.

Conclusion

Because of producing double-zero rapeseed in large volumes, there will be enough materials for preparing biodiesel. Rapeseed biodiesel has become more attractive to replace petroleum fuel. Nowadays the traditional acid and base catalyst are still playing an important role in the technology of industrialization. The base catalysis is preferred to acid catalyst routes, which is often used commercially. Conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts. Lipase-catalyzed and Supercritical transesterification have proceeded to the experiment of industrialization. Nano materials have present many particular properties in many fields. There will be a new approach to resolve the problem in catalyst. Green and environmental catalysts will be the important research field of catalytic chemistry. The nano solid base catalyzed transesterification is the promising area of research for production of biodiesel.

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