Biodiesel Production

Brief Technology Overview

Introduction

In the biofuel industry, the enzymatic process is theoretically known to be better than the chemical process because it can operate under mild temperature and pressure and co-produce glycerol with higher purity. However, people have come to believe that enzymes are expensive and have short lifespans. In addition, an overwhelming amount of journal papers overlook the negative effects of the second liquid phase that forms during the reaction, further contributing to misconceptions about the enzymatic process. This is why, to date, enzymes have rarely had commercial use in biodiesel production. Beyond lab-scale experiments, enzymes only seemed to add to the already high cost of biodiesel production.

Currently, most if not all of biodiesel production processes use the chemical approach, which involves an acid catalyst, a base catalyst or both. There are two major sources of biodiesel –the oil (triglyceride) and the free fatty acids (FFA) contained with oil, both of which require alcohol to convert to biodiesel. The difference lies in the co-product of the reaction. For oil, biodiesel is produced with glycerol as a co-product in a transesterification reaction. For FFA, biodiesel is produced with water as a co-product in an esterification reaction (See equations **1** and **2** below).

$$\text{Transesterification: Oil} + \text{Alcohol} \rightleftarrows \text{Biodiesel} + \text{Glycerol} \quad (1)$$

$$\text{Esterification: FFAs} + \text{Alcohol} \rightleftarrows \text{Biodiesel} + H_2O \quad (2)$$

Limitations of the Chemical Approach

Aside from acid and base, the chemical approach is further divided into liquid and solid catalysts. If only one type of catalyst is used, feedstock with high FFA content cannot be fully utilized. To overcome this problem, the use of two processes was proposed. For a clearer understanding of the chemical approach, problems related to acid and base catalysts are briefly discussed as follows.

A. Limitations of a Base Catalyst

The foremost limitation of a base catalyst is that it can be applied only for transesterification. It is limited to feedstock with low water and FFA levels. When a liquid type base catalyst is used, the resulting soap formation not only consumes the catalyst but also makes the separation of glycerol and biodiesel difficult. It also involves wastewater disposal problems and results in low quality

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glycerol co-product.

B. Limitations of an Acid Catalyst

An acid catalyst is normally applied only for esterification. The basic limitation in using a liquid acid catalyst is corrosion of the process equipment. Because of the corrosion problem that occurs when an acid catalyst is used, specialized metal containers and parts become necessary, even though they cost more. Furthermore, an acid catalyst needs lengthy reaction time and excess alcohol to drive the reaction towards biodiesel formation. In addition, neutralization remains unavoidable for the purpose of removing the homogeneous acid catalyst.

C. Limitations of Solid Catalysts

Solid catalysts eliminate the need for water washing, reducing wastewater from plants. However, this kind of process normally requires high pressure and temperature. This leads to the decomposition of glycerol and other negative side effects. The formation of the secondary liquid phase, whether it be glycerol or water, also negatively affects the reaction by deactivating the solid catalyst. Similar to liquid base catalysts, solid base catalysts are also subject to strict feedstock water and FFA levels. On the other hand, solid acid catalysts still require the use of excess alcohol.

To avoid the deactivation of the catalyst by the second liquid phase formed by glycerol or water, high temperature is employed. The temperature needed for a base-catalyzed process can be as high as 180-210°C. While some processes use temperatures that may not be as high, it is enough to cause alcohol to evaporate. To suppress this, the reaction pressure is maintained at a high level. This means that, for solid catalysts, it is hard to avoid problems that arise due to high pressure and temperature.

One of the biggest drawbacks of high temperature is thermolytic reactions [**1**]. Cleavage of bonds and formation of many different kinds of compounds (alkenes, dimers, polymers, polycyclic compounds, CO, and CO_2) result in high safety requirements to protect against fugitive emission and produce impurities. High temperatures may also promote radical formation and, hence, polymerization. Therefore, while it offers some advantages over liquid catalysts, solid catalysts require more energy for operation and result in a higher capital investment.

Technical Advantages of the Enzymatic Approach

The main advantage of the enzymatic approach is that the reaction can be carried out in mild conditions. The enzymatic approach can handle both transesterification and esterification simultaneously. In the past, applications of the enzymatic approach did not make use of an inert solvent. As such, the reaction time was deemed too long and the biocatalyst was eventually deactivated by glycerol or water. Only a batch operation was possible and the overall operating cost was determined to be high. Even then, product quality is unpredictable as the immobilized lipase deactivates after several runs.

[1] M.G. Kulkarni and A.K. Dalai, Waste Cooking Oil –An Economical Source for Biodiesel: A Review, *Ind. Eng. Chem. Res.*, **2006**, 45, 2901-2913.

Sunho Biodiesel's Enzymatic Transesterification Process (ET Process) makes use of an inert solvent that protects the lipase so that it can have a long lifespan. The reaction can be done at ambient temperature and pressure in a continuous, integrated process. Because there is no water washing involved after the reaction, biodiesel and glycerol can be recovered with high purity. The reaction time is also reduced to less than 30 minutes, hence allowing for better time and cost efficiency.

Summary

Catalyst	Liquid	Solid
Acid	➢ *limits esterification normally*	
	• strict feedstock water level • equipment corrosion • lengthy reaction time • needs neutralization • needs excess alcohol	• needs high temperature and pressure • needs excess alcohol • lengthy reaction time
Base	➢ *limits transesterification*	
	• strict feedstock water and FFA levels • needs neutralization and water washing • low quality glycerol co-product	• strict feedstock water and FFA levels • needs extremely high temperature and pressure • glycerol decomposes at high temperatures • thermolytic reactions that result to impurities, including polymers • deactivation of catalyst due to impurities

	Without Inert Solvent	With Inert Solvent
Enzyme	• lengthy reaction time • can only be done by batch operation • biocatalyst is deactivated by glycerol or water • high operating cost due to lipase consumption • unstable product quality	• total green process • lipase can have a long lifespan • operated at room temperature and pressure • continuous, integrated process

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