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Recent development and economic analysis of glycerol-free processes via supercritical fluid transesterification for biodiesel production

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ABSTRACT

In this review, recent development of glycerol-free supercritical fluid transesterification for biodiesel production was discussed. Glycerol-free supercritical fluid processes including single-step and two-step transesterification for biodiesel production were reviewed and subsequently the advantages and limitations were highlighted. Value-added by-product from glycerol-free production such as triacetin is more profitable compared with glycerol produced in conventional biodiesel production. Furthermore, the quality of biodiesel could be enhanced with the presence of triacetin, which is co-produced in supercritical methyl acetate transesterification reaction. However, there are concerns regarding the huge energy required to conduct supercritical reaction at elevated temperature and pressure. Hence, economic consideration in terms of equipment needed and profit margin were discussed in order to study the profitability of glycerol-free supercritical biodiesel production in the industry. Results showed that glycerol-free supercritical dimethyl carbonate process has the highest profit margin, indicating that it is economically competitive and could provide larger revenue to biodiesel producers.

Contents

1. Introduction

Sustainable economic development depends substantially on continuous and steady supply of energy sources. For instance, transportation, agriculture and industrial sectors required huge

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amount of energy sources to accommodate their daily activities. Currently, the main energy sources employed by these sectors are non-renewable fossil fuels such as petroleum, coal and natural gas which inevitably lead to cost escalation and depletion in these natural resources. Furthermore, extensive combustion of fossil fuels also causes detrimental effects to the environment due to excessive emission of hydrocarbon particulates and greenhouse gases such as CO_2, NO_x, O_3 and CH_4 which leads to air pollution and global warming, respectively. Therefore, with alarming environmental degradation phenomenon and increasing awareness among the public regarding harmful effects of employing fossil fuels, researchers throughout the world have been focusing on developing a renewable, sustainable and clean source of energy to replace these natural resources.

One of the most researched renewable energy with enormous potential and prospect to be the main source of clean energy is biodiesel. Biodiesel is considered to be an environmental friendly source of energy because it is made from renewable sources and because of its lower emissions compared to fossil fuels. Biodiesel is derived from oil-bearing crops which absorb carbon from the atmosphere during photosynthesis process. Therefore, biodiesel has the potential to alleviate harmful emission during combustion process compared to fossil fuels as reported by Kumar and Nerella [1] that exhaust emissions in terms of CO, SO_2, and CO_2 compounds decreased with the increment of biodiesel percentage in biodiesel-diesel blend. Therefore, biodiesel could address the issue of energy security and sustainability without compromising our environment.

Refined vegetable oil or even waste cooking oil is commonly employed as the source of the triglycerides (TG) to produce biodiesel through transesterification reaction with alcohol in an alkaline homogenous catalytic system. The most common homogeneous catalysts are sodium hydroxide (NaOH) and potassium hydroxide (KOH). However, these processes may cause unwanted saponification reaction with free fatty acid which decreases catalyst efficiency and biodiesel yield [2,3]. Other than that, these processes may have to couple with an alkaline waste-water treatment in their production plant. Otherwise, untreated waste stream released to the drain could cause adverse effects to the ecosystems. Therefore, numerous methods have been carried out to solve these problems, such as heterogeneous catalysts [4], lipase-catalyzed transesterification [5] and non-catalytic supercritical alcohol transesterification [6,7]. Among these methods, non-catalytic supercritical fluid transesterification has been found to have numerous advantages of being simpler, producing higher yield in a short period of time and easier purification in biodiesel production.

Recently, biodiesel production from vegetable oils has been extensively studied via supercritical fluid transesterification. This novel technology of converting vegetable oil to biodiesel via non-catalytic supercritical alcohol was initially reported by Saka and Kusdiana [6]. The overall transesterification reaction for TG with 3 mol of methanol is shown in Eq. (1). Transesterification reaction refers to a common process of exchanging acyl ($RnCO^-$) group between fatty acid and alcohol. In this reaction, methanol is the acyl acceptor of group found in triglycerides to form fatty acid methyl esters (FAME) and glycerol:

$$\text{Triglycerides} + 3\text{Methanol} \leftrightarrow 3\text{FAME} + \text{Glycerol} \quad (1)$$

It is well known that supercritical methanol process has high reaction rate which allows the reaction to be completed in a short period of time. It is also simpler in its products separation and purification procedure as there is no catalyst in the system. By using supercritical reaction, the existence of high free fatty acids (FFA) and water content in oils/fats do not affect the yield or conversion. Instead, it was found that they enhance the formation of methyl esters as the FFA were also converted to methyl esters as reported by Kusdiana and Saka [8] and Tan et al. [9]. Hence, waste cooking oil which commonly consists of high FFA percentage and water could be employed in supercritical fluid transesterification method without any pre-treatment [10]. This finding shows the superiority of supercritical alcohol technology in producing biodiesel compared to conventional methods which require pretreatment of oils to reduce the water content.

Biodiesel production has experienced a major surge in developed countries such as Germany, Italy, France and United States, as well as in developing countries such as Argentina, Indonesia and Malaysia. Biodiesel production in the world increased substantially from 2.2 million tons in 2002 to an estimated 11.1 million tons in 2008 [11]. In biodiesel production, crude glycerol is the major by-product from the conventional transesterification with the amount produced is approximately 10 wt% of oils/fats employed in the reaction [12]. Consequently, with the huge production of biodiesel throughout the world, excessive crude glycerol has been produced which leads to significant price decline in the world's market [13]. Other than that, the major problem with glycerol in biodiesel production is the contamination of methanol which makes it unsuitable to be processed for consumer market. The only treatment that could refine crude glycerol to pharmaceutical grade is by employing high temperature low pressure distillation [14] which is very costly and uneconomical for this low cost commodity. Even in supercritical alcohol transesterification [15–19], this unprofitable crude glycerol will be produced together with biodiesel. Therefore, in order to improve the economics of biodiesel processing as well as to eliminate waste glycerol in the production stream, some alternative methods need to be carried out, either replacing or transforming crude glycerol into other value-added commodities [20–23].

One of the methods is by employing non-alcohol reactant in the reaction which could produce other invaluable by-product instead of the unwanted glycerol. Glycerol-free process via supercritical fluid transesterification was initially reported by several researchers [21,24,25] by replacing the reactant of alcohol in conventional supercritical transesterification with methyl acetate and dimethyl carbonate. This breakthrough research had initiated a lot of researches in this glycerol-free process via supercritical fluid transesterification for biodiesel production. Therefore, this study aims to review recent progress of glycerol-free supercritical fluid processes including single-step and two-step reaction for biodiesel production and subsequently highlights their advantages and weaknesses. Apart from that, economic analysis will also be discussed in order to examine the profitability as well as potential of glycerol-free supercritical biodiesel production in the industry.

2. Glycerol-free process via supercritical fluid technology

Glycerol-free processes via supercritical fluid technology are basically divided into two methods which are single-step and two-step supercritical fluid transesterification. In single-step supercritical fluid transesterification, reaction takes place only once after the heating of reactant up to its critical temperature and pressure with TG. In two-step subcritical-supercritical fluid transesterification, TG is first induced to FFA and by-product in the hydrolysis reaction. Subsequently, the obtained FFA undergone esterification reaction and produce FAME in supercritical fluid reaction. In this two-step supercritical method, reaction condition is relatively milder with lower operating temperature and pressure.

2.1. Single-step supercritical fluid

It is well known that supercritical fluid transesterification reaction requires high temperature above the critical temperature