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Phospholipid transesterification in sub-/super-critical methanol with the presence of free fatty acids

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ABSTRACT

Phospholipids and free fatty acids (FFA), along with triglycerides, are naturally formed constituents in unrefined vegetable oils and other plant lipids. Presence of phospholipids and FFA in such oils can cause processing difficulties, such as saponification and decrease in catalytic efficiency, thus lead to an adverse process efficiency in the transesterification of such oils for biodiesel production. This phenomenon was also observed in our previous study on converting microalgal lipids to fatty acid methyl esters (FAME) via *in situ* transesterification. This study aimed at further exploring the transesterification of phospholipids and investigating the effects of FFA presence and other processing conditions in biodiesel production from plant oils in sub- and/or super-critical methanol (SubCM/SCM). Experiments were carried out in a batch reactor in SubCM/SCM under various conditions without addition of catalysts. Pure chemicals of lecithin and stearic acid were used as the model compounds for phospholipids and FFA, respectively. The product yield (FAME in mol%) of the phospholipids after transesterification, as affected by the presence of FFA under different conditions, was selected as the respond factor to determine the process efficiency. Experimental results showed that phospholipids can be converted into FAME in such a process. Transesterification of phospholipids is largely affected by the interactive effect of operating temperature and reaction time. The increase in product yield is proportional to the increases in temperature and/or reaction time. The maximum product yield of 68.1 mol% was achieved at 250 °C and 120 min without the presence of FFA. The product yield started to level off once the system reached the SCM state. When temperature was held at 290 °C for 30 min, the product yield dropped to 33.6 mol%. Another phenomenon observed is that the presence of FFA enhances considerably the lipid conversion. The study revealed that phospholipids can be converted to FAME with a highest product yield of 93.9 mol% at 250 °C for 120 min in SCM without catalysts and with the presence of FFA. However, the FFA enhancement became less significant when the system was operated for a longer period of time than 120 min.

1. Introduction

Microalgal lipids have been widely used in biofuel studies due to their similar fatty acid (FA) profiles to those of vegetable oils. However, microalgal lipids possess different chemical composition from the conventional biodiesel feedstocks, mainly in high levels of polyunsaturated fatty acids, free fatty acids (FFA) and other impurities (including phospholipids and pigments) [1]. Chemical properties of phospholipids are different from those of common lipids (i.e., triglycerides, diglycerides, and monoglycerides) due to the existence of both polar and nonpolar molecules. In a uniformed oil sample (unipolar), phospholipids will form micelles, which hydrophobic tails (fatty acid groups) are hidden from alcohol and wrap nonpolar lipids within the micelles structure. Thus, it will result in the nonpolar lipids inaccessible to alcohol and catalysts, and lead to difficulties of phospholipid transesterification. Therefore, the more phospholipids exist in the oil feedstock, the less lipids expose to alcohol and catalysts. This is the key obstacle of biodiesel production through conventional biological and chemical transesterification process with a feedstock high in phospholipid content. This theory has been recognized and claimed that a high content of phospholipids in the raw feedstocks means a concomitant loss of yield in the production of fatty acid methyl esters (FAME), as the fatty acids enclosed in the phospholipid molecules are not accessible to the catalysts for transesterification [2]. It was claimed that the phospholipids present in the oil were not carried over into the methyl esters, and the yield of FAME was reduced by 3–5 wt.% if the phosphorus content in the oil was above 50 ppm [3]. In the traditional techniques for biodiesel production

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from plant oils, phospholipids are commonly eliminated before transesterification through degumming, which is typically carried out by mixing the crude oil with an aqueous solution of phosphoric acid or sulfuric acid and chemically converting the phospholipids into hydratable compounds. Hot water alone can also extract a fraction of so-called hydratable phospholipids. The phase separation after mixing the oil with hot water requires centrifugation. In many cases the initial cost of a centrifuge and its operation cost are too high for small producers. Therefore, people pay attention on how to produce biodiesel without degumming phospholipids.

Phospholipids still contain valuable components of fatty acid groups, which potentially are able to be converted to biodiesel. Successful conversion of phospholipids will increase the efficient use of the valuable feedstock and the productivity. However, converting phospholipids possesses serious challenges. In order to convert phospholipids via transesterification with high efficiency, both biological and chemical catalysts can be used [3–7]. Enzymatic transesterification was frequently studied for phospholipids conversion due to many characteristics, such as mild reaction conditions, easy recovery of glycerin, no need for further purification, and no chemical waste production. In addition, the enzymatic process tolerates a certain water content in oils and avoids the typical soap formation due to alkaline transesterification, thus increasing the biodiesel yield [8]. A FAME yield beyond 90 wt.% was frequently achieved in the studies of enzymatic transesterification with high phospholipids content [5,9,10]. A FAME yield of 94 wt.% was obtained by immersing lipase in crude oil (phospholipid content of 0.36 wt.%) at 40 °C for 120 h [9]. A similar FAME yield was also obtained for refined oils. Therefore, research has proved that immersing lipase in oils could improve both the reaction rate and methyl ester yield significantly by increasing the accessibility of lipases to lipids. In a recent study, a mobilized lipase NS81006 used to catalyze phospholipids-containing oil (10% phospholipids content) for biodiesel production and achieved a best result of 95% FAME yield [5] through a two-step process (hydrolysis and then transesterification).

Other than enzymatic transesterification, acid/base catalysts also work on oil samples to remove phospholipids from microalgal lipids [11]. The principle of acid/base catalytic transesterification is also to hydrolyze phospholipids at acyl ester bond to produce FAME. Unfortunately, a high content of phospholipids in raw feedstocks will lead a concomitant loss of yield in FAME production, as the fatty acids enclosed in the phospholipid molecules are not accessible to the catalysts for transesterification [2]. A two-step catalytic conversion (i.e., degumming and then acid catalytic transesterification) was experimented to produce microalgal biodiesel with high phospholipid and FFA contents [12] and proved that phospholipids could be converted to FAME (56 wt.% yield) under appropriate conditions. However, the incomplete reaction of phospholipids can result in loss of the product yield by as much as 45 wt.% due to the phospholipid precipitation and saponification [12]. Furthermore, base catalysts (i.e., KOH, calcium methoxide, and calcium oxide) were also studied in order to successfully perform phospholipid transesterification. The work of Balasubramanian and Obbard concluded that the transesterification of phospholipids and soybean oil mixture, catalyzed by KOH, calcium methoxide and calcium oxide, resulted in a FAME yield in excess of 90 wt.% at a reaction condition of 60 °C, 250 min with an oil to methanol molar ratio of 1:12 (catalyst concentration of 3 wt.%) [4]. The phosphorus (P) content in FAME from this procedure remained at a high level (0.081 wt.% P/FAME). In addition to the challenge of catalyst removal from the FAME layer, the phosphorus content in the biodiesel is still above the EN 14214 and ASTM D6751 standards of a maximum of 10 ppm in the final biodiesel. Therefore, it is also important to know the phosphorus content in the biodiesel process and control the phosphorous content in the product. A study of phosphorus balance through a biodiesel production process from un-degummed vegetable oil was conducted [7]. Un-degummed soybean oil and coconut oil containing FFA, triglycerides, and phospholipids were used as the feedstocks in a base catalyzed transesterification process and an acid wash of the raw product mixture was followed to acquire FAME. The mass balance of phosphorus compounds showed that only 1 wt.% of the initial phosphorus compounds remained in the biodiesel phase and 97 wt.% of initial phosphorus stayed in the glycerin phase. This makes a good point that phosphorous distribution in the streams in biodiesel production favorable for biodiesel quality control.

Although scientific research has proved that phospholipids can be eliminated or converted by pretreatment or catalytic transesterification, their presence increases the complications of final product purification and the cost of production. In addition, phospholipids are abundant components in various feedstocks, such as microalgal lipids, and have the chemical property that does not favor the transesterification reaction without catalysts [8]. Fortunately, under a critical thermal condition (such as super-critical methanol or SCM condition), the miscibility of lipids and alcohol is reinforced. Previous scientific studies have proved the advantages of using supercritical fluid (SCF) in transesterification reaction for biodiesel production and the research group from Japan have made promising contributions on such technique [13–19]. Thus there is a potential that phospholipids are converted to FAME without the aid of catalysts. Besides, FFA is an organic acid that can be an effective acid catalyst under high temperature conditions [20]. The chemical polarity of methanol is enhanced, the chemical activity boosted and the acidity of FFA is increased, especially when methanol was heated up to a higher temperature (i.e., 250 °C). Therefore, the presence of FFA could promote the overall reaction yield in the system of phospholipids and methanol for transesterification reaction.

Numerous researches have successfully demonstrated that lipid transesterification can be achieved in SCF either with or without the aid of catalysts but few records had shown the phospholipid transesterification conversion for biodiesel production purpose under similar conditions. In our previous study of *in situ* transesterification for microalgal biodiesel production, microalgal lipids were converted into FAME with sub-critical methanol (SubCM) and/or SCM successfully without the addition of catalysts [21]. This study was to further investigate the transesterification of phospholipids in SubCM/SCM without and with the presence of FFA. Hence, the ultimate goal of this study was to explore the transesterification of phospholipids and the effects of processing conditions and presence of FFA in sub- and/or supercritical methanol for biodiesel production without the addition of catalysts. Due to the favorable nature of SCF for transesterification, an increased FAME yield (mol%) was expected with the conversion of phospholipids to FAME and with the enhancement of FFA under SubCM and/or SCM conditions.

2. Material and methods

2.1. Materials

In this study, phosphatidylcholine (i.e., lecithin), the most abundant of all phospholipids found in eukaryotes [4], was selected as a model phospholipid to study its conversion. L-α-lecithin (3-sn-Phosphatidylcholine) in powder form derived from egg yolk was purchased from Acros Organics (Geel, Belgium). The FA profile of lecithin specified by the manufacture was approximately 33 wt.% of palmitic acid (C16:0), 13 wt.% of stearic acid (C18:0), 31 wt.% of oleic acid (C18:1), and 15 wt.% linoleic acid (C18:2). The average molecular weight of the lecithin is approximately 768 g/mol.