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Phospholipids Conversion in Biodiesel Production

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Introduction

Phospholipids are a group of chemical compounds that consist of two fatty acids and a phosphate group attached to a glycerin backbone (Fig. 1), different than that of triglycerides in which three fatty acids attach to a glycerin backbone. Phospholipids are major components of cell membranes. Therefore, when oils are extracted from oilseeds, presence of phospholipids in oil is inevitable, typically at concentrations of 2%~5% [1]. If hydrated, phospholipids become insoluble and precipitate out, which is commonly known as gums.

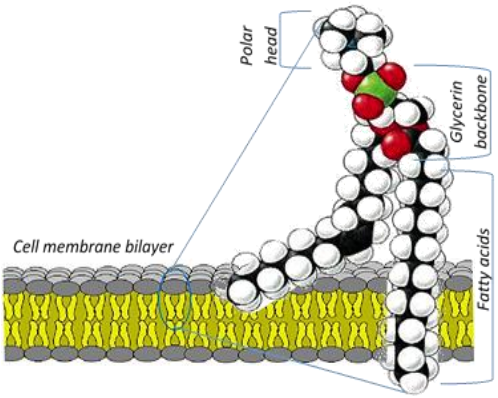

Figure 1. Illustration of phospholipid molecules.

Although long-chain fatty acids are also contained in phospholipids like that in triglycerides, they cannot be converted into FAME (fatty acid methyl esters) under the conventional reaction conditions in biodiesel production. Presence of gums in oils poses processing challenges and potentially leads to the biodiesel being off-spec due to the insolubility of the gums. Therefore, gums need to be removed, typically by water washing, before the oils are transesterified into biodiesel. However, de-gumming by water washing not only involves added costs of operation but also results in the yield loss of biodiesel because two fatty acids on phospholipids could be utilized to produce biodiesel. One way of converting the fatty acids on phospholipids into biodiesel is enzymatic conversion by lipases, which bear many pros and cons (e.g., [2]). *In-situ* trans-esterification of oils and fats under super-critical methanol was also researched for its advantages of high tolerance to impurities, including free fatty acids (FFA) and phospholipids, and a catalyst-free process [3, 4].

Microalgal oils are at present considered as promising feedstock for biodiesel production. The noticeable differences between microalgal oils and other seed oils are the considerably high in FFA and other impurities including phospholipids. Special conversion practices are needed to turn microalgal oils to biodiesel. At the University of Idaho, we have explored the feasibilities of producing biodiesel *in situ* from microalgal biomass [4] and converting phospholipids into FAME with the presence of high levels of FFA [5].

Study on Phospholipid Conversion to FAME

In our study of phospholipid transesterification, lecithin derived from egg yolk was used as the model phospholipid. Lecithin, or chemically called phospha-tidylcholine, is considered as the most commonly seen phospholipid in microorganisms [6]. The objectives of this study were to explore the phospholipid conversion into FAME under sub-critical and/or super-critical methanol conditions (170˚C-290˚C) and the FFA effect on phospholipid conversion efficiency as measured by the FAME yield in percentage on molar basis. Experiments were systematically conducted in batch mode and no catalysts were added to the system.

Experimental Findings

In stage one of the study, we tested the phospholipid conversion without the presence of FFA. It was shown that maintaining a super-critical condition of methanol (i.e., 240˚C & 7.93 MPa) is critical to achieve significant conversions of lecithin to FAME. The highest FAME yield was observed at 250˚C for 120 minutes of reaction time (Fig. 2). Shorter reaction of 30 min at 250˚C did not show a similar FAME yield, indicating an extended period of reaction time is necessary. If the operating temperature was increased to 290°C, a decrease in FAME yield was observed. It was found that this was being caused by the polymerization and sedimentation of phospholipids under temperatures that were too high [6].

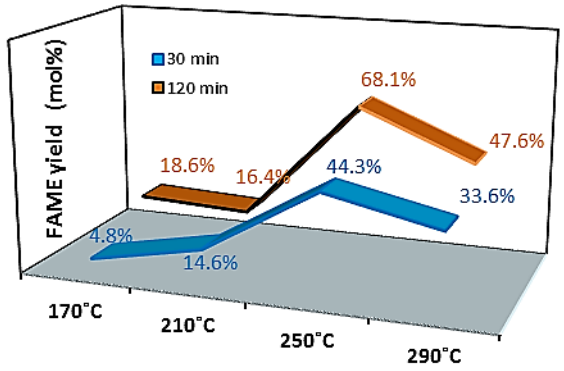

Figure 2. FAME yield without the presence of FFA.

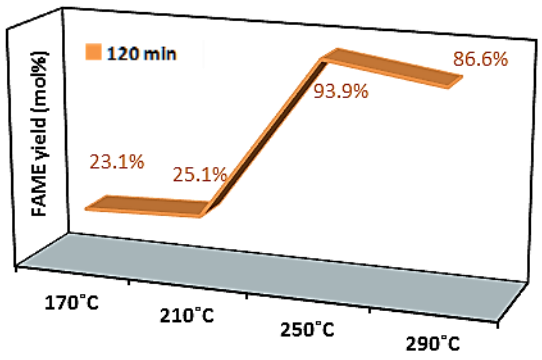

Figure 3. FAME yield with the presence of FFA.

In stage two of our study, FFA effect on phospholipids conversion was examined. Microalgae are typically high in FFA. Although strong acids, such as sulfuric acid, can be used as catalysts in transesterifying high FFA feedstocks, such as waste vegetable oils, to biodiesel, fatty acids are considered too weak to perform a catalytic role. However, this can be changed if high temperatures are used. The acidity of weak fatty acids can increase dramatically under the state of super-critical methanol. Meanwhile, FFAs react with methanol to form FAME via the esterification reaction.

Experimental results have shown that the presence of FFA in the phospholipid reaction system effectively increases FAME yield, and the optimal reaction temperature for the best yield of FAME was the same as that without FFA, i.e., 250˚C. When 16.6-percent weight of FFA is in the system, which is the FFA content in the microalgal oil in our previous study [4], a FAME yield of 93.9% on molar basis was achieved (Fig. 3). Results also confirmed the phenomenon observed when FFA was present, that FAME yield decreases if the temperature is at 290˚C, although the lower yield was still as high as 86.6% on molar basis (Fig. 3) due to the catalytic effect of FFA. The result also verified that weak organic acids can act effectively as catalysts in the condition of super-critical methanol.

Summary

Experimental results show that phospholipids can be converted into FAME or biodiesel under super-critical methanol condition without an external catalyst application. The optimal reaction temperature is 250˚C and a reaction time of 120 minutes is preferred. Operating conditions under sub-critical methanol or below 240˚C, such as 210˚C, was not adequately proven to convert high yields of phospholipids into FAME. At high temperatures, such as 290˚C, polymerization and precipitation of phospholipids occur, leading to FAME yields. Presence of FFA in the reaction system positively affects the FAME yield, provided that the operating temperature is above 210˚C.

Acknowledgement

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