Bioresource Technology 200 (2016) 153–160

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Glycerin esterification of scum derived free fatty acids for biodiesel production

Erik Anderson, Min Addy, Qinglong Xie, Huan Ma, Yuhuan Liu, Yanling Cheng, Nonso Onuma, Paul Chen, Roger Ruan *

Department of Bioproducts and Biosystems Engineering, and Center for Biorefining, University of Minnesota, 1390 Eckles Avenue, St. Paul, MN 55108, USA

HIGHLIGHTS

- Oil extraction from waste water scum via acid hydrolysis and solvent extraction.
- Acyl-glycerol formation reactions and trends during catalyzed glycerolysis.
- Free fatty acid reduction kinetics of scum derived oil for biodiesel production.
- Inorganic catalyst comparison versus uncatalyzed reaction kinetics.
- Sulfur reduction potential of catalysts during filtration of glycerized oil.

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 7 October 2015
Accepted 8 October 2015

Keywords:
Scum
Solvent extraction
Glycerolysis
Biodiesel
Wastewater treatment

ABSTRACT

Scum is an oily waste stream of the wastewater treatment process that can be used to produce biodiesel. Combining acid hydrolysis and solvent extraction, a free fatty acid and acyl-glycerol rich product was produced. Free fatty acids (FFAs) present were converted to acyl-glycols via a high temperature (238 °C) glycerin esterification process known as glycerolysis. The inorganic catalysts zinc aluminum oxide and sodium sulfate were tested during glycerolysis to compare the reaction kinetics of converting FFA to acyl-glycerols. It was concluded that the zinc-based catalyst increased the reaction rate significantly, from a "*k*" value of 2.57 (uncatalyzed) to 5.63, completing the reaction in 60 min, half the time it took the uncatalyzed reaction (120 min). Sodium sulfate's presence however slowed the reaction, resulting in a "*k*" value of 1.45, completing the reaction in 180 min. Use of the external catalyst Zn–Al_2O_3 showed the greatest catalytic potential, but also assumes additional costs.

1. Introduction

Scum is an oily waste by-product of the wastewater treatment process. Currently, scum is treated either by anaerobic digestion to produce low energy density biogas or by landfilling, the latter of which raises great environmental concern. Research efforts have resulted in a novel process for extracting and converting the oil generated from scum to biodiesel. Scum-sourced oil is a broad mixture of several hydrophobic organic compounds, the most prevalent being acyl-glycerols, glycerides, and free fatty acids. Additionally, the extracted oil contains many impurities that require removal or modification before processing, such as herbicides, insecticides, and other organic macromolecules (Bi et al., 2015). Elemental analysis showed soluble metal and non-metal compounds present in the filtered scum oil. Traditionally, acid washing with water has been the most prominent method for removing such impurities for biodiesel production from alternative fuel sources (Knothe and Van Gerpen, 2010). Based on previous findings, sulfuric acid was chosen over phosphoric and hydrochloric acid for the acid hydrolysis of scum oil (Bi et al., 2015). By combining previously separate purification stages, acid hydrolysis and solvent extraction, a free fatty acid and acyl glycerol rich product can be produced. The resulting oil has an acid value (AV) of approx. 170–174, which correlates to a free fatty acid (FFA) concentration of approx. 86%.

Before the oil can be converted to methyl esters (biodiesel), the FFA needs to be converted to an acyl-glycerol. Without a pretreatment, the FFA will react preferentially with the base-catalyst to form alkali soap. Traditionally, the most prevalent pretreatment method has been the acid-esterification, since it can be done at relatively low process temperatures. Acid esterification is the

* Corresponding author. Tel.: +1 612 625 1710; fax: +1 612 624 3005.
E-mail address: ruanx001@umn.edu (R. Ruan).

http://dx.doi.org/10.1016/j.biortech.2015.10.018
0960-8524/

direct conversion of FFA's into methyl esters using sulfuric acid as a catalyst, with an excess of methanol (Knothe and Van Gerpen, 2010). During acid esterification, each mole of fatty acid converted to methyl esters produces one mole of water. The resulting wet methanol must then be decanted, neutralized, and dried via fractional distillation with high reflux rates before the methanol can be re-used. Methanol drying columns can cost millions of dollars and consume the largest percent of processing plants' energy. By not having to dry wet methanol after acid esterification, biodiesel plants can cut their thermal energy consumption in half (Anderson, 2014).

Alternatively, glycerin esterification or "glycerolysis" can reduce FFA in low-grade oils without the use of acid, methanol or vacuum stripping (Jackam et al., 2014). When glycerin is combined with the scum-derived oil at a temperature of approximately 238 °C, the free fatty acids will react with glycerin to form an acyl glycerol or glyceride and water. The resulting glycerides formed during glycerolysis can then be converted directly to biodiesel via base-catalyzed trans-esterification. Since glycerolysis is done at such high temperatures, any water formed is driven out immediately via a nitrogen purge. The continuous removal of water throughout the process via a nitrogen purge is important for multiple reasons. Drying the feed oil to moisture levels below 0.5% avoids the formation of excess soaps during base-catalyzed trans-esterification and the decanting problems that can occur (Leung et al., 2010). Purging the water from the system will also shift the reaction equilibrium toward the product side, allowing the free fatty acid concentration to fall below 0.2%. This is the result of Le Chatelier's principle, or "the equilibrium law", which states that when a system at equilibrium is subjected to change (i.e., removal of water at low concentrations), the system will readjust itself to counteract the effect of the change, establishing a new equilibrium. This principle has been used to manipulate the outcomes of reversible reactions, often to increase the yield of a specific product (Atkins, 1993). Along with water, volatile organic compounds and light carboxylic acids are removed during the purge. These compounds are the result of organic oxidation and can be very odorous. Blanketing the system with nitrogen avoids any further oxidation of the oil components at high temperature.

The only reagent needed for successful glycerolysis is glycerin, a co-product of the trans-esterification of acyl glycerols. In plants using glycerolysis, the glycerin produced during trans-esterification can be recycled back into the process, and the excess glycerin can be refined for sale as a valuable byproduct (Kome et al., 2013). Catalysts present in the glycerin phase after trans-esterification must be neutralized using an acid then removed via filtration. Sulfuric acid is a cheap and available mineral acid that will form sodium sulfate when used to neutralize the base catalyst sodium methoxide. As shown later, the presence of sodium sulfate in glycerin bound for glycerolysis can have benefits extending beyond reaction rate and acyl glycerol formation.

The rate of the glycerolysis reaction is determined by two variables: initial concentration of FFA and temperature. In batch systems using refined free glycerin, FFA concentrations over 90% have been reduced to below 0.3% in only 3 h of reaction time. The optimum temperature range for non-catalyzed glycerolysis is between 221 and 238 °C (Jackam et al., 2014). The presence of an inorganic catalyst can also have a large effect on reaction rate and may serve to lower reaction temperatures. The majority of biodiesel plants run their processes at operating temperatures of 176 °C or below. Although glycerolysis can be run at lower temperatures, reaction rates are vastly improved when run at temperatures around 232 °C (Anderson, 2014). Operating temperatures approaching 260 °C are not recommended due to possible glycerin decomposition (Albin, 1962).

Catalyzed free fatty acid reduction via glycerolysis is one approach being studied to address production limitations. Different inorganic catalysts were tested during high temperature glycerolysis (238 °C) in order to study the reaction kinetics of converting free fatty acids (FFAs) to mono-, di-, and tri-acyl-glycerol. The glycerin introduced during glycerolysis must be removed in subsequent processes. A combination reflux distillation, mid-condenser phase separation, and adsorbent filtration are being researched in order to remove residual unbound glycerin. By modeling of all reactions present, reaction conditions and residence times can be optimized to produce biodiesel as energy efficiently as possible. The process serves the dual purposes of converting scum to a higher value product (biodiesel) and reducing environmental pollutants in both landfills and water resources. As a result, 70% of the dried and filtered scum oil can be converted to biodiesel, the equivalent of approximately 140,000 gallons of biodiesel and \$400–500K profit per year (Haas et al., 2006). A scum-to-biodiesel conversion process for the treatment and complete utilization of scum has the potential to be both more economical and environmentally sound than current practices.

The objective of the research performed was to compare two different inorganic catalysts during high temperature glycerolysis (238 °C) against a third uncatalyzed reaction. By analyzing the concentrations of all of the reaction components, the catalytic potential of each scenario could be assessed, assuming a first-order reaction. Factoring in the catalytic potential along with projected catalyst costs, the economic potential of each scenario could also be determined. Additionally, different acyl-glycerol formation reactions were studied in order to understand the effects of metallic catalysts on glyceride formation. Understanding the final concentrations of various acyl-glycerols could allow for improved modeling data for changes in bulk density and volume throughout glycerolysis. The sulfur reduction potential of the catalyst was determined by removing the catalyst after glycerolysis. Any reduction in sulfur levels was attributed to the binding or complexing of the metal catalyst with sulfur.

2. Methods

2.1. Material and reagent

The scum samples were collected from Metropolitan Wastewater Treatment Plant at St. Paul, MN. Sulfuric acid (98%, AR) and hydrochloric acid (36.5–38.0%, AR) were obtained from Mallinckrodt Baker, Inc., Paris, Kentucky. Phosphoric acid (85.0%, GR) was obtained from EM Industries, Inc. Butanetriol (1000 mg/ml), tricaprin (8000 mg/ml), and N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) were obtained from Sigma–Aldrich, Inc. Sodium methoxide (30% in methanol), methanol (anhydrous, 99.8%), n-heptane (HPLC grade), potassium hydroxide concentrate (0.1 N), ~50 micron filter paper, and glycerol (99.9%) were obtained from Thermo Fisher Scientific, Inc. Distilled water was obtained from Premium Waters, Inc., MN, USA.

2.2. Oil rendering process and experimental design

The general process for the preparation of scum derived oil can be summarized according to the following six steps:

$$\text{Heat Scum} \rightarrow \text{Filter} \rightarrow \text{Acid Hydrolysis} \rightarrow \text{Solvent Extraction} \rightarrow \text{Solvent Distillation} \rightarrow \text{Glycerolysis}$$

The detailed experiment procedures are described as follows.