Fuel Processing Technology 124 (2014) 70–77

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Esterification of free fatty acids to fatty acid alkyl esters in a bubble column reactor for use as biodiesel

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ARTICLE INFO

Article history:
Received 17 May 2013
Received in revised form 5 February 2014
Accepted 7 February 2014
Available online 12 March 2014

Keywords:
Biodiesel
Fatty acid methyl ester
Free fatty acid
Trap grease
Esterification

ABSTRACT

Biodiesel is readily produced from refined vegetable oils; however, many low-value degraded and waste oils contain a high concentration of free fatty acids, which are difficult to convert to fatty acid alkyl esters for use as biodiesel. This paper evaluates the performance of an acid-catalyzed bubble column reactor that is highly robust for the esterification of free fatty acids to fatty acid alkyl esters. The bubble column reactor typically operated at 120 °C and ambient pressure; methanol bubbling through the reactor reacts with free fatty acids and strips by-product water, which enables high conversions and makes the reactor more robust to water than other reactor designs. This paper shows the effects alcohol, feedstock type and quality, alcohol flow rate, and oil feedstock on the reactor performance. Most reaction conditions produce greater than 98% conversion in less than 2 h, including reactions with alcohols containing 10% water by volume and lipids extracted from trap grease.

1. Introduction

Rising prices of crude oil and concerns about carbon dioxide emissions have led to increased research into alternative fuels and renewable energy. There are several other pressures for increased research into renewable fuels including: worsening air quality by emissions of sulfur oxides, particle matter, and other gases; security of domestic energy supply; and limited long-term supply of petroleum. This paper analyzes performance of a bubble column reactor for producing biodiesel from low-value lipid feedstocks containing high concentrations of free fatty acids (FFA); these low-value lipids can be obtained from non-food crops grown on marginal land or from waste fats, greases, and oils.

Biodiesel is a promising renewable fuel. Biodiesel is a name given to fatty acid alkyl esters that are suitable diesel substitutes. Biodiesel is typically produced chemically by reacting plant or animal derived lipids with an alcohol. The majority of biodiesels are produced by reacting lipids with methanol to produce fatty acid methyl esters (FAME). Throughout this paper, the term FAME is used to refer to the reaction product. Before selling FAME as biodiesel, it is necessary to demonstrate that the product satisfies the full suite of ASTM specifications for biodiesel as a diesel substitute. The majority of current biodiesel is produced from refined lipids with low FFA concentrations, such as soybean oil (in USA), rapeseed oil (in Europe), and palm oil (in Asia), which are agricultural crops that are relatively high-cost, require significant fertilizer and chemical inputs, and compete with food crops for land. However, biodiesel is not a complete solution for the United States energy demand. Van Gerpen [1] noted that only about 14% of current diesel demand can be replaced by biodiesel produced from crop-based lipids. Other waste lipid feedstocks can add significant production capacity [2].

Published techno-economic analyses of biodiesel production processes have predicted attractive conversion economics, but the results are highly sensitive to the feedstock used. Apostolakou et al. [3] and Haas [4] showed that the cost of raw materials can be 75%–90% of the cost of manufacturing. Marchetti et al. [5] reported three scenarios for producing biodiesel from lipids containing 5% FFA, and all three processes were profitable with raw materials being more than 80% of the manufacturing costs. Zhang et al. [6,7] compared four biodiesel processes; the production of biodiesel from refined lipids had the lowest capital expense and highest cost of raw materials. Processes converting waste lipids to biodiesel required more methanol and larger distillation columns to recover methanol for recycle. Because feedstock is a major fraction of the manufacturing costs, processes that use low-value feedstocks (such as waste oils) are likely to show much greater economic profitability [2,4].

The reactor described in this paper has several potential advantages related to sustainability including: flexibility to varying FFA content, flexibility for alcohol feed, robustness to moisture, and reduced energy requirements. The results section of this paper presents parametric studies of how the bubble column reactor performance varies with some key process variables. A robust reactor that can handle a variety of feedstocks without additional pretreatment will reduce economic

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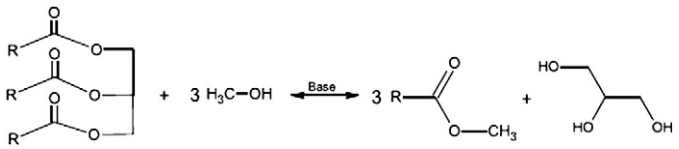
http://dx.doi.org/10.1016/j.fuproc.2014.02.003
0378-3820/

hurdles to constructing and operating biodiesel production facilities and will result in lower consumer prices of biodiesel products.

1.1. Chemistry for production of fatty acid methyl esters

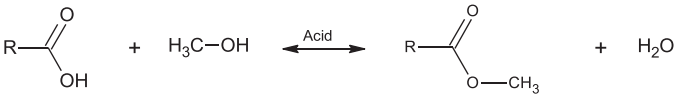
The most common reaction pathway for producing FAME is the transesterification of triacyl glycerides (TAG), or triglycerides. During transesterification, a TAG molecule reacts with three alcohol molecules to form three FAME molecules with by-product glycerin:



(1)

In this reaction equation, the alcohol is methanol, and R represents a long aliphatic fatty acid chain, which typically contains 8–22 carbon atoms [8]. The reaction in Eq. (1) is a simplification of a series of three reactions in which TAG sequentially reacts with methanol molecules to form a diacyl glyceride molecule (DAG), a monoacyl glyceride (MAG), and finally glycerin with one FAME molecule produced at each step. Industrial biodiesel processes predominantly use transesterification reactions and base catalysts because this reaction requires low operating temperature and achieves high conversions within a couple of hours. A major drawback of the base-catalyzed transesterification reactions is that the lipid feedstock must be high purity in TAG; if the FFA content exceeds 1%, the soaps that form from the reaction between the base catalyst and the FFA hinder transesterification and downstream purification [1,9,10]. The alternative acid-catalyzed reactions do not form soaps with FFA, but acid-catalyzed transesterification reactions are much slower than base catalyzed transesterification reactions [1,11].

For high-FFA lipids, acid-catalyzed esterification is effective for producing FAME from FFA:



(2)

The esterification of FFA by Eq. (2) catalyzed with acids like sulfuric acid have been the subject of a number of studies [9,12–18]. Esterification reactions are reversible and are equilibrium-limited by the accumulation of the by-product water. The presence of water generally limits the conversion to FAME that can be achieved in an acid-catalyzed reactions, and its continuous removal has been shown to dramatically increase yields [14]. The bubble column reactor described in this paper is effective at continuously removing water from the system, which results in high yields of FAME when using FFA feedstocks.

1.2. Biodiesel process feedstocks

The quality and the price of potential lipid feedstocks are related to their FFA content. Edible lipids have low FFA content and high prices. Inedible lipids tend to be high in FFA and have low prices. The high-FFA lipids are mostly waste products and have limited commercial value, while low-FFA lipids tend to be viable food sources. For example, soybean oil currently sells for about $3.52 per gallon, and yellow grease (filtered and dewatered waste cooking oil with FFA content <15%) sells for $2.19 [19]. Trap grease is a potential source of high-FFA lipids; wastewater utilities charge $0.06 or more per gallon to dispose of trap grease [20]. Trap grease contains 2%–10% lipids, and lipids separated from trap grease can be over 95% FFA; more details about trap grease are provided in Section 3.4 [2]. Producing biodiesel from high-FFA lipids entails low feedstock costs and is less prone controversies associated with creating fuels from food-grade lipids [21,22].

1.3. Process options for the esterification of high-FFA lipids

There are several technologies available for converting high-FFA lipids to FAME; acid-catalyzed esterification is effective over a large range of FFA concentration and is often used for pretreatment prior to base-catalyzed transesterification in a two-step process. A significant disadvantage of acid catalysts is slower reactions. There are several ways to increase acid-catalyzed esterification reaction rates, including the following: increasing temperature, increasing catalyst concentration, and removing by-product water. For feedstocks containing 1%–10% FFA, a two-step process (low-temperature acid-catalyzed esterification followed by base-catalyzed transesterification) is the most common method. For feedstocks containing more than 50% FFA, multiple moderate-pressure reactors with intermediate removal of water are used effectively [23]. Multiple, identical reactors with intermediate water removal not only increases the reaction time and conversion, but it also increases the capital and operating costs significantly. To achieve acceptable reaction rates, temperatures above the boiling point of methanol are often used, which requires elevated pressure to maintain methanol in the liquid phase; for example, Van Gerpen reports using 240 °C and 90 bar [1] and Berry and Ratigan report 115 °C and 5.4 bar [23].

However, Kocsisova et al. [13] showed that high conversion can be achieved with acid-catalyzed reactions by bubbling methanol vapor through FFA at ambient pressure and elevated temperature. Bubbling methanol vapor through hot lipid provides several benefits: use of high temperatures corresponds to faster reaction kinetics, simultaneous removal of water reduces equilibrium limitations, and intensive agitation of the reaction mixture enhances mass transfer. Kocsisova et al. [13] demonstrated that esterification in a bubble reactor at temperatures 50%–60 °C higher than the boiling point is effective and requires lower amounts of methanol (methanol:FFA molar ratio of 3:1 to 4:1 is sufficient) for high conversion. Kocsisova et al. [13] claims that feeding the methanol as a liquid into the reactor and local excess of methanol near the feed were necessary for high conversion. The reactor described in this paper extends on the work of Kocsisova et al. [13] by using a column reactor configuration and by providing a more detailed study of how the rate of methanol fed to the reactor affects reaction conversion.

2. Materials and methods

2.1. Chemicals and materials

Oleic acid was used to model an FFA feedstock for the experiments in this paper unless otherwise noted. Oleic acid at technical grade purity (>90%) as well as toluene and methanol with purities above 99% were purchased from Sigma Aldrich and used without further purification. Ethanol was anhydrous and denatured with 5% isopropyl alcohol and was also purchased from Sigma Aldrich. Isopropyl alcohol was purchased from Azer Scientific and was 99.99% purity. Sulfuric acid at 93% weight (66° Baume) was purchased from Fischer Scientific. Paratoluenesulfonic acid (PTSA) was purchased from Sigma-Aldrich and dissolved in methanol for use. Triglyceride samples were refined soybean oil purchased from local supermarkets. Trap grease was donated by Russell Reid waste management, and more information about the experiments with trap grease is included in Section 3.4.

Fig. 1 displays a schematic of the reactor system. The primary reaction chamber was a jacketed glass column with several pumps used for alcohol feeds and recirculation. Throughout the system, all parts wetted by the reactants and products were glass, stainless steel, or PTFE. The reactor and the alcohol-vaporizer/lipid-reheater were heated by circulating hot silicone oil from a heating bath.