Bioresource Technology 214 (2016) 826–835

Contents lists available at ScienceDirect

Bioresource Technology

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

Review

A novel process for low-sulfur biodiesel production from scum waste

Huan Ma[a,b], Min M. Addy[b], Erik Anderson[b], Weiwei Liu[b,c], Yuhuan Liu[d], Yong Nie[e], Paul Chen[b], Beijiu Cheng[a], Hanwu Lei[f], Roger Ruan[b,d,*]

[a] School of Life Sciences, Anhui Agricultural University, 130 Changjiang West Road, Hefei 230036, China
[b] Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Avenue, St. Paul, MN 55108, USA
[c] School of Engineering, Anhui Agricultural University, 130 Changjiang West Road, Hefei 230036, China
[d] MOE Biomass Engineering Research Center, Nanchang University, Jiangxi 330047, China
[e] Separation Engineering Institute, Zhejiang University of Technology, Hangzhou 310014, China
[f] Department of Biological Systems Engineering, Washington State University, Tri-Cities Campus, Richland, WA 99354, USA

HIGHLIGHTS

- A new process was developed to convert scum to low sulfur biodiesel.
- Solvent extraction combined with acid washing was used to clean the scum oil.
- Activated carbon was integrated with reflux distillation to reduce sulfur content.
- 70% filtered and dried scum was converted to biodiesel with sulfur content $\leqslant$15 ppm.
- Biodiesel from new process showed better properties than that from other processes.

ARTICLE INFO

Article history:
Received 19 March 2016
Received in revised form 9 May 2016
Accepted 10 May 2016
Available online 13 May 2016

Keywords:
Scum
Biodiesel
Solvent extraction
Adsorptive desulfurization
Glycerolysis

ABSTRACT

Scum is an oil-rich waste from the wastewater treatment plants with a high-sulfur level. In this work, a novel process was developed to convert scum to high quality and low sulfur content biodiesel. A combination of solvent extraction and acid washing as pretreatment was developed to lower the sulfur content in the scum feedstock and hence improve biodiesel conversion yield and quality. Glycerin esterification was then employed to convert free fatty acids to glycerides. Moreover, a new distillation process integrating the traditional reflux distillation and adsorptive desulfurization was developed to further remove sulfur from the crude biodiesel. As a result, 70% of the filtered and dried scum was converted to biodiesel with sulfur content lower than 15 ppm. The fatty acid methyl ester profiles showed that the refined biodiesel from the new process exhibited a higher quality and better properties than that from traditional process reported in previous studies.

Contents

1. Introduction . . . 827
2. Method . . . 827
  2.1. Material and reagent . . . 827
  2.2. Process design and experiment design . . . 828
    2.2.1. Basic process . . . 828
    2.2.2. Experimental design . . . 830
  2.3. Analytical methods . . . 830
    2.3.1. Acid value (AV) determination . . . 830
    2.3.2. Fatty acid methyl ester (FAME) analysis . . . 831
    2.3.3. Sulfur analysis . . . 831

* Corresponding author at: Center for Biorefining and Department of Bioproducts and Biosystems Engineering, University of Minnesota, 1390 Eckles Avenue, St. Paul, MN 55108, USA.
E-mail address: ruanx001@umn.edu (R. Ruan).

http://dx.doi.org/10.1016/j.biortech.2016.05.029

3. Results and discussion . . . 831
3.1. Effect of solvent type on the sulfur removal . . . 831
3.2. Process comparison for low-sulfur biodiesel conversion . . . 831
3.2.1. Sulfur removal performance . . . 831
3.2.2. Oil yield comparison . . . 832
3.2.3. FAME comparison . . . 832
3.3. Fuel properties of the scum-derived biodiesel from different processes . . . 833
3.3.1. Cetane number (CN) and Kinematic viscosity (KV) . . . 833
3.3.2. Cloud point and acid value . . . 834
3.4. Future work . . . 834
4. Conclusion . . . 834
Acknowledgements . . . 834
References . . . 834

1. Introduction

Biodiesel production has attracted considerable attention in recent years due to the global energy crisis and awareness in environmental pollution. To date, biodiesel conversion from vegetable oils has been the primary route for biodiesel production (Sivakumar et al., 2011). However, production of vegetable oil based biodiesel competes with food production by engrossing agricultural cropland. A major obstacle to the commercialization of biodiesel production is the high cost associated with the oil feedstock, which makes up nearly 75–85% of the total production costs (Demirbas, 2009). Therefore, low-cost feedstocks such as used cooking oil, spent oil, grease, or low-quality oil are regarded promising high potential feedstocks for biodiesel production (Abedin et al., 2016; Li et al., 2014; Wang et al., 2016).

Scum is a floatable waste by-product from the wastewater treatment process. It is an oil-rich material containing grease, animal fat, vegetable oil, food wastes, plastic material, soaps, wax, and many metallic and non-metallic impurities. The oil content of scum could be as high as 60% (Bi et al., 2015), making it a promising alternative feedstock for biodiesel production. Attempts have been made to convert scum to biodiesel (Anderson et al., 2016; Bi et al., 2015; Mu et al., 2016). Bi et al. (2015) proposed a novel six-step method to produce scum-based biodiesel. In this process, a combination of acid washing with acid catalyzed esterification was used to remove impurities and convert free fatty acid to methyl esters, followed by base-catalyzed transesterification to produce fatty acid methyl ester (FAME). Converting scum to biodiesel is potentially a more profitable process than scum combustion and anaerobic digestion. It was reported that scum to biodiesel conversion yielded 29% and 104% more profit than scum combustion and anaerobic digestion, respectively (Mu et al., 2016).

Although scum holds a great potential as a biodiesel feedstock, one of its major issues is of its high sulfur content ranging from 600 to 1000 ppm. The sulfur compound presented in the scum primarily comes from sulfur-containing organics in the wastewater from restaurants, households and other facilities. The sulfur goes to the atmosphere as sulfur dioxide during the combustion of biodiesel, causing significant environmental and health problems (Bu et al., 2011; Jung and Jhung, 2015). To regulate sulfur in biodiesel, the American Society for Testing and Materials (ASTM) D6751 (2015) specifies the sulfur content in biodiesel to be less than 15 ppm. In a previous study (Bi et al., 2015), the scum-based biodiesel contained 33.6 ppm sulfur, which is twice the sulfur limit allowed by the ASTM specifications. In addition, there was a drawback in the acid-esterification which was used to convert free fatty acid (FFA) into methyl esters in the previous study. The resulting wet methanol from the acid-esterification must be dried for reuse, which causes two times higher thermal energy consumption in biodiesel plants than the process without drying (Anderson et al., 2016). Therefore, a novel process to lower the sulfur content in biodiesel with higher energy conversion efficiency was proposed in this study.

In the present work, solvent extraction incorporated with glycerolysis and desulfurization distillation was investigated. Solvent extraction combined with acid washing can deep clean the scum oil by removing slightly polar and non-oil impurities, including a part of organosulphur compounds. Heptane, hexane, and petroleum ether were investigated and compared for sulfur reduction in the solvent washing step. Instead of traditional acid esterification, glycerin esterification or so called "glycerolysis" was used to reduce FFA in low-quality scum. Glycerolysis does not consume any acid and methanol, therefore the vacuum stripping required for methanol recycle can also be eliminated. In addition, a new distillation system integrating the traditional reflux distillation and adsorptive desulfurization was developed to further remove sulfur impurities from the biodiesel. Sludge-derived activated carbon was used as the adsorbent in the new distillation system. The activated carbon was packed on the top of the distillation column and steel wool was used to fill the rest of the column. Consequently, the adsorptive effect was enhanced due to increased surface contact when fatty acid methyl esters (FAME) were in vapor phase during the reflux distillation. For comparison, two other processes were explored to prepare scum-based biodiesel, both of which used the same reflux distillation system without addition of adsorbents in the column, with one process including solvent extraction step and the other excluding the solvent extraction step. The change in sulfur-content in each step of the three processes was recorded and compared in order to understand desulfurization performance of the new process and evaluate the sulfur reduction potentials of these three different processes. In addition, the oil yields of different steps in three routes were determined to assess the conversion efficiency of each process. Furthermore, the properties such as cetane number, kinematic viscosity, and cloud point of the final biodiesel from different processes were evaluated based on their FAME profiles.

2. Method

2.1. Material and reagent

The scum samples were collected from the Metropolitan Wastewater Treatment Plant in St. Paul, MN. Sulfuric acid (98%, AR) was purchased from Mallinckrodt Baker, Inc., Paris, Kentucky, butanetriol (1000 mg/ml), tricaprin (8000 mg/ml), and N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) 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%) from Thermo Fisher Scientific, Inc., distilled water from Premium Waters, Inc., MN, USA, and Supelco 37 component fatty acid methyl ester (FAME) mix from Sigma–Aldrich, Inc.