Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

# Recovery of slaughterhouse Animal Fatty Wastewater Sludge by conversion into Fatty Acid Butyl Esters by acid-catalyzed esterification

Christopher Wallis, Muriel Cerny, Eric Lacroux *, Zéphirin Mouloungui

*Laboratoire de Chimie Agro-industrielle (LCA), Université de Toulouse, INRA, INPT, Toulouse, France*

ARTICLE INFO

*Article history:*
Received 9 March 2016
Revised 13 June 2016
Accepted 2 July 2016
Available online xxxx

*Keywords:*
Biodiesel
Fatty Acid Butyl Esters (FABE)
Esterification
Homogeneous acid catalysis
4-Dodecylbenezenesulfonic acid (DBSA)
Response surface methodology

ABSTRACT

Two types of Animal Fatty Wastewater Sludges (AFWS 1 and 2) were analyzed and fully characterized to determine their suitability for conversion into biofuel. AFWS 1 was determined to be unsuitable as it contains 68.8 wt.% water and only 32.3 wt.% dry material, of which only around 80% is lipids to be converted. AFWS 2 has only 15.7 wt.% water and 84.3 wt.% dry material of which is assumed to 100% lipids as the protein and ash contents were determined to be negligible. The 4-dodecylbenzenesulfonic acid (DBSA) catalyzed esterification of AFWS with 1-butanol was performed in a novel batch reactor fitted with a drying chimney for the "in situ" removal of water and optimized using a non-conventional Doehlert surface response methodology. The optimized condition was found to be 1.66 mol equivalent of 1-butanol (with respect to total fatty acid chains), 10 wt.% of DBSA catalyst (with respect to AFWS) at 105 °C for 3 h. Fatty Acid Butyl Esters (FABEs) were isolated in good yields (95%+) as well as a blend of FABEs with 1-butanol (16%). The two potential biofuels were analyzed in comparison with current and analogous biofuels (FAME based biodiesel, and FABE products made from vegetable oils) and were found to exhibit high cetane numbers and flash point values.



## 1. Introduction

Today biodiesel has firmly established itself as a major bio-alternative to fossil fuels for motor vehicles as well as liquid fueled generators. Biodiesel itself consists primarily of fatty acid methyl esters (FAMEs) that are synthesized either *via* the base catalyzed trans-esterification of glyceride material, such as vegetable oils or animal fats; or *via* the acid catalyzed esterification of free fatty acids (FFAs), such as those found in trap greases or waste cooking oil (Helwani et al., 2009; Demirbas, 2008; Leung et al., 2010). In both cases, and in accordance with current legislation, methanol is the alcohol of choice, usually used in a 2 fold excess, in order to achieve high yields of the FAMEs. Due to its evermore common usage the possible sources of biodiesel have become as important as its production. Whilst the current technologies employed are very effective when applied to clean sources of oils or fats (100% glycerides or 100% FFAs), they are far less effective when applied to mixtures of glycerides and FFAs, or if there is significant amount of water present (5 wt.% or more) (Lam et al., 2010). For mixtures of triglycerides and FFAs the problem remains that whilst basic catalysts are extremely active for the trans-esterification of the triglycerides, the opposite is true for the acidic catalysts used for the esterification of FFAs. Thus there are only a few reported catalysts capable of simultaneous trans-esterification and esterification (Ramalinga et al., 2002; Kulkarni et al., 2006; Kalemba-Jaje et al., 2014; Jin et al., 2014; Chai et al., 2014).

An even greater inhibiting factor is water. The condensation reaction performed during the formation of biodiesel produces one mole water for every mole of FAME. If water is already present in the origin source of oil or fat, either dissolved or emulsified, it limits the desired reaction from proceeding due to Le Chatelier's Principle (Kusdiana and Saka, 2004). In addition, the highly active acid-resin type catalysts have been reported to be poisoned by the presence of water, as the water swells their pores and inhibits their activity (Park et al., 2010). 4-dodecylbenezenesulfonic acid (DBSA) was shown in 2001 by Kobayashi et al. to be a highly effective active acid catalyst for performing esterification reactions in water (Manabe et al., 2001). Their study elucidated the mechanism of action of the DBSA to be that of a micellar catalyst that forms hydrophobic pockets in which the organic reagents condensate with the expulsion of a molecule of water from the hydrophobic core. Based on this study we presumed that DBSA would potentially be an excellent catalyst for the esterification of FFAs emulsified in water into their corresponding fatty acid esters (biofuel).

* Corresponding author.
*E-mail address:* eric.lacroux@ensiacet.fr (E. Lacroux).

http://dx.doi.org/10.1016/j.wasman.2016.07.003
0956-053X/

Animal Fatty Wastewater Sludge (AFWS), like animal fats, represent an important source of glyceride and free fatty acid material for potential conversion into biodiesel (Chakraborty et al., 2014; Da Cunha et al., 2009; Jeong et al., 2009). Any bio-fuel made from AFWS would be classified as a non-consumable, 2nd generation raw material and is considered to 'count double' on carbon emissions savings according to the Renewable Energy Directive (RED 2009/28/CE) of the EU, thus sources such as used cooking oil, are already being exploited for their economic and environmental benefits (Jørgensen et al., 2012; López et al., 2010; Tu and McDonnell, 2016). AFWSs can vary greatly in their nature depending on their origin and the manner in which they are collected. In general, the washings of the slaughterhouse are drained through a scraper that removes any large pieces of insoluble material (bones, feathers, skin, etc.) and collected in a floatation tank. Here the animal fats float to the top of the tank, (hence they are often referred to as floatation greases), and are separated by skimming off the fat into a secondary container, normally exterior to the slaughterhouse and open to air. Due to their collection and treatment AFWSs are generally regarded to be completely hydrolyzed to the free fatty acids (FFAs), however, as our analysis shows they can contain up to 20% of un-hydrolyzed compounds, namely the tri-, di- and mono-glycerides. The amount of un-hydrolyzed material generally depends on the amount of time the lipids are left to stagnate (open to air) before being collected. Currently there are no commercial uses for AFWSs and thus slaughterhouses are obliged by law to pay for its destruction. For the purposes of this work, we will report on two very different, but very representative types of AFWS and our efforts to convert the lipid material contained within them into liquid biofuels.

Whilst the current legislation allows for only FAMEs to be used as biodiesel, there have been many reports in the literature that suggest that fatty acid esters made from short-chain alkyl alcohols ranging from $C_1$ to $C_4$ carbon atoms are equally effective as potential biofuels (Hellier et al., 2012). In some cases, the fuel properties of the fatty acid esters are superior to that of FAMEs, particularly with respect to cloud point, cetane number, viscosity, etc. (Knothe et al., 2003; Knothe, 2005). In particular, Fatty Acid Butyl Esters (FABEs) made from either the trans-esterification of triglycerides, or the esterification of FFAs with 1-butanol (Bynes et al., 2014), have recently become of considerable interest as a potential biofuel with their cost of production and their physical properties (cetane number, cloud point, viscosity, etc.) having been found to be equal, or superior, to those of the current biodiesel FAMEs (Sanchez et al., 2015). The global production of butanol is expected to grow from its current production of 1.3 billion gallons per year to 9.4 billion gallons by 2018 (Jin et al., 2011), mainly due to the massive increase in bio-butanol either as its straight chain (*n*- or 1-butanol), or its branched (*iso*- or 2-butanol) form, made from 2nd generation fermentation processes of biomass (Berezina et al., 2012), and is predicted to overtake bio-ethanol as the bio-additive of choice for drop-in fuel blends of petrol and bio-alcohol (Bio-butanol: The game changer, 2013). These increases in production will undoubtable drive down the cost of butanol on the market making it an inexpensive raw material for potential industrial transformations. It is therefore unsurprising to find recent reports on the engine tests of FABE based biodiesel (Knothe et al., 2003) and blends of biodiesel with 1-butanol (Yilmaz et al., 2014), all of which suggest that it is highly feasible to consider biofuels made of blends of 1-butanol and FAMEs, or biofuels made exclusively of FABEs. We wished to exploit the currently unused and discarded AFWSs by undertaking a study with the aim of converting AFWS into biofuel *via* the DBSA catalyzed esterification of the lipids with 1-butanol. We will demonstrate the effectiveness of a novel reactor designed and patented in our laboratory that allows for the simultaneous removal of the excess water emulsified in the AFWS, as well as promoting the desired transformation to butyl esters (Mouloungui et al.). We intend also to present a FABE-1-butanol blend as a novel potential liquid biofuel synthesized directly from AFWS with minimal post-treatment or purification required.

## 2. Materials and methods

### 2.1. Materials

AFWS 1 and 2 were received without treatment, *via* our project partners, from a slaughterhouse and meat processing plant respectively. 1-Butanol, DBSA and Lewatit MP 500 were purchased from Sigma-Aldrich (France) and used without further purification.

### 2.2. Characterization of Animal Fatty Wastewater Sludges and esterified samples

The moisture (Standard NF EN ISO 662, 2001) and ash (Standard NF EN ISO 6884, 2012) content of AFWS 1 and 2 were determined by European standard protocols. The total lipid contents were determined by Soxhlet extraction in cyclohexane and are reported as an average of at least three separate extractions (Table 1). The protein contents were determined on a Foss Tecator 2020 Digester and a Foss Kjeltec 8400 and were given as a total of nitrogen content in the AFWS by the method of Kjeldahl, using a standard conversion factor of 6.25.

The FFA profile of AFWS 1 and 2 (Table 2) was determined by taking up 20 mg of sample in *t*-butylmethyl ether (1 ml). To 100 µl of this dilution in *t*-butylmethyl ether was added 50 µl of trimethylsulfonium hydroxide (0.5 M MeOH solution) before mixing at room temperature. The samples were characterized on a G.C. Varian 3900 CPG-FID Instrument (Varian, USA) fitted with a CP-select CB for FAME fused silica WCOT column (50 m × φ0.25 mm × 0.25 µm) using helium at a flow rate of 1.1 ml/min which was coupled to a flame ionization detector (FID). The injector split 1:100 (1 µl) temperature was 250 °C for 55 min. The oven temperature ramp was programmed to be 185 °C for 40 min, rising by 15 °C per minute until 250 °C, where the temperature was held constant for 10 min. The temperature of the detector (FID) was set at 250 °C.

**Table 1**
Characterization of AFWS 1 and 2.

| % Content | AFWS 1 | AFWS 2 |
|---|---|---|
| Dry material | 32.3 (± 6.6) | 84.3 (±3.4) |
| Water | 68.7 (±6.6) | 15.7 (±3.4) |
| Lipids (total of dry material) | 80.6 (±8.6) | 97.4 (±0.6) |
| FFAs | 100 | 81.6 |
| T.G.s | 0 | 16.4 |
| D.G.s | 0 | 2.0 |
| M.G.s | 0 | 0 |
| Proteins (% of dry mat.) | 3.6 (±0.3) | 1.1 (±0.1) |
| Ashes (% of dry mat.) | 2.5 (±0.3) | 0.1 (±0.1) |

**Table 2**
Composition of the principle free fatty acids in AFWS 1 and 2.

| Free Fatty Acid (FFA) | AFWS 1 (%) | AFWS 2 (%) |
|---|---|---|
| Myristic acid (C14:0) | 3.1 | 1.3 |
| Palmitic acid (C16:0) | 59.5 | 23.8 |
| Palmitoleic acid (C16:1) | 0.2 | 2.7 |
| Stearic acid (C18:0) | 14.3 | 10.6 |
| Oleic acid (C18:1) | 10.6 | 41.9 |
| Lineoleic acid (C18:2) | 0.8 | 11.2 |

Please cite this article in press as: Wallis, C., et al. Recovery of slaughterhouse Animal Fatty Wastewater Sludge by conversion into Fatty Acid Butyl Esters by acid-catalyzed esterification. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.07.003