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

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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 dodecylbenzenesulfonic 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).

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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 C₁ to C₄ 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 undoubtedly 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 bio fuel 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

All esterified samples for Gas Chromatography analysis were prepared in the same manner: 10 mg of sample were taken up in 10 ml of cyclohexane, to which 100 μ l of internal standard solution was added, (heptadecane 10 mg in 1 ml cyclohexane). To 160 μ l of this solution was added 40 μ l of the silylating agent BSFTA and the sample was heated at 103 °C for three minutes. For analysis 1 μ l was injected directly onto the column. The samples were characterized on a Perkin Elmer Autosystem XL Instrument (Perkin Elmer, USA) fitted with a Restek Rtx 5 column (15 m \times ϕ 0.32 mm \times 0.25 μ m) using helium as carrier gas at 15 psi of pressure which was coupled to a flame ionization detector (FID). The injector temperature was 55 °C for 30 s, and then ramped at 200 °C per minute to 340 °C. The oven temperature ramp was programmed to be 55 °C for 0.5 min, rising by 45 °C per minute until 80 °C, then 10 °C per minute up to 360 °C where the temperature was held constant for 16 min. The temperature of the detector (FID) was set at 360 °C.

2.3. Selection of experimental design parameters

A non conventional Doehlert Experimental (Doehlert, 1970) design was made for process variables optimization. We identified four major parameters for our process: (1) the temperature of the reaction; (2) the time of the reaction; (3) the quantity of catalyst used; and (4) the quantity of butanol required. The temperature of the reaction was set at 105 °C and the time of the reaction was set at 3 h, both based on our preliminary experiments (see Section 3.2). The experimental design was, therefore, set to factor two variables: the quantity of DBSA catalyst (as wt.% of AFSW 2) and the quantity of butanol (mole/mole equivalence calculated based on the total mole content of fatty acids, carboxylic acid chains in AFSW 2).

The ranges of experimental parameters were selected based on our preliminary experiments (see Section 3.2) and in order to remain within the realms of a potential industrially applicable procedure, the maximum/minimum limits were set between 1 wt.% and 10 wt.% for the DBSA catalyst, and between 1.1 and 2 equivalence of butanol. The two factor ($k=2$) network needed seven experiments plus three repetitions at the center of the experimental domain, giving 10 experiments in total that are shown in Table 3. The response value Y is expressed as a % yield of conversion of FFA chains into FABLEs (calculated based upon total lipid content determined by G.C. analysis). A second order polynomial model of the design was used to evaluate the FABLE content response value (Y), as a function of three variables: wt.% of DBSA catalyst (X_1 is the coded value); molar equivalence of 1 butanol (X_2 for the coded value); and the interaction between the two (X_1 and X_2). The behavior of the system can be described by the following equation:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2$$

Table 3
Calculated non-conventional Doehlert design factors for optimization of process parameters (1-butanol and DBSA), and experimental results (% content FFAs/FABLEs).

Entry	% Catalyst (wt.% vs AFSW wt.)	Quantity catalyst (g)	1-Butanol (mol. Eq. vs FFAs)	Quantity 1-Butanol (ml)	% Content FFAs	FABLEs
1	10.0	1.72	1.55	8	4.4	95.3
2	3.0	0.52	1.55	8	7.9	92.1
3	7.8	1.34	1.94	9.5	5.3	94.5
4	3.3	0.57	1.16	6	13.8	78.7
5	7.8	1.34	1.16	6	12.1	87.4
6	3.3	0.57	1.94	9.5	3.7	92.9
7	5.5	0.95	1.55	8	6.9	92.8
8	5.5	0.95	1.55	8	4.4	93.1
9	5.5	0.95	1.55	8	5.8	93.0
10	5.5	0.95	1.55	8	5.2	91.4

Our experimental results from the non conventional Doehlert design factor determined all the necessary the coefficients: a_0 is the response at the center of the experimental domain; a_1 and a_2 are linear coefficients; a_{12} is an interaction coefficient; a_{11} and a_{22} are quadratic coefficients. X_1 and X_2 are coded values for the two variables of our design experimental and can be expressed as:

$$X_1 = \frac{x_1 - 5.5}{4.5} \text{ and } X_2 = \frac{x_2 - 1.55}{0.45}$$

Here x_1 and x_2 are an expression of the real values of our two variables: wt.% loading of DBSA catalyst and molar ratio of 1 butanol/moles FFA chains, respectively.

2.4. Esterification of AFSW 2

The batch reactor was loaded with AFSW 2 (17.2 g, 56.3 mmol. of FFA chains) and the required amount of 1 butanol and DBSA catalyst (see Table 3). The emulsified reaction mixture was heated with stirring at 105 °C for 3 h during which time the mixture became a dark brown liquid. The reaction mixture was then cooled to room temperature with stirring and filtered. The resulting brown liquid was passed through a column of silica gel, any excess volatiles were removed on a rotary evaporator and a sample was taken for G.C. analysis.

2.5. FABLE 1 butanol blend and FABLE production

A 2 L batch reactor was loaded with 800 g of AFSW 2 (2.6 mol of FFA chains), 1 butanol (400 ml, 1.66 mol. eq.) and DBSA (80 g, 10 wt.%), and was fitted with an internal thermometer. The reaction mixture was heated until the internal thermometer read 105 °C and held at this temperature for 3 h. After which time the reaction was allowed to cool to room temperature. The resulting brown liquid was neutralized by the addition of $\text{Ca}(\text{OH})_2$ (16 g, 20 wt.% of DBSA) and left to decant at 4 °C. The FABLE 1 butanol blend was thus isolated at this stage by filtration, and sent for analysis. The 1 butanol content of the FABLE 1 butanol blend was determined by distillation of the 1 butanol from the blend (50 °C, 40 mbar), and calculated to be 16.33%.

For isolation of the concentrated FABLE products the reaction mixture is filtered after decantation, and Lewatit MP 500 (50 g) added. The reaction mixture is agitated for 2 h before filtration and evaporation of the volatiles, yielding 506.3 g (62.5% yield by weight) of FABLE (based on total FFA chains converted to FABLEs in AFSW 2).

3. Results and discussion

3.1. Analysis of Animal Fatty Wastewater Sludge 1 and 2

AFWS 1 and 2 demonstrate the variability in composition of slaughterhouse wastes. AFSW 1 is nearly 70% water, with relatively high protein content in the dry material (Table 1). The dry material itself only represents around 30% of possible lipid material for conversion. AFSW 2, on the other hand, consists of around 80% lipid material with negligible quantities of proteins and ashes. Given that there is so little lipid material contained in AFSW 1 we decided that it would be of little interest to conduct any further investigations upon this material. In fact, our investigation suggests that if a potential AFSW contains less than 50% dry material (and 95% lipid content of the dry material), it is unfeasible to conduct any biodiesel conversion, as the process would be too costly given the small amount of biofuel produced.

The FFA profile of AFSW 2 (Table 2) is consistent with animal fats, in that it contains a ratio of saturated to unsaturated FFAs of

approximately 50:50. This is potentially very promising as a bio fuel as saturated FFAs are known to produce biofuels with high cetane numbers and good oxidation stability. For the purposes of this work we assumed that 100% of the dry material in AFWS 2 is lipids, given that the protein and ash content of AFWS 2 is so small we assume that is negligible with respect to the investigation undertaken. The molecular weight of the lipids in AFWS 2 was based on the total number of FFA chains and calculated using the method of Sanchez et al. (2012) (257.45).

3.2. Preliminary investigations leading to the selection of reagents and conditions

Our efforts initially focused on attempts to produce the well established fatty acid methyl esters (FAMEs) with methanol (64.7 °C, 2 h, 10 wt.% DBSA) as alcohol, but the low boiling point of methanol, and its miscibility with water, led to the result that only 50% of the FFAs were converted to FAMEs. Surprisingly, switching to ethanol (79 °C, 2 h, 10 wt.% DBSA) only produced a 30% conversion of the FFAs, presumably due to the differences in reactivity of the two alcohols in water (Marchetti and Errazu, 2008). We therefore suspected that a more lipophilic alcohol, such as 1 butanol, would be highly compatible with the AFWS and produce a higher yield of butyl esters compared to the more hydrophilic alcohols such as methanol and ethanol.

AFWS 2 was reacted with 1 butanol and DBSA as catalyst (10 wt.%) at 80 °C and gave 90% conversion of the FFAs and glycerides into their corresponding FABLEs after only 2 h. DBSA has previously been reported to be an active catalyst for the *trans* esterification of triglycerides with methanol; however, Alegria et al. (2014) reported that upon addition of 5 vol.% of water to the reaction mixture increased the time for 100% conversion from 2 to 9 h. Our work suggests that by using a more hydrophobic alcohol such as 1 butanol, we can achieve high yields of FABLEs within 2 h despite having a significantly higher quantity of water present (20 wt.%). Despite the catalysis yielding a high quantity of FABLE, the reaction mixture remains a homogeneous stable emulsion even at the end of the reaction; therefore the isolation of the desired FABLEs would require either, the addition of organic solvents or reagents to break down the emulsion, all of which would make any potential industrial process unfeasible and costly.

Current technologies for performing dehydrative condensation reactions usually use a classic Dean Stark apparatus or the addition of molecular sieves to the batch reactor in order to remove/absorb the water produced from the condensation reaction performed within. Either technique would mean the addition of costly co reagents and/or solvents, both of which we wished to avoid. Thus we fabricated a novel reactor for performing the esterification of AFWS and 1 butanol to FABLE using DBSA as catalyst by combining a standard batch reactor with a drying chimney. In order to test our design we heated only the AFWS in our new reactor at 105 °C and found that all the water was removed from the material and a monophasic liquid produced after 3 h. At this point addition of the DBSA catalyst and 1 butanol, followed by a further 3 h of heating at 105 °C produced FABLE in 95%+ conversions. We then tested the "in situ" removal of the water whilst also converting the lipids into FABLE by combining the AFWS, 1 butanol and DBSA catalyst from the beginning. We found that a monophasic liquid was obtained after 3 h and conversion to FABLE were around 95%. The experimental plan was thus undertaken to optimize the reagent quantities necessary to obtain 95%+ conversions to FABLE using our new reactor and reaction conditions of 105 °C for 3 h. Thus the reactions for the experimental plan were performed at 105 °C where we presume that the water already present in the AFWS, and the water produced by the esterification reaction, would be removed by evaporation and subsequently trapped within the dry

ing chimney (Mouloungui et al.). The butanol, on the other hand, condenses in the drying chimney and returns to the reaction mixture, thus as the reaction precedes the water concentration of the reaction mixture decreases, whilst the concentration of butanol remains relatively constant allowing for high conversions to FABLE.

3.3. Results of experimental design

We sought to optimize our process using experimental design to calculate the optimum reaction process conditions for obtaining FABLE yields superior to 95%. Table 3 shows the range of calculated experimental non conventional Doehlert design parameters (Doehlert, 1970) with respect to DBSA loading and quantity of 1 butanol needed for optimization of the process, along with the corresponding experimental results in terms of % content of FABLEs and remaining FFAs. All reactions were performed in batch at 105 °C for 3 h. The four fold replicated centers (entries 7-10) all consistently give % FABLE contents between 91.4 and 93.1%, thus demonstrating the reproducibility of our system.

Applying determined coefficients in order to resolve the second order polynomial equation of the design gives

$$Y = 92.85 + 3.77X_1 + 6.15X_2 - 4.09X_1X_2 - 0.83X_1^2 - 5.70X_2^2$$

Substituting values of X_1 and X_2 into our mathematical model gives:

$$Y = 92.85 + 3.77((x_1/4.5) - (5.5/4.5)) + 6.15((x_2/0.45) - (1.55/0.45)) - 4.09((x_1/4.5) - (5.5/4.5))((x_2/0.45) - (1.55/0.45)) - 0.83((x_1/4.5) - (5.5/4.5))^2 - 5.70((x_2/0.45) - (1.55/0.45))^2$$

An *F* test and a Student's *T* test were used to check the statistical significance and suitability of the model. The *F* value (1.87) was less than the Fisher *F* parameter at the 95% confidence level (10.13), meaning that the mathematical model is a good fit with the experimental data set.

A graphical representation of the response surface for the selected variables (Fig. 1) shows the evolution of the conversion of FFAs into FABLEs in relation to the wt.% of DBSA catalyst and quantity of 1 butanol used. Unsurprisingly, and in agreement with similar reports in the literature (Leung et al., 2010; Bynes et al., 2014), the predicted conversion of FFAs increases with an increase in 1 butanol and DBSA catalyst applied. We sought to use the

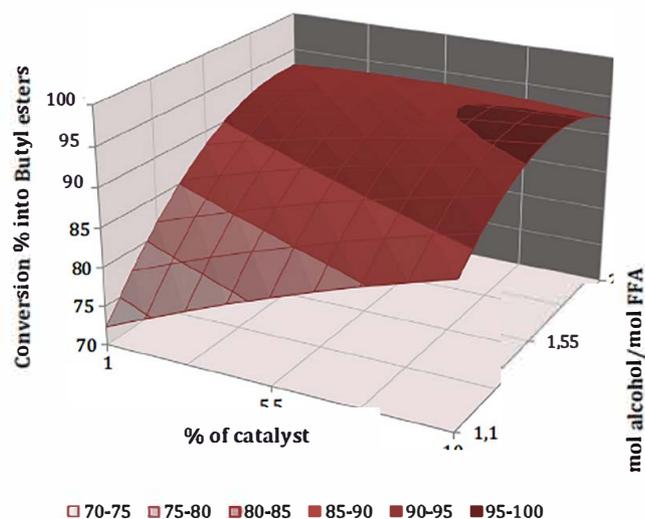


Fig. 1. Graphical representation of the surface response for optimization of % FABLE content versus 1-butanol quantity and DBSA loading.

graph in order to obtain the optimal quantities of DBSA and 1 butanol necessary to achieve 95% conversion of the lipids in ASFW 2. This should, in theory, give us a FAME content of our reaction mixture close to that of the FAME content currently required for biodiesel (96.5%, EN 14214). Thus using the graph gave an optimal DBSA catalyst loading of 10 wt.% with respect to the total weight of ASFW 2; and a molar ratio of 1.66 for 1 butanol with respect to the total FFA chains in ASFW 2.

Experiments performed under these optimized values gave FAME contents of 95.2% (for a 50 g scale reaction performed, as stated in Section 2.4), as well as two 800 g scale reactions (see Section 2.5) giving FAME values of 95.8 and 95.7%. These results validate the experimental design and the robustness of our system as we do not see a decrease or change in conversion of FFAs in AFWS 2 on increasing the scale of the reaction (17.8 g through to 800 g).

Once this mathematical model was validated by the experimental results it is now possible to use it as a method for determining the catalyst loading and amount of butanol necessary to achieve a specific FAME yield. For example, if the catalyst loading were to be rigorously fixed at 1 wt.% the model predicts that it is possible to achieve FAME yields of 90% with a butanol mole equivalence of 1.64 or higher. However, to obtain FAME yields close to that of the desired 95% or higher, a catalyst loading of 10 wt.% was necessary at a butanol loading of 1.66 mol equivalent according to our model.

The lipid profiles of the reaction mixtures (Fig. 2) suggests that the use of our specific reactor with DBSA and 1 butanol as alcohol is capable of transforming 90% of all the lipid material contained in AFWS 2 into FAMES. The only case where the % content of FAMES was less than 90% (entry 4) is where the 1 butanol content is close to stoichiometric (1.16 equivalent) with respect to the FFA chains in the AFWS 2. Whilst the 1 butanol content may remain too low to

achieve a higher conversion to FAMES, the glyceride material is completely hydrolyzed under the reaction conditions. The triglyceride (T.G.) content diminishes from 16.4% to 1.7% presumably due to hydrolysis by the 15.7 wt.% water content in AFWS 2; the temperature (105 °C); and the acidic conditions (DBSA). This advantageous phenomenon of our system and the nature of AFWS 2 mean that we can convert the glycerides and the FFAs within the raw material equally without inhibition of our catalyst or loss in conversion rates.

3.4. Production of FAME 1 butanol blend and FAMES as biofuels

FAME productions were performed on 800 g scales (see Section 2.5), using the same concept of reactor as for the smaller scale reactions. The reactor allows for the isolation of a monophasic liquid at the end of the reaction without needing excess solvents or co reagents. The FAME 1 butanol blend can be isolated by addition of Ca(OH)₂ (to neutralize and trap the DBSA) and filtration to yield a blend of FAME and 16.3% 1 butanol (25% of the initial 400 ml of 1 butanol added). A recent report in the literature has suggested that blending 1 butanol (up to 20%) with FAME based biodiesel produces a combustible fuel with similar emission and performance characteristics to that of the parent biodiesel fuel (Yilmaz et al., 2014). Blending alcohols, particularly bio ethanol with existing fossil fuel based petrol is already common practice and has been seen as a way to prolong the life of the ever dwindling fossil fuel reserves. As previously mentioned, butanol, especially bio butanol, is predicted to overtake bio ethanol as the alcohol of choice for a drop in fuels, as it can mixed at higher concentrations (up to 16%) and gives a higher energy output (90% cf. 70% for ethanol) (Jin et al., 2011).

Table 4 shows the fuel characteristics of the FAME 1 butanol blend and the FAME product in comparison to the current

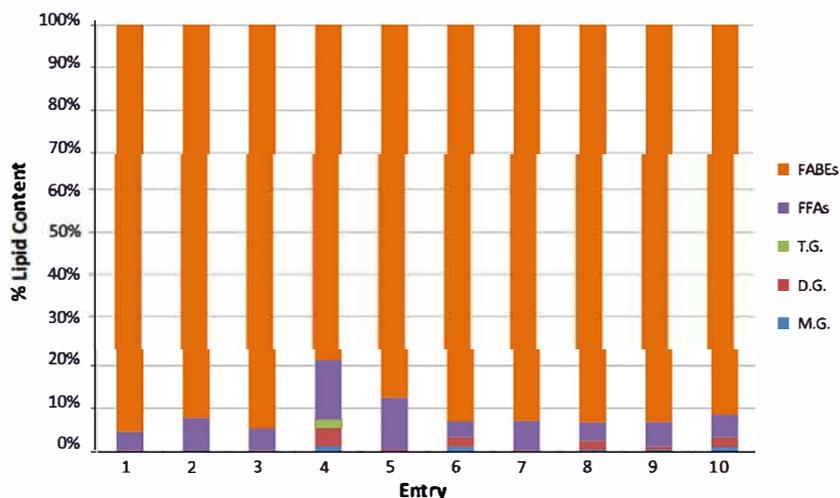


Fig. 2. Lipid profile of the reaction mixtures performed with DBSA catalyst and 1-butanol after 3 h at 105 °C.

Table 4
Fuel characteristics of FAME, FAME-1-butanol and other biofuels.

Fuel	Density @ 20 °C (kg m ⁻³)	Viscosity @ 40 °C (mm ² s)	Cetane number	Flash point (°C)	Reference
EU standards	860–900	3.5–5.0	>51	>120	EN 14214
Diesel	815	2.95	52	70	Knothe et al. (2003)
Biodiesel (FAME)	855	4.57	52	126	Knothe et al. (2003)
FAME (from soybean oil)	–	28.3	49	–	Yilmaz et al. (2014)
FAME (from sunflower oil)	–	30.6	33.4	–	Yilmaz et al. (2014)
FAME (from AFWS)	903.4	7.39	63.0	74.5	This work
FAME-1-butanol (from AFWS)	900.5	9.35	46.9	51.5	This work
Butanol	808	2.63	25	35	Knothe et al. (2003)

European legislation values of EN 14214, diesel, FAME based biodiesel, and two FABE products made from vegetable oils. The FABE product produced in this work from AFWS 2 has a cetane number higher than that of diesel, biodiesel or FABE made from vegetable oils. Due to the fact that AFWS 2 contained around 50% unsaturated FFA (40% oleic acid and 10% linoleic acid), the resulting FABE product has a cetane number more similar to that of butyl oleate (61.6). The cetane number for the FABE made from animal fats is considerable higher than that for the FABEs made from vegetable oils (Singh and Anbumani, 2011). This is unsurprising as animal fats contain a higher percentage of saturated FFAs compared to vegetable oils, and it is well established that the corresponding esters of saturated FFAs give higher cetane numbers compared to their unsaturated analogues (Knothe et al., 2003). In addition, the animal fat based FABE exhibits a flash point equivalent to that of diesel, but lower than that of FAME based biodiesel due to the presence of the butyl group.

The FABE 1 butanol blend exhibits both a lower cetane number and flash point due to the effect of the 16% butanol which causes these values to decrease as the butanol itself has a much lower cetane number and flash point value. The cetane number for the FABE 1 butanol blend, however, remains comparable to that of diesel and thus remains a potentially interesting blended biofuel.

4. Conclusion

Animal Fatty Wastewater Sludge 1 and 2 have been characterized and analyzed and determined to be highly variable in terms of their composition and quality. Due to the analysis AFWS 1 was determined to be too insufficient in terms of its lipid content to be considered for further transformation into a biofuel. AFWS 2, however, was converted by DBSA catalyzed esterification into FABEs and a FABE 1 butanol blend in good yields (95%+ of FFA chains converted). The optimal conditions for the esterification of AFWS 2 are 1.66 mol equivalent of 1 butanol, 10 wt.% of DBSA catalyst, and a temperature of 105 °C for 3 h. Our reactor fitted with a drying chimney allow for simultaneous transformation and water removal of the AFWS without the need of organic solvents or the addition of co reagents to the reaction mixture. After minimal post treatment we isolated two potential biofuels: A FABE 1 butanol blend, being a 16% blend of 1 butanol and FABE and, after further work up a FABE product. Both products show good potential as plausible biofuels as they contain high cetane numbers and flash point values, partly due to the high content of saturated FFAs present in the original fatty animal source, thus demonstrating further the potential of the currently unexploited AFWS as a bio source for novel biofuels. In conclusion, we have determined that if the raw material contains over 50% water (by weight) it is unfeasible to convert the AFWS in FABE based bio fuel due to the production costs of achieving the sufficient conversion and water removal. On the other hand, as long as the AFWS employed in the catalytic system contains no more than 50% water content, and that the remaining dry material constitutes at least 95% or more of lipids then it is possible to be converted into a FABE based biofuel.

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