

ENHANCED FATTY ACID GENERATION FROM MEAT PROCESSING DISSOLVED AIR FLOTATION SLUDGE

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ABSTRACT: The hydroesterification process is a two-stage biodiesel production process that integrates a hydrolysis step and an esterification step to circumvent the challenges of the high free fatty acid content and high moisture content of low-grade lipid sources. These challenges limit the feasibility of such low grade lipid sources as the feedstock for biodiesel production via the conventional alkaline catalysed transesterification process, due to unwanted saponification side reactions. The esterification step is normally completed efficiently. However, the high temperature and high pressure operating conditions and the concentrated mineral acid catalyst utilised in the initial hydrolysis step constitute major concerns, because a large mass of superheated steam, high pressure pumping systems, and expensive corrosion resistant equipment are required. This study therefore investigated the feasibility of an in-situ lipid hydrolysis of meat processing dissolved air flotation sludge to generate fatty acids. This in-situ lipid hydrolysis process was catalysed using a polystyrene sulphonic microporous resin to enhance fatty acid generation. Such an in-situ approach will enable the invention of a single step lipid extraction and lipid hydrolysis process that will bypass the need for preliminary drying and lipid extraction operations, with the lipid hydrolysis achieved under moderate conditions.

Keywords: Meat processing dissolved air flotation sludge; In-situ lipid hydrolysis; Polystyrene sulphonic microporous resin; Fatty acid generation.

1 INTRODUCTION

The commercialisation of hydroesterification biodiesel processes in the USDA and Biobrax plants in Brazil clearly demonstrates the maturity of the biodiesel production pathway as a suitable method that facilitates the utilisation of low grade lipid sources as biodiesel feedstocks [1, 2]. The hydroesterification process which integrates an initial hydrolysis step for producing fatty acids with an esterification process for the methylation of the generated fatty acids is however fraught with a number of challenges. These challenges are typically associated with the requirement for high pressure (50 bar) and superheated steam (260 °C) for lipid hydrolysis and the problems associated with the alternative introduction of a cocktail of concentrated mineral acids to catalyse the lipid hydrolysis reaction [3-5]. The highlighted challenges result in a highly capital intensive lipid hydrolysis process due to the required high pressure superheated steam and the required installation of expensive corrosion resistant reactors due to the highly corrosive concentrated mineral acid catalysts utilised [6, 7]. Environmental concerns also persist since the utilisation of concentrated acid mixtures to catalyse lipid hydrolysis reactions will also lead to secondary toxicity effects, thus requiring the incorporation of complex downstream neutralisation operations which will further increase operational costs [8].

The present study therefore seeks to circumvent these limitations by investigating the possibility of utilising a polystyrene sulphonic microporous resin, Dowex 50WX2 as a catalyst for the lipid hydrolysis reaction. Dowex 50WX2 is environmentally benign and is capable of catalysing reactions via H⁺ ion exchange under appropriate reaction conditions [9-11]. It is therefore hypothesised that Dowex 50WX2 possesses the capacity to catalyse lipid hydrolysis reactions via a so called 'in-situ' process, thus eliminating the need for preliminary energy intensive drying of the feedstock and lipid extraction operations and for additional energy intensive downstream separation and complex neutralisation

processes required by mineral acid catalysed lipid hydrolysis reactions. The selection of this specific polystyrene sulphonic microporous resin is also justified by its lower price relative to other resins and larger pore volume in the hydrated state relative to other commonly available ion exchange resins [12].

In this study, the high lipid and moisture containing dissolved air flotation sludge has been investigated as the low grade lipid source. This is because of the abundance of the waste stream, with previous work establishing the sustainability of the meat processing waste stream as a biodiesel feedstock [13]. In the present study therefore, the following research questions will be resolved:

- How do the major system parameters influence the in-situ lipid hydrolysis process?
- How effective is the polystyrene sulphonic microporous resin as a catalyst for enhancing fatty acid yield feasible from the catalysed in-situ lipid hydrolysis process?
- Can the 'exhausted' polystyrene sulphonic microporous resin be efficiently recovered and subsequently regenerated for reuse?

2 MATERIALS & METHODS

2.1 Materials

Bulk quantities of DAF sludge samples were acquired from a local meat processing plant according to the ASTM D-2013 protocol and subsequently dried using standard methods [14]. The lipid content of the dried DAF sludge and the average molar mass of the fatty acids of the DAF sludge lipid were measured to be 0.1298 kg-lipid/kg-dry sludge and 271.7 kg/kmol respectively, as described in Reference [15]. Hexane (labserve 99% purity, Dunedin), 95% ethanol and KOH pellets (Sigma-Aldrich chemicals, Auckland), diethyl ether, distilled water and commercially available polystyrene sulphonic microporous resin, Dowex 50WX2-100-200mesh (Sigma-Aldrich chemicals, Auckland), were utilised in the experiments.

2.2 Experimental procedure, Design of experiment and statistical analysis

In this study, the influence of the polystyrene sulphonic microporous resin load (m_{cat}), set reactor temperature (T), moisture content (wet basis) of the DAF sludge (W_{DAF}) and the reaction time (t), on the fatty acid (FA) yield (%) via the in-situ lipid hydrolysis of DAF sludge have been investigated using the central composite design (CCD) method [16]. These parameters have been selected, based on the previous researches in the area of lipid hydrolysis [17, 18]. In this study therefore, the four factors have been investigated by undertaking 29 experimental runs using a five-level rotatable central composite design (CCD). The central point of the design was replicated 7 times for the determination of the experimental error. Table I therefore summarises the coded and the actual levels of the process variables investigated in this analysis.

Table I: Coded and actual levels utilised in the CCD experimental method

Parameters	Coded and actual values for the levels for experimental design				
	low axial	low	centre	high	high axial
Levels	-2	-1	0	+1	+2
Set temperature (°C)	55	80	105	130	
Reaction time (h)	1	2	3	4	5
Mass of catalyst* (g)	0.125	0.250	0.375	0.500	0.625
Moisture content (%)	86	90	94	98	

Experimental investigations were not performed for the calculated high axial values for temperature and moisture content which have been determined to be 155°C and 102% respectively. This is because the upper thermal stability limit for Dowex 50WX2 is 150°C, implying that the influence of the resin on the reaction cannot be properly investigated at temperatures greater than 150°C [19]. Clearly a moisture content of 102% cannot be investigated since the value has no physical meaning. The exhaustive conditions of the values of the experimental runs based on a full factorial CCD design has been presented in Table II.

In the experiments, oven dried DAF sludge (0.5 g), was introduced to a batch reactor and the polystyrene sulphonic microporous resin load, moisture content and set temperature and reaction time were imposed according to the specified rotatable CCD experimental design runs shown in Table II. The batch reactor was a 0.5 L stainless steel autoclave reactor (Zhengzhou Keda, China), equipped with a Proportional-Integral-Derivative (PID) temperature controller and a J-type thermocouple. At the specified residence time, the in-situ lipid hydrolysis process was stopped by rapidly cooling the contents of the reactor and opening the reactor. The rapid cooling was achieved by passing cold water through the reactor internal cooling coil while simultaneously immersing the reactor vessel in an ice bath. The non-aqueous phase containing the fatty acids generated was

recovered using hexane. The hexane-oil mixture was subsequently dried to remove the hexane solvent leaving only an oil phase and the fatty acid yield (FA) determined titrimetrically using standard AOCS official methods, Cd 3d-63 [20].

Table II: The levels of the experimental parameters and the results of the experimental runs

Exp. No.	T (°C)	W_{DAF} (wt. %)	m_{cat} (g)	t (h)	FA (%)
1	105	94	0.375	3	35.59
2	105	86	0.375	3	52.33
3	80	98	0.5	4	60.70
4	105	94	0.375	3	35.59
5	80	90	0.25	2	66.98
6	130	98	0.25	2	29.31
7	130	98	0.5	2	41.86
8	55	94	0.375	3	46.05
9	105	94	0.375	3	36.11
10	105	94	0.375	3	35.59
11	130	90	0.5	4	41.86
12	130	90	0.25	4	39.77
13	130	90	0.5	2	50.24
14	105	94	0.375	3	36.11
15	80	98	0.5	2	71.17
16	80	98	0.25	2	25.12
17	80	90	0.25	4	32.97
18	130	90	0.25	2	23.03
19	80	98	0.25	4	12.56
20	105	94	0.375	3	35.59
21	105	94	0.625	3	87.92
22	80	90	0.5	4	75.36
23	105	94	0.375	3	35.59
24	105	94	0.125	3	25.12
25	130	98	0.5	4	32.97
26	105	94	0.375	5	32.97
27	80	90	0.5	2	83.73
28	130	98	0.25	4	23.03
29	105	94	0.375	1	41.86

Exp. No is the number of experimental runs undertaken in this study

3 RESULTS AND DISCUSSIONS

The fatty acid yield results of the experimental runs undertaken are presented in Table II. The statistically average independent effect of each operating variable on the fatty acid yield based on the experimental results is illustrated in Fig. 1. This figure will be extensively discussed in subsequent subsections.

3.1 Effects of the operating parameters on in-situ lipid hydrolysis

In Fig.1, Fig.1A shows the variation of the fatty acid yield with reaction time, at a moisture content of 94 wt.%, a set temperature of 105°C and a catalyst load of 0.375 g, respectively. It is seen that the fatty acid yield initially increases with the residence time. However a decrease in the fatty acid yield is observed as the residence time is extended beyond a so called optimum residence time condition. This observation is due to the reduction of the fatty acid product as a result of the splitting of the long chain fatty acid, which is a consequence of sustained heating.

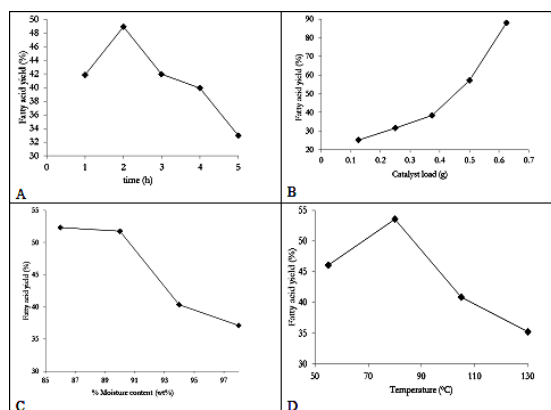


Figure 1: The statistically average independent effect of each operating variable on the percentage fatty acid yield.

Fig.1B shows the variation of the fatty acid yield with the catalyst load, at a moisture content of 94 wt.%, a set temperature of 105°C and a reaction time of 3 h. The results shown in Fig.1B suggest that the polystyrene sulphonic microporous resin has a favourably enhanced effect on the in-situ hydrolysis reaction of DAF sludge. This observation is expected since the amount of H^+ ions available for ion exchange increases with the mass of the resin.

Fig.1C shows the variation of the fatty acid yield with the moisture content, at a set temperature of 105°C, a reaction time of 3 h, and a catalyst load of 0.375 g. The results in Fig.1C show the negative effects of excessive moisture on the fatty acid yield. This suggests that, while catalyst hydration is crucial to the catalytic activity, excessive moisture is not advantageous, because of the reduced accessibility of protons which are crucial in catalysing the hydrolysis reaction. This reduced accessibility is due to increased competition of the hydroxyl (OH^-) group from the water molecules for the available protons necessary for ion exchange. Indeed previous researchers have reported the loss of catalytic activity (Bronsted-Lowry acids) due to the reduction of the available H^+ ions or Bronsted sites [21, 22].

Fig.1D shows the variation of the fatty acid yield with the set temperature at a moisture content of 94 wt.%, a reaction time of 3 h, and a catalyst load of 0.375 g. It is seen that an increase in the reaction temperature results in an initial increase in the fatty acid yield. The fatty acid yield however does not continue to increase with a further increase in the reaction temperature. Beyond an optimum temperature condition, the fatty acid yield decreases. This is due to the thermally induced splitting of the long fatty acids to shorter chain non-fatty acid molecules as the temperature increases or the heating time increases [23, 24]. Some authors suggested that the splitting of the long chain fatty acid is further enhanced by secondary oxidation reactions leading to the formation of free radicals that form dimers and other oxidation products such as epoxides [25, 26]. The results shown in Fig.1D therefore reinforces the need for moderate reaction temperatures in the in-situ lipid hydrolysis process of DAF sludge.

3.2 Maximum percentage fatty acid (FA) yield obtainable from the in-situ lipid hydrolysis using Dowex 50WX2.

The operating conditions for a maximum fatty acid yield were obtained using a fitted function of the

experimental fatty acid yield. These are: the reaction temperature of 92.5°C, reaction time of 1 h, DAF sludge moisture content of 92 wt.%, and resin catalyst load of 0.09216 wt. resin/wt. wet fresh DAF sludge. Under these conditions, a calculated value of 99.99% of the lipids present in the dry DAF sludge exists in the oil phase as fatty acids. The estimated conditions for the optimised fatty acid yield have been tested experimentally using the in-situ lipid hydrolysis experimental procedure described in section 2.2 above. Quadruplicate experiments were undertaken and an average value of the fatty acid yield was obtained. The fatty acid yield under the estimated optimum conditions, in the presence and absence of the resin, is presented in Fig.2.

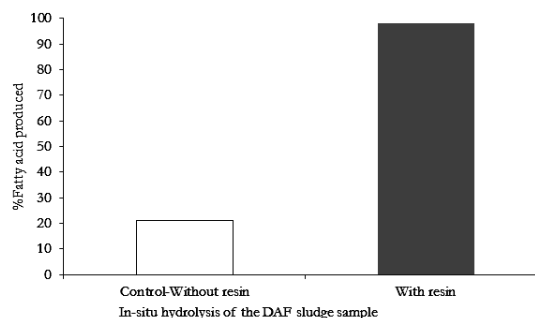


Figure 2: Comparative assessment of the fatty acid yield with and without the resin catalyst.

Fig.2 shows that in the presence of the microporous resin, a fatty acid yield of 98% of the original DAF sludge lipid content can be generated. The fatty acids production enhanced by the resin catalyst represents approximately a 5 fold increase, compared to fatty acid yield (21%) obtained under similar conditions in the absence of the catalyst. Thus utilising the DAF sludge feedstock as a low grade lipid source, the almost complete hydrolysis (98%) of all lipids present is feasible when the polystyrene sulphonic microporous resin was utilised.

4 RESIN RECOVERY FOR REGENERATION AND REUSE

In the present study, a 'layered-sieve' system schematically presented in Fig.3 was utilised. The separation system was built using Endecott meshes (Endecott, Australia) 60, 63, 230 and 300 which will enable the screening out of particles with diameters greater than 0.25 mm, 0.238 mm, 0.063 mm and 0.048 mm respectively.

The sieve of mesh 230 enabled the separation of most of the polystyrene sulphonic microporous resin beads with the recycling of the water sustained until no increments in the collected particles was observed on the sieve of mesh 230. Elemental analysis of the hydrolysed DAF sludge, after resin separation on the sieve of mesh 230 has been undertaken using a Carlo-Erba EA1108 elemental analyser (FISONS, Milan, Italy). This is to determine if any residual resin remain unseparated. From our calculations and elemental analysis, after multiple washes the dried DAF sludge-resin mixture still contained as much as 0.12 g of the resin/g of the dried DAF sludge-resin mixture, thus suggesting that the layered sieve method cannot be considered as a viable

method for comprehensive resin recovery for regeneration and reuse. It is therefore suggested that further investigations be undertaken to improve the catalyst recovery.

The recovered particles on the sieve of mesh 230 was subjected to a series of acid treatments and washes and the activity of the resin was measured. The activity (γ) of the resin is defined as the ratio of the FA acid yield obtained using the regenerated catalyst to the fatty acid yield obtained using the fresh catalyst. The results of several catalyst treatment steps are presented in Fig.4.

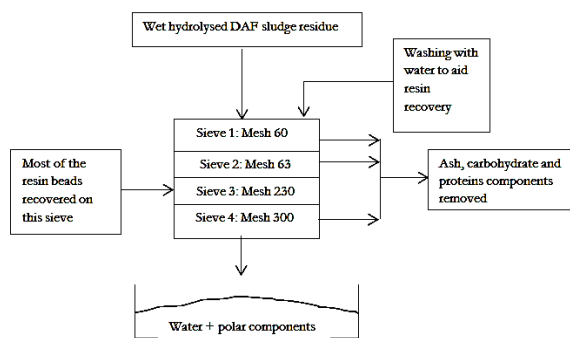


Figure 3: A low cost resin separation set up.

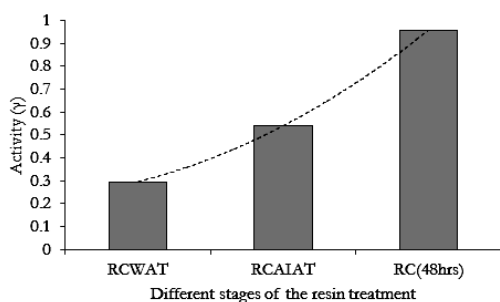


Figure 4: Activities of the catalyst at different levels of treatments.

In Fig.4, the RCWAT step represents the catalyst recovered without any acid treatment and washing. Without any treatment, the recovered catalyst was very dirty due to the presence of DAF sludge particulates. The RCAIAT step indicates the catalyst recovered with an initial acid treatment using H_2SO_4 of 2M concentration and the RC (48 h) step denotes the catalyst recovered after acid treatment using H_2SO_4 of 2M concentration for 48 h and washing treatment using distilled water. From Fig. 4, it is seen that prior to acid treatment the catalytic activity (30%) of the dirty recovered resin was very low. This is due to the combined effects of the resin poisoning and the fouling of the resin by dirt particles [27]. After an initial acid treatment followed by multiple washes using distilled water, most dirt particles and metallic sulphates generated in the displacement reaction between the H_2SO_4 and any metallic ions were removed, with the activity of the recovered resin improved to be 54%. Longer time (48 h) acid treatment and washes of the resin using distilled water resulted in a comprehensive recovery of the activity of the recovered resin to be 96%.

Our preliminary tests therefore suggested that it is possible to regenerate the polystyrene sulphonic microporous resin using combined acid treatment and

washing with distilled water. Crucially, the results also indicated that the meat processing DAF sludge in this investigation does not contain chemicals that leads to an irreversible poisoning of the polystyrene sulphonic microporous resin catalyst utilised in the in-situ lipid hydrolysis of DAF sludge.

5 CONCLUSION

In this paper, the enhanced generation of fatty acids from low grade lipids using a polystyrene sulphonic microporous resin catalyst has been investigated. It was demonstrated that the polystyrene sulphonic microporous resin, Dowex 50WX2, can serve as a suitable catalyst that enhances fatty acid production in an in-situ lipid hydrolysis process of low grade lipids present in meat processing DAF sludge. This work also demonstrated the sufficiency of moderate conditions of reaction temperature, pressure and reactor residence time of 92.5°C, 1 bar, and 1 h respectively, to facilitate a high lipid conversion to fatty acids of almost 100% under the action of the polystyrene sulphonic microporous resin catalyst.

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