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Glycerin Revalorization Using Anaerobic Digestion of Organic Waste

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A novel process for the revalorization of glycerine from biodiesel production is proposed. Glycerol is converted to short chain oils by reaction with volatile fatty acids. The volatile fatty acids can be obtained from anaerobic digestion of organic waste streams. It is shown that there is a minimum viscosity according to the oil chain length. Therefore the obtained short chain oils present viscosity values that make them useful as biodiesel additives increasing its lubricant properties. Listing some experimental results from literature, the process requirements are determined providing a maximum reaction rate to the desired volatile fatty acids, i.e. high substrate content and low acid content. A novel process satisfying these requirements with a low energy demand is provided. A frying potatoes factory is used as illustrative example.

1. Introduction

High dependence on fossil fuel has caused increase of carbon dioxide concentration in the atmosphere. The actual political trends are towards an increased use of renewable fuels. Biodiesel is one of the main products of the European bio-refineries. The main reaction involved in biodiesel synthesis produces large amounts of glycerol as by-product. The inclusion of a percentage of biodiesel in the commercial diesel has generated a large surplus of glycerol. As most of the nowadays markets for glycerol are already saturated, wide research is focused on the revalorization of glycerol as raw material (e.g. Da Silva et al, 2012) or for energy purposes, including the synthesis of biodiesel additives. The energetic valorisation by combustion is useful for any organic waste including glycerol. New processes available, involving high purity glycerol, avoid the generation of harmful combustion compounds. However, from the sustainability point of view, a residue valorization to a valuable chemical compound is preferable than burning it, as the combustion products cannot be used further as industrially useful raw materials and are usually disposed to the environment. A diesel additive has a higher added value than the energy of burning it alone. It is preferable a less degrading process, such as a partial combustion to syngas (Peres et al, 2010) useful to produce biodiesel raw material methanol, than a total combustion. Instead of high temperature combustion, glycerol can be converted to hydrogen or methane by microbial means. However, it is preferable to produce syngas, hydrogen or methane from a lower quality organic residue than from breaking down glycerol. On the other hand, glycerol can even be converted again to oils by yeasts producing 4.7 g of lipids for each 40 g of glycerol (Amaretti et al, 2012).

One feasible revalorization path, without breaking down or glycerol mass losing by microbial metabolism and growing, is the esterification with acetic acid to produce triacetin. The reaction of organic acids with glycerol can be catalyzed by supported sulphonic acids (Ladero et al, 2009). When a distillate water flow rate is collected according to the stoichiometry of the reaction, a total conversion to triacetin can be obtained by means of a reactive distillation column (Bonet et al, 2009, Hasabnis and Mahajani, 2010). Triacetin has been proved to be a good biodiesel additive (Casas et al, 2010). The use of methyl acetate instead of methanol in the biodiesel synthesis would avoid the glycerol generation (Casas et al, 2011).

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However, acetic acid has the main advantage over methyl acetate that it can be obtained by anaerobic acidogenic digestion of most agro-industrial waste streams or hydrolysis of lignocellulosic biomass. Acetic acid is also obtained as byproduct of some biological processes, e.g. the biotechnological processes can convert low grade residual streams to valuable compounds. The anaerobic process breaks down any organic residual stream first to short chain acids (acetic, propionic, n-butyric, iso-butyric, caproic, etc) and to methane when it proceeds further in anaerobic conditions. Therefore, methane is a low grade molecule. The use of short chain acids and glycerol to generate short chain oils provides the highest material use of residue streams.

The present study extends the glycerol revalorization to short chain oils mixtures (triacetin, glycerol trilactacte, glycerol tripropionate, glycerol tributyrate, glycerol triisobutyrate and glycerol trihexanonate) as biodiesel additives. The biotechnological processes must be adapted to each particular scenario, according to the bio-resources available and chemical compounds demand. In this study, the best short chain oils from the viscosity point of view are identified and some examples of volatile fatty acids obtained by anaerobic digestion are provided. However, the examples list can be extended as volatile fatty acids are also obtained as by products of many alcohols (e.g. Ferreira et al, 2012) and acids (e.g. Vlysidis et al, 2011) produced by biotechnological means. Finally, a snacks factory with residual vegetable oil and potatoes peels is presented as illustrative example.

2. Useful oils as biodiesel additives

The first diesel engine used by Diesel was powered by peanut oil, but the fossil oil was cheaper and the diesel engines evolved to be used with diesel from fossil oil. The nowadays diesel engines are not able to burn vegetable oil due to its high viscosity compared to diesel. The oils present good lubricity in the engine but the fuel atomization is affected by viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion and increased exhaust smoke and emissions. Most common vegetable oils have a number of carbons in the fatty acid chains typically ranging from C_4 to C_{22}, depending on the type of oil, although the most common lengths are around C_{18} (C_{16} to C_{22}). Although, some oils such as coconut oil or palm kernel oil are quite packed with fatty acids around C_{12}-C_{14} and their viscosities are still too high. Most vegetable oils are too viscous as diesel fuels, the shortest carbon chain oils can be taken into consideration. Casas et al (2010) proved that triacetin improves the properties of biodiesel, therefore the maximum quantity of triacetin (C_2) is limited in EU by the current law and not by technical reasons. The USA biodiesel standards would allow its inclusion. In the following paragraphs, some other short chain oils apart from triacetin (C_2) are shown to be good candidates in biodiesel formulation.

Figure 1 shows the viscosity values for glycerol and several oils of different carbon chain length at temperatures of 20, 40 and 60 ˚C. Notice that the viscosity scale is logarithmic. Although it is a quite short molecule, glycerol (C_0) has a very high viscosity due to the hydrogen bounds between the molecules. When the carbon chain enlarges, then the effect of the hydrogen bounds decreases abruptly and its viscosity depends mainly on the chain length. Therefore, between glycerol, which presents a high viscosity, and the large oil molecules with high viscosity, there are some oils that exhibit a minimum viscosity; these are the tripropionin (C_3) and tributyrin (C_4). Therefore, these two compounds are able to decrease the viscosity of biodiesel even more than triacetin (C_2), increasing its lubricity. As triacetin (C_2) is proved to be a good biodiesel additive, the compounds with a similar viscosity should be also useful as biodiesel additives, i.e. triisovalerin (C_5) or tricaproin (C_6). Although these short chain oils are rare in vegetable oils, the corresponding acids are easily generated by anaerobic digestion or hydrolysis of organic waste. Although tripropionin (C_3) or tributyrin (C_4) could be in large amounts in biodiesel, it would not affect negatively the biodiesel to too low viscosity values. The kinematic viscosity of tripropionin (C_3) and tributyrin (C_4) at 40 ˚C would be around 4.7 and 5.3 cSt, which is in the range of viscosities of rapeseed methyl-ester (4.4-5.7 cSt). Triacetin (C_2), which presents a slightly higher viscosity, has been proved to give good results in practice, in mixtures with biodiesel at any proportion (Casas et al, 2010).

Therefore, the short chain oils derived from volatile fatty acids mixtures would be useful as biodiesel additives, tripropionin (C_3) and tributyrin (C_4) being preferable due to the decrease of biodiesel viscosity. As the branched molecules freeze at a lower temperature than the linear ones, triisobutyrin is expected to be also a desirable biodiesel additive. Therefore, anaerobic digestion favouring the formation of propionic, tributyric and isobutiric acids is desirable, although the presence of other volatile fatty acids such as acetic acetic. Tributyrin (C_4) viscosity data from 0 to 60 ˚C from LBD (2013) can be adjusted to Eq(1).

$$v\left(mPa\cdot s\right)=21\pm 2\cdot e^{3.1\pm 0.1} \tag{1}$$

The reaction of glycerine with a mixture of volatile fatty acids will not generate only oils with the three chains equal. Instead, a large number of feasible combinations of three short volatile fatty acids are feasible. For instance, it could be obtained a butyric chain in one end, a propionic chain in the other end and an acetic in the middle. However, the overall proportion of the volatile fatty acids defines the properties of the additive.

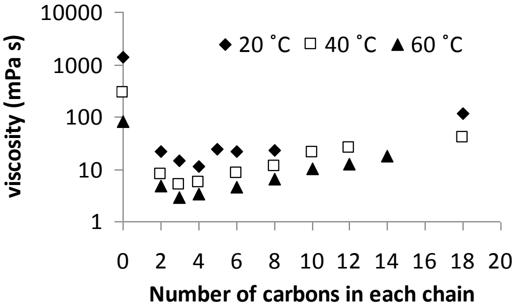

Figure 1: Viscosity of glycerol and several oils (LBD, 2013).

3. Anaerobic production of volatile fatty acids

Most of the studies on anaerobic digestion are focused on the production of methane or hydrogen and even on treating propionic acid instead of producing it; relatively few papers are focused on the production of volatile fatty acids (VFA). The VFAs production is attributed to anaerobic microorganisms such as Firmicutes of the genera Bacillus, Paenibacillus and Clostridium which growth can be promoted by a reactor packing (Bertin et al, 2010). The spectrum of organic acids produced is mainly a function of feed substrate composition and concentration and it changes along the time until the inhibition due to the acidification is reached. The ratio of valeric and isovaleric acids versus acetic acid increases when protein rich waste activated sludge is added to a primary sludge. The acetic, propionic, butyric and isobutyric acids are formed directly from the fermentation of carbohydrates, proteins and lipids, while the higher molecular weight VFAs are largely linked to the proteins fermentation. This means that the process must be modelled by each particular residue taking into account its concentration. The present section discusses several results from literature related to anaerobic acidogenic digestion of several organic waste residual streams to VFAs.

Table 1: Some anaerobic reactor experiments inputs to obtain volatile fatty acids

Waste	Temperature (K)	Residence time (d)	COD (g/L)	Source
Olive mill wastewater	288	1.3	17	Bertin et al (2010)
Waste activated sludge	298	5	10.95	Yuan et al (2011)
High strength molasses-based synthetic wastewater	328	1.5	10.2	Wijekoon et al (2011)
			16.1	
			23.9	
Secondary sludge	310	4-7	9.5	Rajagopal and Béline (2011)
Pre-treated sludge		4-7	9.5	
Pig slurry		0.5	9.5	
Cattle slurry 1		2	9.5	
Cattle slurry 2		2	9.5	
Glucose	308	1	30	Syngiridis et al. (2013)
			50	
			130	
			200	

Tables 1 and 2 show that a great variety of organic residual streams are appropriate for biodiesel additives production. Recently, Syngiridis et al (2013) have proposed the use of sugars anaerobic digestion as a simultaneous source of alcohols and VFAs for biodiesel production. However, the acids inhibit the microorganisms and relatively low concentrations of ethanol are achieved.

Therefore, the concentration of substrate must be kept high to promote the butyric and isobutyric acids and the acids formed should be continuously removed from the reaction media to avoid the inhibition of the reaction rate.

Table 2: Some anaerobic reactor experiments and the obtained volatile fatty acids

Waste	C2	C3	C4	iC4	C5	iC5	Ethanol
Olive mill wastewater	55.7	21.5	14.4	0	0	0	-
Waste activated sludge	41	28	17	0	12	0	-
High strength	43.2	41.2	8.2	0	0	0	-
molasses-based	42.9	44.2	7.1	0	0	0	-
synthetic wastewater	42.2	48.3	5.6	0	0	0	-
Secondary sludge	34.2	22.5	7.4	5.9	7.9	22.1	-
Pre-treated sludge	32.8	23.4	9.3	5.3	8.2	21	-
Pig slurry	37.2	21	20.6	9.5	0	11.7	-
Cattle slurry 1	46.6	17.6	11.4	2	5.4	17	-
Cattle slurry 2	46.4	9.8	5.6	2.8	0	35.4	-
Glucose	40.5	8.1	48.9	2.5	0	0	5.57
	73.8	0.7	22.9	0	0.8	1.9	4.9
	92.2	0.2	7.6	0	0	0	4.55
	78.2	0.1	13.2	0	0	8.4	33.1

4. Process proposal

Based on the available information previously discussed, a novel continuous process for glycerol revalorization is proposed (Fig. 2). An organic waste stream with a high concentration in substrate, at least 10 g/L, is fed to an anaerobic biological reactor. The high substrate concentration assures the formation of the desired volatile fatty acids (e.g. butyric and isobutyric acid), the remaining operating parameters should be optimized from an economic point of view according to the waste stream available. The reactor is followed by a decanter to eliminate the microorganisms generated by the biological reaction and purge the possible compounds that could get accumulated in the system. The recycle stream continuously removes the volatile fatty acids (VFAs) from the bioreactor to avoid the inhibition due to the acidification of the media. The VFAs, due to their acid nature, are efficiently retained in an adsorption column charged with a basic ion exchange resin.

Due to the basic character of the resin, the acids are efficiently retained meanwhile the aqueous substrate is recycled back. Resins with high basicity are most suitable for the acid removal applications from aqueous solutions since they yield high resin capacity utilization. The approaching of the break point of the resin could be easily detected by the increase of pH at the adsorption column. In order to continuously operate the system, two adsorption columns are required. While one column is on duty, the other is regenerating. To regenerate the column, glycerol can be used. The ion exchange resins act also as catalyst and glycerol is converted to monoglycerids, diglycerids and triglycerids. When the column is totally regenerated with glycerol, then monoglycerids and diglycerids, water and excess of glycerol are present in the product. As the short chain triglycerids are an additive to be mixed with biodiesel, the biodiesel could be used as liquid/liquid extractor of the short chain triglycerids, but the diglycerids also are extracted by the biodiesel. Moreover, a distillation column would be required to separate the water from non reacted glycerol. Therefore, a total regeneration of the resin is not desirable. The presence of high quantity VFAs adsorbed at the exit of the column assures the total conversion to triglycerides. The proposed process scheme is shown in Figure 2.

Therefore, using an organic waste stream, glycerol from the biodiesel synthesis is converted to short chain triglycerides useful to be mixed with biodiesel as additives, improving the biodiesel properties. As there is not any distillation used, the energy required by the process is very low. Notice that glycerol itself could be used as organic waste stream to produce the VFAs, but it is better to use a lower grade organic waste stream, i.e. a mixture of a large amount of chemical compounds usually is not useful as chemical reactant but it is useful as biochemical feed.

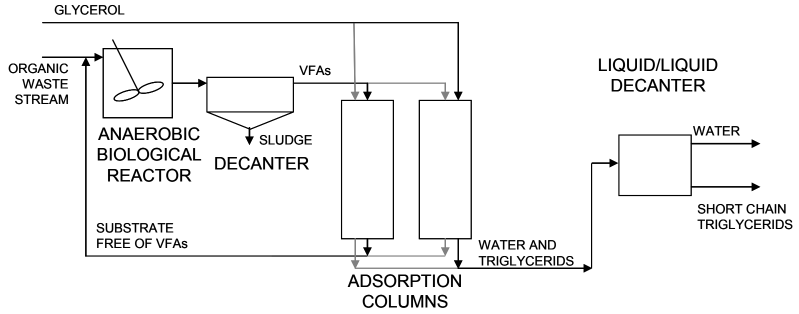

Figure 2: Process scheme for the revalorization of glycerine using an organic waste stream.

5. Illustrative example

The proposed process scheme is a general idea that needs to be fitted to each particular case, being required laboratory experiments. As a particular example, a process of frying potatoes is presented. The residual frying oil is a plausible source to produce biodiesel, and the potatoes peel is a plausible organic waste stream for the revalorization of glycerine. The experimental kinetic data of solid potato waste anaerobic digestion to VFAs is retrieved from Parawira et al (2004), which was performed at 37 ^{o}C using anaerobic sludge from a municipal wastewater treatment plant. When 1 kg of solid potatoes waste is mixed with 1 L of water, a solubilised substrate concentration 31.9 g/L results, having an equivalent formula of COH_2 for the substrate. The substrate reacts to form VFAs approaching a first order reaction with a molar kinetic constant of $2.74 \cdot 10^{-6}$ s^{-1}. A total solubilised substrate conversion is achieved due to the recycle stream, although the advance of the reaction in the bioreactor would be small. The process is calculated assuming a basis of 100 kg/d of residual potatoes. A higher concentration requires a smaller reactor volume, but higher flow rates are pumped (Figure 3). A higher composition of substrate in the reactor promotes a higher amount of isobutyric and butyric acids versus acetic acid and the required glycerol quantity decreases (Figure 4). Applying mass balances, 450 kg of potatoes produce around 100 kg peels which triturated generates 3.2 kg of substrate that are converted to VFAs. The VFAs react with 1.3 kg of glycerol, which comes from around 13 kg of residual vegetal oil converted to biodiesel.

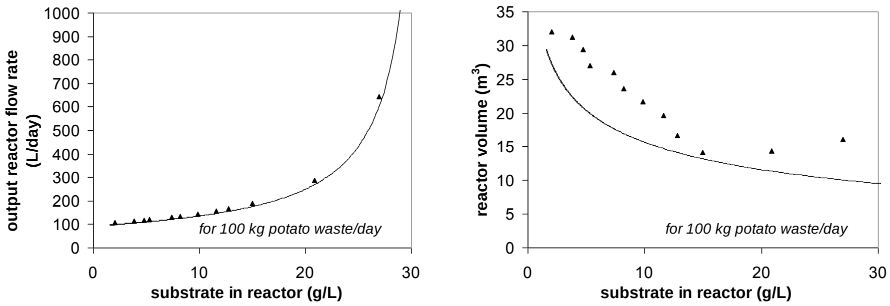

Figure 3: Reactor volume and flow rates versus the substrate concentration in the reactor.

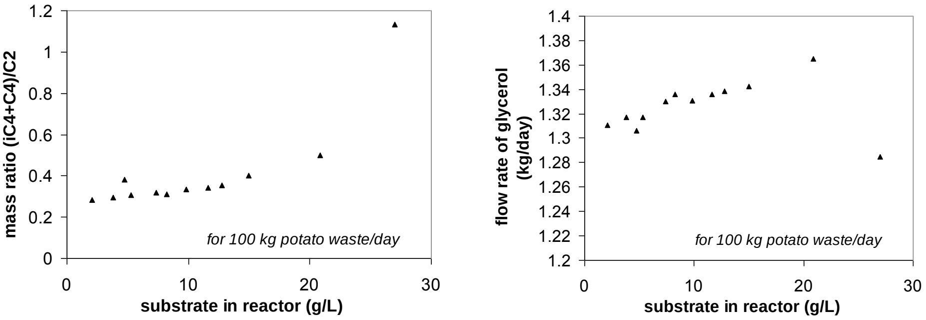

Figure 4: Product distribution for an anaerobic bioreactor behaviour for 100 kg/d potatoes waste.

6. Conclusions

The reaction of volatile fatty acids with glycerine collected from the biodiesel synthesis produces short chain oils useful as biodiesel additives. The volatile fatty acids can be obtained from anaerobic digestion of a great variety of organic wastes, preferably with low content of proteins. A rich substrate media with low acid content promotes the reaction rate to isobutyric, butyric and propionic acids, which produce the short chain oils more suitable as biodiesel additives from viscosity point of view. The volatile fatty acids produced in the bioreactor are separated by means of a basic exchange resin. The resin is regenerated using glycerol, producing water and volatile fatty acids, which can be separated by phase split. An illustrative example of frying potatoes process shows the above mentioned facts, but the process proposed should be fitted to each particular case according to the residual streams available. The future work is to verify experimentally the performance of the short chain oils in the biodiesel formulation in a diesel engine and find the optimal formulation.

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