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Properties and Sustainability of Biodiesel from Animal Fats and Fish Oil

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This work presents and analyses the fat and fuel properties and the methyl ester profile of biodiesel from animal fats and fish oil (beef tallow, pork lard, chicken fat and sardine oil). Also, their sustainability is evaluated in comparison with rapeseed biodiesel and fossil diesel, currently the dominant liquid fuels for transportation in Europe. Results show that from a technological point of view it is possible to use animal fats and fish oil as feedstock for biodiesel production. From the sustainability perspective, beef tallow biodiesel seems to be the most sustainable one, as its contribution to global warming has the same value of fossil diesel and in terms of energy efficiency it has the best value of the biodiesels under consideration. Although biodiesel is not so energy efficient as fossil diesel there is room to improve it, for example, by replacing the fossil energy used in the process with renewable energy generated using co-products (e.g. straw, biomass cake, glycerine).

1. Introduction

Currently dominant feedstocks for biodiesel production, in particular vegetable oils, are problematic as they are normally expensive and may have limited availability due to seasonal, social and economic constraints. Thus, there is strong interest in using lower cost feedstocks (Caetano et al., 2012) that do not interfere with important aspects of human societies and contribute to increase its role in sustainability. One interesting possibility is to use fatty residues from food processing or waste collecting systems, such as: spent coffee grounds (Caetano et al., 2013b), animal fats (Mata et al., 2011), fish wastes (Vilela et al., 2010), brewer's spent grains (Caetano el al., 2013a) among others, representing this an opportunity for waste valorisation. This study focuses on the usage of animal fats and fish oil for biodiesel production, analysing their properties and evaluating their contribution to sustainability in comparison with rapeseed biodiesel and fossil diesel, in order to determine which feedstocks are more adequate, and which issues need to be addressed to effectively use these abundant residues as fuel sources.

2. Materials and Methods

2.1 Animal fats and fish oil extraction

The animal residues were collected in slaughterhouses and food processing companies. They were melted, at around 110 ºC, to remove moisture (about 70 %) and separate the liquid fat (beef tallow, pork lard and chicken fat) from solids (gums, protein residues, and suspended particles) by percolation and filtering.
The fish's viscera and heads were collected at the local fish market. They were first cooked thoroughly in boiling water and the supernatant oil was placed in a separating funnel, where it was washed (with distilled water at 60 °C) and separated from water and solid particles. Then, the fish soapstock was squeezed to

release crude fish oil and separate it from the cake of fish dregs. Since this crude fish oil still contained some solid impurities, it was centrifuged and placed in a separating funnel to be washed as described above. Finally, the fish oil was vacuum filtered to remove any remaining impurities.

2.2 Biodiesel production and purification

Biodiesel was produced in stirred flasks operating in batch mode by alkali-catalysed transesterification, using KOH as catalyst and methanol. In a typical experiment 300 g of fat were weighed in a screw cap Pyrex bottle, with 500 mL of capacity, and placed in a thermostatic bath to heat the fat up to the reaction temperature (60 °C). Excess methanol was used in an approximated molar alcohol/oil ratio of 6/1. Around 3 g of KOH catalyst (p.a., Pronalab) were measured and dissolved in a closed cup in the required volume of absolute methanol (Pronalab), slightly warming and stirring the mixture. This operation took place in a hood for about 5 minutes (approximate methanol dissolution time). Then, the alcohol/catalyst mixture was added to the previously pre-heated oil and shaked vigorously in order to promote contact between the reactants. This bottle was placed in the thermostatic bath where the reaction took place for 2 hours at 60
°C and at 60 rpm of stirring speed. After completing the reaction time the flask was removed from the bath, and the mixture was allowed to settle for about half an hour in a separating funnel to remove the heavier glycerol phase, that was transferred to a previously weighed beaker to determine its mass.
The lighter phase (biodiesel) was subjected to distillation at 80 °C to recover the excess alcohol, and then placed in the separating funnel, where it was neutralized with hot water slightly acidified with concentrated phosphoric acid. The washing procedure was repeated several times using hot water until a clear phase was obtained with neutral pH. The purified biodiesel was placed in a beaker and about 2 g of diatomaceous earth was added to remove any water remaining in biodiesel. The mixture was stirred for about 15 min, after which biodiesel was left to stand, and then vacuum filtered through cellulose membranes (4-7 µm pore) to remove the diatomaceous earth. Finally biodiesel was stored in dark glass flasks for subsequent characterization.

2.3 Characterisation of animal fats, fish oil and biodiesel

Animal fats, fish oil and the corresponding biodiesels were characterized using the standard methods described in Table 1. In particular, for the animal fats and fish oil, the acid value, iodine value, kinematic viscosity at 40 ºC, density at 15 ºC, and higher heating value were determined. The resulting biodiesels were characterized following the EN 14214:2009 standard that defines the FAME quality requirements, in particular for the following parameters: acid value, iodine value, kinematic viscosity at 40 ºC, density at 20
ºC, water content, flash point, copper corrosion, CFPP, FAME content, and higher heating value (not an EN 14214 standard requirement).

Table 1: Standard methods applied for the animal fats, fish oil and biodiesel characterization

Parameter	Method
Acid value	Titrimetric method, ISO 14104:2011 standard
Iodine value	Titrimetric method with Wijs reagent, EN 14111:2009 standard
Kinematic viscosity	Glass capillary viscometers Cannon-Fenske Series 200, ISO 3104:1994
Density	Hydrometer method, EN ISO 3675:1998 standard
Water content	Karl Fischer coulometric titration, NP EN ISO 12937:2003 standard
Flash point	Rapid equilibrium closed cup method, ISO 3679:2004 standard
Copper corrosion	Copper strip test, ISO 2160:1998 standard
CFPP	Standardized filtration equipment, EN 116:2002 standard
FAME content	Gas chromatography (GC), EN 14103:2010 standard
Higher heating value	Oxygen bomb calorimeter, ASTM method D240-87

2.4 Sustainability evaluation

For the sustainability evaluation the methodology described by Mata et al (2013) was considered, in which the full fuel value chain is taken into account. Two sustainability indicators were selected for this study the life cycle energy efficiency (LCEE) and the contribution to global warming (GW) calculated as Eq (1) and (2), respectively. LCEE is the ratio of the total energy output, consisting of the energy content of the biofuel, plus that of byproducts only if they are used to supply energy to the biofuel production system, to the amount of energy expended to obtain the biofuel (dimensionless). The GW measures the potential contribution of different GHG emissions to global warming, expressed as equivalent CO_2 emission per unit energy of fuel product (kg CO_2-eq/MJ fuel).

$$Life\ Cycle\ Energy\ Efficiency(LCEE) = \frac{Total\ energy\ Output}{Total\ energy\ Input} \quad (1)$$

$$Contribution\ to\ Global\ Warming\ (GW) = \sum_i GWP_i \times E_i \quad (2)$$

where E_i is the mass of compound *i* emitted to the air and GWP_i is the global warming potential of the compound *i*, calculated as the net GHG emissions through the fuel life cycle.
For these indicators calculation, life cycle inventory data was obtained from literature for biodiesel from beef tallow (R-Power, 2013), fish oil (Ronde et al., 2010), rapeseed (Reinhardt and Jungk, 2001) and fossil diesel (Mata et al., 2013). It is assumed that there are no significant differences among the sustainability of animal fats (beef tallow, chicken fat and pork lard).

3. Results and Discussion

3.1 Fat and fuel properties and quality requirements

Tables 2 and 3 present the characteristics of the animal fats and fish oil and biodiesel produced from them, respectively, and Table 4 presents the FAME profiles for the several biodiesels obtained by gas chromatography.

Table 2: Animal fats and fish oil properties

Fat or oil property	Unit	Chicken fat[a]	Beef tallow[a]	Pork Lard[a]	Sardine oil[b]
Density at 20 ºC	kg/m^3	932	929	948	923
Kinematic viscosity at 40 ºC	mm^2/s	41.06	46.37	39.53	41.06
Acid value	mg KOH/g fat	0.56	1.07	0.63	0.56
Iodine value	g iodine/100 g fat	76.7	45.3	77.9	76.7
Higher heating value	MJ/kg fat	39.6	38.9	39.5	39.6
Average molecular mass	g/mol	856.1	846.6	860.0	873.7

(a) Mata et al., 2011; (b) Vilela et al., 2010

Table 3: Properties of biodiesels from animal fats and fish oil

Biodiesel property [a]	Chicken fat [b]	Beef tallow [b]	Pork Lard [b]	Sardine oil [c]	EN 14214 limits
Reaction yield (wt%)	76.8	90.8	91.4	89.5	–
Higher heating value (MJ/kg biodiesel)	39.4	40.0	39.9	39.7	–
Density at 15 ºC (kg/m^3)	883	870	872	886	860-900
Kinematic viscosity at 40 ºC (mm^2/s)	5.85	5.40	4.96	4.33	3.50-5.00
Water content (mg/kg)	1237	585	149	200	≤ 500
Iodine value (g iodine/100 g biodiesel)	76	45	76	163	≤ 120
Acid value (mg KOH/g biodiesel)	0.32	0.21	0.20	0.20	≤ 0.50
Group I metals ($Na^+ + K^+$) (mg/kg)	53.5	3.9	39.7	13.0	≤ 5.0
Copper strip corrosion (3 h at 50 ºC)	1B	1B	1B	1A	class 1
Flash point (ºC)	171	172	147	160	≥ 101
CFPP (ºC)	+3	+10	+5	-1	≤ +5 [d]

(a) Reaction conditions were: 6:1 Alcohol/oil or fat molar ratio; 2h Reaction time; 60 ºC reaction temperature, 1 % catalyst (KOH)/fat weight percentage; (b) Mata et al. 2011; (c) Vilela et al. 2010; (d) Limit for temperate climates.

With the exception of chicken fat, conversions to biodiesel of at least 90 % were obtained, showing that the transesterification reaction conditions were adequate. In this case an esterification pre-treatment was not needed, since as shown in Table 2, the acid value of all fats was below 1 mg KOH/g fat (corresponding to less than 3 % acidity) (Mata et al., 2011). Biodiesel density generally decreases with increased reaction time and temperature, and is lower as the biodiesel molecular mass is lower and its degree of unsaturation is higher (Mata et al., 2010). Table 3 shows no significant difference among biodiesel densities.
Biodiesel viscosity is another important parameter as it influences atomization and thus, the quality of fuel combustion in the vehicle engine. High viscosity values may promote the formation of deposits in the engine, reducing their efficiency and resulting in costly repairs. This is the main reason why fats and oils

are transesterified to biodiesel, to reduce viscosity by one order of magnitude. The kinematic viscosity of fats and oil is within 39 and 46 mm^2/s and that of the corresponding biodiesel within 4 and 7 mm^2/s (Tables 2 and 3). Generally, viscosity increases with the number of CH_2 moieties in the fatty ester chain (corresponding to larger molecules), and generally decreases with the increasing number of double bonds between carbon atoms in their molecules (Knothe, 2008), which is confirmed by the data presented in Table 4.

Table 4: FAME profile of some biodiesels from animal fats (in terms of relative weight percentage)

FAME relative percentage, wt%	C14:0	C16:0	C16:1	C17:0	C18:0	C18:1	C18:2	C18:3	C20:0	Others
Chicken fat [(a)]	–	34.8	–	–	4.9	44.4	14.2	1.7	–	–
Beef tallow [(a)]	9.2	30.1	–	–	17.1	38.3	4.2	0.6	0.4	–
Pork lard [(a)]	–	29.8	–	–	11.4	37.5	18.5	2.8	–	–
Sardine oil [(b)]	7.4	18.7	7.7	20.3	2.5	11.5	0.0	3.1	14.3	14.5

(a) Mata et al. 2011; (b) Vilela et al. 2010

The cold-filter plugging point (CFPP) is used to characterize biodiesel and determine its adequacy for usage at low temperatures. Biodiesel derived from animal fats generally has significant amounts of saturated esters, which leads to higher CFPP values when compared with biodiesel from vegetable oils, because those compounds have higher melting points, making it difficult or even impossible to use it in pure form during cold weather periods.

In Table 3, beef tallow methyl esters displayed very high CFPP value of 10 ºC, above the standard limit of 5 ºC, an indication that those fats contain large amounts of saturated fatty compounds, as shown in the FAME profiles of Table 4.

On the other hand, biodiesel of animal origin has positive properties, such as large values of heating value (HHV) and cetane number (CN) (Lebedevas et al., 2006). The heating value, or heat of combustion, is a measure of the energy available from the fuel. Generally, it increases with increasing chain length and decreases with increasing unsaturation. Although the heating value is not specified in the biodiesel standard EN 14214, the EN 14213 specifies a minimum heating value of 35 MJ/kg for using biodiesel as heating oil. The heating value of the various biodiesels is around 39-40 MJ/kg biodiesel, slightly lower than that of fossil diesel (45 MJ/kg diesel), but all above the minimum value given in the standard EN 14213.

The acid value of biodiesel indicates the presence of free fatty acid (FFA), which can have a significant effect on the fuel storage stability and thermal properties, as a high amount of FFA corresponds to a more reactive fuel, with more potential to oxidize and corrode the engine metal components (Mata et al., 2010). However, the acid values in Table 3 are all below the standard limit of 0.50 mg KOH/g biodiesel.

The copper strip corrosion test is used for detecting the potential corrosiveness of biodiesel, as corrosion affects the metallic materials in contact with the fuel, particularly the engine components and the storage and maintenance equipment (Mata et al., 2012). Table 3 shows the lowest level of corrosiveness for all cases, meaning that corrosion is not a problem.

The alkaline metals (potassium and sodium) concentration should be below the standard limit of 5.0 mg/kg, as their presence is related to the possibility of formation of metallic soaps or abrasive solids that can clog filters and injectors in the vehicle's engine. Table 3 shows a higher concentration of these metals in several biodiesels, which can be reduced by improving the purification step (Mata et al., 2012).

Concerning the water content, during water washing and storage biodiesel can absorb a certain amount of water leading to the presence of moisture, which should be limited as much as possible. The presence of water in biodiesel can cause problems in cold climates and increases the risk of microbial proliferation in the engine that will clog engine filters. Table 3 shows for some biodiesels (chicken fat and beef tallow) a water content higher than the standard limit (500 mg/kg) that may be due to an incomplete drying step.

The flash point is one of the most important advantages of biodiesel relatively to fossil diesel, as biodiesel has higher flash point, resulting in safer storage, handling and transportation. Yet, it also depends on how much of the excess methanol used in transesterification is removed during the final biodiesel purification. All biodiesels' flash points are much above the minimum standard limit (101 ºC), meaning that the distillation step was effective and independent of the specific chemical composition of the residual fats.

The iodine value is a measure of the unsaturation degree, and gives an indication of the biodiesel oxidative stability. Unsaturated compounds contain molecules with double bonds, which are very reactive toward iodine, and give a measure of the reactivity with oxygen. The higher the iodine value the more reactive, less stable, softer, and more susceptible to oxidation and rancidification is the fat or biodiesel. Although unsaturated esters (especially polyunsaturated) have reduced oxidative stability, undesirable for a diesel fuel, they have lower melting points, desirable to improve biodiesel low-temperature properties

(Knothe, 2008). Normally biodiesels from animal fats have lower iodine value and lower degree of unsaturation than biodiesels from vegetable oils (Mata et al., 2010). Table 3 shows that iodine values of biodiesel from animal fats, with the exception of sardine biodiesel, are below the maximum standard limit (120 g iodine/100 g biodiesel). It was expected that the iodine value of sardine biodiesel was also below this limit, because the sardine oil has a much lower Iodine value and its FAME profile has the largest relative amounts of saturated fats. Yet, the FAME profile has also the largest relative amount of other components, and that may have contributed to this result. However, as those compounds were not identified, more experiments are needed to identify the real culprit. For the remaining residual fats the rule holds true, as beef tallow has the lowest iodine value and the largest percentage of saturated esters. Most biodiesels from animal fat are mainly comprised of C16:0 and C18's FAME, but sardine oil biodiesel presents a lower percentage of C16:0, a very low percentage of C18:0 and C18:2 and a significant amount of C17:0, C20:0 and others.
Among unsaturated esters, special attention should be given to linolenate (C18:3) with a maximum standard limit of 12 % (w/w). This is verified by the biodiesels FAME profile in Table 4. Verification of the linolenate standard limit is relevant because this ester is more susceptible to oxidation, and has a lower cetane number than other esters (i.e. lower tendency to ignite and more difficulty to combust).

3.2 Biodiesel sustainability evaluation

Table 5 presents and compares the sustainability evaluation of biodiesel from beef tallow and fish oil with rapeseed biodiesel and fossil diesel.

Table 5: Sustainability evaluation of biodiesel from beef tallow, fish oil and rapeseed and fossil diesel

Outputs/ Inputs/ Indicators	Beef tallow biodiesel[(a)]	Fish oil biodiesel[(b,e)]	Rapeseed biodiesel[(c)]	Fossil diesel[(d,e)]
Energy (MJ/MJ biofuel):				
- Farming/ Cultivation	-	-	0.62	-
- Rendering/ Pressing/ Extraction	0.35	0.43	0.14	0.06
- Transesterification/ Refining	0.12	0.06	0.19	0.10
- Fuel energy output	1.00	0.99	1.00	1.13
GHG emissions (kg CO_2 eq/MJ biofuel):				
- Farming/ Cultivation	-	-	0.06	-
- Rendering/ Pressing/ Extraction	0.02	0.04	0.01	0.01
- Transesterification/ Refining	0.01	0.01	0.01	0.01
- Tailpipe emissions[(d)]	0.07	0.07	0.07	0.09
- CO_2 sequestration	-	-	0.07	-
Sustainability indicators[(e)]:				
- LCEE (dimensionless)	2.11	2.04	1.05	7.03
- GW (kg CO_2-eq/MJ biofuel)	0.10	0.12	0.08	0.10

(a) R-Power, 2013; (b) Ronde et al., 2010; (c) Reinhardt and Jungk, 2001; (d) Mata et al., 2013; (e) This study

Results show a LCEE above the unit for all biodiesels, meaning that their production is energy viable, although they are still far from fossil diesel that presented the best value. This is because the petroleum refining process is already highly optimized and energy integrated. The biodiesel process can also follow the same principle, according to the biorefinery concept, using for example the co-products (straw, biomass cake and glycerine) as energy sources in the process. Also, the heat capacity of fossil diesel is higher than that of biodiesel, which gives it a higher fuel energy output.
The LCEE of rapeseed biodiesel is lower than that of animal and fish wastes. Rapeseed needs to be cultivated and harvested, each of these steps involving energy. For residual fats farming is not considered as an energy consumption step since its purpose is meat production for human food and not for biofuel. Thus, there is only energy consumption for rendering the animal wastes and for the transesterification steps. However, in terms of GW, rapeseed biodiesel is advantageous over animal and fish biodiesels because there is CO_2 sequestration by plants during their growth which compensates for the tailpipe emissions during the fuel combustion.

4. Conclusions

This study analyses the fat and fuel properties of biodiesel from animal and fish wastes, and evaluates their sustainability in comparison to rapeseed biodiesel and fossil diesel. Results show that biodiesel properties such as density, flash point, heat of combustion, acid value and copper strip corrosion depend on the type of waste fat, in particular on its esters profile. Important fuel properties that can be estimated

by the esters profile of a biodiesel are the oxidative stability, low-temperature properties, and kinematic viscosity. Relatively small amounts of minor components (e.g., linolenate and some contaminants) can have a significant effect on the fuel properties (especially on the oxidative stability and low-temperature properties). Beef tallow and sardine oil biodiesels seem to be the best waste fat options to be used alone, even though there may be some problems such as iodine value or CFPP. Nevertheless, a possible blend of these fats may result in a biodiesel that fully complies with the EN 14214 standard, as there might be compensation effect. An efficient conversion of animal and fish wastes to biodiesel must take into account the differences between them, and more studies are necessary to identify the optimal operation conditions, in particular for the transesterification reaction and potential pre and post treatment steps. Regarding sustainability considerations, from the biodiesels under consideration, Beef tallow biodiesel seems to be the most sustainable one, as its GW value is the same as the one of fossil diesel and the LCEE is the highest of the biodiesels under consideration.

References

Caetano N.S., Moura R.F., Meireles S., Mendes A.M., Mata T.M., 2013a, Bioethanol from Brewer's Spent Grains: Acid Pretreatment Optimization, Chemical Engineering Transactions, 35, 1021-1026.

Caetano N.S., Silva V F.M., Melo A.C., Mata T.M., 2013b, Potential of Spent Coffee Grounds for Biodiesel Production and Other Applications, Chemical Engineering Transactions, 35, 1063-1068.

Caetano N.S., Silva V.F.M., Mata T.M., 2012, Valorization of coffee grounds for biodiesel production, Chemical Engineering Transactions 26, 267-272, DOI: 10.3303/CET1226045.

Knothe K., 2008. "Designer" Biodiesel: Optimizing Fatty Ester Composition to Improve Fuel Properties, Energy & Fuels, 22, 1358-1364.

Lebedevas S., Vaicekauskas A., Lebedeva G., Makareviciene V., Janulis P., Kazancev K., 2006, Use of waste fats of animal and vegetable origin for the production of biodiesel fuel: Quality, motor properties, and emissions of harmful components, Energy Fuels, 20, 2274-2280.

Mata T.M., Caetano N.S., Costa C.A.V., Sikdar S.K., Martins A.A., 2013. Sustainability analysis of biofuels through the supply chain using indicators, Sustainable Energy Technologies and Assessments 3, 53- 60.

Mata T.M., Cardoso N., Ornelas M., Neves S., Caetano N.S., 2011, Evaluation of two purification methods of biodiesel from beef tallow, pork lard, and chicken fat, Energy Fuels, 25, 4756-4762.

Mata T.M., Sousa I.R.B.G., Vieira S.S., Caetano N.S., 2012, Biodiesel production from corn oil via enzymatic catalysis with ethanol. Energy Fuels, 26, 3034–3041.

Mata, T.M., Cardoso, N., Ornelas, M., Neves, S., Caetano, N.S., 2010. Sustainable production of biodiesel from tallow, lard and poultry fat and its quality evaluation. Chemical Engineering Transactions 19, 13- 18. DOI: 10.3303/CET1019003.

Reinhardt G.A., Jungk N.C., 2001, Pros and Cons of RME versus conventional diesel fuel. In: Bartz W. J., ed., Proceedings of the 3rd International Colloquium Fuels 2001, 17-18 January 2001, Ostfildern, Technische Akademie Esslingen, 247-256, Ostfildern.

Ronde H., Ranne A., Pursiheimo E., 2010, Integrated Renewable Energy Solutions for Seafood Processing Stations, The Technical Research Centre of Finland VTT, Finland. Accessed 10/11/2013 at http://www.enerfish.eu/uploaded/downloads/downloads_5.pdf

R-Power, 2013, Life Cycle Analysis of the R-Power Tallow Biodiesel Fuel Pathway. Accessed 10/11/2013 at: http://www.arb.ca.gov/fuels/lcfs/2a2b/apps/rpw-rpt-121511.pdf

Vilela L., Mata T.M., Caetano N.S., 2010, Biodiesel Production from Fish Oil with High Acidity. In: Third International Symposium on Energy from Biomass and Waste (Venice 2010), November 8-11, Venice (Italy), Paper 322.