WASTES

solutions
treatments
opportunities

III

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The Wastes Selected Papers Series presents the latest theoretical research and innovative technologies and techniques in the waste field, as well as tools and strategies to improve corporate environmental performance.

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The potential of biodiesel production from WWTP Wastes

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ABSTRACT: The biofuel incorporation in fossil fuels is a measure that promotes energy sustainability and reduction of fossil fuels dependency. The European Union established a target of incorporating 14% renewable energy in the transport sector by 2030. The biodiesel is one of the most widely used biofuel in Europe mainly from vegetable oils. Land use to grow biodiesel feedstock may have negative environmental impacts. It is necessary to look for an alternative feedstock for biodiesel production that consider the sustainability, and which can contribute to the decarbonisation. The wastewater contains fat, oil and grease (FOG) that can be used in the biodiesel production to reduce the carbon footprint and to promote the circular economy. This work analyses the potential of biodiesel production from FOG collected in WWTP. Considering the quantity and quality of FOG separated, it can be verified that this may be an important alternative feedstock for biodiesel production.

1 INTRODUCTION

Oil and grease (O&G) can be found in wastewater and they need to be removed in wastewater treatment plants (WWTP) by a separation process. The storage can release odours to the atmosphere and the final treatment of this fraction is still a problem for the WWTP management. The floating mixture, scums, composed of inert and fat oil and grease (FOG) is removed for a storage device and seldom go for a specific treatment at WWTP. For many wastewater treatment facilities, FOG and scums, preceded or not by a concentration step, are mixed and treated with activated sludge in an anaerobic digestion process. Other wastewater treatment facilities will treat FOG and scum as a waste product, either incinerating it or sending it to landfill.

These solutions, apart from the incorporation of the FOG and scums in the anaerobic digestion, represent economic costs which include transportation, energy (pumping and aeration), labor, storage and final destination. Regarding the incorporation of FOG and scums into the solid phase treatment line, although the economic costs may be relatively small but present disadvantages. The presence of FOG in the affluent to anaerobic processes can be a problem for two reasons: inhibition of methanogenesis by long chain fatty acids and sludge flotation due to hydrophobicity and lower specific mass of these compounds in relation to water. The inhibition of methanogenesis may be associated with the adsorption of long chain fatty acids on the cell wall or membrane of the organisms responsible for methanogenesis, interfering with the functions of substrate transport. To maintain a stable operation of an anaerobic treatment system and promote the degradation of FOG a loading of less than 1.0 kg $m^{-3} d^{-1}$ is needed (Tchobanoglous et al. 2014). Moreover, to the drawbacks of FOG and scum incorporating into anaerobic digestion, in a recent work, Kumar et al. (2019) suggests that scum to biodiesel was 9.6 times more energetically favorable than scum to methane.

New sources of O&G to produce biodiesel are one of the challenges nowadays to avoid reduce greenhouse gas emissions from diesel, so the reutilization of the FOG waste separated at WWTP to produce biodiesel is extremely interesting. The potential of this waste as a raw material should be evaluated.

To reduce greenhouse gas emissions and dependence on fossil fuels and promotes energy sustainability, the European Union established in the Renewable Energy Directive a target of introducing 10% renewable energy (such as biodiesel) in the transport sector by 2020 (Directive 2009/28/EC) and increased the percentage to 14% in the revision of this Directive in 2018 (Directive (EU) 2018/2001).

Biodiesel is considered one of the best solutions as an additive to the diesel to reduce the CO_2 emissions and particles to the atmosphere.

Biodiesel can be used directly in the vehicle at 100% or mixed with diesel. Its biodegradability, non-toxicity and being free of sulfur and aromatics makes it advantageous over the conventional petrol diesel. It emits less air pollutants and greenhouse gases. In addition, it is safer to handle because it is less toxic and easy to store than petroleum (Gebremariam & Marchetti, 2018). However, despite these environmental advantages, biodiesel cannot be extensively applied as a complete substitute fuel for conventional diesel. The main reason is its higher cost of production, which is about one and a half times more expensive than petroleum diesel fuel. The reasons are the price of raw materials and the high cost of production.

Biodiesel is a mixture of fatty acid alkyl esters (FAME) that can be produced from different lipid feedstock or alcohol with or without the presence of a catalyst (Abdullah et al. 2017). Depending on the nature of the lipid feedstock the reaction is called transesterification or esterification (Diamantopoulos et al. 2015). The selection of an appropriate catalyst to the type of reaction and the lipid feedstock depends on the amount of free fatty acids in the oil (Abdullah et al. 2017; Diamantopoulos et al. 2015), and can be homogeneous (acid or base) or heterogeneous (acid or base, or enzymatic).

Vegetable oils, edible or non-edible, are the main source of biodiesel, according to a review carried out by Sajjadi et al. (2016). The same authors indicate that more than 95% of the world biodiesel is produced from edible vegetable oils, being rapeseed (84%) the main source of edible oil, followed by sunflower (13%), palm (1%), soybean and others (2%). The most commonly used edible oil in EU Member States is rapeseed oil (70.2%), but oil from soybean (5.8%), palm (5.0%), are also used (Ecofys, 2014). The use of raw material waste like animal fat waste (Kirubakaran & Selvan 2018), waste cooking oil from the restaurant industry (Abed, et al. 2018), microalgae (Chen et al. 2018a, Shomal et al. 2019) have been extensively investigated. Biodiesel production from wastes like cooking oil or animal fats is gaining a foothold, and more capacity is expected in the coming years. In European Union 11.4% of biodiesel is produced from cooking oil and 4.6% from animal fat (Ecofys, 2014). The increased demand for animal fats to produce biodiesel has resulted in the price of animal fats increasing significantly and there are also difficulties in obtaining the enough waste cooking oil to ensure production based on this waste source.

A life cycle assessment and economic analysis of the scum-to-biodiesel done by Mu et al. (2016) shows that the technology provides great benefits to the environment by reducing fossil resource depletion, CO_2 emissions, and N and SO_2 discharge to the environment. When comparing the impact of biodiesel from scum to conventionally produced biodiesel from soybean and vegetable oil, scum as a feedstock has less environmental impacts per kg diesel produced in all impact categories, fossil fuel use, GHG emissions, eutrophication, and acidification.

The aim of this study was to evaluate the potential of biodiesel production from scums and FOG removed in Portuguese WWTP. Extraction of FOG from the separated fraction was studied in Portugal by extraction the raw material for the biodiesel production and produce biodiesel using this O&G source.

2 MATERIALS AND METHODS

2.1 *Chemicals*

Methanol, *n*–Hexane and sulfuric acid were purchased from Panreaç (Panreac, Portugal) and sodium hydroxide was purchase from Merck (Merck, Portugal).

2.2 *Solid sample collection in WWTP and FOG extraction*

The area selected for this study is in the metropolitan area of Lisbon (Lisbon and Setúbal districts), where an important populated and industrialized region is responsible for the existence of several wastewater treatment plants. Ten WWTP were selected and all the WWTP are activated sludge processes, with exception to WWTP n°8 which is a biofiltration process. All the WWTP have aerated channels for the FOG waste removal, with exception of WWTP n°5. Total annual solid waste fraction collected in degrease separators (ton/year) was kindly provided by WWTP management.

Wet solid samples were collected in PET bags and preserved at +4°C. Samples were homogenized and dried in an oven at 100°C. This dried fraction was then used for FOG extraction and to determine the inert and non-oil fraction.

The extraction of FOG was carried out by soxhlet, where 3.0 g of sample were extracted with n-Hexane for 3 h. Extracts were concentrated under vacuum at 69°C with a rotary evaporator. The FOG extract was completely dried in an oven at 50°C and the mass of FOG was measured. The FOG extract previously pre-treated with an extraction step as clean-up process was then used for the biodiesel production. The extraction was carried out in duplicates.

2.3 *Biodiesel production process*

The acid or basic catalysis selection for the transesterification reaction was defined according to the acid value determination of the FOG extracts. The acid value determination was carried out according to the ASTM D 6751-08 standard. Acid value of the extracts less than 4 mg g^{-1} KOH suggests that the transesterification should be under alkaline catalysis, if higher the catalysis should be acidic (Nair et al. 2012). FOG extracts of the WWTP separators were in the range of 7 to 15 mg g^{-1} KOH so the transesterification reaction was catalyzed under acidic conditions for the biodiesel production from WWTP FOG extracts.

The acid catalyzed process was carried out by taking a WWTP FOG extract sample and dilute with n-Hexane in the proportion of 1:20 (w/w), adding 20 times of stoichiometric amount of methanol and 3.6% (w/w) of sulfuric acid and leaving the mixture to react for 1 h at 65°C (Wang et al. 2006). Then, excess of methanol was recovered under vacuum at 50°C with a rotational evaporator, and the mixture was left to settle for separation into two layers. The upper oil layer was the FAME mixture of biodiesel and some unreacted triglyceride, and the down layer was sulphuric acid and glycerol. After this period, the mixture was transferred to a settling device to separate the biodiesel of the glycerin and the pH of the biodiesel fraction was neutralized with NaOH. The biodiesel was washed by 10% of water at 80°C to remove soap which was produced by reaction of the alkali and the free fatty acid (FFA). The wet biodiesel was dried under vacuum at 70°C with rotational evaporator for 1 h.

3 RESULTS AND DISUSSON

3.1 *FOG recovered in the WWTP*

The solid waste removed in the WWTP degrease system was composed of wastewater, inert material and FOG. Combining the information of reported annual solid waste fraction collected in degrease separators with the percentage of FOG found in these samples (black dashed line), Figure 1 was constructed. As seen in Figure 1, in some WWTP the total solid removed was mainly FOG (e.g.

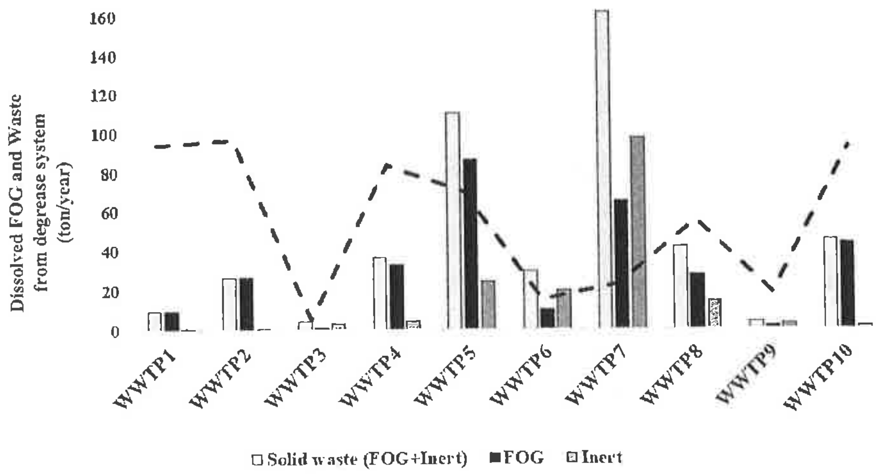

Figure 1. Total amount of FOG recovered from the solid waste in the degrease system (t.y^{-1}). Black dashed line is % of FOG in the solid waste recovered from the WWTP separator.

WWP 1, 2, 4, 5, 8 and 10) and in others only a little fraction of FOG was found suggesting that these WWTP were not interesting sources of FOG for biodiesel production (e.g. WWTP 3 and 9).

In the ten WWTP, it is possible to recover 469 ton per year (dry weight) of total solid where 303 ton per year correspond to FOG and only 166 t y^{-1} to inert material.

At least in seven WWTP, the total solids are composed mostly by FOG (e.g. WWTP 1, 2, 4, 5, 7, 8 and 10). The FOG and water content of the WWTP 3, 6 and 9 suggests that the separation system is less efficient. A large amount of wastewater is present in the sample, so it contains a very little percentage of FOG.

The FOG percentages found were higher than 80% for five of the ten WWTP studied (e,g 1, 2, 4, 5 and 10). The potential source of FOG collected in the degrease separators of WWTP can give an important source contribution for biodiesel production when compared with other sources. The amount of FOG found WWTP degrease separators in this study was higher than the one found in grease trap waste (GTW) (Almeida et al. 2016, Hums et al. 2016, Montefrio et al. 2010), or in other WWTP wastes like sewage sludge (Chen et al. 2018b, Demiirbas 2017, Melero et al., 2015, Pastore et al., 2013) or in scum from other systems (Almeida et al. 2016, Anderson et al. 2016a, b, Anderson et al. 2018, Bi et al. 2015, Bitonto et al. 2015, Kumar et al. 2019, Pastore et al., 2014).

According to our knowledge one of the highest FOG content obtained with scum was a value of 60% (Bi et al. 2015), this indicates the exceptional potential of some of the WWTP studied as sources of biodiesel raw material, since half of them have 80% or higher of FOG content. This study reveals that the FFA content of FOG derived from grease interceptors did not exceed 8% (w/w) due to constant influx of fresh FOG from wastewater. However, if the FOG can hydrolyze without dilution, the FFA content can reach 15% (w/w) in more than 20 days (Montefrio et al. 2010).

Nevertheless, not all WWTP have degrease separators, or even having them, cannot be considered as feedstock for biodiesel production, since according to Olkiewicz et al. (2012) the amount of extracted lipids for primary sludge was 25.3% compared to 21.9%, 10.1% and 9.1% (dry wt) for blended, stabilized and secondary sludge, respectively, and the FAMEs yield obtained for primary, blended, secondary and stabilized sludge were 13.9%, 10.9%, 2.9% and 1% (dry wt), respectively, showing that an important amount of O&G are mixed in the sludge fraction.

In can be concluded that in the metropolitan area of Lisbon FOG from WWTP degrease system can be a very interesting possibility to increase the amount of O&G for biodiesel production,

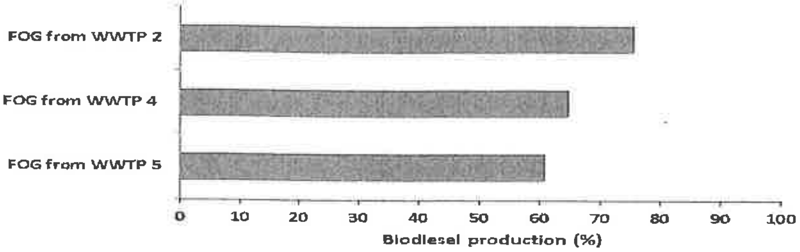

Figure 2. Percentage of biodiesel obtained from WWTP FOG.

ensuring both a more sustainable supply of this feedstock and a way to reuse this waste and reduce its treatment and disposal costs in the WWTP.

3.2 *Biodiesel production*

The FOG extracts of the WWTP 2, 4, and 5 were selected to produce biodiesel due to their high FOG content and results are presented in Figure 2.

The biodiesel yield percentage varied from 61 to 75% using the WWTP FOG extracts as raw material for the production. The production was carried out by diluting the biodiesel with n-Hexane as solvent to be comparable to the use of diesel fuel or diesel oil as solvent according to Kojima et al. (2009). The n-Hexane was only used as a solvent to support the occurrence of the reaction for the biodiesel production.

The results of the biodiesel produced from the WWTP agree with the biodiesel produced from a small community with high content of animal fat where they obtain also yields in biodiesel production from 74 to 92% (Phalakornkule et al. 2009). In other hand, when other FOG sources are used such as feather meal, only 7–11% of biodiesel can be obtained (Kondamudi et al. 2009).

Pokoo-Aikins et al. (2009) extracted lipids from sewage sludge using different organic solvents, and obtained lipids yields close to 25 wt%. A two-step production of FAME from municipal waste water sludge using n-Hexane in acidic ambient followed by methanolysis with sulfuric acid allowed FAME yields between 12 and 22 wt%. Huynh et al. (2010) reported the in-situ production of FAME, from untreated wet activated sludge under subcritical water and methanol conditions with sulfuric acid. Additionally, Mondala et al. (2009) investigated the feasibility of using homogeneous acid catalysts to produce biodiesel from primary and secondary sewage sludge by in-situ transesterification process, with sulfuric acid and n-Hexane to improve the solubility in the reaction mixture; obtaining FAME yields close to 15 wt% from primary sludge and 3 wt% from secondary sludge (Melero et al., 2015). According to these studies, it can be concluded that biodiesel produced by FOG from degrease separation process at the entrance of the WWTP have an exceptional potential when compared with other studies and sources of O&G from wastewater processes.

4 CONCLUSION

The total amount of FOG available in WWTP is much higher compared with other sources as feather meal, algae or biomass lipids of primary and secondary sludge. The average yield of biodiesel production from FOG extracts of WWTP obtained was higher than 60%. This work suggests that production of biodiesel should be considered as an option for O&G WWTP disposal, avoiding the problems associated with the addition of O&G to anaerobic digestion, and reinforcing a circular economy with energy produced from waste and reduction of CO_2 emissions to the atmosphere. This work provides an important contribution, revealing not only a new raw material source of O&G but also the feasibility of biodiesel production from these waste material. The amount of the

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REFERENC

Abdullah, S.H.
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feedstock available and the final characteristics of biodiesel produced justify further investments in this process.

REFERENCES

Abdullah, S.H.Y.S., Hanapi, N.H.M., Azid, A. Umar, R., Juahir, H., Khatoon, H., Endut, A. 2017. A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. *Renewable and Sustainable Energy Reviews* 70: 1040–1051.

Abed, K.A., El Morsi, A.K., Sayed, M.M., El Shaib, A.A., Gad, M.S. 2018. Effect of waste cooking-oil biodiesel on performance and exhaust emissions of a diesel engine. *Egyptian Journal of Petroleum* 27: 985–989.

Almeida, H.S., Corrêa, O.A., Eid, J.G., Ribeiro, H.J., Castro, D.A.R., Pereira, M.S., Mâncio, A.A., Santos, M.C., Souza, J.A.S, Borges, L.E.P., Mendonça, N.M., Machado, N.T. 2016. Production of biofuels by thermal catalytic cracking of scum from grease traps in pilot scale. *Journal of Analytical and Applied Pyrolysis* 118: 20–33.

Anderson, E., Addy, M., Chen, P., and Ruan, R. 2018. Development and operation of innovative scum to biodiesel pilot-system for the treatment of floatable wastewater scum. *Bioresource Technology* 249: 1066–1068.

Bi, C., Min, M., Nie, Y., Xie, Q., Lu, Q., Deng, X., and Ruan, R. 2015. Process development for scum to biodiesel conversion. *Bioresource Technology* 185: 185–193.

Bitonto, L., Lopez, A., Mascolo, G. Mininni, G. 2016. Efficient solvent-less separation of lipids from municipal wet sewage scum and their sustainable conversion into biodiesel. *Renew. Energy* 90: 55–61.

Chen, J., Li, J., Dong, W., Zhang, X., Tyagi, R.D., Drogui, P., Surampalli, R.Y. 2018a.The potential of microalgae in biodiesel production. *Renewable and Sustainable Energy Reviews* 90: 336–346.

Chen, J., Tyagi, R.D., Li, J., Zhang, X. Drogui, P. Sun, F. 2018b. Economic assessment of biodiesel production from wastewater sludge. *Bioresource Technology* 253: 41–48.

Choi, O.K., Song J.S., Cha, D.K. Lee, J.W. 2014 Biodiesel production from wet municipal sludge: Evaluation of in situ transesterification using xylene as a cosolvent. *Bioresource Tech.* 166:51–56.

Demirbas, A. 2017. Biodiesel from municipal sewage sludge (MSS): Challenges and cost analysis. *Energy Sources, Part B: Economics, Planning, and Policy* 12 (4): 351–357.

Diamantopoulos, N., Panagiotaras, D., Nikolopoulos, D. 2015. Comprehensive Review on the Biodiesel Production using Solid Acid Heterogeneous Catalysts. *J. Thermodyn. Catal* 6(1): 143.

Directive 2009/28/EC of the European Parliament and of the Council, of 23 April 2009. Renewable Energy Directive. *Official Journal of the European Union.*

Directive (EU) 2018/2001 of the European Parliament and of the Council, of 11 December 2018. Renewable Energy Directive. *Official Journal of the European Union.*

Ecofys, 2014. Renewable energy progress and biofuels sustainability.

Gebremariam, S.N., Marchetti, J.M. 2018. Economics of biodiesel production: Review. *Energy Conversion and Management* 168: 74–84.

Hums, M.E., Cairncross, R.A., Spatari, S. 2016. Life-Cycle Assessment of Biodiesel Produced from Grease Trap Waste. *Environ. Sci. Technol.* 50: 2718–2726.

Huynh, L. Kasim, N., Ju, Y. 2010. Extraction and analysis of neutral lipids from activated sludge with and without sub-critical water pre-treatment, *Bioresource Technology* 101(22):8891–6

Kirubakaran, M. & Selvan, V.A.M. 2018. A comprehensive review of lowcost biodiesel production from waste chicken fat. *Renewable and Sustainable Energy reviews* 82: 390–401.

Kojima, S., Du, D., Sato, M., Park, E.Y. 2004. Efficient production of fatty acid methyl ester from waste activated bleaching earth using diesel oil as organic solvent, *J. Biosci. Bioeng.* 98 (6): 420–424.

Kondamudi, N., Strull, J., Misra, M., Mohapatra, S.K. 2009. A green process for producing biodiesel from feather meal, *J. Agric. Chem.* 57: 6163–6166.

Kumar, L.R., Yellapu, S.K., Zhang, X., Tyagi, R.D. 2019. Energy balance for biodiesel production processes using microbial oil and scum. *Bioresource Technology* 272: 379–388.

Melero, J.A., Sánchez-Vázquez, R., Vasiliadou, I.A., Castillejo, F.M., Bautista, L.F., Iglesias, J. Morales, G., Molina, R. 2015. Municipal sewage sludge to biodiesel by simultaneous extraction and conversion of lipids. *Energy Conversion and Management* 103: 111–118.

Montefrio, M.J., Xinwen, T., Obbard, J.P. 2010. biodiesel production. *Appl. Energ.* 87(10): 3155–3161

Mu, D., Addy, M., Anderson, E., Chen, P., and Ruan, R. 2016. A life cycle assessment and economic analysis of the Scum-to-Biodiesel technology in wastewater treatment plants. *Bioresource Technology* 204: 89–97.