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PRODUCTION OFSUSTAINABLE BIODIESEL FROM WASTE SLUDGES BY MICROWAVE-ASSISTED PYROLYSIS

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Abstract

Purpose: Disposal of sewage sludge is becoming one of the most important issues in wastewater treatment: the 2005EU sludge production was estimated at9,5 million tons dry weight, up 54% in ten years. Sludge disposal costs may constitute 30-50% of the total operationcost of WWTPs. Sewage sludge still contains resources that may be put to use, like nutrientsand energy, that can be recovered through a variety of approaches.

Methods: Pyrolysis is a thermochemical decomposition process occurring by applying heat in absence of oxidizing agents; this way, chemical bonds are broken, with formation of simpler molecules, producing solid, gaseous and oil fractions that can be used as fuel or as prime material for chemical products. By combining pyrolysis and microwave heating to sludge under treatment, the more desirable production oil and gas fractions is increased and the residual solid fraction decreases.

Results: Microwave-assisted pyrolysis of urban waste sludge was applied for the production of oil and (Syn)gas, that were afterwards characterized and compared to mainstream alternative fuels (biodiesels). An energetic balance of the process is performed and described. A key factor in deciding the positivity of the energetic balance (and therefore the economic validity of the process) is the correct "tuning" between microwave source and treated sample.

Conclusions: Based on our experiments, the overall energy balance of the process is not always immediately favorable, however, by appropriately "tuning" the wave source and minimizing reflected radiation (lost energy) an energy-positive recovery of resources on one side, and considerable reduction of sludge volumes on the other may be achieved.

Keywords: wastewater sludge, biodiesel, pyrolysis, microwaves, sustainable, sludge disposal

Introduction

The safe disposal of sewage sludge is becoming one of the most important issues in the wastewater treatment cycle: at the European Union level, the 2005 sludge production was estimated in 9,5 million tons dry weight, up more than 54% in ten years, and is expected to reach 12.9 Mt in year 2020, a further increase of more than 30% [1]. Sludge disposal costs may constitute up, and sometimes above, 30-50% of the total cost of operation of a WWTP. Most common disposal options at the moment are: landfilling, disposal in agriculture (about 40% EU-wide), incineration or co-incineration, use in industrial production of bricks, asphalts, concrete. Sewage sludge, however, still contains resources that may be put to beneficial use: among the others, nutrients, that can be recovered through specific processes (e.g. precipitation as struvite) and energy, recoverable through a variety of approaches.

On the other hand, to reduce fossil fuels consumption and carbon emissions, energy industry and government policies worldwide are promoting the use of biodiesel and other non-petroleum biofuels.The current EU commitment under Directive 2003/30/EC on the promotion of biofuels for transport, sets a target of 5.75% of all transport fuels by 2010, increased to 10% by 2020 by the recent European Commission energy roadmap [2]. A "biofuel" is defined as a fuel that is produced through contemporary biological processes, rather than by geological ones, such as those involved in the formation of fossil fuels. An ongoing debate on biofuels sustainability has emerged since the biofuels industry gathered momentum. While 1st generation biofuels were (and are) mainly produced with feedstock with food value for humans or animals, 2nd generation biofuels are increasingly being produced from lignocellulosicand waste materials and could enable far greater reductions in greenhouse gases (GHG) emission.

Traditionally, sewage sludge is processed in anaerobic tanks to produce biogas, a mixture of CH_4 and CO_2, [3, 4], that can be used as such or further refined to obtain bio-methane, a renewable fuel with characteristics practically identical to those of fossil methane. However, recent work has demonstrated that the production of biodiesel using the lipids extracted from sewage sludge could be economically feasiblebecause of the remarkably high yield of oil and low cost of this feedstock, as compared to conventional biodiesel feedstocks. The authors demonstrated this using a thermochemical process under ambient pressure in a continuous flow system [5].

In this study, the effectiveness of microwave-assisted pyrolysis to obtain biodiesel from sewage sludge has been investigated. Pyrolysis is a thermochemical decomposition process that occurs by applying heat in the absence of an oxidizing agent (usually, oxigen); in this way, the original chemical bonds are broken, with formation of simpler molecules. From the process, a solid, a gaseous and an oil fractions are produced, and either one can be used as a fuel or, in the case of the oil fraction, also as a prime material for chemical products. The final products of pyrolysis are influenced by the process' operating conditions (heating rate, final temperature and Hot Areas Residence Time "HART" of volatile substances), therefore the process could be optimized in order to maximize the production of the most desirable residual fraction. It has been observed that, by combining pyrolysis and microwave heating to the sludge under treatment, the (usually) more desirable production of oil and gas fractions is increased, and the residual solid fraction decreases [6, 7]. In this paper, microwave-assisted pyrolysis of urban waste sludge was applied for the production of SSPO (Sewage Sludge Pyrolysis Oil) and Syngas, that were afterwards analytically characterized and compared to mainstream alternative fuels (biodiesel). An energetic balance of the process is described to evaluate process efficiency.

Materials and methods

The apparatus shown in Figure 1 was used for the sludge samples microwave assisted pyrolysis [8]. The experimental apparatus consists of a pure quartz cuvette (Fig. 1[a]), capable of withstanding temperatures exceeding 1000°C, with a cavity (Fig. 1 [b]) containing the sludge sample (15 or 25 g) being treated.

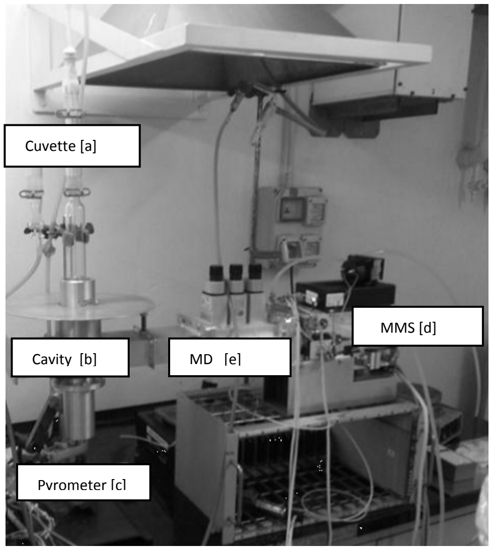

Figure 1. Microwave apparatus used for dry pyrolysis tests

Figure 2. Flask withcollected pyrolithic oil

The sample itself was located between two layers of quartz wool, thus allowing the generated gas flux while impeding the movement of the solids. In order to purge the cuvette from atmospheric oxygen, it was fluxed with helium prior to each test. Temperature was measured by means of an infrared pyrometer (Fig. 18 [c]), allowing the measurement of temperatures up to 1000°C.

The monomodal microwave synthesizer (MMS, Fig. 18 [d]) used in these tests was built in the Microwave Laboratory of the Department of Electronic Engineering at the University of Pavia. A MMS unlike a conventional (multimodal) cooking microwave oven, is capable of matching the impedance between the load to be irradiated and the microwave-generator (magnetron), thus maximizing the power transfer to the samples. With an MMS appropriately tuned, it is also possible to irradiate dry samples, a task impossible to achieve with traditional microwave ovens that heat contents indirectly, by agitation of the water molecules contained in the "samples".

The microwave source worked at a frequency of 2.45GHz generating an electromagnetic field that could reach 3 kW of power, and was completed with "dummy load", in order to dissipate return energy from the load, and with a power sensor, measuring both emitted and reflected power levels. A specially designed tuner (impedance adapter) was also used to minimize the quantity of reflected (wasted) power. Power output was regulated by PLCs, offering both the possibility of regulating power emission, and measuring process variables (P_{out}, P_{refl}, temperature and pressure). A triple-stub matching device from Alter Systems (MD, Fig. 1[e]) connected with the magnetron was also used to balance reflective coefficients within the system, allowing the tuning of incoming and reflected waves in order to create an optimal electric field intensity in the cavity containing the sample.

Analyses of samples and product oils (Figure 2) were conducted by means of FT-IR spectroscopy, and GC-MS spectroscopy for pyrolysis oils.

Sludge samples were prepared from waste sludge obtained from the municipal WWTP of the city of Pavia. The sludge used in these tests has already undergone an anaerobic digestion process, from which biogas (CH_4 and CO_2) had already been produced, thus the expected biodiesel yield is in fact lower than the one extractable from a "fresh" sludge. Sludge samples were further desiccated at 60^oC for 24 hours in order to further reduce their water content, while minimizing any possible reaction that could modify their organic content. Dry sludge was then ground to a fine powder, and further characterized for humidity and organic content. Sludge characteristics are presented in Table 1.

Table 1. Test sludge characteristics

Sample	Dry fraction	Humidity	Volatile fraction
Desiccated sludge at 60^oC/24 hrs	26.10%	73.87%	
Dried sludge at 105^oC/24 hrs	85.38%	14.62%	
Dried sludge at 600^oC/3 hrs	53.60%		46.40%

Sludge samples heating up to the temperature required for pyrolysis was achieved through the MMS apparatus described; by means of the PLC interface, furthermore, it was possible, in addition to record process data (ever ¼ s), to set up automatic process temperature control. In order to minimize process disturbances, ranging from sample expansion in the cuvette, due to residual water vapors formation, wetting of the quartz wool containing the sample, inhibiting the gas flow, hot-spot formation, and others, a controlled, step-increasingly temperature profile was adopted for the experiments (Figure 3).

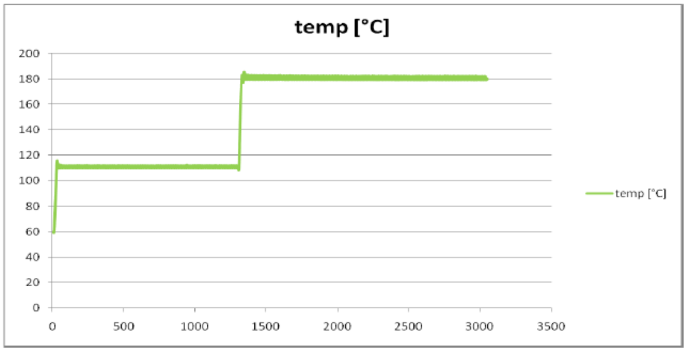

Figure 3. Temperature profile in the cuvette during pyrolysis experiments at 180^oC (time in s)

Pyrolytic processes were conducted in inert atmosphere (helium) at different temperatures and durations (Table 2). Pyrolysis-generated oils were estracted with solvent using a Soxhlet estractor, and desiccating the extract with a vacuum rotating evaporator (rotavapor). Both the liquid extract and the solids were analyzed in ATR IR spectroscopy, oils were also analyzed with GC-MS and tested for calorific content.

Results and discussion

Table 2 shows temperature, duration and quantity of extracted oils from the tests conducted. The greatest oil yields were observed between 270 and 500^{o}C. Below 200^{o}C the oil quantity obtained is very low; over 500^{o}C, there is still good production. These result confirm earlier results obtained in literature [9].

Test 9 (270^{o}C) was the shortest (8 min total process time), yet it yielded the absolute highest oil production. Test 1, conducted at a similar temperature but for longer time, showed a much lower oil yield.

Results of the three tests at 400^{o}C (nos. 3, 6 and 10) show that the oil yield increases in an inverse proportionality to the duration of the test. However, in test 3 a partial carbonization in the cuvette was observed, and this might have contributed to the lower oil production in this experiment.

Tests at 500^{o}C (nos. 4 and 7) were characterized by difficulties in adjustment of the MMS to synchronize outgoing and reflected waves. This resulted in hot spots within the system, high irradiated energy and somewhat lower oil yield. This is even more evident in test no. 7.

Table 2. Tests conditions and oil yields

	Max Temp. ^{o}C	Time at T_{MAX} [min]	Total process Time [min]	% oil to total sludge	% oil to sludge org. fraction
TQ	60	=	=	3.57*	7*
TEST 1	270	20	55	9.68	19
TEST 2	180	28	50	3.30	7
TEST 3	400	5	55	8.64	17
TEST 4	490	1	54	10.25	21
TEST 5	600	3	56	8.71	17
TEST 6	400	6	46	11.79	24
TEST 7	500	9	51	7.63	15
TEST 8	650	-	60	7.38	15
TEST 9	280	2	8	12.52	25
TEST 10	400	2	18	10.77	22

*extraction with solvent from original sample

The two tests conducted above 600^{o}C (nos. 5 and 8) had a fair yield of oil: the temperature in this case was however above the optimal range for oil production. Expansion (swelling) of the sample in the cuvette was observed. In test 8 some of the process data were lost due to a security block of the PLC that recorded temperatures over the safety range.

Figure 4 shows the results of the ATR-IR spectroscopy analysis of some of the oil samples. The graphs record the presence of lipids (2900 and 2800 cm^{-1}), carbonyls, C=O, due to protein by-products (1650 cm^{-1}), and cresole-like aromatic compounds (below 1000 cm^{-1}) [10]. The presence of these compounds was also seen via GC-MC analysis.

GC-MC analyses on diluted samples (using dichloromethane) showed the following curves (Figure 5) . Note that toluene and styrene do not show in some of the resulting lines due to the high dilution ratio adopted, however, they were detected in the oil samples by other analyses. From lower to higher retention times (left to right in the graphs) mass spectra identify aromatic hydrocarbons (containing one or more aromatic rings in their molecular structure), nitrogenous compounds, alkanes, carboxylic acids (containing the –COOH or the –OH groups linked to a carbonyl group C=O), sterols and derivatives.

Comparing the graphs obtained for tests at different temperatures, a reduction of peaks to the right-hand side of the curves (carboxylic acids and sterols) can be observed with increasing temperatures. This is due to the final higher process temperatures, as heat splits the larger sterol molecules in the oil, thus forming smaller ones pertaining to the alkanes, nitrogenous, and aromatics groups. In the extraction test with solvents ($T=60^{o}C$, non-pyrolyzed sample), on the other hand, aromatics are practically absent, alkanes are scarcely present, and most of the oils consist of fatty acids, sterols and derivatives.

In general, the observed oil characteristics are not too dissimilar to those of common feedstock biodiesel, although with a lower lower calorific value (LCV) equal to about 33 kJ/g (range 33-35 kJ/g), against that of corn and safflower at 42-43 kJ/g, or the one produced by coconut at 38 kJ/g. Compared with petroleum-diesel, therefore, sludge-derived oils have a LCV that is about 30% lower [11]. This however was expected since pre-digested sludges were used in the tests, therefore part of their energetic content had already been converted to biogas, which contribution to this analysis is not accounted for.

Table 3 summarizes the energy balance of all tests conducted. The table shows the energy emitted by the magnetron, that reflected within the irradiation apparatus, and that absorbed by the sample; it also shows the quantity of oil produced in each test and the energy that can be recovered from this oil.

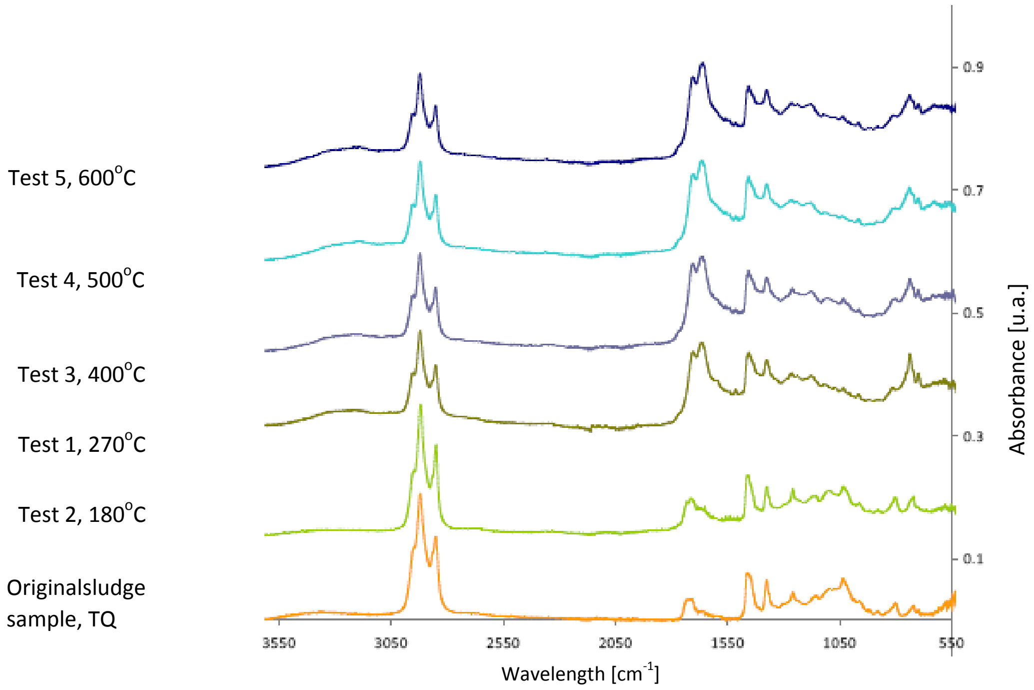

Figure 4. ATR analysis of some oil samples

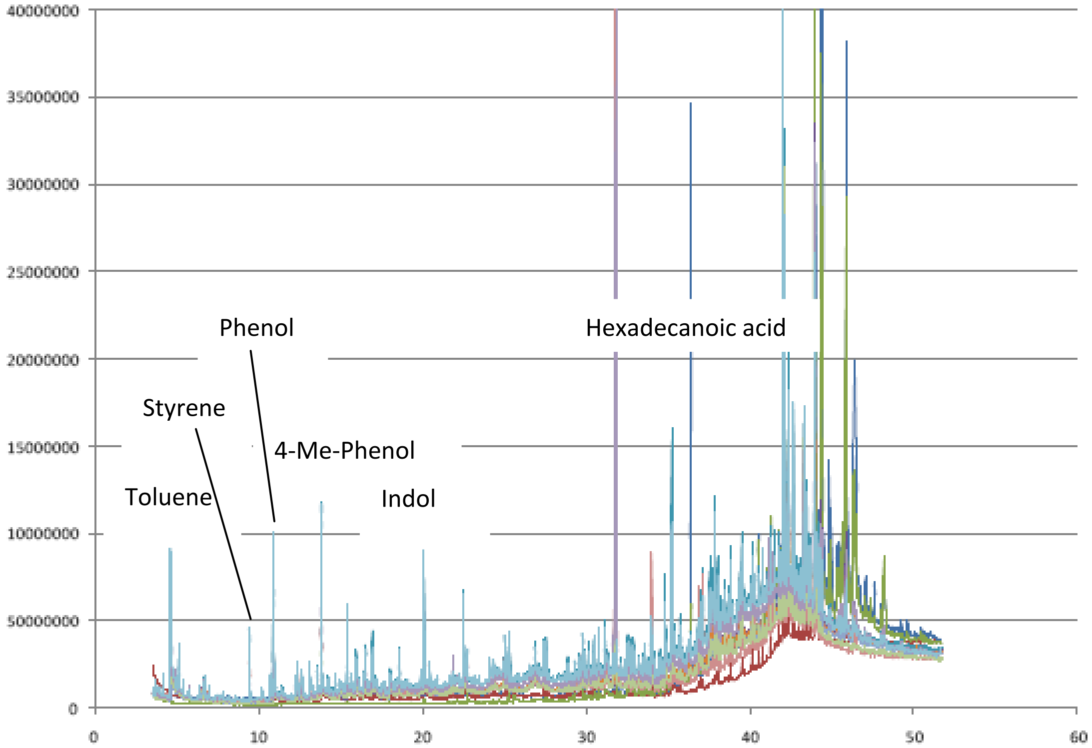

Figure 5. Summary of MC-GC analyses results for all sludge samples

Table 3. Energetic balance summary of tests conducted

Test no./ Temp. °C	Emitted Energy [kJ]	Reflected energy [kJ]	Absorbed Energy [kJ]	Oil yield [g]	Recoverable Energy [kJ]	Process Efficiency Gross [%]	Process Efficiency Net [%]
1/ 270	49.36	13.96	35.40	1.7164	**56.6**	**114.67**	**159.89**
2/ 180	65.94	23.82	42.11	1.7894	59.1	89.63	**140.35**
3/ 400	47.22	25.08	22.14	1.5621	**51.5**	**109.06**	**232.61**
4/ 490	76.07	31.85	44.22	1.0775	*35.6*	*46.80*	*82.54*
5/ 600	44.09	21.53	22.56	1.1365	37.5	85.05	**166.22**
6/ 400	90.64	62.7	27.94	1.8413	60.8	67.09	**217.61**
7/ 500	60.19	18.79	41.40	1.022	*33.7*	*55.99*	*81.40*
8/ 650	94.51	33.31	61.20	0.86221	*28.4*	*30.05*	*46.40*
9/ 280	92.99	19.17	73.82	1.4137	*46.7*	*50.22*	*63.26*
10/ 400	134.62	33.34	101.28	1.4077	*46.6*	*34.61*	*46.01*

The last two columns, process efficiency, Gross and Net, are given respectively by the ratio between recoverable and emitted energy (Gross Efficiency) and the ratio between recoverable and absorbed energy (Net Efficiency). Gross Efficiency incorporates the energy losses due to reflected energy in the irradiation system, indicating that a process overall positive efficiency was achieved "as was" during the experiments, if the value reported is greater than 100. Net efficiencyestimates, on the other hand, neglects such losses, indicating that the process *may* become energy efficient if the "reflected energy" losses could be reduced to zero (or close value). Net efficiency thus expresses a sort of "potential" process positive efficiency index, if the value shown is greater than 100. It might in fact be possible, through more extensive studies and better calibration of the apparatus, to achieve this goal and reduce the differences between net and gross efficiencies. These estimates do not include the conversion efficiency of electric energy into microwaves of the magnetron:

this was estimated at 65% in the present case, but it may vary substantially, depending on the magnetron type and its construction. Also, the energy balance is not actually complete, as the energy yield from pyrolysis gases (generated, but quantified and not considered in this energetic balance) should also be added to it.

It can be seen that in two cases (tests 1 and 3), the gross process efficiency is favourable, indicating that the energy recoverable from the oils is greater than the one used to complete the pyrolysis process. Considering net efficiency, that is the efficiency determined considering only the energy *absorbed* by the samples during the process, favourable cases turn out to be five over ten experiments: this means that, by substantially reducing the reflected energy, *corresponding to a loss* in the system, also in these conditions more energy could be recovered, than that used for completing sludge pyrolysis.

One of the problems influencing process efficiency is that the dielectric constant of sludge (that in turn influences impedance minimization) varies with temperature, rendering manual wave tuning quite difficult. The problem could be solved by designing a circuit to automatically detect and adjust the observed dielectric constant, allowing self-tuning between wave generator and sample, with resulting automatic minimization of reflected energy.

Finally, Figure 6 shows the reduction (percent) of solids before and after the process: this generally is proportional to the operating temperature and reaches values of up to 51%, approximately halving the disposal costs of residuals compared with the initial sludge quantities.

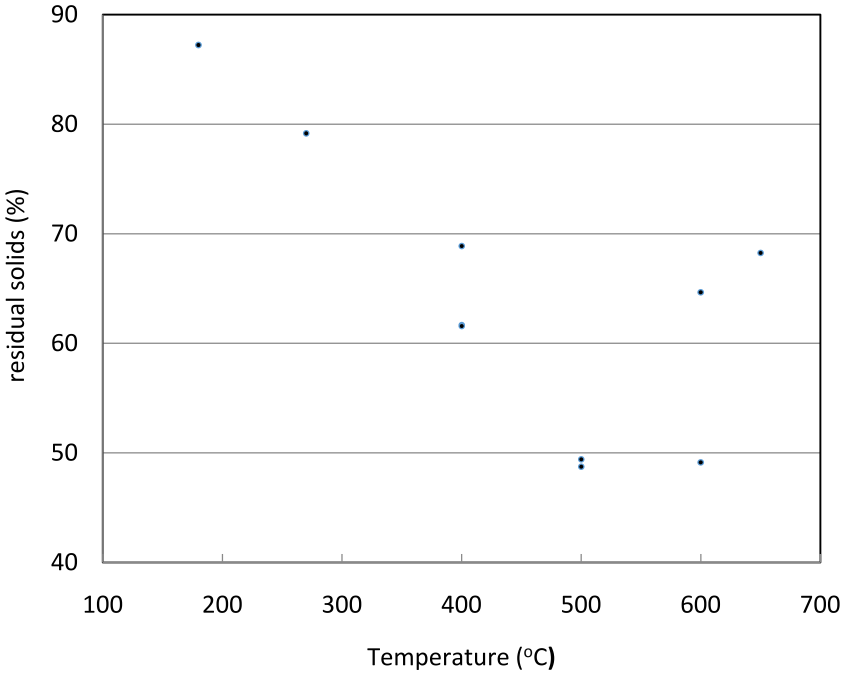

Figure 6. Sludge solids residual (%) after sample processing

Conclusions

Biodiesel-like oil, or Sewage Sludge Pyrolysis Oils (SSPOs) was produced through microwave-assisted pyrolysis of municipal waste pre-digested sludge. Process yield varies according to operating conditions, and depends on the achievement ofa proper tuning between MMS and sludge samples, in order to minimize reflected (non-absorbed) energy in the system. As this is equivalent to an energy loss, it influences the ultimate energetic balance of the process. Obtained oil composition is quite similar to that reported by other authors, and not dissimilar to that of biodiesels obtained from common feedstock (food-) crops, with a slightly lower calorific value. This was expected since the pre-digested sludge had released some of its contained energy during anaerobic bio-gasification: the additional energetic value of the biogas previously generated was not considered in this analysis.

Based on the conducted experiments, the overall energy balance of the process is not always immediately favorable: in just two cases over ten the oil-recoverable energy was higher than the MMS-emitted energy under adopted process conditions. However, in five cases over ten the energy balance turned out to be potentially positive if the reflected (lost) energy in the system were neglected. With a more accurate tuning between wave generator and sample, incoming wave absorption could be improved (reducing the quantity of reflected waves), thus turning the energy balance into a positive figure. This task could be achieved with more sophisticated, automatic equipment capable of tracking the dielectric constant of sludge samples during the process. Also, in the energy balances herein presented, the positive energetic contribution of the generated syngas component (the gas fraction generated during pyrolysis) was neglected for simplicity.

In conclusion, microwave-assisted, pyrolysis processes couldconstitute an interesting technology for the production of biodiesel and syngas fuels from a waste component such as sewage sludge, that currently requires expensive processing for its disposal. The process may allow, as shown, an energy-positive recovery of resources on one side (under the right circumstances), and at the same time (in any case) reduce original sludge volumes, consequently reducing disposal costs regardless of other factors. The fractioned fuel yield can be shifted towards the most desirable product type (oil, gas or solid) for the specific useby appropriately adjusting the process. Application of the process to non-processed (undigested) sludge should further improve energetic yield in terms of extracted oil and gas, however, integral energetic yields balancesunder different process combination options should be investigated attentively in order to achieve the best final option.This process could substitute 1st generation biodiesel (from food crops) with a sustainable, waste-derived renewable energy source. In addition to thedirect benefits from energetic recovery, considerable economic and energetic savings due to the reduced quantity of final residues to be disposed of (less than 50% of initial sludge quantity), should also be factored into the overall process balance.

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