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Innovative Strategies For Ozone Treatment Of Industrial Wastes: Hydrothermal Liquefaction Of Surfactant Wastewater And Leacheate Evaporation

Juan J. Mascarella,\*, Jose M. Abelleira-Pereiraa, Belén García-Jaranaa Juan R. Portelaa, Enrique Martínez De La Ossaa, José L. García-Moralesb

aDepartment of Chemical Engineering and Food Technology, Faculty of Sciences, University of Cádiz, International Excellence Agrifood Campus (CeiA3), 11510, Puerto Real (Cádiz), Spain.

bDepartament of Environmental Technologies. Faculty of Marine and Environmental Sciences, University of Cádiz, IVAGRO institute, 11510 Puerto Real (Cádiz), Spain.

[jotero.litio@gmail.com](mailto:jotero.litio@gmail.com)

In this paper, ozonation is used as a pre-treatment for two different kinds of wastewaters. The first purpose is the study of the effect of ozonation on a landfill leachate treated by a reverse osmosis process prior a concentration step in an atmospheric evaporator. At first sight, an ozone treatment can supply three effects: Defoaming capacity, biocide effect, and pH acidifier to avoid the ammonia striping in the evaporation process. The second purpose of this paper is regarding hydrothermal liquefaction (HTL) of wastewaters. HTL can produce a liquid fuel, normally called crude-oil, alternative to fossil fuels, as well as other products of industrial interest (phenols, furfurals, etc.). The second objective is the study of the possible positive effect that a pre-treatment with ozone can have on the performance of the subsequent HTL. In this work, HTL is applied to liquid surfactant wastes obtaining up to 7% crude-oil yield, with a High Heating Value (HHV) higher than 8.000 cal/g. These results are compared with those obtained when an ozonation pre-treatment is applied before the HTL process. Ozone treatment shows a slight defoaming capacity for the leachate feed but don’t seem to show a significant difference in the HHV of the crude-oils obtained from liquid surfactant. However, there is a noticeable difference in the solid residue generated for this later. Less aggregates of solid particles and a weight reduction of 20% in the filtering step were obtained from ozonated liquid surfactants. The reduction of solid by-products is of great interest for dimensioning an industrial-scale HTL plant due to the problems that these solids can generate in pipes and valves.

* 1. Introduction

Ozonation is a type of advanced oxidation process whose most common application is the disinfection of waters. Ozone is able to attack all microorganisms, as well as for the degradation of organic and inorganic pollutants involving the production of very reactive oxygen species. Ozone is a strong oxidant, capable of participating in numerous chemical reactions with inorganic and organic substances. The reactions can occur mainly by two mechanisms: Direct reactions are nonspecific reactions, attacking double bonds and some functional groups; and indirect reactions are a consequence of the action of hydroxyl radicals resulting from the decomposition of ozone in water. With regard to waste treatment by ozonation, as a general rule, the less organic matter the waste contains, the better the result of ozonation. However, if the organic matter is recalcitrant, it can be a way of eliminating it since its oxidation either leads to its mineralization or can improve its biodegradability. (Gripa et al., 2020).

On the other hand, hydrothermal liquefaction (HTL) is a thermochemical process that can convert organic matter into a biocrude oil with physicochemical properties similar to petroleum. Artificial transformation of biomass requires prior knowledge of the prevailing reaction routes and products. By appropriately modulating the operating conditions of hydrothermal processes, there are immense possibilities to transform a large amount of feedstock into a large amount of valuable products. In this way, the value and advantages of particular wastes that currently have no better way of disposal than pyrolysis could be exploited, opening the door to a valorisation for what could be the waste from the surfactant-producing industry; a type of waste that is abundant and for which no satisfactory management procedure has been developed so far. In first instance, the idea of using ozonation as a pre-treatment for HTL could make this latter more efficient, although saturated bonds, such as the aliphatic chains of surfactants, hinder the good performance of ozonation. It would therefore be expected that ozonation would not be cost-effective as a complete treatment, but it may have important benefits as a pre-treatment prior to HTL of surfactants.

Many studies in the literature (Akhtar and Amin, 2011; Toor et al., 2011) demonstrate the applicability of HTL to biomass residues, showing that hydrothermal conversion routes to liquid fuels are favoured and have a large extent for biopolymers (cellulose, hemicellulose, lignin), proteins and lipids. For example, in the conversion of cellulose, the main component of biomass, depolymerization by hydrolysis occurs, and oligosaccharides are obtained, which undergo dehydration and retro-aldol condensation, to be transformed into furfurals and carboxylic acids. On this basis, it is feasible to hypothesise that HTL is satisfactory for some other organic aqueous wastes, as there is no reason why some organic molecules of industrial origin cannot be converted into liquid fuels by liquefaction. 300°C is the selected HTL temperature as it provides the best crude-oil yield in agreement with a considerable number of authors for HTL of biomass (Karagöz et al., 2004; Qu et al., 2003; Shuping et al., 2010; Sugano et al., 2008; Yin et al., 2010; Zhang et al., 2009). The study's main contribution is is to evaluate how much improvement would be achieved by pre-treating these wastes with ozone prior to HTL. It is also intended to study the composition of the crude-oils obtained.

* 1. Material and methods

The wastewaters used for the study and their analytical parameters are presented in Table 1. Landfill leachate wastewater is a brown liquid with great presence of salts and chlorides, while industrial surfactant wastewater is a dense liquid disposed of cleaning a production line in a liquid surfactant manufacturing company. Both wastewaters were reverse osmosis concentrated at origin.

*Table 1. Main analytical parameters of the wastewaters*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Landfill leachate wastewaters |  |  | Industrial surfactant  wastewaters |
| pH | 7.7 |  | pH | 4.3 |
| Conductivity (mS/cm) | 75.29 |  | Conductivity (mS/cm) | 4.97 |
| TOC (mg/L) | 6,692 |  | TOC (mg/L) | 63,660 |
| DOC (mgC/L) | 3,481 |  | DOC (mgC/L) | 54,560 |
| Chlorides (mg/L) | 24,536.14 |  | COD (gO2/L) | 233.61 |
| Sodium (mg/L) | 11,841.34 |  | Chlorides (mg/L) | 2,573.7 |
| Bicarbonates (mg/L) | 8,944.10 |  | Sulphates (mg/L) | 630.8 |
| Potassium (mg/L) | 2,757.47 |  | Nitrates (mg/L) | <50 |
| Ammonium (mg/L) | 2,751.03 |  | Zinc (mg/L) | 19.34 |
| Carbonates (mg/L) | <25 |  | Copper | 4.21 |
| Copper | 23.43 |  | Lead | 1.3 |
| Other metals: As, Pb, Hg, Cr, Ba, Se, Cu… (mg/L) | <1 |  | Other metals: As, Hg, Cr, Ba, Se, Ni… (mg/L) | <1 |

2.1. Ozonation of landfill leachate

The ozonation plat consists of a laboratory-scale test bench with small contactors and a semi-continuous reactor, being the ozone generator Zonosistem GZ07 the main unit. A 1L polycarbonate test tube was used for ozonation of landfill leachate wastewater, being filled with 500 mL of a 1/2 dilution of leachate waste in deionized water. For these experiments, 10 minutes of an ozone stream of 52.8 mgO3/L·min at a flow rate of 0.3 NL/min is bubbling through a diffuser located at the bottom. The procedure is repeated on another identical feed, but this time increasing the ozone concentration to 85 mgO3/L·min. Total organic carbon (TOC), conductivity and pH is measured in order to know the chemical changes made in compassion with the original feed. Subsequently an air stream at a flow rate of 0.3 NL/min is bubbling through the diffuser and the volume of foam generated is measured every minute until the overflow is reached.

2.2.1 Ozonation of liquid surfactant wastewater

Unlike the case for leachate, a 2L polycarbonate test tube was used for liquid surfactant wastewaters due 1L test tube is insufficient for operating at this level of foam generation due to the surfactant nature. The circuit is completed with an airtight stopper, from which a sample-taking tube and the ozone inlet and ozone outlet tubes to the analyzer come out. 800ml of a 1/2 dilution in two batches (400ml each time to reduce the generation of foam, which will then be mixed) is introduced into the ozonation reactor. The ozone dose applied depends on three variables: ozone concentration, gas flow rate, and reaction time. For this experiment 12 minutes of an ozone stream of 85 mgO3/L·min and a flow rate of 0.3 NL/min is bubbling through a diffuser located at the bottom. An input-output balance of the ozone stream is carried out, firstly to the empty system that will serve as a target and then to the experiment. The dose applied (absorbed by the residue) is 39.83 gO3/L for the HTL1 tests, which will end up presenting a paler blue color than the one that was not subjected to ozonation (HTL0).

2.2.2 Hydrothermal liquefaction

An Autoclave Engineers' stirred batch reactor (300 ml) was used for HTL treatment. Typical range: 150-320 ºC and 50-180 bar. The equipment includes temperature control, stirring speed, pressure, and injection measurement system, and sample collection. All parts of the equipment are made of 316 stainless steel.

150 ml of the sample are introduced at room temperature into the reactor. Then the reactor is closed, and the headspace is purged for 15 minutes with a stream of N2 gas to remove the oxygen present in the air headspace, as the presence of an oxidant has a negative effect on HTL, as shown in the literature (Akhtar and Amin, 2011). After that, the reactor is pressurized to 30 bar with N2. The pressure level for this specific reactor was set so that the reaction takes place in the liquid phase when the temperature reaches 300ºC and 100 bar. Once the operating conditions are achieved, the response is stopped by cooling down the reactor. Once cooled, a sample of the gases is collected, analysed and depressurized. The reactor is opened and the effluent is taken. The effluent is vacuum filtered, dried and weighted. The crude-oil is extracted using dichloromethane that will be recovered in a rotary evaporator at atmospheric pressure and 50ºC, keeping the crude-oil in the boiler. The yields obtained for both the char and the crude are referred to by weight and are calculated by taking the weight of the undiluted feed as a reference. To carry out the comparative study of HTL applied to the target waste, two identical samples of these wastewaters were subjected to the same operating conditions, without pre-treating with ozone and pre-treating it ozone.

2.3. Analytical methods

Calorimetric analysis of the crude-oil was carried out using a PARR 6400 Calorimeter. For this analysis, approximately 0.6 g of the crude-oil sample is introduced and burned in a high-pressure oxygen atmosphere; the energy released by the combustion is absorbed inside the calorimeter, recording the temperature variation and its high heating value. Ultimate analyses of crude-oils were carried out using LECO TRUSPEC CHNS MICRO equipment, where the proportion of CHNS of the samples was obtained.

* 1. Results and discussions

**3.1. Ozonation of landfill leachate**

Figure 1. Foam generation in the bubbling stage

The figure 1 illustrates the result of the air foaming experiments on the leachate. The first thing that can be observed is a different curve form in the foams of the ozonized and non-ozonized leachate. While the untreated leachate still maintains an upward curve after 5 minutes of air bubbling, the ozone-treated leachate reaches a stable value with 4 minutes of treatment. The foam reduction was 28.3% but it would be even higher if the experiment continues, but the limitation of the tube sample volume did not allow it before overflowing foam.

Table 2. Analytical parameters and foam volume of non ozonated and ozonated leachate in bubbling stage.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Air | O3 A | O3 B |
| pH | 8.01 | 7.81 | 7.80 |
| Conductivity (mS/cm) | 41.6 | 42.2 | 40.7 |
| TOC (g/L) | 2,378 | 2,396 | 2,219 |
| Foam volume (mL) | 300 | 210 | 220 |

As seen in table 2, the pH of the ozonated diluted feed waste was 7.81 (A) and 7.80 (B) for both experiments with ozone, similar but slightly lower than the original one, that is 8.01. Less remarkable is the conductivity, that keeps between 42.2 mS/cm (A) and 40.7 mS/cm (B) near the original value of the diluted feed (41.6 mS/cm). It was not possible to measure a reliable value for the Chemical Organic Demand (COD) due to interferences caused by the high presence of chlorides in this particular wastewater, as shown in table 1. TOC was similar in all cases, that means that no organic matter was lost in the process. No other significant differences were observed more than a paler color for the highest ozone dose. However, it is remarkable that despite applying almost twice ozone for experiment B, a proportional response was not obtained. This behavior may be caused, in major part, to the large amount of bicarbonates contained in the leachate (table 1), which rapidly consumes the ozone and dampens the effects described above.

**3.2. Ozonation and HTL of surfactant wastewater**

As a reference, a dry sample of this wastewater is 13.9% of the original weight, and the HHV of this dry sample reached 6,242 cal/g at the calorimetry test. The table 3 summarises the mean results obtained for each battery of experiments (triplicates).

Table 3. Results obtained for HTL study.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Raw feed  (HTL0) | | | Feed pre-treated by Ozonation (HTL1) | |
| Sample | Feed | Effluent | Feed | Effluent |
| pH | 5.98 | 4.17 | 5.41 | 3.99 |
| Conductivity (mS/cm) | 7.42 | 13.80 | 8.42 | 14.78 |
| TOC (g/L) | 33.90 | 22.13 | 33.46 | 24.57 |
| COD (gO2/L) | 117.59 | 82.55 | 116.90 | 85.25 |
| Crude-oil yield (%) | 7.03 | | 7.20 | |
| Char yield (%) | 0.08 | | 0.06 | |
| H.H.V (cal/g) | 8,382 | | 8,381 | |
| Ashes (% wt) | 1.95 | | 1.90 | |

Ozonation affects the pH in the pre-treated feed, but that effect is negligible when comparing the effluents. O3 pre-treatment reduces the feed pH by 0.6 units, while the effluents in HTL0 and HTL1 are quite similar (there is only a pH decrease of 0.18 units). The effect of ozone on the pH of the feed may be explained by the hydrolysis reactions and breaking of double bonds in the molecules that occur, as well as oxidation of intermediate carbons. However, it is discarded that ozone has affected inorganic components, i.e., CaCO3, as no inorganic carbon was detected in the feed. Despite the use or not of ozone, both HTL effluents end up at pH around 4, slightly acidic, due to the HTL reactions that acidify the medium. There is an increase in the conductivity of the ozonated feed from 7.42 mS/cm to 8.42 mS/cm. The presence of sulphates, nitrates, and phosphates in the surfactant residue increases the conductivity as mineralization occurs. In the case of the effluents, the experiment that was not ozone treated is 13.8 mS/cm, while the experiment that was ozonated is 14.8 mS/cm. There is variability, although ozone does not seem to substantially alter the conductivity of the feed. In contrast, HTL increases the effluent conductivity to almost double in all cases. For the raw feed, the TOC results were 33,90 mgC/L and 33,46 mgC/L when ozonated. The difference is insignificant, so ozonation does not seem to affect the feed TOC. Thit is the desired behavior because the objective is to not reduce the organic carbon, to later be converted to crude-oil. The same cannot be said for the effluent from the ozonated feed because exists enough variability (3,896 units) that overlaps the range of the ozonated feed, making it impossible to draw a reliable conclusion.

Despite the large variability in the COD of each replicate, the conversion that occurs when feed is subjected to HTL is very similar, 30% for the non-ozonated waste and 27% for the ozonated waste. It does not seem to be affected by pre-treatment at HTL. The average crude yields appear to be slightly higher when pre-treatment is applied (+0.17%); however, the variability between replicates was high, so it cannot be assured that it has a noticeable effect on the HTL reaction as in previous sections. This may be a consequence of the numerous steps involved in the production method and the small volumes of crude-oil generated in each experiment. In terms of generated char, less filters were needed in the cases where ozone pre-treatment was used (from four to one), reducing the char by 25% and presenting smaller particle sizes retained by the filters. This behavior is similar to the observed changes in the sludge dewatering index after treatment with ozone (Kosowski et al., 2020). The ash resulting from the calorimetry tests of both crude-oils shows a slight decrease (2.6% reduction) for the ozonated experiment. Ultimate analysis of the crude-oil was carried out in triplicate to determine its elemental chemical composition.

Table 4. Ultimate analysis of crude-oil without ozone pre-treatment (HTL0) and with ozone pre-treatment (HTL1). \*The oxygen content is obtained by difference from the total sum.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Experiment | C (%) | H (%) | N (%) | S (%) | O (%)\* |
| HTL0 | 65,79 | 10,56 | 0,22 | 1,05 | 22,39 |
| HTL1 | 64,76 | 10,33 | 0,35 | 1,14 | 23,42 |

As shown in table 4, the composition of both crude-oils is very similar, which is consistent with their almost identical HHV. The relatively low Sulphur content (<3%) and ashes (<5%) fulfill the acceptance requirements for alternative liquid fuels.

|  |  |
| --- | --- |
|  |  |

Figure 2. Gas analysis for untreated and pre-treated feeds in HTL.

Figure 2 shows the mole percent of gases after HTL reaction. Left columns represent the composition of the gases in the headspace, including the nitrogen gas introduced prior to the reaction. The right columns represent the normalized composition after subtracting all nitrogen gas used as an inert gas in the tests.

Hydrogen couldn’t be detected in any of the experiments, but there exist noticeable differences in the gas composition of HTL without and with ozone pre-treatment. HTL of the raw feed does not produce carbon monoxide in the gas phase, and only carbon dioxide is produced. However, the HTL of the pre-treated feed generates carbon dioxide and up to 16% of carbon monoxide.

* 1. Conclusions

Regarding to the leachate treatment, it was possible to verify two of the three positive mentioned effects of ozone. Indeed, foam generation was reduced in 28% and the pH was not increased in the process. The biocidal effect could not be measured due to the nature of the leachate, which contains so many ions, metals and salts that it is unlikely that micro-organisms can grow in this medium. However, further studies on other wastewaters are required to determine the biocide effect of ozone at the same doses applied. Regarding HTL ozonation compared with the reference dried RAW feed, HTL provides a better energy valorization product in terms of HHV (8,382 cal/g versus 6,242 cal/g). These crude-oils could be, therefore, considered a feasible alternative to conventional fuels. From the technical and economic point of view, the conditions chosen in materials and methods should be considered as the starting point if the scaling up of the process to an industrial level is to be attempted. Here is where the pre-treatment takes place. Ozonation reduced the char yield by 25%, but char is considered more of a by-product in this study, being the crude-oil the main and preferred product which yield and HHV don’t seem to be affected. At the same time, ozonation reduced drastically the cost of filters in the filtration step up to 75%. The ozone pre-treatment also slightly reduced ashes by 2.6%. Ashes are undesirable in combustion processes and can be a problem at industrial scale operation. Finally, it is necessary to point out that the 16% of carbon monoxide generated by HTL over ozonated feed is another valorizable and toxic by-product. All these minor improvements and risks need to be taken into account as they involve an additional cost to be pondered when calculating the cost-effectiveness of the overall process. There is no doubt that further studies will be required before ozonation can be applied to the production of fuels for HTL from industrial wastes on a bigger scale. More experiments with higher ozone doses are scheduled to complete this study.

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