Monitoring and management of the wastewater produced in Galp Energia biodiesel factory, Enerfuel, in Sines.

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ABSTRACT

The present work aimed to monitor all wastewater sources in the biodiesel factory *Enerfuel*, relative to quantity and quality, identify the critical spots of contamination and suggest procedure modifications or final treatment alternatives in order to minimize the financial and environmental impact from the wastewater produced in the plant operation.

Until the beginning of the present work, March 2014, the most penalized parameters were Oils and Grease (O&G) and COD (Chemical Oxygen Demand). Both parameters represented a 83% share of all penalizations until the specified date.

After analyzing the produced wastewater, the main sources of contaminants identified were equipment cleaning and washing (e.g.: *Glycerin Reboiler*), with COD up to 100.000 mg O_2/L, and flush of aqueous solution from glycerin dewatering (RWA), which reached values approximate to 25.000 mg O_2/L until May 2014.

Therefore, changes to procedures were implemented and monitored which led to no COD penalties in the last month of monitoring, August 2014. However, some penalties were applied to O&G, probably due to insufficient capacity of the separators. As a solution, a prototype for equalization and control of the feeding wastewater flow to the separator system was installed. Thus, reducing by half (≈ 2m^3/h) the inflow rate of the O&G separator, previously installed in the plant, resulted in COD removals between 67-80%, against a maximum of 56% obtained previously, and no sample presented a penalizing value or a COD higher than 1000mgO_2/L (Class IV).

1. INTRODUCTION

1.1. Biofuels

Nowadays, the impact of production and consumption of fuels by men is not only part of common knowledge but its awareness is on the highest level in history. It is increasingly common to hear about alternative energies and alternative fuels capable of supporting the development of human civilization with minimal impact on the environment. Even knowing zero impact is considered barely impossible, it is important to discuss alternatives with less impact then the existing solutions in order to invert the pollutant recent pass trend to minimum emission consumption habits. It is with technology development, but also and mainly with the change of mentality, that rises the biggest interest in biofuels, or bio-based fuels.

According to data provided by *World Bank* [1] and *IEA* [2] it is possible to confirm the growth tendency of fossil fuel emissions. For example, in 2010, this fuel usage resulted in approximately 91% of total emissions worldwide and since 1870 the CO_2 emission profile, derived from fossil fuel combustion, follows an exponential growth (Figure 1).

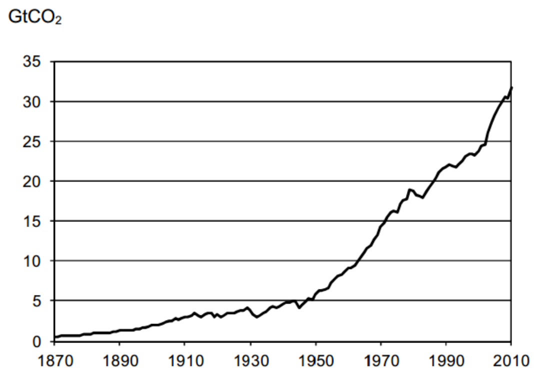

Figure 1 – Worldwide CO_2 emissions from fossil fuels combustion.

The *IEA* 2013 [2] report states that coal combustion represents, globally, the major source of CO_2 emissions, but oil corresponds to the biggest share in energy production. Relatively to alternative energies, namely biofuels, it can be verified that against a 18% TPES (Total Primary Energy Supply), they assume a 1% share in global CO_2 emissions. It should be noted that the use of biofuels is only in the transport sector.

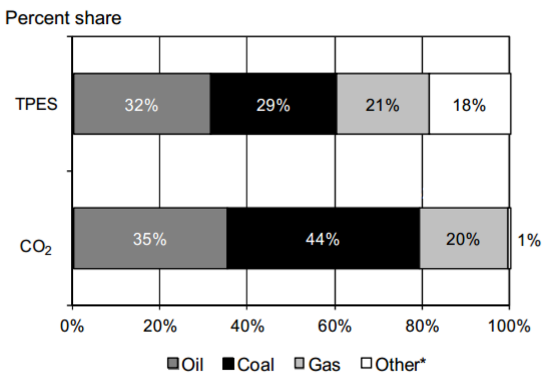

Figure 2 – Primary energy and emission sources worldwide. Share by fuel in 2011. **Other* includes nuclear, hydro, geothermic, solar, tides, wind, biofuels and residue reuse.

However, despite all the advantages associated to the use of biofuels as an energy source, there have been some setbacks in its implementation. Among these stands out the ethical and social problem of using raw food and the occupation of agricultural land for energy crop production while we witness a worldwide struggle against food scarcity. As a result of several factors, namely some climatic issues that affected the regular world market supplies and a higher demand for food raw materials, there was an abnormal food price increase due to the biofuels market. An example of this scenario was the worldwide food price that doubled between 2000 and 2011. In fact, the growth of the US corn-based bioethanol market was followed by the rise of this food product price. The production of bioethanol from corn quadrupled between 2005 and 2013 in the USA, reaching a 15% use of total produced corn for conversion into biofuel [3], [4].

The aforementioned problems associated to 1st generation biofuels have spurred the development of 2nd generation biofuels. These are produced from non-food raw materials such as lignocellulosic wastes used to produce ethanol or animal fats, waste oils and even oils from non-food crops like *Jatropha Curcas* oil used to produce biodiesel [5][6]. Finally, there are the so-called 3rd generation biofuels, which use, for example, oils extracted from microorganisms such as microalgae, or other technologies still poor developed which may also be an interesting alternative to use various new raw materials in a more or less near future.

Aiming to promote the sustainable use of biofuels in medium and long term, in 2009 the European Commission issued the Directive 2009/28/EC, designated as RED (Renewable Energy Directive) [7]. Among other aspects, this Directive imposes a mandatory target, for all Member States, that consists in 10% of renewable energy in the transportation sector until 2020. Simultaneously, it sets some sustainability criteria for biofuels and bioliquids which compliance is crucial to its accounting, including a minimum reduction in CO_2 of 35% by 2017, relatively to fossil fuels combustion. For the next years, it is demanded a reduction no less than 50% in emissions from 2017 and 60% from 2018 [8][9]. Also in 2009, it was published the Fuel Quality Directive (FQD) that defines an increasing rate of incorporation of biodiesel in diesel (7% v/v) and ethanol in gasoline (10% v/v) [7].

1.2. Enerfuel

Following this trend, in 2012, Galp Energia acquires *Enerfuel* biodiesel plant in Sines, for production of fuel from waste products as animal fats and used cooking oils. This unit was bought from Enersis and is equipped with Austrian process technology from BDI (BioDiesel International). It started producing in 2013 and it has an annual production capacity of 27 thousand tons of biodiesel, which allows Galp Energia to contribute to national incorporation in diesel, according to the European target (RED). In addition, the European Commission is discussing the possibility of limiting the contribution of 1^{st} generation biofuels to 5,5% in order to meet the 10% uptake target of biofuels by 2020 [10].

The production process in Enerfuel uses almost exclusively animal fat as feedstock. It consists in a first stage of esterification of free fatty acids (FFA), with acid and methanol, followed by a step of alkaline transesterification with methanol (catalyst added as potassium methoxide CH_3OK). There are also several steps for methanol recovery and product separation and purification, namely washing, distillation, decantation and drying stages [11]. In addition, unlike the usual biodiesel factories, the wastewater produced in the biodiesel washing is re-introduced in the process and afterwards acidified for FFA (Free Fatty Acid) and methanol recovery.

Among all process steps and stages there are only some that produce wastewater that follows to the industrial sewer and subsequently to the wastewater treatment plant of *Águas de Santo André*. These are equipment washing, like the Glycerin Reboiler or the potassium sulphate dryer, flush of water from the glycerin dryer (RWA), floor washing and utilities purge, such as from reverse osmosis in the water treatment system, from the boiler and the cooling tower. Regarding the wastewater quality, these may be mainly contaminated with fats, biodiesel, glycerin, methanol, salts, etc. Thus, it is expected high COD (Chemical Oxygen Demand) values and possibly high levels of oils and fats (O&F). COD measures the amount of biodegradable and non-biodegradable organic compounds.

The industrial sewer collector in Enerfuel leads all wastewater produced, except the domestic volumes from the administration building, to five oil and fat separators with $1m^3$ each. After the effluent passes through all the separators goes straight to the AdSA collecting room for later analysis. The sample analyzed by AdSA is a composed sample, a mixture of small volumes collected recurrently in short periods of time that represents the total volume of flushed wastewater in a period of operations.

Águas de Santo André (AdSA) is the responsible entity for managing the system *Santo André* in order to ensure quality water supply to the covered population and industries and collection and treatment of wastewater from the covered areas. The billing system consists in applying fares depending on the wastewater quality. There are 5 classes, which class V represents the worst composition, and there's a level of penalty, over class V, that increases according to the excess of each parameter (Table 1) [12].

Table 1 – Penalizing parameters according to AdSA classification system [12].

Parameter	Penalizing Load
pH	<4.5 or >10
COD (mg/L)	> 2,000
Total Suspended Solids (mg/L)	> 1,000
Oils & Fats (mg/L)	> 100
Sulphides (mg/L)	> 20
Phenols (mg/L)	> 40

1.3. State of the art

There are some precedent works that describe different biodiesel wastewater treatments

XIE *et al* [13], for example, studied the effect of acidification and coagulant addition to an effluent with high glycerin concentration, from biodiesel washing. It was obtained removals of 96% for COD, 93% for BOD_5 (Biochemical Oxygen Demand for 5 days), 98% of TSS (Total Suspended Solids), 100% of soaps, 86% of methanol and 65% glycerin.

NGAMLERDPOKIN *et al* [14] compared a chemical treatment with an electrochemical on a biodiesel washing effluent. After acidification, the chemical treatment with $Al_2(SO_4)_2$ achieved COD, BOD_5 and O&F removals of 98%, 97% and 98%, respectively. On the other hand, the electrochemical treatment, after acidification, removed 99,6%, 91,5% and 98,7% of COD, BOD_5 and O&F, respectively.

SHIRAZI *et al* [15] tested the accelerating effect of NaCl addition in biodiesel – water separation. This experiment resulted in a 100% acceleration of the glycerin phase decantation when added 1 gNaCl/100mL to the initial mixture.

It has already been tested other treatments to typical biodiesel plant wastewaters, such as processes based in adsorption or biological principals[16][17][18][19][20][21] . However, usually these consist in more complex and more expensive setups.

2. MATERIALS AND METHODS

2.1. COD Analysis

The COD analysis followed the *Standard Methods for the Examination of Water and Wastewater* protocol 5220B [22]. The reagents used were $K_2Cr_2O_7$ (VWR Chemicals), $HgSO_4$ (Merck), Ag_2SO_4 acidic solution (VWR Chemicals), FAS - Ferrous Ammonium Sulphate (VWR Chemicals) and ferroin (VWR Chemicals). For the heat digestion a TR 420 Spectroquant from Merck was used to subject the samples to 150±2^{o}C for 2h.

2.2. Coagulation – flocculation jar test

Concerning the jar test, it was used $FeCl_3$ (Sigma-Aldrich) as coagulant, magnafloc 1011 (Rivaz Química S.A.) as anionic flocculant and zetag (Rivaz Química S.A.) as cationic flocculant. The procedure consisted at first in a 175rpm agitation for 3 min and a final 25rpm agitation for 12 min.

2.3. NaCl tests

Regarding the Sodium Chloride tests, it was used a Panreac salt dissolved with 30min of magnetic agitation followed by 30min of settling.

3. RESULTS AND DISCUTION

Analyzing the AdSA reports from Enerfuel wastewater, it stands out that COD and O&F are the most penalized parameters during the plant operations (Figure 3). In fact, they both represent an 83% share of total occurrences until March 2014.

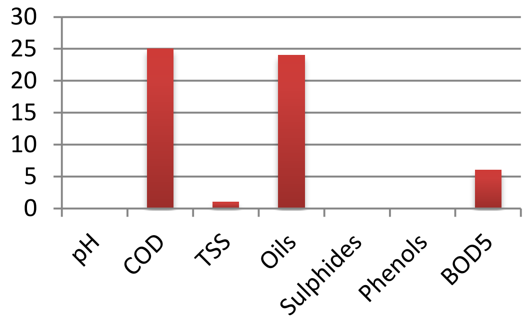

Figure 3 – Number of penalties applied to each parameter monitored by AdSA.

3.1. COD Monitoring and Procedure Intervention

The first samples collected and analyzed were from the biodiesel washing, utilities purges, and several spots in the plant during a washing/cleaning procedure of the glycerin dryer, or glycerin reboiler.

Regarding the biodiesel washing, a direct sampling was made from the transesterification reactor after the washing steps. A COD of approximately 385,000 mgO_2/L was obtained, thus, it is important to avoid flushing this wastewater to the industrial sewer.

As for the purges' COD, the obtained values are presented in Figure 4. As it can be verified, these wastewater sources do not represent critical COD values for contamination.

A sample was collected after the separators, before and during a glycerin reboiler washing, and analyzed afterwards (Figure 5). The results showed a COD during cleaning 31 times higher than before the event, so it was implemented a procedure modification that consisted in storing the first volumes of wastewater produced for further dispatch and proper treatment.

Financially this intervention might as well be favorable considering the lower fee applied when a contaminated wastewater is received by AdSA separately from the industrial sewer. In order to monitor the impact of this intervention, samples were collected from the contained flushes produced during this process, in two different days. In 19th May were contained 3m^3 of wastewater in three IBCs (Intermediate Bulk Container), 1m^3 each, and in 22nd May was contained only 1m^3 but a 1L sample was also collected to represent the first volume that went to the industrial sewer.

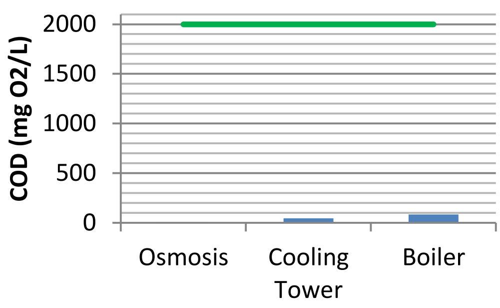

Figure 4 – COD values of each utility system purge. Blue bars represent purges COD and green line the COD penalty limit imposed by AdSA.

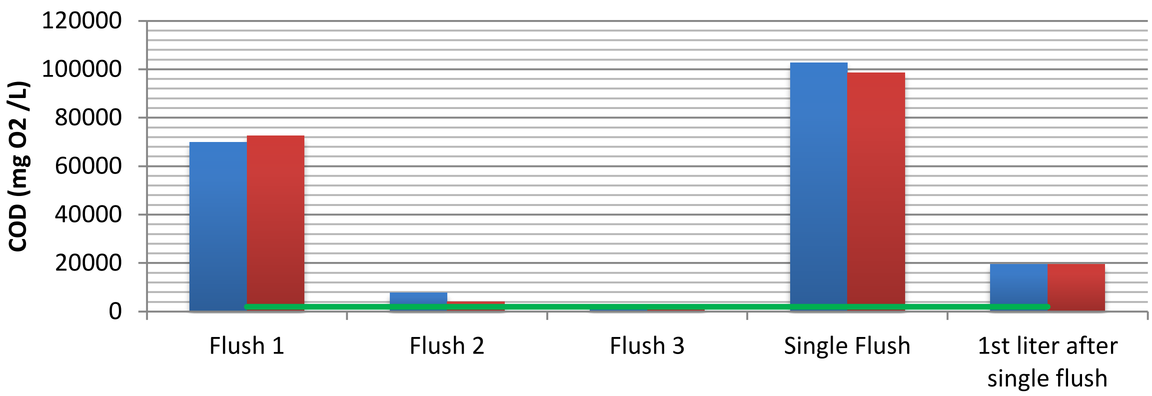

Figure 5 – COD values of the first 3 flushes from the 19th May reboiler washing, the single flush from the 22nd May reboiler washing and the first liter thrown to the industrial sewer. Blue bars represent the COD from the homogenized samples, red bars the COD from the supernatant after 15 day of the sample natural sedimentation and the green line the COD penalty limit.

The results presented in the previous Figure show that this wastewater isolation is beneficial to the final effluent quality. In fact, the flush 3 COD is close to the penalty limit (≈ 2,500 mgO$_2$/L), however, it is recommended to be contained. Additionally, the whole effluent produced should be isolated in order to prevent final contamination and subsequent penalizations.

The last sample analyzed in this campaign was the water from the glycerin dewatering which is stored in the RWA tank. The COD analysis showed that this effluent, that is intermittently unloaded to the industrial sewer, has a correspondent value close to 25,000 mgO$_2$/L. As this COD is a lot higher than the penalty limit (2,000 mgO$_2$/L) several treatments were studied in the laboratory to try reducing it.

3.2. Experimental COD reduction treatments

3.2.1. Coagulation – Flocculation in Jar test

The addition of coagulant and flocculant agents to a RWA and post-separators' sample was studied in jar test. The experiment followed the method and used the materials described in Section 2 – Materials and Methods, moreover a blank was prepared without coagulant or flocculant. The essay consisted in studying the effect of zetag in RWA wastewater collected in 16/04/2014, the effect of magnafloc in RWA collected in 22/05/2014 (referred as RWA' in this test) and magnafloc in a sample gathered after the separators (Figure 6).

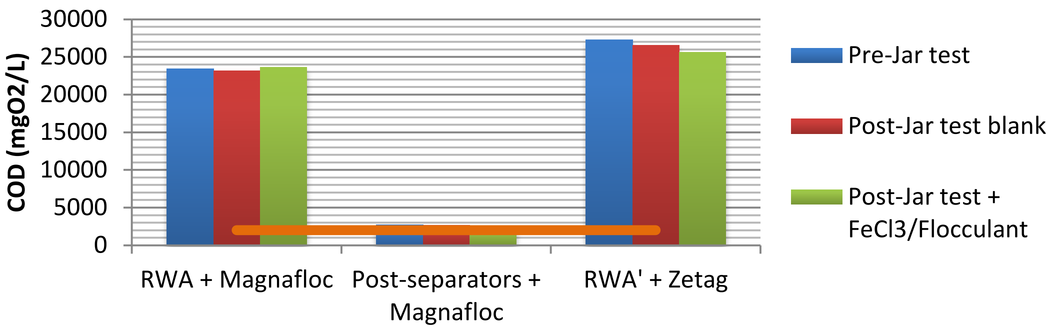

Figure 6 – COD values obtained in the jar test with addition of $FeCl_3$ + zetag or $FeCl_3$ + magnafloc, against COD value of the blank sample.

The results presented in the previous figure showed that the addition of anionic or cationic flocculants had no effect on the sedimentation of suspended particles. As a matter of fact, even the blank sample remained with a similar COD value after de jar test. Therefore, eventually both RWA and post-separators wastewater have few suspended organics compounds able to settle down. The highest COD removal was 14% in the post-separators sample with FeCl3 and magnafloc.

3.2.2. Sodium Chloride Tests

It was tested the addition of NaCl in order to achieve COD reductions in wastewater. As the RWA found to be one of the major contaminant source of organics, this was the selected wastewater for the experiment.

The RWA' used in this test had an initial COD of 27,300 mgO_2/L. Furthermore, 1 g and 5g of NaCl were added to 50mL of raw RWA' and to RWA' after the coagulation/flocculation test described previously. The results are shown in Figure 7.

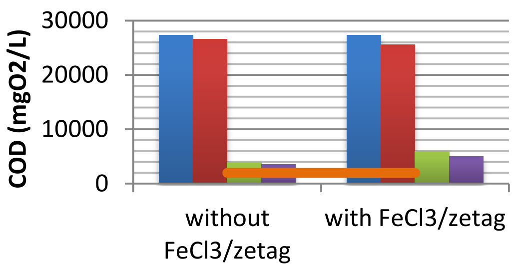

Figure 7 – Blue, initial RWA' COD; Red, RWA'COD after test without NaCl; Green, RWA' COD after test with 1g NaCl; Purple, RWA' COD after test with 5g NaCl; Orange, COD penalty limit.

According to the COD values obtained, the NaCl addition led to a significant decrease of the organic matter in the middle zone of the beaker used in the experiment (sampling zone for COD analysis). The highest removal was 87% of COD in the raw RWA' sample, obtained without coagulant/flocculant and with 5 gNaCl/ 50mL (Figure 8).

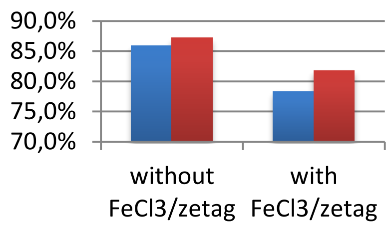

Figure 8 – COD removals in the RWA' samples after NaCl addition test.

In addition, further NaCl tests were done but none achieved the same results as this first. This might indicate that this procedure is only effective in high organic concentrations (glycerol or methanol). Unlike this first sample (27,000 mgO_2/L) the other tested samples had initial CODs below 12,000 mgO_2/L. Another possible explanation is the high methanol content in the first sample relatively to the next RWA collected samples. After a reflux ratio modification in the demethanolization step, the RWA COD dropped significantly, possibly due to the sharp fall of methanol concentration in this wastewater. This process alteration was also found beneficial in improving the final effluent quality.

3.3. Oils and Fats Monitoring

After COD, Oils and Fats is the most penalized parameter in Enerfuel wastewaters (Figure 3). Indeed, as can be seen in Figure 9, since April 2014, due to modifications made in the factory process, the frequency of COD penalties has been decreasing. On the other hand, the Oils and Fats monthly penalties have become more frequent.

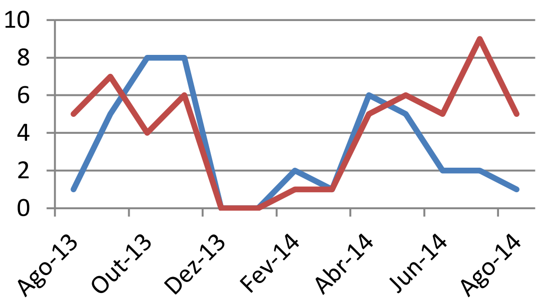

Figure 9 – Number of monthly COD penalties applied to Enerfuel (blue) and Oils and Fats (red), since August 2013 to July 2014.

The Oils and Fats contamination were identified to be mainly from equipment washing/cleanups and floor washing. The solution to prevent the first source is identical to the one described for reducing the COD contamination: containing the washing effluents. Regarding the second identified source, the problem can be also solved with wastewater retention in IBCs, however, given the existence of the five separators already installed, it was decided to first study this operation aiming its optimization.

3.4. Oils and Fats Separators Optimization – Equalization System Prototype

As described by *Metcalf & Eddy* [23], in order to prevent oversizing in wastewater treatment plants which have widely varying discharging volumes is convenient to install equalization tanks. Thus, in order to study the effect of reducing the separators inflow rate in the equipment efficiency, it was installed a prototype for containment and flowrate control. The prototype system consisted in five IBCs, $1m^3$ each, connected to a single pipe as shown in Figure 10. One of the containers is fed from the effluent well and in one end of the connecting pipe there's a valve that controls the discharge flowrate to the first separator surface. Thus, it is expected that with the increase of the capacity of volume containment, the separators inflow rate can be controlled reducing the turbulence inside and increasing the residence time. Figure 11 shows the system impact in COD values before and after the separators.

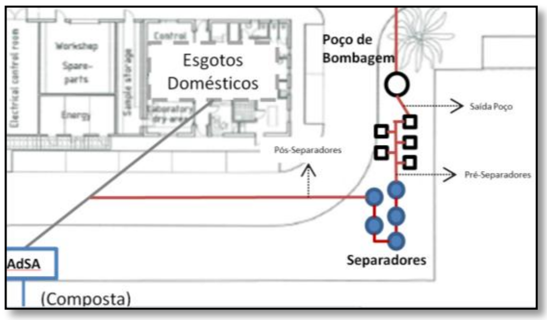

Figure 10 – Scheme of equalization system prototype setup in the plant. Blue – O&F separators; White circle – Effluent Well; White squares – equalization IBCs.

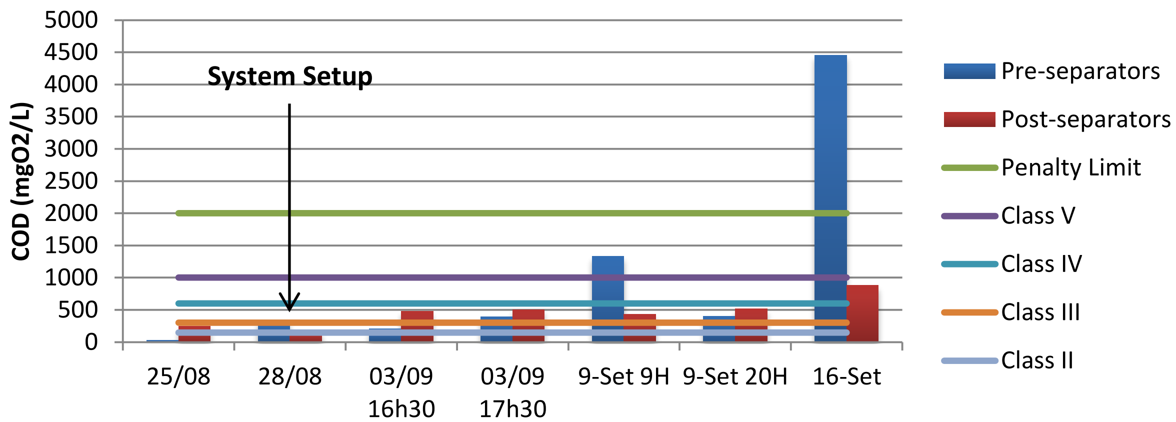

Figure 11 – Pre and Post-separators COD values before and after the equalization system prototype setup.

According to Figure 11, after the prototype setup there was an increase in the separators efficiency. Actually, when the separators inflow rate was approximately 2 m^3/h, against the previous 4 m^3/L, it was verified a 67% COD removal in the separators at 9h of 9th September and 80% on the September 16th. These are the highest COD removals obtained since the beginning of the present work. In fact, previously, it was only obtained a maximum of 56% COD removal, however this happened to an effluent with 720 mgO_2/L COD which means a smaller amount of organics retained in the separators. Moreover, following the AdSA wastewater classification, none of the post-separators sample was classified over class IV, even when the wastewater enters the separators with a 4,500 mgO_2/L COD (16th September).

3.5. Analysis to the Produced Wastewater Volume

Several analysis were made aiming to better understand the produced wastewater volume in Enerfuel. In order to identify the regular effluent quantity flushed to the AdSA sewers during a normal production period, it was calculated the total formed effluent volume per ton of FAME produced since February 2014. The produced values are presented in Figure 12 and shows two peaks of wastewater volume and two levels of stabilization. The first peak was caused by several washing procedures to equipments and a low FAME production. On the other hand, the second peak was caused by the total flush of the boiler water system before an equipment modification.

Regarding the stabilization levels, the first one (April 2014 – June 2014) shows a ratio wastewater/produced FAME between 0.60 and 0.75 m^3/ton and the second one indicates a ratio between 1.0 and 1.6 m^3/ton. This parameter has two different stabilization tier values probably due to the increase of purge with the mentioned boiler system modification.

3.6. Current Enerfuel Effluent Quality

In the last monitored month, August 2014, the factory was laboring steadily and with a high FAME production. Nevertheless, it was verified an improvement in the wastewater quality, especially in COD. The only penalized parameter during this month was O&F, which can be possibly solved with the equalization system setup, according to the obtained results in section 3.4.

3.7. Conclusions

- The main COD sources are equipment cleanup and RWA flush. The first can be contained in IBCs for dispatch and the second was partially solved with the demeth reflux ratio modification.
- NaCl addition to the RWA wastewater can lead to a significant COD reduction when higher methanol content is verified.
- The main O&F sources were equipment cleanup and floor washing. The first will be solved with the referred intervention for COD reduction and the second can eventually be solved with the installation of an equalization tank for the separators inflow rate reduction.
- Avoiding penalties will at least eliminate an average cost of €3,400/month.

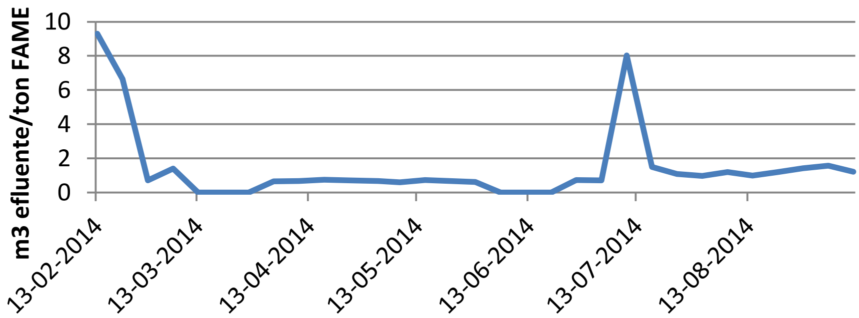

Figure 12 – Flushed wastewater volume per ton of FAME produced since February 2014.

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