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USE OF BOMB CALORIMETRY TO ASSESS RECOVERY OF WASTE INDUSTRIAL MINERAL OILS THROUGH REGENERATION

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Abstract

This paper shows an application of bomb calorimetry used in the procedure of regeneration of waste industrial mineral oils. Using the treatment here reported a recovery of nearly 50% of the used oils was achieved. Furthermore, the oils so recovered contain concentrations of potentially contaminant elements far below the requirements of the European Union (EU). Generally speaking, it can be said that the used oil treatment is based on the proper combination of two main procedures, namely the addition and mixture of certain chemicals–precipitant, flocculant and demulsifying agents– in a permanently stirred reactor, at high temperature, and the centrifugation of the mixture. This oil, recovered through the technique of oil regenerating, cleaning, and fitness, can be used either as a raw material for the elaboration of new oils or as a fuel to be used for cogeneration of thermal or electric energy. The treatment described is highly remunerative, both as regards to cost –used oil is subject to a low-cost process, especially if compared to its elaboration from raw materials– and as regards to ecology, since it is recycled, thus saving a great amount of raw materials.

Keywords: calorimetry, environmental and regeneration, used industrial mineral oils

Introduction

Out of almost 500000 tons [1, 2] of used oils generated in Spain every year, nearly 40% come from the industry. Of these residual oils, almost 60% are thrown away without any control whatsoever, so causing serious environmental problems:

– In the aquatic environment, by preventing a proper water oxygenation, the spreading of contaminants and increasing the organic load in the water.

– In the atmosphere, by releasing heavy metals and other highly polluting materials, harmful to human health (SO_3, HCl and other particles and hydrocarbons).

– On land, by polluting the soil as well as surface and underground water layers.

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Out of the remaining 40%, only 5% are recycled, whereas 95% are used as a fuel, dubiously safe for the environment.

The main source of the oils used in industry is mineral, i. e., they derive from the distilled fraction of crude. Different other products are then added to these lubricant bases, so that they may be fit for the functions they were designed for. These additives deteriorate with use, so becoming waste oils. The final composition of a used oil makes it to be classified as a hazardous toxic waste (HTW).

It is known that oil is never degraded but its additives deteriorate.

Our experimental procedure is based on the separation of such additives and the recuperation of the lubricant basis, which is not degraded. This recovered oil is used as the basis for new oils, ready to receive the relevant additives. One of the key parameters to consider used oils as regenerated is the recovery of calorific values, that is the energy content in a mass unit of fuel.

The regeneration of used oils is beneficial in two ways:

– Ecologically, as it helps to save raw materials when elaborating oils, since we are using recovered materials.

– Economically, as the oil recovered through the procedure here described is cheaper than conventional base oils, hence more competitive.

The main target, therefore, was to develop a new technique thus making possible the recovery of the largest amount of lubricant basis that could be used again as a basis for new oils [3]. To achieve this, it is necessary:

– To determine the main impurities contained in these hydrocarbons and residual oils to study which reagent/s will allow an effective separation through a centrifugation procedure.

– To recover their calorific power so as to know their yield of energy. The higher heating values (HHV), that is, the quantity of heat generated by complete combustion, in a bomb calorimeter, of a unit mass of sample in an oxygen atmosphere, assumming that both the water contained in the sample and that generated from the combined hydrogen remain in liquid form.

Experimental

Waste used oils constitute a very heterogeneous material. For this reason the collection of a representative bulk sample is a hard and very important task. In a previous study, waste oils were split into five groups: fuel-oil slops, industrial oil slops, gas-oil slops, mineral oil slops and synthetic oil slops. The present study was carried out with industrial oil slops, gas oil slops and mineral oils slops. As it was reported [4], synthetic oils are used, after treatment, as fuels to be used for cogeneration of electric and thermal energies. For our study, sampling was carried out during 30 days along six months, giving a final 400 tons bulk sample for every type of residue. The different used waste oils studied were homogenized as much as possible in big tanks provided with continuous stirring systems and then stored in 50 L polypropylene cylinders to avoid loss of properties during transport to the laboratory. The different cylinders contained waste oils of same composition as those received in the treatment plant. Once characterized, the various waste oils were mixed to achieve a 'base mixture'. This staple mixture consists of 20% fuel-oil and gas-oil slops, and 80% industrial mineral waste oils. The cylinders containing this waste oils were continuously stirred in order to obtain a final homogeneous mixture 500 cm^3 of which were used for our study. The optimization of the restoring process needs the knowledge of different data. To determine them, a first series of tests must be carried out:

– Viscosity: ASTM D-1745/60, D-445/61, INTA ISO21819 Part 25 [5].
– Flash point: ASTM D-92 Part 23 [6].
– Water content: ASTM D-95/70 Part 23 [6,7].
– Water and centrifuged sediments: ASTM D-96773 Part 23 [6].
– Density: ASTM D-1298/67 Part 23 [6].
– Higher heating value (HHV) following the procedure given by Hubbard *et al.* and Núñez-Regueira *et al.* [8, 9].
– Elementary composition, determined by a Carlo Erba elementary analysis equipment, heavy metal contents, by atomic absorption spectrophotometry, and poly(chloridebiphenyls) contents (PCB).

Once characterized the waste oil 'base mixture', the purifying process starts. This process consists of a series of steps trying to restore the original values of physico-chemical properties and thus to allow the mixture be declassified as a hazardous toxic waste (HTW). With this purpose, the following steps were carried out:

1. Heating the samples to 80–90°C by a heating blanket JP SELECTA FIBROMAN O and homogenization by continuous stirring during 15 min using a HEIDOLPH RK 3 motor.

2. Demetallizing process. In this process, different chemical compounds were used to produce a combined effect by which flocculation and precipitation of the heavy metals contained in the residual oils were achieved after 1 h of centrifugation. With this aim, ammonium salts were used as demetallizers [10–12], the flocculant was a commercial LZ5957, and different sodium salts were used as precipitants. All these products were prepared in our laboratory.

3. Centrifugation experiments. This step started by the search for the optimum time and speed of centrifuging. Both are key parameters from the economic point of view. Once found, the step went on with the separation of the different phases resulting from centrifugation: lubricant base, water and sediments. The lubricant base was under the same physico-chemical experiments that the used oils in order to check the recovery of physical properties and thus to corroborate the optimization of the process carried out for mineral used oil treatment.The experiments were carried out using a 600 ml SELECTA-Meditronic centrifuge at 4800 rpm.

4. Other determinations of interest that are usually carried out were the study of the evolution of pH over the experiment, using a Crison micropH 2000, and the determination of the cokefaction index according to standard ASTM D-189/76 [12–14].

5. Finally, the resulting oil mixture obtained after treatment was compared to the waste oil as received, and to some other regenerated commercial oils to show the

many advantages of the method here proposed, both from the point of view of the final product and from the point of view of the experimental procedure developed. In this step, the calorific value of the samples was determined using a static bomb calorimeter under an oxygen atmosphere [8, 9].

Results and discussion

Table 1 shows results obtained after centrifugation of a residual oil/ammonium salt (diammonium phosphate or DAP) mixture after 15 and 60 min respectively of centrifuging. Concentration of chemical reagents was varied in the range 0.31–10 g L^{-1} in order to find the optimum value. One other point to be taking in account from the economical point of view is the speed and time of centrifuging. To search for optimum values, speeds in the range 1000–7000 rpm, and times from 5 to 60 min were tested. Next step was the election of diammonium phosphate (DAP) [9–11] as a demetallizing agent. From results shown in Table 1 it was found that 5 g L^{-1} lead to a percentage separation 42% of a well looking recovered oil, 10% of an interphase easily separable by mechanical means, high percentage of extracted water (41%), and 7% of a compact sediment of the total oil treated. It can be also observed that these numbers were not significantly improved by an increase in the time of centrifuging (60 min). Because of this, a time of 15 min was considered very adequate with the subsequent economical savings.

Table 1 Percentages of the different phases after centrifugation of a residual oil/ammonium salt (DAP) mixture

	Phase after centrifugation/%							
	Oil		Interface		Water		Sediments	
DAP added/g L^{-1}	15′	60′	15′	60′	15′	60′	15′	60′
0.00	–	15	47	33	48	47	5	5
0.31	40	40	12	14	43	41	5	5
0.62	41	40	12	14	42	41	5	5
1.25	36	36	18	24	43	35	5	5
2.50	32	27	24	28	37	38	7	8
5.00	42	38	10	10	41	44	7	8
10.0	40	39	10	12	42	40	8	8

In a second series of runs, different amounts of reagent were added before centrifugation: sodium salts (0.5–1 g L^{-1}): sodium acetate and sodium oxalate, and flocculant (6 g L^{-1}). Results after centrifugation are shown in Table 2. For this second centrifugation a ratio used oil/ammonium salt: 500 cm^3/5 g L^{-1} was chosen same as the one chosen for the previous series. As it can be seen from this table, the best results were obtained using preparation 1, (as a recovery of 38% of the used oils was achieved, using sodium acetate (cheaper than oxalate) and separation between the oil phase and the re-

Table 2 Second centrifugation using a 500 cc/5 g L^{-1} recovered lubricant base/DAP. In all the experiments, a concentration of 6 g L^{-1} of a commercial flocculant was used

	Phase after centrifugation/%							
	Oil		Interface		Water		Sediments	
Sampling	15′	60′	15′	60′	15′	60′	15′	60′
1	38	36	9	9	46	47	7	8
2	36	38	13	12	43	41	7	8
3	38	36	8	10	47	46	7	8
4	38	38	7	10	47	43	8	9

1: Sodium acetate 0.5 g L^{-1}

2: Sodium acetate 1 g L^{-1}

3: Sodium oxalate 0.5 g L^{-1}

4: Sodium oxalate 1 g L^{-1}

Table 3 Chemical composition of sediments and interphase resulting from centrifugation of the treated oil

	Interphase	Sediments
HHV/kJ kg^{-1}	29 889.57	11 727.23
Sediments/%	37.50	100
Ashes after bomb combustion/%	6.57	20.65
Cl/%	0.20	0.10
S/%	0.27	0.24
N/%	0.89	0.10
Fe/ppm	227.30	53
Mn/ppm	11.70	1.25
Zn/ppm	280.50	168.25
Pb/ppm	60.75	90.60
Cd/ppm	9.30	6.20
Cu/ppm	10.30	9.70
Ni/ppm	–	–
Cr/ppm	–	–
Al/ppm	48.50	19.70
P_2O_5/ppm	290.65	360

mainder material was easier because the interphase was better defined. Moreover, the time needed was shorter thus reducing operation costs.) For this same reason, a centrifuging time of 15 min was selected. For this reason, this preparation was chosen for our experiments obtaining a 38% of used oils recovery, which means a recovery of 76 000 T of oil. Sediments (7%), and interface (9%) constitute a residue to be adequately treated before dumping in a security dumping place. Sodium acetate and sodium oxalate were used to achieve a higher stability in phases. It can be seen that preparation 1 makes the phases more differentiable and stable thus meaning that this compound (sodium acetate) is very favourable for the separation of the oily phase from the rest of residual phases. The use of a flocculant improves both the demetallizing process and, at the same time, the sedimentation of particles suspended in the waste oil, thus optimizing the phase separation. As it can be seen in Table 3, this residue contains the most part of pollutants [14]. Alternatively, due to their large HHV, close to 30 000 kJ kg^{-1}, these residues can be used as a fuel in incineration plants. Ashes generated from combustion of these residues contain very low pollutant concentrations.

Table 4 shows chemical composition of ashes generated by the combustion of the interphase and sediments combustion. This table together with Table 3 shows that pollutant elements are mainly fixed in the interphases and sediment. Because of this, the concentration of pollutants in the water separated after centrifugation (46%) is very low thus making it very easy to be treated following conventional procedures [15–17].

Table 4 Ashes chemical composition after combustion of interphase and sediments of the treated oil

	Interphase/%	Sediments/%
SiO_2	4.98	22.85
P_2O_5	36	19.40
Fe_2O_3	9.70	25.20
CaO	38.30	22.20
MgO	5.31	4.26
MnO	0.95	2.17
Na_2O	<0.01	0.02
K_2O	<0.01	<0.01
ZnO	1.23	1.48
PbO	0.03	0.38
NiO	0.04	0.11
Cr_2O_3	0.03	0.05
CuO	0.08	0.17
Al_2O_3	0.63	1.97
Cd	16 ppm	8.20 ppm

Table 5 shows HHV and LHV before and after treatment. It can be seen the enormous increase in HHV that changes from 18 438.44 kJ kg^{-1} before treatment to 45 199.73 kJ kg^{-1} after being treated. This fact shows the good election of the experimental procedure used for recovering the waste oil as an energy source [4]. HHV of the regenerated oil is very similar to that of the commercial original one. The increase in HHV is due obviously to a decrease in water content (45% on the case of used oils) and of some of the impurities that oils add with use.

Table 5 HHV and LHV of the different oils

	HHV/kJ kg^{-1}	LHV/kJ kg^{-1}
No-treated used oil	18 438.44	14 363.81
Treated oil	45 199.73	40 035.73
Original industrial oil	47 462.95	42 298.95

Table 6 Different parameters corresponding to used oils before and after treatment

	Before treatment	After treatment
Moisture content/%	56.22	<0.1
Viscosity$_{20°C}$/cps	255	13.2
Flash point/°C	195	125
HHV/kJ kg^{-1}	18438.44	45199.73
Sediments/%	10.08	<0.1
Ashes after bomb combustion/%	4.48	<0.05
Cl/%	0.50	0.4
S/%	0.29	0.5
N/%	1.10	1.65
Fe/ppm	217.75	55
Mn/ppm	33.75	1
Zn/ppm	188.18	10
Pb/ppm	66.32	14
Cd/ppm	7.5	1
Cu/ppm	26	8
Ni/ppm	316.75	–
Cr/ppm	100.50	–
Al/ppm	35.38	12
P_2O_5/ppm	80.5	–

– bellow detection limits

Table 6 shows the results of different parameters corresponding to used oils before and after treatment. It can be seen:

- The almost total elimination of water.
- The recovery of the initial viscosity of the oils.
- A 64% reduction in the flash point.

– A small increase in S and N as a consequence of the reagents used in the treatment.

– Big reductions in the concentration of all the heavy metals present in the used oil, especially those of Cr and Ni, that disappear totally in the treated oil, and those of Pb, Zn, and Cd for their importance in the phenomena of environmental contamination.

– Reduction in ash percentage (<0.05%)

Conclusions

The results here reported demonstrate that the procedure TERBIPROMAT-SADER to recover used oils is suitable. The recovered oil contains concentrations of pollutants very below those demanded by the EU [18, 19]. This recovered oil is an ideal base for the obtention of new industrial oils both from the ecological and the economical points of view since the procedure developed makes the price of this oil to be much lower than that of the prime matters necessary for its elaboration.

The simplicity of the procedure here used makes it very suitable for any firm dedicated to waste oil regeneration and, at the same time, the low cost of the products used in this treatment make the final product very competitive from the economical point of view.

The recovery of approximately 80 000 T per year is not only viable and adequate from the economic point of view but also from the ecological point of view (the cost of treatment of polluting waters, interphase, and slops is low and at the same time, the techniques are well developed).

After treatment, the regenerated oils can be used either as fuels for cogeneration systems or as a source to elaborate new oils. On the one hand, the fact they present great HHV (45 000 kJ kg^{-1}) and very low moisture content (<0.1%), and low amount of ashes (<0.5%) make them very convenient to be used in combustion engines for cogeneration of electric or thermal energies, with low corrosion and low solid deposition in the engine. On the other hand, the fact that they recover viscosity, flash point and some other physical properties make their use possible as a base for elaboration of new oils. The final choice of using this regenerated oil in one or the other way is based only on economic reasons or on the actual demand.

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