Used Lubricating Oil Processing for Energy Recovery
I. Applied pyrolysis

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Applied pyrolysis is used in this work as a treatment technique for hydrocarbon fraction recovery of used lubricating oils (ULO) with the aim of its further energetic valorisation. Applied pyrolysis bring also the advantage of a better management of metallic compounds that will be concentrated in the solid residue. In this work, technical parameters have been evaluated to establish their influence on the process evolution with the aim of identifying the adequate parameters for obtaining the maximum liquid fraction. It was found that, for an equilibrated energy balance, the final pyrolysis temperature should not exceed 460°C and the main parameter that affect the pyrolysis oil yield and its physical-chemical properties is the heating rate in the thermal range of decomposition. Activated Zeolites (HZSM-5 type) and Na_2CO_3 were used as catalysts. The catalysed pyrolysis tests were performed using direct contact between ULO and catalyst, the materials being mixed before processing. Experimental results showed that in non-catalysed pyrolysis an increasing heating rate is slightly reducing the yield of liquid fraction. On the other hand, by using catalysts, the liquid fraction is decreasing. Thus, the highest liquid ratio (81 wt.%) was obtained when the Na_2CO_3 is used and the process is run under a heating rate of 3-5°C/min. But then, the zeolite HZSM-5 is leading to the highest overall conversion, 95 wt.% at 15-17°C/min, and is positively influence the formation of gas fractions.

Keywords: Used lubricating oil, pyrolysis, environment, energy

Used lubricating oils (ULO) and industrial oils pose serious pollution problems and it is estimated that less than 45% of available waste oil are collected worldwide while the rest is either misused or improperly disposed by the end user [1]. As a result, there are different studies carried out to highlight certain strategies to control the ULO issue that has become an important concern of modern society [2]. The diverse nature of waste oils makes finding a universal treatment for them difficult task. Concerns about the material recovery or reuse of various types of natural oils used as lubricants in different fields have been since the 1970s, generally correlated with the various economic crises in which the oil price was a major player [3]. This is understandable considering the chemical composition of these oils, up to 95% being represented by hydrocarbons and 5% by additives [4].

Thus, experimental studies where focused on different topics such as removing various pollutants contained in waste lubricating oil and simultaneously reusing the residue as valuable products; metal distribution and solvent extraction and reuse; etc. [1-3, 5, 6]. Mainly, re-refining processes were applied in these studies highlighting the most important disadvantage of this treatment the oil loss during the processing (up to 16% of the hydrocarbon content) [3].

Furthermore, economical assessment of different proposed processing paths has been done in order to identify the appropriate way of dealing with the continuously increasing amount of the used lubricating oils [7, 8]. Complex processes such as *Mohawk Technology Five-Stage Process* have been analysed, and it was found that a high quality oil may be obtain only after the several stages of controlled distillation and hydro-treatment. Thus, an economically feasible system for oil recovery from ULO is possible to be implemented only if the process plant is located near a refinery or petrochemical plant where hydrogen can be easily supplied to ensure high profitability [7].

Moreover, related to the chemical composition of these used oils, another route of revaluation would be the energetic one. For this, simple or catalytic pyrolysis appears as an economical way to process ULO, with maximum demanding temperatures of 450-500°C. Pyrolysis techniques are today studied at different technological readiness levels with the aim of reducing different bulky industrial waste or neutralising the polluting effect of these materials. Since the process is leading to gas, liquid and solid fractions, different studies focussed on optimising the obtaining of a specific fraction and finding integrated solutions for co-products use, depending on the chemical composition of subjected waste [9-14].

Related to ULO processing through catalysed pyrolysis technologies, Bhaskar et al. [4] used thermal and catalytic treatment of waste lubricant oil with silica-alumina (SiO_2-Al_2O_3) and alumina (Al_2O_3) supported iron oxide (10 wt% Fe). The used Fe/SiO_2 catalyst was able to decrease the sulphur content from 1640 to 90 ppm and induced the breaking of heavy hydrocarbons into low molecular weight hydrocarbons. As well, Fe/SiO_2-Al_2O_3 (86%) and Fe/Al_2O_3 (90%) catalysts could decrease the sulphur content; however with an increase in reaction time, the desulphurization activity was found to decrease [4]. Wang at al. [14] performed co-pyrolysis of ULO with biomass and proved that the use of zeolite and magnesium oxide (HZSM-5/MgO) mass ratio of 3:2 favoured reactions of aromatic hydrocarbons formation.

However, as stated above, the wide variety of lubricating oils that are collected together make a given technology to be successfully applied only for certain cases. Thus, each

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ULO stock will have to be characterized and processed by appropriate methods.

In this paper, catalysed pyrolysis applied at laboratory level to a specific ULO recuperated from a light car lubricating system is reported. The aim of the experimental work was to determine the optimal thermal range of running the pyrolysis process in order to develop further an integrated continuous process for liquid hydrocarbon fraction production. This liquid should have appropriate physical and energetic characteristics that enable its blend with regular petroleum fuels. In the first part of the study, the effects of heating rate and catalysts type on pyrolysis fractions distribution were investigated.

Experimental part
Materials and methods
Raw Materials

The ULO used in the present study was dark brown, containing carbon soot and some types of gum and various additives originally present in lubricating oils. Before pyrolysis, the ULO was subjected to proximate and ultimate analysis. It was found that he ULO has a high viscosity (122 mPa×s) and a higher heating value of 45.75 MJ/kg. The elemental analyses was performed with a Thermo-Fisher CHNS/O Analyser and the results are presented in Table 1.

In order to establish the thermal range of decomposition (R_T), the temperature of highest process intensity (T_{max}) and the mass loss (wt%) under different heating rates thermo-gravimetric (TG) analysis was employed. The device used for this work was a SETARAM modular simultaneous TGA & DTA / DSC thermal analyser, which requires Helium as vapour fraction carrier and Argon as protective gas. The registered curves are shown in Figures 1-3.

For the tests run in laboratory-scale installation, two commercial catalysts were used:

-Acidic catalyst: Zeolites powder (HZSM-5) - sodium alumina-silicate powder, with a high silica to alumina ratio (up to 32) used for catalytic cracking of residual hydrocarbon-based material. The particles have an average pore diameter of 4Å, while the surface area is higher than $450m^2/g$.

-Basic catalyst: Na_2CO_3 - Sigma Aldrich, reagent plus grade with a of pKa = 10.35, and characterised by a density of $2.5g/cm^3$, and a melting point of 851°C;

Applied pyrolysis procedure

Pyrolysis reactions were carried out in a laboratory scale installation that includes a stainless steel reactor with a volume of 0.8L, equipped with two thermocouples for reference and internal temperatures measurement. The reactor is connected to a glass-made condensing system for pyrolysis vapours exiting the reactor and their separation into non-condensable (gases) and condensable (liquid) phases. The reactor is heated by an electrical heater able to ensure 500°C at the external wall of the reactor. Laboratory scale pyrolysis set-up was already used for other pyrolysis tests applied to hydrocarbon-based waste [11, 15].

Experimental tests under three heating rate (3-5°C/min, 10-12°C/min and 15-17°C/min) were performed in laboratory-scale reactor in order to correlate the identified thermal parameters with TG analysis, in three experimental cases: (i) non-catalysed pyrolysis, (ii) Na2CO3-catalysed pyrolysis, and (iii) HSZM5- catalysed pyrolysis.
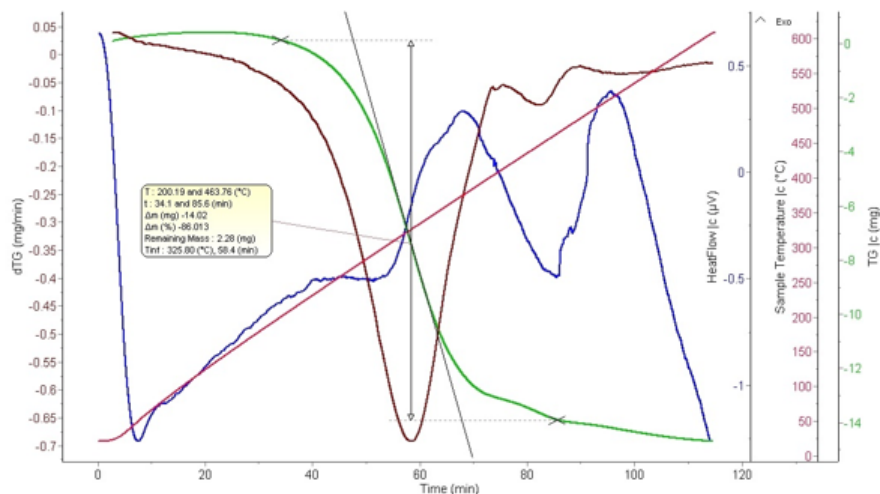

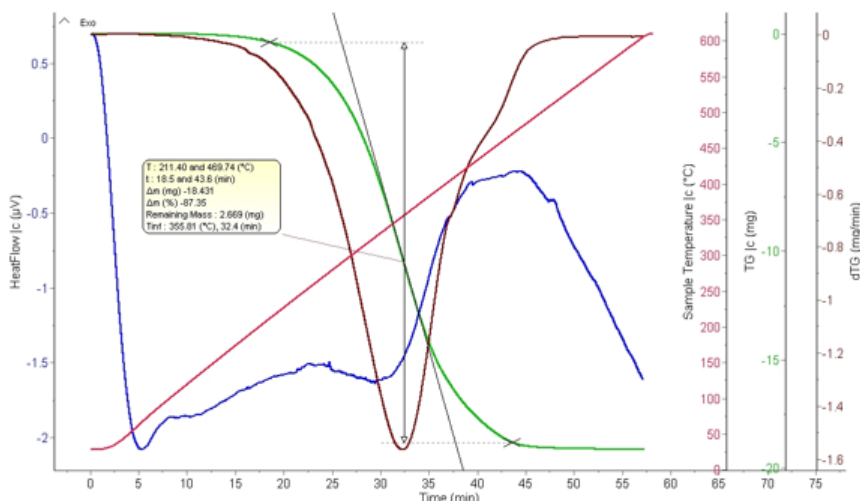Fig. 1. TG Analysis of ULO under a heating rate of 5 °C/min

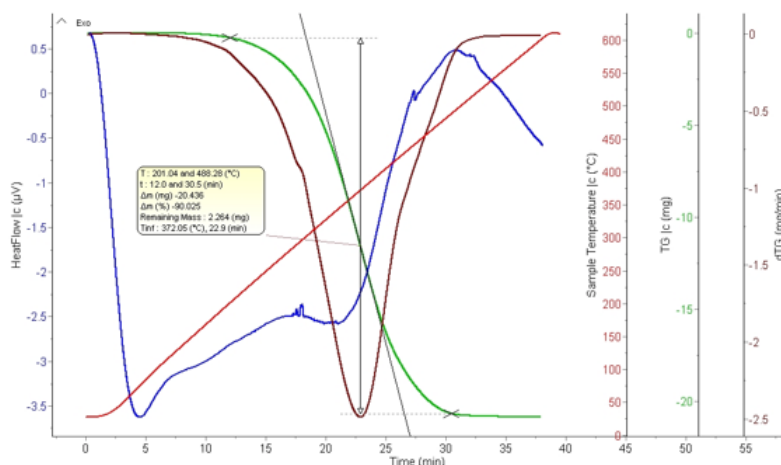Fig. 2. TG Analysis of ULO under a heating rate 10 °C/min

Fig. 3. TG Analysis of ULO under a
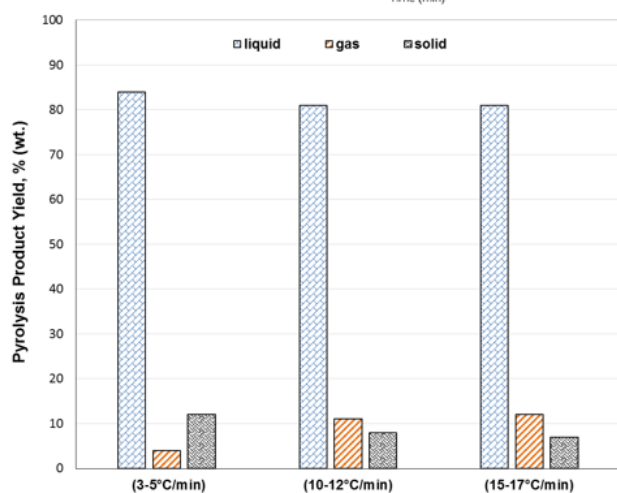heating rate of 15 °C/min

Fig. 4. Distribution of pyrolysis products yield in non-catalyzed
pyrolysis

The pyrolytic reaction products were classified into three groups: gas fraction, pyrolytic oil (liquid fraction) and residual coke (solid fraction). The yield of pyrolytic oil was defined as the amount of liquid collected whereas the yield of residual coke was the amount of char remaining in the reactor after the experiment, while the gas yield was the calculated by the difference. The liquid and solid fraction have been subjected to elemental analysis and the results are presented in the Table 1.

Results and discussions
TG Analysis

In the Figures 1-3, the green curve is showing the mass loss (TG) in Helium atmosphere, the brown curve represents differential of thermogravimetry (DTG), the blue curve shows differential scanning calorimetry (DSC), and the red curve represents the sample temperature.

Product	C, % (wt.)	H, % (wt.)	O, % (wt.)	N, % (wt.)	S, % (wt.)
Diesel Fuels	80 - 85	14 - 18	1.1 - 1.3	nd	nd
Used Lubricating Oil	82 - 86	12 - 14	1.5 – 1.8	nd	0.2 – 0.5
Liquid Fraction – non-catalysed pyrolysis					
3-5°C/min	82 - 88	11 - 13	0.5 – 1.1	nd	0.2 – 0.3
10-12°C/min	79 - 82	12 - 15	1.7 – 2.1	nd	0.2 – 0.4
15-17°C/min	78 - 82	13 - 15	1.8 – 2.4	nd	0.3 – 0.5
Solid Fraction – non-catalysed pyrolysis					
3-5°C/min	40 – 43	5.2 – 5.5	4.8 – 5.5	0.2 – 0.4	0.5 – 0.7
10-12°C/min	39 – 43	3.5 – 4.0	6.5 – 7.5	0.4 – 0.9	0.8 – 1.5
15-17°C/min	34 – 35	2.2 – 2.4	7.1 – 8.0	0.3 – 1.1	1.8 – 2.1
Liquid Fraction – Na_2CO_3-catalysed pyrolysis					
3-5°C/min	82 - 86	10 - 14	0.5 – 1.8	nd	nd
10-12°C/min	82 - 84	11 - 14	2.5 – 2.8	nd	nd
15-17°C/min	79 - 81	14 - 16	2.2 – 2.4	nd	nd
Solid Fraction – Na_2CO_3-catalysed pyrolysis					
3-5°C/min	42 – 43	4.5 – 4.8	4.5 – 4.6	0.2 – 0.4	0.6 – 0.9
10-12°C/min	39 – 40	4.3 – 4.7	5.5 – 6.0	0.3 – 0.6	1.2 – 1.7
15-17°C/min	37 – 38	3.7 – 3.9	7.5 – 8.0	0.9 – 1.3	2.4 – 2.8
Liquid Fraction – zeolite-catalysed pyrolysis					
3-5°C/min	77 - 80	14 - 16	2.6 – 3.0	nd	nd
10-12°C/min	80 - 83	12 - 14	2.2 – 2.8	nd	nd
15-17°C/min	82 - 84	12 - 14	1.8 – 2.0	nd	nd
Solid Fraction – zeolite-catalysed pyrolysis					
3-5°C/min	39 – 41	3.7 – 3.9	4.9 – 5.2	0.2 – 0.4	0.9 – 1.3
10-12°C/min	29 – 32	3.1 – 3.3	7.5 – 7.7	0.4 – 0.8	1.8 – 2.0
15-17°C/min	24 – 28	1.8 – 2.1	8.5 – 9.5	1.1 – 1.3	2.5 – 2.8

Table 1
ELEMENTAL ANALYSIS OF RAW
MATERIAL AND PYROLYSIS
FRACTIONS COMPARED TO
DIESEL FUELS[*)]

*) the detection limit of the apparatus is 0.2% ; nd – non detected

Fig. 5. Distribution of pyrolysis products yield in Na_2CO_3-catalyzed pyrolysis
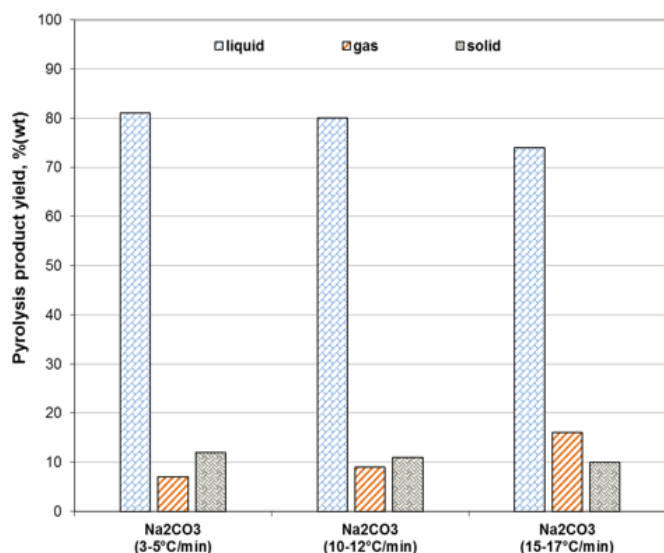

Fig. 6. Distribution of pyrolysis products yield in zeolite-catalyzed pyrolysis

TG Analysis showed that by increasing the heating rate, the start point of decomposition stays at 200 - 211°C while the end point is growing from 464°C for 5°C/min to 488°C for 15°C/min. following these results, it was established that the tests in laboratory-scale reactor will be run at the final temperature of 500°C. At the same time, the temperature of the maximum decomposition rate is increasing with the heating rate, from 326°C for 5°C/min to 372°C for 15°C/min. The mass loss continuously varied, with an increasing trend from 86% for 5°C/min to 90% for 15°C/min. In pyrolysis performed at 5°C/min the DTG curve reveals two stages decomposition process, 200 – 396 °C and 410-475 °C, characterised by a temperature of the maximum decomposition rate of 326°C and 460°C, respectively. The second stage fades at 10°C/min and 15°C/min. However, the registered DTG curves shape are still showing a hump at 10°C/min, which become less prominent at 15°C/min. Moreover, the TG curves (Figures 2 - 3) are clearly exhibiting this segment with completely different slope.

In DSC curves upward peaks correspond to exothermic reactions, while the downward peaks endothermic reactions, as the mark on the DSC axis shows. The heat flow in ULO pyrolysis evolves with the increasing temperature and peaks at 313°C for 5°C/min, 328°C for 10°C/min and 348°C for 15°C/min. In slow pyrolysis (5°C/min) a major DSC peak is identified at 440°C closely related with the second thermal range of decomposition, which might be attributed to the decomposition of coke resulted during thermal cracking of hydrocarbons.

Pyrolysis Products Yields
Taking into account the results from TG Analysis, the tests in laboratory-scale reactor have been scheduled to be run by using 50g ULO. A condenser of 0.5m length and 0.07m internal diameter has been used to separate the liquid and gaseous fractions. The liquid recovery flask was immersed in an ice/water bath, to ensure the complete condensation of pyrolysis vapours.

The effects of the pyrolysis heating range and catalysts on the yields of pyrolytic oil, gas and residual coke are presented in Figures 5-6.

In absence of catalysts, the maximum amount of liquid fraction, 84%wt., is obtained at low heating rate (3-5°C/min). At higher heating rates, the liquid fraction slightly decline at 81%wt. while strong variations are observed in solid and gas fraction distribution.
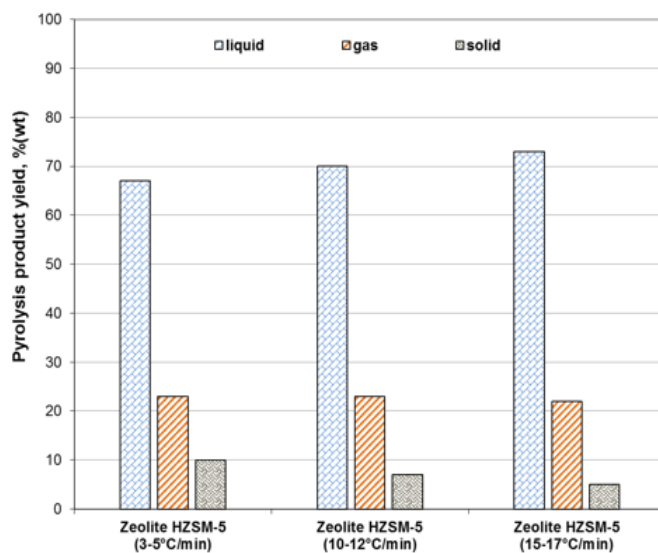
In catalysed pyrolysis, in terms of liquid yield, the highest amount of oils was achieved in the presence of Na_2CO_3, which reached 81 %wt. at 3-5°C/min and decreased continuously with increasing heating rates. Since the solid fraction yield was constantly decreasing with the heating rate rise, it can be concluded that the heating rate is positively influencing the gas fraction formation in the presence of basic catalysts. Increasing of heating rate at 10-12°C/min is accompanied by small differences in the distribution of pyrolysis products. However, growing further the heating rate at 15-17°C/min, the yield of liquid fraction is decreasing at 74%wt., and the gas formation is strongly favoured. Taking into account that the rising heating rate does not significantly affect the amount of solid residue, we can presume that, in presence of Na_2CO_3, faster pyrolysis process involves quick rupture of marginal C-C bonds and favours secondary breakage reactions of hydrocarbons with medium molecular masses. The results from elemental analysis of liquid and solid fractions (see Table 1) consolidate this presumption, showing a clear tendency of lower carbon content in both fraction at increasing heating rate.

It appears that zeolite-based catalyst has opposite influence regarding the liquid fraction and, in the applied experimental conditions, it has led to a better overall conversion of the ULO at higher heating rate. Also, a growing heating rate conclusively promotes the liquid fraction formation in the presence of acidic catalysts, while maintaining a constant the amount of gaseous fraction.

Conclusions
Used lubricating oils (ULO) are posing an environmental hazard when the disposal is not well managed. Their high calorific value recommends naturally the energetic use pathway as an economically alternative of waste management. Direct combustion of such waste materials lead to hazardous emissions that affect both water air quality due to their relatively high content of pollutants such as heavy metals. To mitigate these unwanted effects, treatment techniques need to be employed in order to extract hydrocarbon-based fractions and separate the inorganic matter.

The results of this study show that pyrolysis may be a valuable technique that can be used to recover both liquid and gas hydrocarbon fractions from ULO, which can be used further as fuels. Nevertheless, a compromise between

the optimal parameters of the process in term of energy balance, overall conversion and the main pyrolysis product need to be done. Neither the liquid nor the gas fractions can be separately obtained, the treatment system requiring the takeover and management of the two fluids.

The best yield of pyrolytic liquid was obtained at low heating rate (slow pyrolysis) in absence of catalysts. Also, evolving heating rate are favouring the overall ULO conversion, the solid residue yield continuously decreasing. By using Na2CO$_3$ as catalyst, the gas fraction is increasing mainly by breaking volatile molecules released during pyrolytic decomposition, while in the presence of zeolites a better conversion is registered at higher heating rate and the gas formation is favoured regardless of heating rate value.

Further experimental work will be performed with the aim of characterising the fuel quality of liquid and gas fractions in order to allow a better and accurate assessment of energy balance in applied pyrolysis for energetic purposes use of ULO.

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