Waste and Biomass Valorization (2021) 12:2131–2143
https://doi.org/10.1007/s12649-020-01155-6

ORIGINAL PAPER

Experimental Investigation on Petroleum Sludge Valorization into Fuel via Pyrolysis Process

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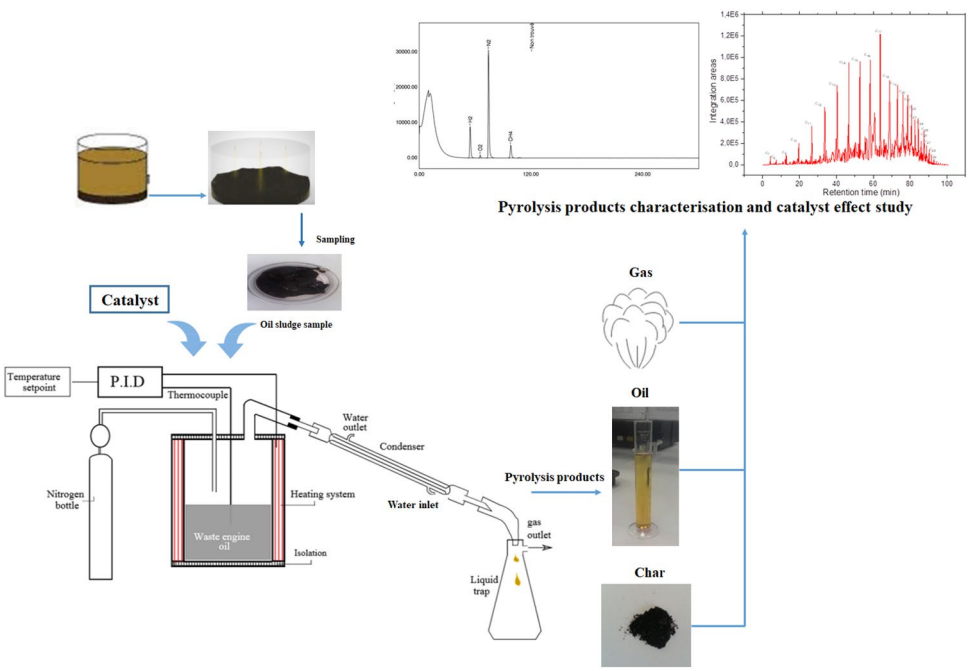
Received: 18 November 2019 / Accepted: 6 July 2020 / Published online: 13 July 2020

Abstract

Oil sludge (OS) has been of key concern due to its continuing effect on the environment degradation. The huge quantities thrown yearly of this waste contain a high proportion of hydrocarbons which are valuable for recovery. This study focused on the oil sludge conversion into a fuel for a diesel engine by thermal/catalytic pyrolysis process. The experiments were conducted at atmospheric pressure in a batch reactor operated without and with two catalyst types: TiO_2 (3 and 5 wt%) and Al_2O_3(3 and 5 wt%). Overall all test conditions followed in the OS pyrolysis, a considerable liquid fraction is recovered (around 70%), as compared to the gaseous fraction (around 25%) and the solid residue (around 5%). The characterization of the pyrolytic oil samples, containing approximately 11.70% of oxygen, showed also that the use of 5% of Al_2O_3 catalyst in the OS cracking provide the best fuel quality with a minimum viscosity value (3.5 mm^2/s), a maximum heating value (45.72 MJ/kg) with a hydrocarbon compounds in the range (C_7–C_{32}) which are detailed by GC–MS analysis. The others properties (density, flash point, pour point and cloud point) are found to be close to those of diesel fuel. Also, the catalysts effect is studied on the others pyrolysis products. The obtained results allow to predict the good usability as a diesel like fuel. Further tests to control engine performance and pollutant emissions could be done

Graphic Abstract



Extended author information available on the last page of the article

Keywords Oil sludge · Pyrolysis · Catalyst · Diesel fuel

Statement of Novelty

This investigation aims to find solution relating to petroleum sludge treatment in the Algerian refinery industry. The effect of catalysts selected, with a low content in the pyrolysis reaction, on the products quality has not been yet studied neither pyrolytic oil composition and physical–chemical properties are analyzed. Further study has been included in this manuscript on the gaseous and char products.

Introduction

The environment has never been so threatened as nowadays namely by the oil industry including drilling, transportation, storage, and refining. All these activities generate important amounts of hazardous wastes. According to the Statistical Annual Report (ANP), the effective global refining capacity in 2009 was estimated to be 14 400 000 m^3/day with a worldwide petroleum production of 12 600 000 m^3/day with at least 190 000 m^3/day of generated sludge [1]. In Algeria, the petroleum refineries represent the major source of this waste, which constitutes the deposit of crude oil in storage tanks. Oil sludge is one of the most significant hazardous wastes according to Environment Protection Act and Hazardous Wastes Handling Rules [2]. This residue is a semi-solid pasty material with high heating value (HHV) composed of hydrocarbons (HC), water, heavy metals, minerals and sediments [3]. In fact, it contains dangerous pollutants such as aromatics hydrocarbons, heavy metals, accreted harmful microorganisms, and radioactive substances [4]. Due to the presence of these hazardous pollutants, OS accumulation can cause negative impacts on the environment and human health [2]. Soils contamination and the subterranean water pollution lead to a deterioration of the ecological environment but also cause a huge waste of oil resources [1, 5]. Due to the growth in energy demand (oil and gas), the OS transformation into an energy resource has become crucial. Presently, major research projects are launched to develop appropriate and environmentally friendly standards in order to reduce the accumulated sludge in the petroleum industries. Therefore, a various of OS treatment methods and technology have been proposed by many researchers [5–11] such as solidification/stabilization, biodegradation, solvent extraction, centrifugation, pyrolysis, hydrothermal liquefaction technology, etc. [5, 7].

The choice of the treatment method is based on the composition and physicochemical properties of the OS [12]. Compared to other methods, pyrolysis is a promising treatment which converts oil sludge wastes into three main products, char (solid fraction), gas and pyrolytic oil (liquid fraction) with a higher heating value than that of the raw oil sludge [13]. Several promising studies of fuel recovery from pyrolysis OS process have been reported in the literature. Schmidt and Kaminsky [14] recovered about 84% of oil from oil sludge by pyrolysis in a fluidized bed reactor in the range of temperature 460–650 °C. Karayildirim et al. [15] studied the fixed-bed pyrolysis of OS by using thermogravimetry analysis (TGA). Based on their results, the large amount of oil obtained is in the HC range C_{12}–$C_{28,}$ and the oil properties are close to those of the commercial diesel.

Hu et al. [16] provided the pyrolysis characteristic of petrochemical sludge using TGA with different heating rates. They found that the maximum weight loss rate of petrochemical sludge has happened in the range of 111–526 °C, 113–542 °C and 122–445 °C at 10 °C/min, 20 °C/min and 30 °C/min respectively. In addition, it has been deduced that the stage of maximum weight loss rate moves towards higher temperature with the increase of heating rate.

In OS non-catalytic pyrolysis, the reaction time is long and requires a lot of energy [17] and the produced liquid mainly consists of heavy hydrocarbons that may affect the oil quality [18]. The catalysts addition in pyrolysis reaction has great advantages such as reduced pyrolysis time, lower temperatures, while improving both the quantity and the quality of the produced oil [4].

Shie et al. [19] have studied the effect of two inexpensive metal additives: Aluminum compounds (Al, Al_2O_3 and $AlCl_3$) and Iron compounds (Fe, Fe_2O_3, $FeSO_4 \times 7H_2O$, $FeCl_3$ and $Fe_2(SO_4)_3 \times nH_2O$) on OS pyrolysis. The results revealed that the addition of Fe_2O_3 and $Fe_2(SO_4)_3$. nH_2O improves the pyrolytic oil quality. Nonetheless, the addition of Al and $Fe_2(SO_4)_3 \times nH_2O$ leads to optimum liquid yields. Fly ash, oil sludge ash, waste DAY-zeolite and waste polymer of polyvinyl alcohol (PVA) addition were used as low-cost source for catalyst to improve oil sludge pyrolysis reaction [20]. It was found that all these catalysts lead to the improvement of the pyrolysis oil quality in the following order: fly ash > oil sludge ash > PVA > DAY-zeolite > no additives. Lin et al. [21] have studied the effect of potassium hydroxide (KOH) on the oil pyrolysis quality and found that the oil pyrolysis quality can be improved by adding KOH in terms of smaller molecular weight, lower viscosity, higher heating value and lighter straight chain hydrocarbons. Metal oxidess are easily available and effective catalysts, Metal ions at the active sites on the surface may react with carboxylic acid, sulfur components in the sludge and help to break C–C bond to form relative light component. By far, metal oxides were the most studied catalysts in the literature [4].

TiO_2 loaded MCM41 was used as catalyst and its effect was investigated on oil sludge pyrolysis. It was proved that TiO_2/MCM41 catalyst helped to improve oil recovery yield and reduce pyrolysis temperature [22].

In the present work, non-catalytic and catalytic pyrolysis of OS have been carried out in a batch reactor at 500 °C in order to improve both the reaction pyrolysis and enhance the pyrolysis oil quality. For this purpose, OS pyrolysis is performed using two catalysts with different mass ratio OS/catalyst (1:0.03 TiO_2, 1:0.05 TiO_2, 1:0.03 Al_2O_3 and 1:0.05 Al_2O_3). In the literature, it is found that the use of Al_2O_3 decrease carbon residue and the migration of S, N and O from the oil sludge to the oil product. Inspired by catalytic technology employed in heavy oil refinery, TiO_2 is used in this study as catalyst to investigate its effect on oil sludge pyrolysis, not only for improving oil recovery yield and reduce pyrolysis temperature as reported in literature, but also to investigate its effect on the overall properties of the pyrolytic oil for diesel engine application. Furthermore, low-cost solids are taken into account to make the chemical recycling process economically reliable. The obtained pyrolysis oils were characterized by FTIR, elemental analysis (for solid and liquid product), chromatographic analyses (GC analysis for gas, and GC-MS-FID analysis for oil) to determine the composition, and to study the effect of catalysts on the obtained oil. The effect of the tested catalysts on oil quality were then discussed and compared.

Materials and Methods

Experimental Setup

The OS sample was picked up from the waste park of a refinery that produces about 8000 tons of oil per day, located in North Algeria. Periodically, the crude oil storage tanks are cleaned by removing the accumulated OS residue which is and stored in so-called waste parks or basins. The quantity of sludge stored in these basins amounts to more than 2000 tons.

Experimental pyrolysis consists in heating samples (400 g ± 0.1 g) of OS in a lab-scale fixed-bed reactor at 10 °C/min. The reactions were performed at 500 °C under inert atmosphere (2 mbar; nitrogen) as shown in Fig. 1. Two series of reactions are carried out: with and without catalysts. The catalysts used are TiO_2 and Al_2O_3 which have been purchased from Sigma-Aldrich with a purity of 96 and 97% respectively. The tested catalysts are physically mixed with the OS in the reactor (four experiments were carried out with different mass by loading 12 g of TiO_2 and Al_2O_3, 20 g of TiO_3 and Al_2O_3 respectively). The experimental error is given by calculating absolute error from the average of three manipulations.

The yields of pyrolysis reaction products are calculated using the following equations:

$$Oil\ yield\ (wt\%) = \frac{m_O}{m_{OS}} \times 100 \quad (1)$$

$$Char\ yield\ (wt\%) \frac{m_r}{m_{OS}} \times 100 \quad (2)$$

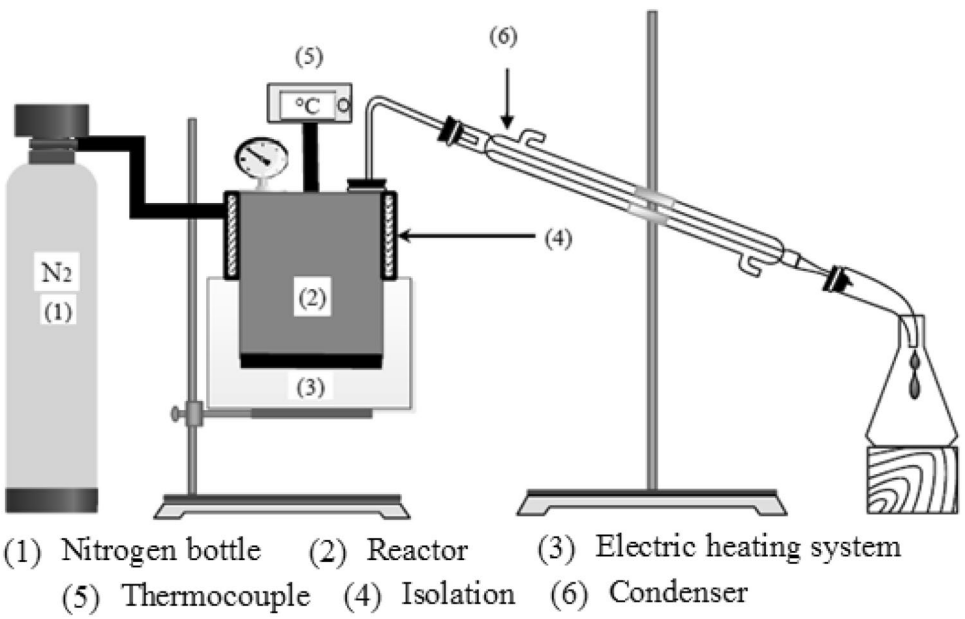


Fig. 1 Experimental setup of OS pyrolysis

$$Gas\,yield\,(wt\%) = \frac{m_{OS-}(m_O + m_r + m_w)}{m_{OS}} \times 100 \quad (3)$$

m_{OS} : $initialOS(feedstock)$

m_O : $oilmass$

m_w : $massofwater$

m_r : $mass\ of\ char$

Gas yield was calculated by difference.

Instrumental Settings

Raw Material (OS)

The OS metal composition is determined by spectrometric analysis by ASTM D 6595 in a Spectral M instrument. The mineral composition by X-ray diffraction (XRD) is performed using XPERT-PRO machine with the application of Bragg's law. Ultimate analysis CHNS/O is carried out using a Thermo Finnigan Flash Model 1112, EA-CHNS/O equipment. Oxygen content is determined by subtracting the sum of C, H, N, S, and ash from 100%. Calibration and sample analysis were done in three replicates, averages were taken. The OS HHV is determined using an adiabatic bomb calorimeter (Parr 6200 type) up to 0.05–0.1% precision, while the viscosity is measured by a VIBRO SV-10 viscometer with 1% error. Moisture is determined by KARL FISCHER method (870 KF Titrino plus equipment).

The SARA (Saturate, Aromatic, Resin and Asphaltene) composition of the OS is measured, according to ASTM D2007, by gas chromatography (capillary HP 6890 with flame ionization detector FID) using 1 mg of waste diluted in 4 ml of dichloromethane. Toluene, hexane and dichloromethane are used to separate aromatic, aliphatic and resins, respectively. The analysis is carried out at an initial temperature of 60 °C, a heating rate of 4 °C/min, an initial time of 1.5 min, a final temperature of 280 °C and a final time of 10 min. TGA coupled to Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) (Setsys Evolution 16/18 SETARAM balance under nitrogen/argon atmosphere at a heating rate of 10 °C/min) is carried out to investigate the thermal degradation of OS components as temperature function. The aim is to determine the optimal conditions of OS pyrolysis and collect information about initial and final temperatures of thermal degradation [23]. The DSC is used to assess the heat capacity and quantify of the heat flow in each reaction using the Derivative Thermogravimetry (DTG). It is to be noticed that the thermogravimetric baseline was established to reduce the experimental error before the thermogrametric experiments, the equipment's resolution is: +/−2 µg for TGA, +/−1 µW for DSC and +/− 0,1 °C for temperature sensor of K type.

The percentage of mass loss is calculated according to the Eq. 4 [2]:

$$\%Mass\ loss = \frac{(m_i - m_a)}{m_i} \times 100 \quad (4)$$

m_i is the initial mass (g) of sludge, m_a is the actual mass (g).

Pyrolysis Oil

Pyrolysis oil physical properties such as viscosity, density, cloud point, pour point, flash point and cetane number are measured according to standard methods mentioned in Table 1. The HHV and CHNS/O elementary composition are also determined.

Chemical functions present in the pyrolysis oil are determined by FTIR (Perkin Elmer equipment, analysis mode ATR). The chemical composition is studied by Perkin-Elmer Clarus 680 Mass spectrometer coupled with a gas chromatograph and a Flame Ionization Detector (GCMS-FID). An Agilent SLB-5MS column (30 m × 0.25 mm; 0.25 µm film thickness) is used with a helium flow rate of 1 ml/min. The injection temperature is 275 °C, the oven temperature is 30 °C for 10 min, then it rises to 100 °C at the rate of 2 °C/min then to 300 °C at 5 °C/min and it is held at this temperature for 5 min (total run time 90 min). The mass spectrometer is set at an ionizing voltage of 70 eV and a mass range of m/z 30–450. The identification of organic compounds is performed by comparing the mass spectra of the resolved components using the NIST library and confirmed by their retention time.

Gas Pyrolysis Analysis

A micro-chromatograph (micro-GC) Agilent 3000A is used to analyze the gaseous product which is collected in a gas sampling bag. This instrument is equipped with two detectors. The first is a flame ionization detector (FID) to analyze hydrocarbons gas, and the second is a thermal

Table 1 Standards used to characterize the produced oil

Analyses	Standards
Viscosity (at 40 °C)	ASTM D445
Density (at 15 °C)	ASTM D4052
Cloud point	ASTM D5772
Flash point	ASTM D92
Distillation	ASTM D86
Cetane index	ASTM D976

conductivity detector (TCD) for H_2, CO and CO_2 analysis. The first channel (10 m × 0.32 mm × 12 µm) is a 5 Å molecular sieve, the second channel is PLOT Q column (PLOT Q, 10 m × 0.32 mm × 10 µm).

The HHV of the obtained gas is calculated according to the ASTM D 3588–98 using the following formula 5:

$$HHV = \frac{\sum_{j=1}^{n} x_i M_i HHV_i}{\sum_{j=1}^{n} x_i M_i} \quad (5)$$

where *xi* is the mole fraction of gas component *i*, *Mi* is the molar mass of components *i* and HHVi (kJ/mol) is the HHV of gas component *i*.

Solid Residue

The analysis of solid residues CHNS/O is performed in the Thermo Finnigan Flash Model 1112 previously mentioned; and the O composition is determined by difference. The HHV of the solid residues is measured by the adiabatic bomb calorimeter previously mentioned. The metal composition was analyzed using an X-ray spectrometer (Rainy series EDX-700HS) equipment.

Results and Discussion

OS Characterization

As shown in Table 2, the OS contains an important fraction of Ca and heavy metals such as Fe and Pb, which are its main contents. The SARA analysis shows (Table 3) that the saturated hydrocarbons (linear and branched alkane) represent the main OS components [24], 26 wt% of aromatic hydrocarbons and 16 wt% of resin (condensed aromatic) [25]. Due to its high concentration of organic matter and its high HHV, OS can be considered as a promising source of energy. From the elementary analysis, the sludge contains a high concentration of carbon 77 wt%, whereas sulfur was not detected by the equipment used indicating that its concentration is below the detection limit.

Table 2 Metal composition (as received basis) of OS

Metal element	Concentration (ppm)
Fe	300
Cr	0.6
Pb	94.5
Cu	1.1
Al	24.4
Ni	0.8
Ag	0.2
Mo	0.9
Ti	1.1
V	0.8
B	0.2
Mg	19.2
Ca	85.9
Zn	22.3
Si	89.5
Na	59.4

Table 3 Properties and composition of the OS sample

	Concentration
Proximate analysis (wt% on as received basis)	
Moisture	9.0
Organic matter	89.2
Ash	1.8
pH	6.3
Element analysis (wt% on as received basis)	
C	77.8
H	12.1
N	–
S	–
O[a]	8.2
HHV(MJ/kg)	30.2
Viscosity (Pa.s) at 40 °C	9.5
SARA composition (wt% on as received basis)	
Saturated hydrocarbons	52
Aromatic hydrocarbons	26
Resin	16
Asphalten	7

[a]Determined by difference

The TGA and DTG curves are shown in Fig. 2, and DSC curves in Fig. 3. The TGA shows the thermal degradation of OS. Based on the obtained results, the thermal behavior of OS can be divided into three regions as found in literature [16, 25, 26]. The first mass decreased is observed in the temperature range of 100–160 °C where the water and light fractions elimination takes place [26]. The weight loss is about 7.3% of initial OS weight. In this region, exothermic peaks appear in DSC curves with a heat flow of −0.162 mW/ mg, which may represent a flash point or auto-ignition. In the second region corresponding to 160–500 °C the mass loss is more pronounced and reach about 98%. Volatilization and cracking of organic matter take place (light and heavy kerosene–diesel fuel) [16, 19]. This important mass loss is accompanied by a succession of DTG peaks. It is also observed that the maximum weight loss takes place when a maximum mass loss rate of 5.1%/min is reached at a temperature corresponding to 451 °C. In this region, endothermic peaks appear on the

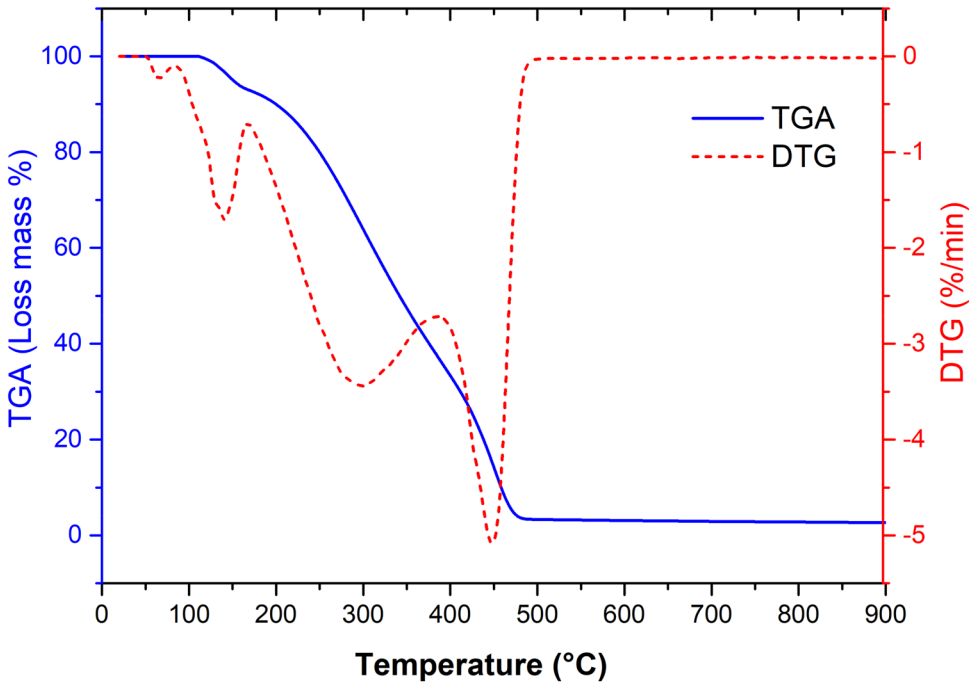


Fig. 2 TGA curve, DTG curve of OS

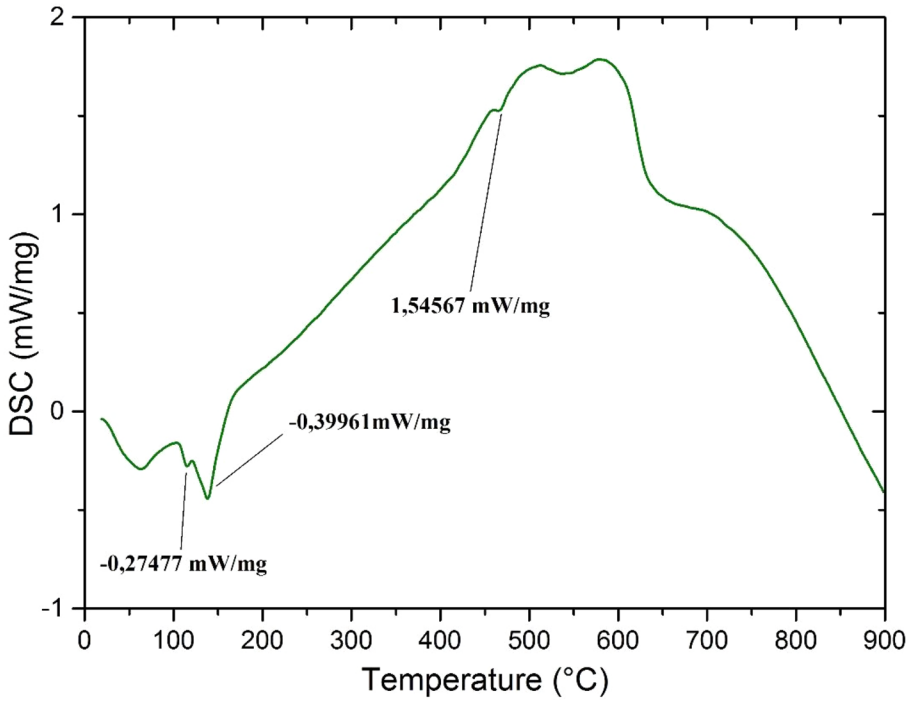


Fig. 3 DSC curve of OS

DSC curves corresponding at pyrolysis reaction as shown in Figs. 3, 4.

The third region 500–900 °C represents the degradation of the inorganic like carbonates and clay [16] matter and the carbonization reaction [19], that is the formation of char; and the weight loss rate is about 0.73 wt%.

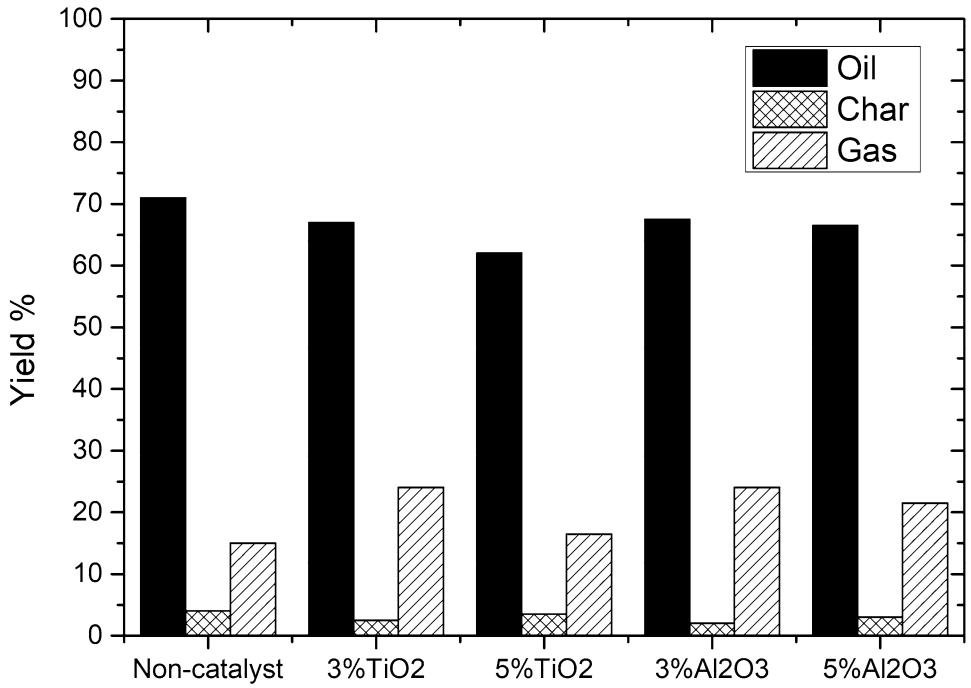


Fig. 4 Product yields of pyrolysis with and without additives

Pyrolysis Reaction

Catalyst Effects on Oil Products

After the reaction, the water phase is separated from the oil phase using a separating funnel, then filtered. The effects of catalysts are studied through the yields, the pyrolysis products quality and specific compounds evolution (oil, gas and char).

The results indicate that the added catalysts have no significant effect on the oil and solid yield whereas an opposite trend is observed in the gas yields.

The properties of the oils obtained by catalytic pyrolysis and those of commercial diesel are given in Table 4 for comparison. The addition of the different types of catalysts lead to a reduction in viscosity which is considered as an advantage for diesel engines. In non-catalytic pyrolysis case, the oil is obtained with a high viscosity compared to the conventional diesel due to the presence of wax in oil, while the catalytic pyrolysis case products a less viscous oil which might be due to the formation of light hydrocarbons [27]. The oil density is decreased with the addition of 5% of TiO_2 compared to that obtained using catalyst free pyrolysis process. For pour point and cloud point the effect is not significant. The flash point value increases with the addition of catalysts. The effect is notable on the HHV which increases with the catalyst addition in all cases and it is found that the highest value is observed for 5% Al_2O_3. Compared to the commercial diesel, the pyrolytic oil obtained contains more oxygen but also higher HHV those reported in the literature due mainly to its high carbon content (Table 5) [15]. Those comparisons and intrinsic pyrolytic oil properties indicate the real potential of OS valorization as fuel for thermic engine.

Table 5 shows the elementary analysis results of the different pyrolytic oil compared to diesel. The sulfur and

Table 4 Effect of the quantity and the type of catalysts on the pyrolysis oil properties

	Viscosity (mm^2/s)	Density (kg/m^3)	Could point (°C)	Pour point (°C)	Flash point (°C)	HHV (MJ/kg)
Non-catalyst	4.70	841.1	3	12	120	43.39
3% TiO_2	3.96	816.1	6	18	98	44.07
5% TiO_2	3.75	816.0	3	15	95	45.60
3% Al_2O_3	4.19	824.9	0	6	110	44.95
5% Al_2O_3	3.50	814.0	3	18	90	45.72
Diesel [15]	2–4.5	810–860	max:− 6	max: −7	min: 55	45.00

Table 5 Elementary composition of the pyrolysis oil

	% N	% C	% H	% S	%O
Non-catalyst	< LD	75.9	12.25	0.029	11.70
3%TiO2	< LD	81.8	13.16	< LD	5.02
5%TiO2	< LD	81.4	13.15	< LD	5.43
3% Al2O3	< LD	78.7	12.61	< LD	8.70
5% Al2O3	< LD	78.4	12.68	< LD	8.90
Diesel [15]	< 0.1	86.5	13.20	< 0.1	–

LD low detection

nitrogen content in the pyrolytic oil are not detected by the analysis instrument: their concentration are below the threshold of detection.

The results show that the catalysts increase the carbon and hydrogen rate compared with the non-catalyst case, this can be explained by the elimination of oxygenate molecule via pyrolysis reaction. The effect is significant with 3% TiO_2 and 5% TiO_2 cases in which C-content is increases from 75.9% to 81.8% and 81.4% respectively, and the H-content from 12.25% to 13.15% which lead to an HHV value upgrading.

The IR spectra of pyrolytic oils obtained by catalytic and non-catalytic pyrolysis reveal that the peaks 2955 cm^{-1}, 2923 cm^{-1} and 2851 cm^{-1} indicate the presence of C–H alkane (aliphatic tendency) [15, 26]; at 1460 cm^{-1} the presence of the bending alkane C–H (branching chain), such as CH_2 group (methylene) and CH_3 group (methyl) [26], peaks at 700 and 900 cm^{-1} indicate an aromatic chain [26] and the peak detected at 909 cm^{-1} indicates the presence of C=C alkene.

It is noticed that the peaks obtained with catalysts are similar to those obtained without catalyst. The Aliphatic compounds, found in oils using FTIR analysis, are detailed by GC–MS analysis.

The carbon number distribution and the quantitative analysis of obtained oils are determined based on the areas of the chromatographic peaks. The hydrocarbons compounds are in the range of C_7–C_{32}. As it can be observed in Fig. 5, the carbon number distribution with the majority of fractions is located in the range C_{10}–C_{28}, and the maximum peak corresponds to C_{17} (9.24%). It is noted that each fraction (Cn) takes into account all the branched (isomeric) and linear hydrocarbons.

Figure 5 shows a comparison between the hydrocarbons distribution present in the oils obtained by catalytic pyrolysis (3% TiO_2 and 3% Al_2O_3 cases) and those obtained by non-catalyst pyrolysis as function of carbon number. As can be seen, the oils derived from catalytic pyrolysis with 3% TiO_2 and 3% Al_2O_3 are distributed in a wide range of carbon numbers (C_7–C_{32+}) with a maximum yield in C_{17} fraction. An increase of the fraction (C_7–C_{12}) is observed with 3% TiO_2, while the obtained oil with 3% Al_2O_3 shows a decrease in light fraction in (C_8–C_9) and an increase in concentration of heavy hydrocarbons.

The distribution of hydrocarbons presents in catalytic pyrolysis oils with 5 wt% of TiO_2 and Al_2O_3 are compared in Fig. 6, It is clearly noticed that both catalysts having

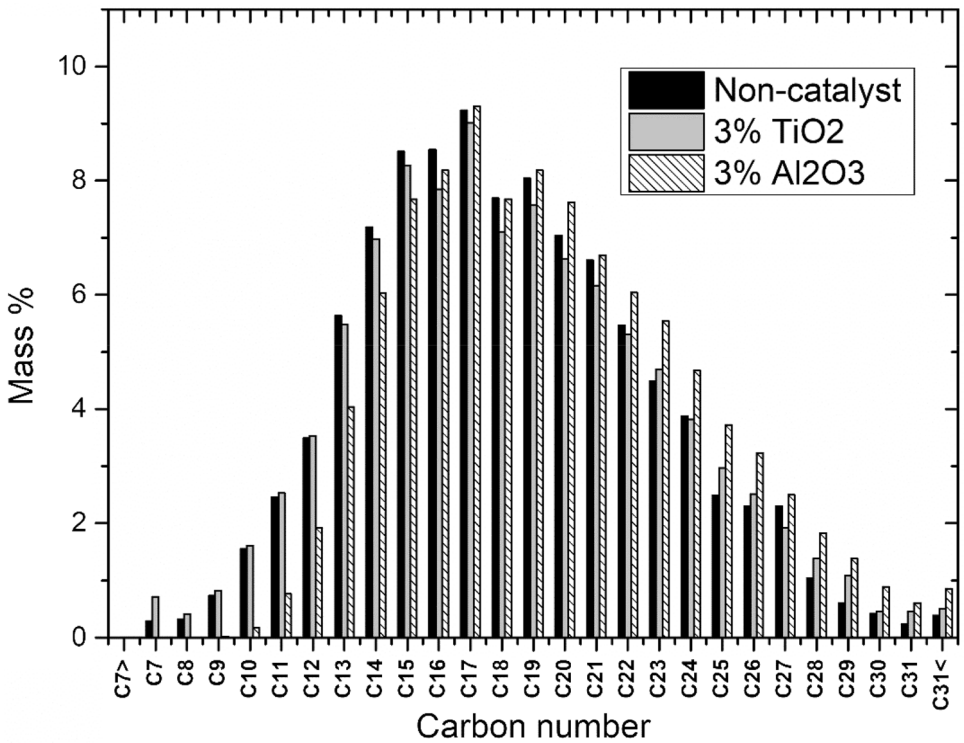


Fig. 5 Carbon number distribution of pyrolysis oil obtained with 3% TiO_2, 3% Al_2O_3 and non-catalyst pyrolysis

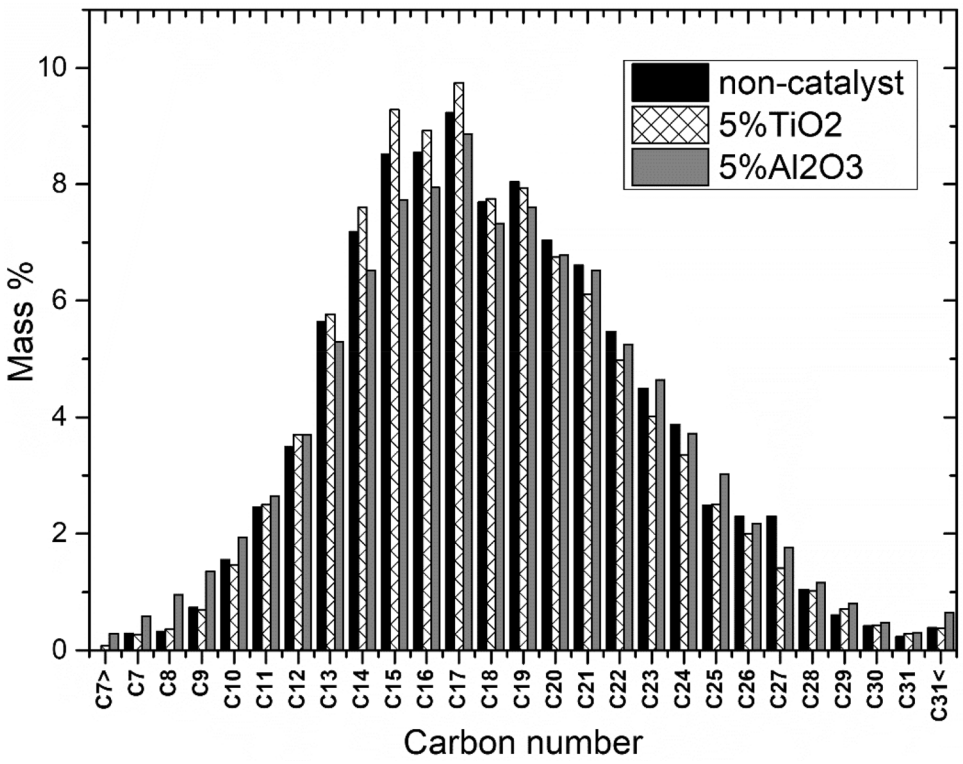


Fig. 6 Carbon number distribution of pyrolysis oil obtained with 5% TiO_2, 5% Al_2O_3 and non-catalyst pyrolysis

Table 6 Hydrocarbon fraction ratio of pyrolytic oil without and with catalysts

	Non-catalyst (wt%)	5% TiO_2 (wt%)	5% Al_2O_3 (wt%)
Heavy fuel (C_{23}–C_{32+})	17.2	16.2	18.7
Gasoil (C_{13}–C_{22})	73.7	74.8	68.8
Gasoline (C_7–C_{12})	8.8	9.1	11.5

an inverse effect on the liquid fraction quality. It seems that 5% TiO_2 catalyst promotes the hydrocarbons formation in the range C_{13}–C_{22}. However, 5% Al_2O_3 use leads to enhance the gasoline (C_7–C_{12}) and the heavy fraction (C_{20}–C_{31}).

The heavy hydrocarbons in the range of (C_{23}–C_{32+}) decrease (Table 6), cause of secondary cracking leading to the formation of lighter hydrocarbons. The increase of light fraction (C_7–C_{12}) concentrations can be explained by the cracking reaction of the middle hydrocarbons in range(C_{13}–C_{22}) [21].

As it can be seen in Table 6, the oil sludge pyrolysis leads to the production of oil with gasoil as the major fraction (C_{13}–C_{22}) (73.7 wt%). The two types of catalysts affect the oil pyrolysis. The addition of TiO_2 has not a notable effect in the three fractions mentioned in Table 6 whereas, the Al_2O_3 has a notable effect in the increase of gasoline fraction (C_7–C_{12}) from 8.84 to 11.5% which due to the cracking of the middle range hydrocarbons (C_{13}–C_{22}), also, the effect is observed in the increase of heavy fuel fraction.

Monocyclic fraction is mainly composed with a cyclohexane part and an aliphatic part (e.g. propyl-cyclohexan) According to the Table 7, it is observed that the monocyclic compounds reacts with catalysts addition, the main evolution is observed with 5% Al_2O_3. The catalysts have a limited effect on the branched alkane composition, as we can see, branched alkane ratio decreases slightly with the increase of catalyst amount.

The evolution of Tribranched alkane for C_{14} and Tetrabranched for C_{17} are given in Figs. 7 and 8 respectively. They were chosen to be followed because they represent a large part of their respective Cn fraction. It is well-known

Table 7 Evolution of linear alkane and branched group compounds ratio with catalysts addition

	Non-catalyst	3% TiO_2	5% TiO_2	3% Al_2O_3	5% Al_2O_3
Linear alkane (%)	26.35	28.10	28.69	29.06	29.66
Branched alkane (%)	66.43	65.56	65.50	66.06	64.04
Monocyclic compounds (%)	2.13	2.61	2.63	2.15	2.91

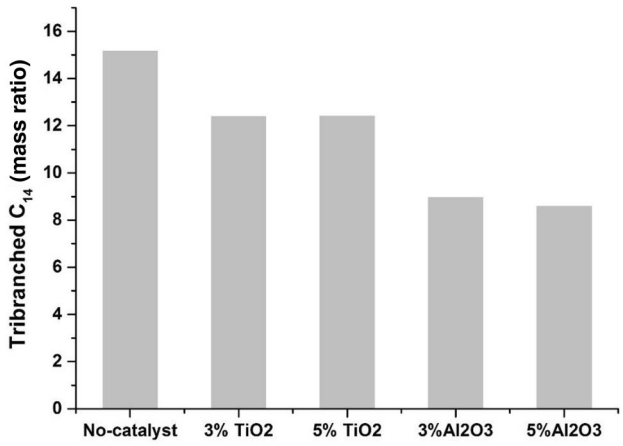


Fig. 7 The Tribranched C_{14} yield with different catalysts load

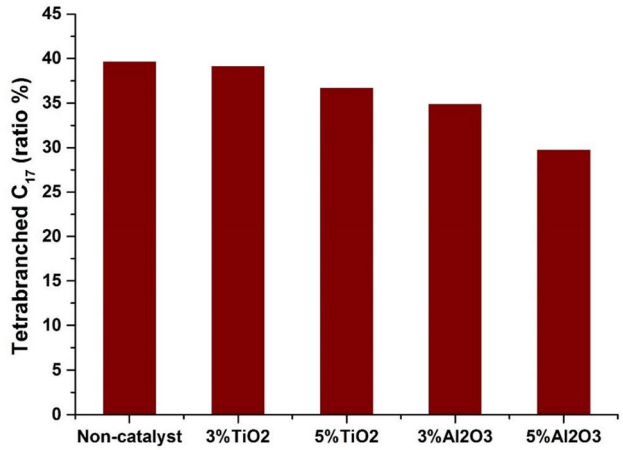


Fig. 8 The Tetranched C_{17} yield with different catalysts load

that in catalytic thermal cracking conditions, there is a competition between two mechanisms. One of them is the basically radical mechanism leading to the formation of a radical with no preference for the most substituted carbon position. In an other hand, you have got the isomerization/cracking mechanism which lead to the formation of an isomer whose will be cracked through a β-scission mechanism. This reaction is extremely favorable in a high branched condition, especially in ααγ position [28]. Tri- and tetra-branched molecule followed are some of the best candidate to a rapid β-scission reaction. Those disappear in the case of Al_2O_3 show the rupture in catalytic or thermal mechanism competition.

Catalyst Effect On Solid Residues

The elementary analysis of the solid (as received basis) are shown in Table 8 after pyrolysis reaction with and without catalysts. As we cannot separate catalysts from the solid residue, catalyst quantity was considered as a constant. The weights of catalyst are not considered in the elemental yield result. Based on these results, carbon is the major element in solid residues but its concentration becomes lower with catalysts addition. The variations of the carbon element in solid residues are important with addition of 3% TiO2 and 5% TiO2 and this is confirmed by the presence of a higher amount of C in the oil pyrolysis products. The C/H ratio value in the char is lower than that without catalysts, this might be due to the reduction of C with catalysts addition, this has not been reported in literature [19, 27]. The presence of catalysts can reduce nitrogen and sulfur contents to very low concentrations which are often undetectable [18]. In Table 9, the metal composition of solid residues (on a dry basis) is determined by X-ray spectrometer (Rainy series EDX-700HS), the results show, that catalyst addition has a net effect on the reduction of heavy metal in the solid residues, the metal ratio decreases with increasing the mass ratio of added catalysts. It is observed that the content of Cr, Ni, Zn, Si and Ca in the pyrolysis chars produced by OS pyrolysis without catalysts was high with the addition of the three catalysts which indicated that the addition of catalysts can reduce the risk of potential contamination to the environment [29] in char landfill condition.

Catalysts Effect on Gas Pyrolysis

The composition of the pyrolysis gas (after elimination of N_2 element) obtained with (5% Al_2O_3 case) and without catalysts addition is presented in Tables 10 and 11 respectively. The results show that the pyrolysis gas mainly contained H_2, CO_2 and hydrocarbons which was consistent with related

Table 8 Effect of the quantity and the quality catalysts on the solid residue (char) pyrolysis composition (% corrected)

	% N	% C	% H	% S	% O	C/H ratio (mass)
No- catalyst	0.34	41.65	2.19	0.07	4.05	19.01
CHAR 3% TiO_2	nd	31.71	3.03	nd	1.04	10.46
CHAR 5% TiO_2	nd	29.09	2.09	nd	0.92	10.03
CHAR 3% Al_2O_3	nd	34.57	3.72	nd	8.59	9.29
CHAR 5% Al_2O_3	nd	30.78	3.21	nd	4.43	9.59

nd no detected

Table 9 Metal analysis of pyrolysis char determined by X-ray fluorescence

Metal element (wt%)	Non-catalyst	3%TiO_2	5% TiO_2	3% Al_2O_3	5% Al_2O_3
Fe	42.9	20.2	18.4	11.3	7.8
Ca	17.5	6.1	4.5	5.1	3.8
Si	13.3	5.6	4.9	3.7	2.9
S	7.0	4.6	3.6	7.0	5.6
Cl	5.4	1.8	1.2	4.3	3.4
Al	5.0	2.4	2.1	61.5	59.8
P	2.3	0.6	0.6	2.0	1.8
Zn	2.0	0.7	0.5	0.5	0.3
K	1.9	0.9	0.7	0.5	0.3
Ti	0.8	56.1	62.4	2.4	0.3
Mn	0.4	0.2	0.2	–	–
Sr	0.4	0.1	0.1	0.1	< 0.1
Cu	0.1	–	–	–	–
Zr	< 0.1	< 0.1	< 0.1	–	–
Br	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

Table 10 Molecular composition of pyrolysis gases obtained by non-catalyst reaction (HHV = 1442 kJ/mol)

Gas element	Volume fraction (%)
H_2	9.8
CH_4	23.4
CO_2	12
$C_2H_2{}^+C_2H_4$	31.8
C_2H_6	17.6
C_3H_8	3.36
C_4H_6	1E–04
C_4H_8	0.8
C_4H_{10}	1.2

Table 11 Molecular composition of the catalytic pyrolytic gases (HHV = 1540 kJ/mol)

Gas element	Volume fraction (%)
H_2	7.3
CH_4	20.3
CO_2	5.7
$C_2H_2{}^+C_2H_4$	26.1
C_2H_6	13.9
C_3H_6	21.6
C_3H_8	3.6
C_4H_6	1.1E–04
C_4H_8	0.2
C_4H_{10}	1.2

work [25]. It's observed that the gas obtained by pyrolysis with catalyst addition, contains high content of propylene (C_3H_6) and it's might due to the hydrogenation reaction which is way interesting for the polymers industry (polypropylene production). In addition, with the high content of ethylene, the gas could be easily valorizing in this kind of industry. The effect of catalysts on the gaseous products and solid residues are not the main focus of our study. For more discussion about catalyst effect, further researches would be needed.

Conclusion

Catalytic pyrolysis of oil sludge is performed to produce a fuel similar to conventional diesel. The pyrolysis reaction is carried out in inert environment by using Nitrogen and either TiO_2 or Al_2O_3 as catalyst at various ratios. The TGA shows that the oil sludge pyrolysis is divided into three parts. The diesel and heavy products form the major fractions of oil sludge hydrocarbons. Both used catalysts have shown an effect on the yield and quality of pyrolysis products. The addition of 5 wt% Al_2O_3 has a net effect on viscosity which very low values while increasing the HHV and the aliphatic hydrocarbons content in oil shown by FTIR spectra. According to elementary analysis results of oil the carbon and hydrogen elements ratio increased with the mass ratio of TiO_2 addition. Based on the GC–MS analysis, the liquid obtained from non-catalytic pyrolysis of oil sludge contains more branched hydrocarbons with a maximum carbon number distribution in the range of C_{13}–C_{22}, whereas the oil obtained by catalytic pyrolysis contains more linear hydrocarbons with a maximum concentration of C_{18} with lower branched hydrocarbons. The addition of catalysts promotes the formation of light hydrocarbons in the produced oil. The obtained oil is rich in oxygen and practically free of sulfur since this latter is not detected, and therefore the oil can be reused as a diesel fraction. In addition, char could be activated and use as activated carbon on gas dehydration process. Oil sludge valorization via pyrolysis process like fuel can solve an environmental problem, the results find their interest in the pyrolysis process and they are very useful to improve the treatment process of oil and gas waste products.

Acknowledgements We would like sincerely to express our thanks to the DGRSDT of the Algerian Ministry of Higher Education and Scientific Research, the environment team of Berraki refinery of Algeria for sludge sampling, Faculty of Technology, University of Boumerdes (Algeria), Department of Energy Systems and Environment of IMT Atlantique (Nantes) of France, Military school (EMP) of BORDJ BAHRI (Algeria), Fuel Analysis Laboratory of NAFTAL, Algerian Petroleum Institute (SONATRACH-Boumerdes) for contribution in

the this work, help and supplying samples and characterization. All our respect.

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