



## Production and characterization of pyrolytic oils by pyrolysis of waste machinery oil

Ali Sınağ<sup>a,\*</sup>, Selen Gülbay<sup>a</sup>, Burçin Uskan<sup>a</sup>, Suat Uçar<sup>b</sup>, Sara Bilge Özgürler<sup>c</sup>

<sup>a</sup> Department of Chemistry, Science Faculty, Ankara University, Ankara 06100, Turkey

<sup>b</sup> Chemistry Program, Izmir Vocational School, Dokuz Eylül University, 35160 Buca-Izmir, Turkey

<sup>c</sup> Çukurova Chemical Industry Corporation, Manisa 45030, Turkey

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### ABSTRACT

The main objective of this work is to propose an alternative method for evaluation of the waste machinery oil which is an environmental problem in Turkey. For this purpose, pyrolysis of waste machinery oil was conducted in a tubular reactor. Effect of the experimental conditions (various temperatures, catalyst type) on the formation of pyrolytic oil, gas, and char was investigated. Nickel supported on silica and zeolite (HZSM-5) were used as catalysts. Properties of the pyrolytic oils were characterized by gas chromatograph equipped with a mass selective detector (GC–MS), gas chromatography with flame ionization detector (GC–FID for boiling point range distribution), nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy, higher heating value measurement, and elemental analysis. The behavior of the metals in the waste machinery oil and the pyrolytic oil samples was also quantitatively detected by inductively coupled plasma (ICP) analysis. As, Cd and Cr contents of the all pyrolytic oils were found as <0.05 ppm, while Cu content of the pyrolytic oils varied between 0.3 ppm and 0.61 ppm. Only Vanadium contents of the pyrolytic oils obtained at 800 °C (0.342 ppm) and in the presence of HZSM5 (0.57 ppm) increased compared to that obtained by waste machinery oil (0.1 ppm). Lower metal contents of the pyrolytic oils reveal that pyrolysis of the waste machinery oils leads to the formation of environmental friendly pyrolytic oils with higher heating values.

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### 1. Introduction

In Turkey, it is estimated that more than 230,000 t/year of waste machinery oil are improperly and illegally, disposed into the backyards, landfills and storm drains by individuals who generate this waste through industrial processes. The composition of waste machinery oils changes with the use, since some contaminants such as sulphur and oxidised compounds, hydrocarbons as well as metals, such as chromium or lead, are present in the virgin oil. All these oils of different origin are often mixed together during collection and storage giving a final contaminated residue which is usually called 'waste machinery oil'. Disposal of waste machinery oil is an important environmental issue. Treatment of wastes has become one of the most important concerns of modern society. The diversity of the nature of wastes makes it difficult to develop a general waste treatment procedure. One of the major problems related to the 1991 Environmental Protection Agency (EPA) report was the attempt to cover a large variety of types and uses of oils, which resulted in a very few samples of any category being tested. The pri-

mary volumes of used oils can be broadly classified as "automotive" or "industrial" [1]. This study basically focused on the evaluation of the waste machinery oil. Waste oils are an excellent example of a high-volume waste that can be processed into valuable products [2]. Pyrolysis may be one option for conversion of waste oils into a more useful product and has received special attention due to the multiphase product variation with different yields in solid, liquid and gas form depending on the process conditions [3,4–7]. Most of the studies reported in the literature on pyrolysis of wastes have focused on solid wastes from different sources [8–10], used tires [11,12] and plastic waste [13,14]. Pyrolysis of lighter paraffinic compounds such as jet fuel components has also been studied by several researchers [15].

The pyrolysis of waste machinery oil has been claimed as an alternative to incineration since the valuable products are obtained [16–18].

In the present study, effect of temperature and catalysts (nickel supported on silica and HZSM-5) on the yields and properties of products obtained from pyrolysis of waste machinery oil was investigated. Characterization of the waste machinery oil and pyrolytic oils obtained from pyrolysis was carried out by GC–MS, GC–FID (for boiling point range distribution) and <sup>1</sup>H NMR analysis. Higher heating values of the oils were also measured to reveal the fuel

\* Corresponding author. Tel.: +90 312 212 67 20x1022; fax: +90 312 223 23 95.  
E-mail address: [sinag@science.ankara.edu.tr](mailto:sinag@science.ankara.edu.tr) (A. Sınağ).

**Table 1**  
Elemental analysis and higher heating value results of the waste machinery oil (WMO).

	WMO
Elemental analysis (wt%, daf)	
C	83
H	13
N	0.11
S	0.8
O <sup>a</sup>	2.8
H/C (mol/mol)	1.87
O/C (mol/mol)	0.03
HHV <sup>b</sup> (MJ/kg)	44.54

<sup>a</sup> Amount of oxygen calculated by deducting the percentage of C, H, N, and S from 100.

<sup>b</sup> Higher heating value.

properties of the oils. Metal contents of the oils were also detected by inductively coupled plasma (ICP) so as to evaluate its effect to the environmental aspects.

## 2. Experimental

### 2.1. Materials and methods

The waste machinery oil was supplied from the Totomak Corporation (Izmir, Turkey). Elemental analysis and higher heating values of the waste machinery oil are given in Table 1. In order to avoid replication, waste machinery oil (WMO) and the pyrolytic oils obtained at 400 °C (PO4), at 600 °C (PO6), at 800 °C (PO8) and obtained at 400 °C in the presence of Ni on SiO<sub>2</sub> (PO4-Ni) and HZSM-5 (PO4 HZSM5) were designated with codes as given in the parentheses throughout the text and in tables and in figures as well.

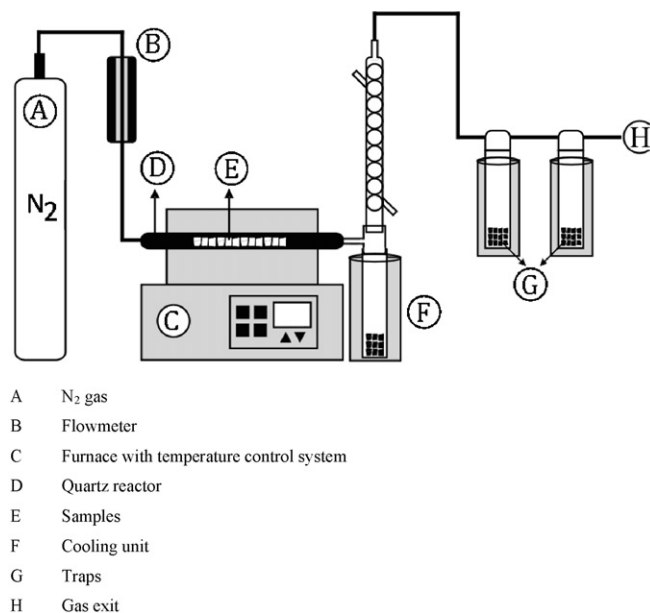
The commercial catalysts used in the experiments were HZSM-5 (Acros, <45 μm) and Ni on SiO<sub>2</sub> (Acros, 70 wt% nickel + 13–19 wt% SiO<sub>2</sub>, surface area; 125 m<sup>2</sup>/g). Among the catalysts, zeolites are in a class of microporous materials that have a well-defined three-dimensional crystalline structure and they are usually composed of aluminum, silica and oxygen atoms.

Zeolites combine high acidity with shape selectivity, high surface area and high thermal stability to catalyze a variety of hydrocarbon reactions.

Reduced silica supported nickel catalyst is generally used for the hydrogenation of benzene, toluene, xylenes, phenol, cresols, and other higher aromatics ring saturation.

### 2.2. Pyrolysis procedure

Pyrolysis procedure was conducted on the system given in Fig. 1. The air of the reactor was removed by purging with nitrogen at a flow rate of 30 mL min<sup>-1</sup> before the experiments for 1 h. The tubular furnace was heated from room temperature to an adjusted temperature. When the furnace temperature reached to the desired experimental temperature, the quartz reactor containing 3.75 g of waste machinery oil in a sample holder was placed into the furnace. Pyrolysis procedure continued until no further liquid was produced. In catalytic experiments, amount of catalysts used was 0.5 wt%. The effluent stream from the reactor was connected to a round-bottomed flask with a reflux condenser where condensation occurred. The reaction mixture was cooled to about 0 °C with an ice-salt bath. The reaction products were classified into three groups: gas, pyrolytic oil and residual coke. The yield of pyrolytic oil was defined as the amount of liquid collected in the round-bottomed flask, and the yield of residual coke as the char remaining inside the reactor after the experiment, while the gas yields were calculated by difference. All pyrolysis tests were duplicated.



**Fig. 1.** Experimental set-up for pyrolysis. (A) N<sub>2</sub> gas; (B) flowmeter; (C) furnace with temperature control system; (D) quartz reactor; (E) samples; (F) cooling unit; (G) traps; (H) gas exit.

### 2.3. Product analysis

The instruments used for the analysis of waste machinery oil and pyrolytic oils and the operating conditions are given below.

#### 2.3.1. Gas chromatography to mass spectroscopy (GC-MS)

GC-MS analysis of the oils was conducted by an AGILENT 6890 GC System 5973 MSD. GC-MS conditions were as follows: (column) HP1 (50 m × 0.32 mm × 0.52 m); (carrier gas) He; (flow rate of He) 0.7 mL min<sup>-1</sup>; (temperature program) initially was held at 50 °C for 15 min, ramp to 300 °C at 5 °C min<sup>-1</sup>, and hold for 17 min. The compounds found in the samples were identified by comparison of their spectra with that in the NIST library of the GC-MS system as their peak area (%) in the total chromatogram.

#### 2.3.2. <sup>1</sup>H NMR spectroscopy

<sup>1</sup>H NMR spectra of the oils were recorded by Bruker Avance DPX-400. <sup>1</sup>H NMR is performed to estimate the hydrocarbon types and to provide an indication of product quality. The hydrocarbon types (aromatics, paraffins) were calculated according to the method described by Myers et al. [19] and Joo and Guin [20] (Table 2).

Aromatics (vol%)

$$= \frac{(A + C/3)0.97 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$$

**Table 2**  
Spectral <sup>1</sup>H NMR regions.

	Type of proton	Chemical shift region (ppm)
A	Ring aromatics	6.6–8.0
B	Olefin	4.5–6.0
C	α-Methyl	2.0–3.0
D	Methine (paraffins)	1.5–2.0
E	Methylene (paraffins)	1.0–1.5
F	Methyl (paraffins)	0.6–1.0

**Table 3**  
Calibration data for ICP-MS.

Elements	R <sup>2</sup> values
As	0.999974
Cd	0.999978
Cr	0.999966
Cu	0.999953
V	0.999996

Paraffins (vol%)

$$= \frac{(D - 2B + E/2 + F/3)1.02 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B}$$

### 2.3.3. Inductively coupled plasma (ICP) analysis

Metal contents of pyrolytic oils (As, Cd, Cr, Cu, V) were analyzed by using ICP-PerkinElmer Optima 2100 DV according to method given in ASTM D 5185 [21]. The samples were prepared as follows.

**2.3.3.1. Sample treatment.** Conostan-S21 Blended Standard was used for calibration in the quantitative analysis. Kerosine was used as the dilution solvent since it is capable of completely dissolving all standards and samples.

The Working standard containing 0, 0.5, 1 and 5 ppm of Conostan S21 standard with 10% (v/v) blank oil (20 cP of viscosity) + 10% (v/v) kerosine and a 20% of blank oil (20 cP of viscosity) solution containing 10% (v/v) kerosine were prepared.

For the calibration, the linear range was established by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analysis of test specimen solutions was performed within the linear range of response as seen in Table 3.

It is extremely important to homogenize the waste machinery oil in the sample container in order to obtain a representative test specimen. So, 1 g of the well-homogenized sample was weighed into a suitable container and 10 g of kerosine (dilution solvent) was added to the sample solution. Thus, the test specimens were ready for analysis and they were analysed in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, etc.).

**2.3.3.2. Gas chromatography with flame ionization detector (GC-FID) analysis.** Gas chromatography with flame ionization detector (GC-FID) analyses of waste machinery oil and pyrolytic oils were performed on a Hewlett-Packard model 6890 GC to determine the boiling point range distributions of oils. The column used in the gas chromatograph is a HP-5 capillary column (30 m length × 0.32 mm diameter) coated with cross-linked 5% phenylmethylsiloxane at a thickness of 0.25 μm. The oven temperature is programmed from 35 (hold 5 min) to 125 °C at a heating rate of 5 °C min<sup>-1</sup> and then up to 250 °C at a heating rate of 3 °C min<sup>-1</sup> and held at 250 °C for 20 min. The data's obtained from GC-FID analyses were used to evaluate the simulated distillation curves of pyrolytic oils according to ASTM D2887 [22].

**2.3.3.3. Higher heating value analysis.** The higher heating values of waste machinery oil and pyrolytic oils (approximately 0.75–1 g) were determined by an IKA C-2000 Basic model calorimeter according to ASTM D240-02 [23]. Oxygen is connected to the system to pressurise the bomb. Measurements are executed in dynamic mode and the calibration of the system is performed with benzoic acid (palleted, C723) of IKA with a higher heating value of 26460 J/g (relative standard deviation of 0.01%).

**2.3.3.4. Elemental analysis.** Elemental analysis of the waste machinery oil and pyrolytic oils was performed with a LECO 932 CHNS elemental analyzer. The sample is burned at a temperature of 1000 °C in flowing oxygen for C, H, N and S analysis in the analyser. The CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub> and SO<sub>2</sub> combustion gases are passed through a reduction tube with helium as the carrier gas for converting the NO<sub>x</sub> nitrogen oxides into N<sub>2</sub> and binding the free oxygen.

The CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub> combustion gases are measured by selective IR detectors. After corresponding absorption of these gases, the content of the remaining nitrogen is determined by thermal conductivity detection. For oxygen, a separate sample is decomposed in a pyrolysis furnace at 1300 °C. The oxygen set free reacts with activated charcoal forming CO. The gas is passed through an oxidation tube with the helium carrier gas and oxidized forming CO<sub>2</sub>. The amount of CO<sub>2</sub> gas is measured as above by an IR detector.

## 3. Results and discussion

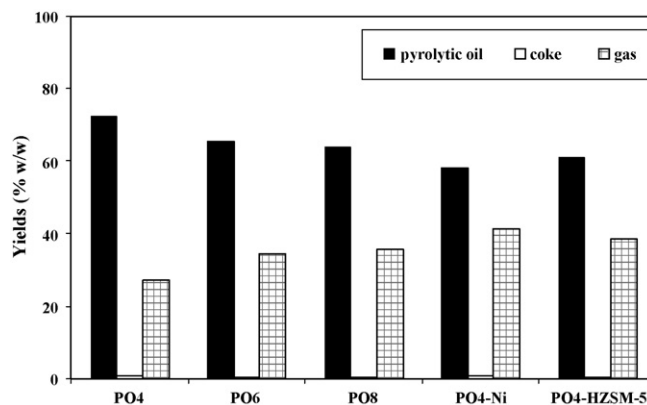
### 3.1. Pyrolysis yields

The effects of the pyrolysis temperatures (400, 600, and 800 °C) and catalysts on the yields of pyrolytic oil, gas and coke are presented in Fig. 2. As the temperature was increased to 800 °C, a slight increase in gas evolution was observed, while pyrolytic oil yields decreased slightly as a result of degradation of oils to gases by free radical mechanism. No remarkable coke formation was obtained. From the point of pyrolytic oil yield, the 400 °C of pyrolysis temperature was selected as optimum and the catalytic experiments were performed at this temperature. The catalysts had important effect on product distribution of pyrolysis. As a result of cracking effect of catalysts, gas yields increased while pyrolytic oil yields decreased. Considering the amount of gases generated, the presence of Ni over silica support was more favorable than HZSM-5.

The aromatic and aliphatic content of the waste machinery oil and pyrolytic oils calculated by Myer's formula is given in Fig. 3. The waste machinery oil and the pyrolytic oil obtained at 400 °C exhibit nearly 80% of aliphatic and 20% of aromatic structures. The higher temperature promotes bond scission and thus mostly lighter aliphatic olefins were obtained.

Decrease in the amount of the aromatic fractions might be attributed to the hydrogenation of the aromatics. This was especially the case at higher temperatures and in the presence of catalysts.

As seen from Fig. 3, the addition of Ni/SiO<sub>2</sub> to the waste machinery oil resulted in the formation of the pyrolytic oil containing less amounts of aromatics than pyrolytic oil from uncatalyzed run.



**Fig. 2.** Effect of the temperature and catalysts on the pyrolytic oil, coke and gas yields.

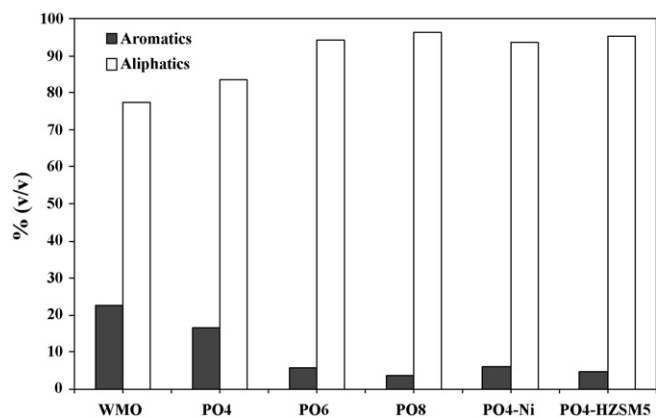


Fig. 3. Composition of the waste machinery oil and the pyrolytic oils.

As known, nickel on  $\text{SiO}_2$  as hydrogenation catalyst was especially used for hydrogenation of higher aromatics such as benzene, toluene, xylenes, phenol, cresols, and other higher aromatics [24]. The waste machinery oil has a paraffinic structure and the hydrogen and carbon atoms are linked in a long linear series similar to a chain. Thus the hydrogen rich structure of waste machinery oil should be mentioned as a source of hydrogen required for hydrogenation. Consequently, this might be the reason why less aromatic and more aliphatic structures were found in the case for  $\text{Ni/SiO}_2$  catalyst.

An interesting result was the pyrolytic oil containing the remarkable amount of paraffins in the presence of HZSM-5. Actually, the formation of aromatics in the presence of HZSM-5 is expected because of the larger extent of cyclization and aromatization reactions that occur within the pores of HZSM-5 [25,26].

This can be explained by the low amount of HZSM-5 (0.5 wt%) used in the present study. Adjaye et al. [27] found that the main effect of HZSM-5 was to increase the extent of cracking and thereby increase the aliphatic hydrocarbon production (below 10 wt% of HZSM-5), while a combination of cracking followed by shape selectivity resulted in the production of aromatic hydrocarbons at the expense of aliphatic hydrocarbons at HZSM-5 amount >10 wt%. It

must be noted that both waste machinery oil and pyrolytic oils contained no olefinic compounds.

### 3.2. GC–MS analysis results

Effect of the experimental conditions (such as pyrolysis temperature, catalyst type, etc.) on the distribution of the most involving compounds identified by GC–MS for the waste machinery oils and pyrolytic oils is summarized in Table 4.

Some of the low molecular-mass compounds such as C5–C9 could not be detected because the MS detector gives no response for species eluted before 5 min.

Pyrolysis parameters (temperature, catalyst type) gave rise to a change in the composition of waste machinery oil. Namely, waste machinery oil consists mainly of aliphatic (linear structures) (<C24) and cyclic hydrocarbons. The amount of aliphatics in the oil obtained by pyrolysis at 600 °C and in the presence of HZSM-5 and Ni on  $\text{SiO}_2$  at 400 °C increased, whereas higher temperatures and addition of catalyst exhibited a slight decrease in the contents of aromatics. Rising pyrolysis temperature also caused to an improved amount of cyclic structures, while a considerable reduction was observed in the amount of linear and branched aliphatics higher than C24 by temperature. Degradation of these products to aliphatics was possibly occurred by catalyst cracking in the presence of catalysts [28]. Another reason for this degradation might be radical formation at higher temperatures.

### 3.3. Fuel characteristics of pyrolytic oils

Elemental compositions of the pyrolytic oils obtained at various temperatures and also in the presence of various catalysts are given in Table 5.

No notable effect of the pyrolysis temperature was found on the elemental composition of the pyrolytic oils. Only oxygen content of the pyrolytic oil slightly decreased compared to the waste machinery oil as seen in Tables 1 and 4. The decrease in oxygen content was due to the decarboxylation which occurred during thermal treatment. The vaporization of the halogenated metal containing oxygen might contribute to the reduction of oxygen. On the other hand, the

Table 4

Main compounds identified by GC–MS for the waste machinery oil and for the pyrolytic oils.

No	R.T. (min)	Purity (%)	Name of compounds	Area (%)					
				WMO	PO4	PO6	PO8	PO4-Ni	PO4-HZSM5
Aliphatics									
1	19.97	97	Tetradecane	2.1	1.3	2.5	1.4	1.1	1.1
2	22.15	98	Pentadecane	5.5	2.8	4.0	2.3	2.6	2.3
3	24.33	98	Hexadecane	2.9	3.8	6.5	3.8	3.7	4.2
4	26.47	97	Heptacosane	4.4	–	–	–	–	–
5	26.47	96	Heptadecane	2.4	–	3.2	2.0	1.8	1.9
6	28.57	99	Octadecane	4.4	3.4	5.5	3.3	3.5	3.4
7	30.57	97	Nonadecane	8.7	5.9	7.5	5.3	8.9	7.5
8	32.54	98	Eicosane	4.9	11.4	6.9	5.7	7.0	21
9	34.40	98	Heneicosane	3.5	3.1	3.2	6.7	2.4	2.5
10	41.63	96	Tetracosane	–	5.4	–	1.7	6.6	7.2
11	42.78	59	Nonacosane	–	5.3	–	–	5.7	4.1
Total area				38.8	42.4	39.3	32.2	43.3	55.2
Aromatics									
12	49.23	93	Pyrene derivative	15.4	5.0	5.2	1.7	11.2	7.7
13	53.41	68	Chrysene derivatives	4.0	3.2	4.5	9.4	2.8	4.2
14	56.25	96	Pyridines derivatives	–	3.5	–	3.8	–	–
Total area				19.4	11.7	9.7	14.9	14	11.9
Cyclic hydrocarbons									
15	32.00	99	Phenanthrene	26.5	28.7	28.3	39.3	36.5	30

**Table 5**  
Elemental analysis and higher heating value results of the pyrolytic oils.

	Type of oil				
	PO4	PO6	PO8	PO4-Ni	PO4-HZSM5
Elemental analysis (wt%, daf)					
C	85	85.3	84.9	84.7	84.8
H	13.3	13	13	13.1	13.20
N	0.1	0.10	0.09	0.12	0.11
S	0.6	0.6	0.99	0.7	0.6
O <sup>a</sup>	0.6	0.77	0.98	1.4	1.3
H/C (mol/mol)	1.87	1.86	1.83	1.86	1.88
O/C (mol/mol)	0.005	0.007	0.009	0.012	0.012
HHV <sup>b</sup> (MJ/kg)	45.7	45.7	45.71	45.65	45.60

<sup>a</sup> Amount of oxygen calculated by deducting the percentage of C, H, N, and S from 100.

<sup>b</sup> Higher heating value.

use of catalyst did not effect the elemental composition of pyrolytic oils.

The higher heating values (HHV) of pyrolytic oils were around 45.7 MJ/kg, which was slightly higher than that of waste machinery oil as seen in Tables 1 and 4. The experimental conditions seem to have not influence on the calorific value of pyrolytic oils obtained. The reduction of oxygen content of pyrolytic oils compared to the original oil contributed to the increase in the HHV of the oils. Actually this value ( $\approx 45.7$  MJ/kg) complies with the higher heating value of commercial diesel, which is 45.7 MJ/kg at 25 °C representing the synthetic fuel potential of the pyrolytic oils.

Boiling point range (BPR) distribution characteristics of WMO, the pyrolytic oils and commercial diesel (for comparison) are represented in Fig. 4. Remarkable effects of temperature increase and Ni on SiO<sub>2</sub> addition to the WMO on the boiling point range of pyrolytic oils were observed. An increase in pyrolysis temperature and adding Ni on SiO<sub>2</sub> to the WMO lead to a decrease in boiling point ranges of the pyrolytic oils compared to WMO.

The pyrolytic oil obtained in the presence of Ni on SiO<sub>2</sub> had a fraction (85%, v/v) boiling between 67 and 68 °C. This could be attributed to C5–C6 (n-pentane–hexane) content of the PO4-NiO<sub>2</sub>, boiling point of which was within this range. PO6 has also 35% (v/v) of C5–C6 fraction, while 35% (v/v) of PO6 and 80% (v/v) of PO8 is within the heavy gas oil range.

The addition of HZSM-5 to waste machinery oil had a small catalytic effect on the production of lighter fractions. Fig. 4 shows that about 75% (v/v) of oil obtained at 400 °C and that obtained in the presence of HZSM-5 were within the heavy gas oil range (320–425 °C). Temperature increase leads to the formation of lighter compounds with low boiling point components due to the increasing cracking of the higher boiling components as expected.

**Table 6**  
Concentration of the metals in the waste machinery oil and the pyrolytic oils (in ppm).

Elements	WMO	PO4	PO6	PO8	PO4-Ni	PO4-HZSM5
As	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cr	0.17	<0.05	<0.05	<0.05	<0.05	<0.05
Cu	0.96	0.308	0.312	0.59	0.57	0.61
V	0.1	<0.03	0.07	0.342	<0.03	0.57

### 3.4. Inductively coupled plasma (ICP) analysis results

The concentrations of metals in both waste machinery oil and pyrolytic oils are presented in Table 6. All oil samples had the lowest concentration of As, Cd, Cr (with the exception of waste machinery oil for Cr). Cu was the most abundant metals in oils. In comparison to the waste machinery oil, pyrolysis conditions (temperature, catalyst type) resulted in a decrease in the amount of Cu content of pyrolytic oils. The content of vanadium after PO4-HZSM-5 treatment was the highest among all the pyrolytic oils. No remarkable effect of Ni over silica on the metal content of the pyrolytic oils was seen from the comparison of metal contents of the pyrolytic oils with and without Ni over Silica at 400 °C except a slight increase in Cu content.

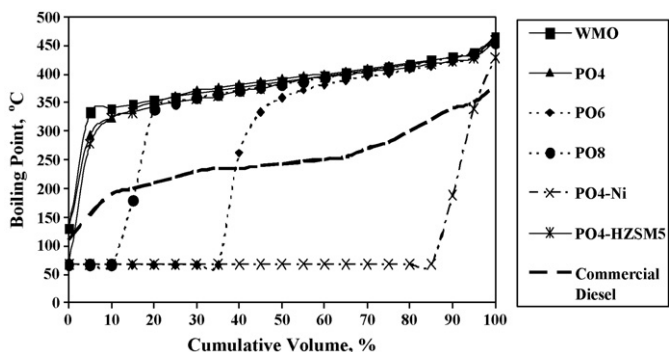
Total chlorine contents of the waste machinery oil together with the volatility of their compounds are the most prominent factors influencing the fate of each metallic compound found in the waste oil [29].

It should also be pointed out that the presence of chlorine enhances the volatilization of most metals [30]. Temperature increase and adding catalyst lead to a slight decrease in the amount of Cr and Cu. This can be attributed to the high volatility (low boiling point) of the compounds CrO<sub>2</sub>Cl<sub>2</sub> and CuCl<sub>2</sub> formed by interaction of Cr and Cu with the high content of chlorine in the waste machinery oil [31,32].

The pyrolytic oil obtained at 800 °C has the highest sulphur content according to the elemental analysis results (Table 5). Vanadium content of this oil found by ICP analysis was also remarkable compared to that obtained by waste machinery oil. This might be due to the lower volatility of vanadium sulphur compared to the other metals [32]. On the other hand, vanadium content in PO8 (0.342 ppm) was found higher than the expected value (around 0.153 ppm). Namely, if the V concentration of the initial oil (WMO) is 0.1 ppm, and in the PO8 pyrolysis run the liquid yield is around 65% and accepting the all V remains in the liquid, the maximum V concentration expected would be 0.1/0.65, that equals 0.153 ppm. Here, it should be mentioned that a mistake in the analytical procedure might be a reason for this situation.

Effect of sulphur on Cu and Cr should also be considered. Copper sulphides have lower solubility constants (thermodynamic constants), whereas Cr do not form insoluble sulphides, meaning that chromium sulphide is more volatile than copper sulphide complying with data given in Table 6 [32].

As given by Contreras et al., each element found in pyrolytic oils is not isolated from other element meaning that the fate of elements is dependent both for their interactions among these elements and their different reactivity towards different atoms such as Cl, S [33]. To simulate the most probably speciation, it is also necessary to take into account the possible interactions which may occur between the elements present in the oils. According to this study, arsenic and cadmium volatilization decrease as a result of the formation of Cd<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> resulting from As–Cd interaction which agrees with the our findings since no variation on the amounts of As and Cd was seen in Table 6. In addition, chromium and arsenic interacted with copper to form CuCrO<sub>2</sub> and Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> as indicated by Lundholm [34].



**Fig. 4.** Boiling point range distribution curves of the oils.

Both of these refractory phases are more stable than the pure chromium and arsenic oxides and thus suppressed the volatility of these elements. Pure oxide of chromium is the least stable phase and it shows higher volatility by increasing pyrolysis temperature.

On the other hand, the observed increase in vanadium content of oil in the presence of HZSM5 can be attributed to the deposition of vanadium on HZSM5 since this metal adsorbs on or near active catalytic sites of HZSM5 as given by Lorenza et al. [35].

In general, a significant reduction of the metal concentration in the pyrolytic oils compared to the content in the waste machinery oil was observed meaning that the pyrolysis of waste machinery oil is a good alternative to direct combustion in terms of an environmental point of view. These metals were expected to be as vapor phase according to the volatility of the compounds involving the metal. On the other hand, metals were mainly involved in such type oils as linked to some organic compounds. All of them were likely transformed during the pyrolysis process and their behaviors were consequently different. This different speciation of each metal could explain why not all the metal content of the waste machinery oil was recovered in the liquid phase or released in the vapor phase.

In future work, it is expected to obtain the pyrolytic oils, boiling point ranges of which are close to that of diesel. In order to achieve this, effect of some experimental parameters, e.g. reaction time, reactor type, catalyst type on the characteristics of the pyrolytic oils will be investigated.

#### 4. Conclusions

Conclusions of this study can be summarized as follows:

- Catalysts lead to the improved gas yields due to the cracking. In the presence of Ni over silica support, more gases were generated over HZSM-5.
- Ni/SiO<sub>2</sub> addition to the waste machinery oil resulted in the formation of the pyrolytic oil containing less amounts of aromatics than pyrolytic oil from uncatalyzed run as a result of hydrogenation occurred in the presence of this catalyst.
- Using low amount of HZSM5 leads to the formation of remarkable amounts of aliphatics instead of aromatics.
- Temperature increase and adding Ni on SiO<sub>2</sub> to the WMO have a significant effect on the boiling point range of pyrolytic oils.
- A decrease in metal contents of the pyrolytic oils was observed due to the different behavior of metals in liquid and gas phases. No effect of temperature and catalysts on the As and Cd content of pyrolytic oils was seen, while temperature increase and adding catalyst leads to a slight decrease in the amount of Cr and Cu.
- High sulphur content of the pyrolytic oil obtained at 800 °C is the reason for the increase in vanadium content of this oil due to the lower volatility of vanadium sulphur compared to the other metals. An increase in vanadium content of oil in the presence of HZSM5 can be attributed to the deposition of vanadium on HZSM5.
- The metal contents of the pyrolytic oils are much lower than the original waste machinery oil meaning that the pyrolysis of waste machinery oil is a good alternative for direct combustion in an environmental point of view.

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