



# Selective production of valuable hydrocarbons from waste motorbike engine oils via catalytic fast pyrolysis using zeolites



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## ABSTRACT

Aged automobile engine oils contain highly oxidized and hazardous organic compounds, and their disposal adversely affects the environment, underground, and surface waters. Therefore, it is imperative to develop innovative strategies to solve the problem of disposal of waste engine oils. One way is to recover value added chemicals and intermediates from it. This study focuses on recovery of useful hydrocarbons from highly oxidized, waste motorbike engine oils via catalytic fast pyrolysis using zeolites belonging to ZSM-5, Zeolite- $\beta$  and Zeolite-Y (ZY) families. Pyrolysis experiments were conducted in a microreactor connected to a gas chromatograph–mass spectrometer. Initially, non-catalytic fast pyrolysis was performed at temperatures from 300 to 800 °C, and it was found that high temperatures led to the formation of C<sub>3–10</sub> alkenes, while low temperatures resulted in high yields of heavy fractions like C<sub>31–60</sub> alkanes and oxidized aromatics. In order to selectively improve the production of C<sub>6–15</sub> alkanes that are valuable as fuel molecules, catalytic fast pyrolysis was performed at 400 °C using 1:1 wt./wt. of oil:zeolites. Hydrogen form of ZY resulted in c.a. 65% of C<sub>6–15</sub> linear, branched, and cyclic alkanes, while other catalysts promoted the formation of alkenes. The yields of C<sub>6–15</sub> linear and cyclic alkanes increased with micropore area, pore volume, and surface acidity of the zeolites. An increase in catalyst quantity significantly increased the yield of C<sub>6–10</sub> alkanes, while reducing the C<sub>11–15</sub> alkane yield and promoting the formation of C<sub>3–5</sub> alkanes. High temperatures led to a significant drop in the production of linear and branched alkanes, but promoted the formation of alkenes and cyclic hydrocarbons. This work has demonstrated that catalytic fast pyrolysis using zeolites is a potential technique to selectively recover value added hydrocarbons from highly oxidized engine oils.

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## 1. Introduction

A large amount of waste automobile lubricating oil is generated every year in the world. About 40 million metric tons of waste engine oil are generated annually, and only 40% of the oil is recycled while the rest is discarded [1,2]. Waste lubricant oils are toxic and hazardous owing to the presence of various elements from additives such as iron, nickel, lead, zinc, magnesium, calcium, and phosphorous, organic compounds like phenolics, oxygenated benzene derivatives, sulfur containing compounds like sulphides and sulfonic acids, polycyclic aromatic hydrocarbons (PAHs) and other carbonaceous solid residues [3]. These toxic and hazardous materials adversely affect the environment, underground, and surface

waters, and also pollute air when oil is incinerated. Many studies have shown that high concentrations of PAHs in sewage effluents and urban runoffs are due to contamination by waste lubricant oils [4–6]. The techniques adopted for recycling and reusing of waste engine oils vary from one country to another. Predominantly, the discarded engine oils, after their first use, enter the secondary market wherein they are used as lubricants for domestic appliances and overhauling purposes. They are also used as furnace oils after the removal of soot and other residual toxic materials via precipitation [7]. In certain processes, regeneration units are utilized to produce re-refined lubricating oils, which possess similar qualities as that of new lubricating oils [8–10]. The Phillips re-refined oil process (PROP) produces high yields of base oils from waste lubes in a two step process that involves chemical demetallization using diammonium phosphate to separate the metal contaminants, and catalytic hydrotreatment to remove nitrogen, oxygen, chlorine, and sulfur compounds [11]. In another process called solvent extraction, the used oil is mixed with liquefied C<sub>3–6</sub> aliphatic hydrocarbons to

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dissolve the oil fraction and isolate the less soluble and insoluble impurities. Solvent recovery is achieved by distillation of the solvent–oil mixture [11]. Ultimately, totally unusable engine oils, after several cycles of reuse and recycling, are currently being discarded into the environment either in water bodies or landfills. Therefore, from environmental, energy, and economic viewpoints, it is necessary to develop innovative strategies to solve the issue of disposal of waste engine oils along with the generation of value added intermediates/fuels.

Pyrolysis is one of the well known thermochemical processing techniques to recover valuable intermediates and chemicals from a variety of renewable and non-renewable feedstocks like waste plastics [12,13], end-of-life tyres [14,15], lignocellulosic biomass [16], coal, petroleum residues [17], and oil shales [18]. A few reports are available on conventional pyrolysis of waste engine oils [1,2,11,19–24]. Fuentes et al. [2] investigated the pyrolysis and combustion of waste lubricant oil using thermogravimetric analyser (TGA) and identified around 30 volatile and 170 semi-volatile compounds at 500 and 850 °C. While PAHs, naphthalene, acenaphthalene, and phenanthrene were observed in significant yields during pyrolysis, naphthalene was the major compound during combustion. In another similar study, waste automotive, hydraulic, machine, and cutting oils were pyrolyzed, and a significant decrease in metallic lead content was observed in the pyrolysis oils [19]. Kim and Kim [20] evaluated the pyrolysis of waste automobile lubricating oil in TGA and proposed a multi-step model involving the formation of C<sub>5</sub>–C<sub>11</sub> compounds from C<sub>12</sub> to C<sub>25</sub> intermediates in the temperature range of 420–440 °C. The average activation energy of decomposition of waste oil was found to be 322.69 kJ mol<sup>-1</sup> in the conversion range of 11–96% with overall reaction order of 1.35 [21]. Arpa et al. [22] blended waste engine oils with different additives and obtained diesel-like product via pyrolytic distillation. Lazaro et al. [23] studied co-pyrolysis of waste lubricating oil with coal, and characterized the tar including C<sub>1</sub>–C<sub>3</sub> alkanes, C<sub>2</sub>–C<sub>4</sub> olefins, and BTX (Benzene, Toluene, Xylene). Bhaskar et al. [24] observed that nearly 95% of sulfur in waste lubricant oil can be removed as H<sub>2</sub>S by catalytic pyrolysis in presence of Fe/SiO<sub>2</sub> at 400 °C. In a series of studies, Lam et al. [25–29] investigated microwave assisted pyrolysis of waste automotive engine oils and obtained valuable products such as hydrogen, light olefins, liquid hydrocarbon oils containing BTX and other benzene derivatives. The effects of microwave operation parameters on yield and quality of pyrolysis oil were evaluated.

Fast pyrolysis is a promising thermochemical conversion technique that yields high amounts of liquid oil compared to non-condensable gases and solid char [16]. This technique involves pyrolyzing the feedstock at moderate temperatures in the range of 350–600 °C at fast heating rates of c.a. 1000 °C s<sup>-1</sup>. Importantly, the involvement of different phases like solid, liquid aerosol, condensed melt, vapor, gas, and aromatic char makes fast pyrolysis a complex process. The liquid product can be upgraded to refinery-ready blendstocks or drop-in fuels. Catalytic fast pyrolysis of biomass to produce bio-oil and biofuels is popular, and commercial scale production of biofuels is now a reality [30,31]. As the existing studies on slow pyrolysis of waste engine oils are performed in TGA and stirred reactors, the product distribution is severely dependent on total reaction time that causes secondary cracking of the primary volatiles. This is one of the reasons for the high yield of low molecular weight (C<sub>1</sub>–C<sub>5</sub>) hydrocarbons observed in most of the studies. However, the product yields and their selectivities are expected to be very different during fast pyrolysis owing to short reaction time scales. Moreover, the mechanism of formation of products can also shift from a conventional gas phase chemistry to a mix of gas phase and condensed phase chemistry.

To the best of our knowledge, this is the first study to report non-catalytic and catalytic fast pyrolysis of waste engine oils to

recover hydrocarbons of specific carbon chain lengths. Compared to the existing re-refining processes, which account for 10% of the reused oils in the United States [32], fast pyrolysis process has the potential to directly yield blendable or drop-in fuels from waste engine oils. In the present work, aged engine oils are subjected to (i) non-catalytic fast pyrolysis at different temperatures, (ii) catalytic fast pyrolysis in presence of six different zeolites at two different oil: zeolite mass ratios and at different temperatures. A thorough analysis of products and their yields is performed, and the optimum conditions that result in high yields of C<sub>6</sub>–C<sub>15</sub> hydrocarbons are established. The role of catalyst in promoting the selective production of saturated hydrocarbons is evaluated by correlating the product yields with various properties of the zeolites like surface acidity, pore size distribution, and specific surface area.

## 2. Experimental

### 2.1. Materials

Two different aged engine oil samples were obtained from a local motorbike service center. Aged engine oil1 (henceforth denoted as oil1) was collected from a four stroke motorbike engine after the first 1000 km run, and aged engine oil2 (oil2) was a mixture of various aged engine oils. Six different zeolites belonging to ZSM-5, ZY, and Zβ categories were obtained from Alfa Aesar. These catalysts varied by Si:Al ratio, acidity, specific surface area, and pore size distribution. The properties of the catalysts are listed in Table 1.

### 2.2. Lubricant analysis

Aged oil samples were characterized by oxidation index, sulfation index, nitration index, antiwear content, and total base number using Fluidscan Q1000 (Spectro Inc.) lubricant monitor in Petrolabs India Private Limited, Hyderabad, India. Fluidscan lubricant monitor is an infrared-based, chemometrically calibrated analyzer that provides the value of the above ageing markers based on increase or decrease in absorbance of a particular organic functional group [33]. The content of heavy metals such as wear metals and contaminants in the oil samples was determined using an atomic emission spectrometer (Spectro Inc.).

### 2.3. Thermogravimetric analysis

Thermogravimetric analysis of the aged oil samples was performed in SDT Q600 TGA (TA Instruments) in presence of nitrogen (100 mL min<sup>-1</sup>). Approximately 2 mg of the oil sample was pyrolyzed under different heating rates, viz. 5, 10, 20, 50, and 100 °C min<sup>-1</sup>. Mass loss and differential mass loss data of the oils during degradation were collected to evaluate the thermal stability of oils and kinetics of ageing.

### 2.4. Evaluation of apparent activation energy of decomposition

Apparent activation energies of thermal decomposition of aged oil samples were evaluated according to the recommendations of the Kinetics Committee of International confederation for thermal analysis and calorimetry (ICTAC) to quantify the stability of the oils [34]. Integral isoconversional method of Kissinger–Akahira–Sunose (KAS) was utilized to evaluate the variation of apparent activation energies of decomposition of oil1 and oil2 with conversion. The functional form of KAS method for a first order decomposition of oil is given by [34]:

$$\ln \left( \frac{\beta_i}{T_\alpha^2} \right) = \ln \left( \frac{A_\alpha \times R}{E_\alpha \times \ln \left( (1 - \alpha)^{-1} \right)} \right) - \left( \frac{E_\alpha}{R \times T_\alpha} \right) \quad (1)$$

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