Cleaner alternative liquid fuels derived from the hydrodesulfurization of waste tire pyrolysis oil

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A B S T R A C T

Waste tires are attractive sources for alternative energy due to their long hydrocarbon chains with a high heating value. However, the condensed (volatile portion) pyrolysis oil derived from waste tires contains a relatively large level of sulfur compounds (1.15 wt%), which is not appropriate for use in combustion engines. Therefore, this research aimed to improve the waste tire pyrolysis oil (WTPO) via hydrodesulfurization (HDS) catalyzed by molybdenum (Mo), nickel–Mo (NiMo) or cobalt–Mo supported on alumina (γ-Al$_2$O$_3$). The maximum % sulfur removal (87.8%) was achieved when the reaction was performed at 250 °C for 30 min using a 2 wt% NiMo/γ-Al$_2$O$_3$ catalyst loading based on the WTPO content and 20 bar initial hydrogen pressure. The amount of sulfurous compounds in the waste tire pyrolysis oil was determined using gas chromatography spectroscopy equipped with a flame photometric detector (GC–FPD). The HDS of the WTPO was effective to reduce the sulfurous compounds, especially thiophene and its derivatives. The results from the simulated distillation gas chromatography (GC–SIMDIS) showed that the hydrodesulfurized WTPO (HDS-WTPO) was mainly composed of a light naphtha fraction (ca. 69%). The heating value of the HDS-WTPO (44 MJ/kg) was similar to those for commercial diesel (45 MJ/kg) and gasoline (gasohol) fuels (47 MJ/kg).

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1. Introduction

The quantity of waste tires is annually increasing due to the numerical and economic growth of the world population with a corresponding increased demand for personal transportation, including within the industrial sectors. Since waste tires are not biodegradable materials, and can generate pollutants during their combustion, such as sulfur dioxide (SO$_2$) and polycyclic aromatic hydrocarbons (PAHs) resulting from the vulcanizing agents and elastomers, respectively, their disposal is problematic. However, waste tires have been considered as an alternative energy source due to their higher heating value (37.7 MJ/kg) [1] than that of terpenoid biomasses such as *Euphorbia rigida* (16.3 MJ/kg) [2] or oil palm wastes (ca. 18 MJ/kg) [3].

Thermal decomposition without oxygen, or "pyrolysis", is an appropriate method to transform waste tires into alternative fuels under inert gas atmosphere and high temperature (300–900 °C)

[4]. The process is irreversible and involves the simultaneous change in the chemical composition and the physical phases of the raw materials. The products derived from pyrolysis can be categorized into the three types: oil (40–60 wt%), char (25–50 wt%) and gases (3–30 wt%) and their yields are dependent on the reactor types and applied conditions [4,5]. Since transportation is the main sector that consumes liquid fuels, waste tire pyrolysis oil (WTPO) containing various organic compounds having 5–20 carbons with an aromatic portion is expected to be used as a fuel or petroleum refinery feedstock. However, WTPO has a high sulfur content (1.0–1.4 wt%) [5,6], which is generated from the vulcanizing agents used for tire production, and this limits its direct application in combustion engines. These sulfur compounds, such as thiols, sulfides, thiophenes, benzothiophenes, dibenzothiophenes and their derivatives, in the WTPO induce undesired properties, such as corrosiveness from the highly toxic SO$_2$ gas that is generated during combustion. Thus, it is necessary to seek a process for the efficient removal of sulfur compounds from the WTPO before using alone or blending with commercial fossil liquid fuels.

Traditionally, the removal of sulfur compounds from petroleum-derived feedstocks has been achieved via hydrodesulfurization (HDS) to convert the sulfur substances to hydrogen sulfide (H$_2$S).

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This reaction is performed on the surface of the catalyst under a high hydrogen (H_2) pressure (30–130 atm) and temperature (300–400 °C). Conventional catalysts used for HDS are the sulfides of cobalt–molybdenum (CoMo) or nickel–molybdenum (NiMo) supported on alumina (Al_2O_3). The removal of sulfur compounds via HDS has been reported for model sulfurous compounds, such as thiophene [7], benzothiophene [8], dibenzothiophene [8,9] and 4,6 dimethyldibenzothiophene [10]. Unlike in conventional fossil liquid fuels, it has been reported that the sulfur compounds found in the WTPO are in forms of sulfur-polycyclic aromatic hydrocarbons, such as dibenzothiophene and its derivatives [11,12]. These sulfurous species would be complicated and difficult to be removed.

Thus, this research focused on the reduction of the sulfur content in the WTPO via catalytic HDS. The performance of three different catalysts supported on γ-alumina, such as molybdenum (Mo/γ-Al_2O_3), nickel–molybdenum (NiMo/γ-Al_2O_3) and cobalt–molybdenum (CoMo/γ-Al_2O_3), on sulfur removal efficiency was individually evaluated. In addition, for each catalyst the effects of the catalyst type and loading level, initial H_2 pressure, reaction temperature and reaction time on the % sulfur removal were investigated. The quality of WTPO before and after HDS treatment in terms of its heating value, and iodine value for evaluation of saturation was also comparatively evaluated.

2. Materials and methods

2.1. Materials

The waste tire powder ($\varnothing$ = 250 μm) was obtained from Union Commercial Development Co., Ltd. (Samut Prakarn, Thailand). For the catalyst preparation, activated γ-Al_2O_3 powder (KHD-12: $\varnothing$ = 150 μm and surface area = 119.0 m^2/g) was supplied from Sumitomo Chemical Co., Ltd. (Japan). Ammonium tetrathiomolybdate (ATTM; [NH_4]$_2$$MoS_4$) (Aldrich, 99.97%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) (QRec, 97%) were used as received. Pure H_2 (99.99% purity), used for the reduction of catalyst and HDS process, nitrogen (N_2, 99.99% purity), used for pyrolysis of the waste tire powder, air (99.95% purity) and helium (He, 99.95% purity), used for the gas chromatography spectroscopy equipped with a flame photometric detector (GC–FPD) analysis, were all supplied by Praxair Co., Ltd. (Thailand).

2.2. Pyrolysis process

The waste tire powder (100 g/batch) was pyrolyzed in a stainless steel tubular fixed bed reactor placed in the tubular furnace and heated at a 25 °C/min increment rate to the pyrolysis temperature of 400 °C under a N_2 atmosphere at a flow rate of 0.1 L/min for 10 min. The obtained vapor from the pyrolysis was condensed in Erlenmeyer flasks immersed in an ice bath to yield the volatile oil fraction or WTPO. When the fixed bed reactor was removed from the tubular furnace, the residual products in the reactor were washed with tetrahydrofuran (THF) to extract the heavy oil fraction from char (residual oil). The amount of the gas fraction was indirectly calculated from the percentage difference in weight. This pyrolysis condition gave yields of WTPO, residual oil, char and gas fractions of 42.0, 4.00, 41.6 and 12.4 wt%, respectively. Since the WTPO was obtained in the highest yield, and so was more practical to be scaled up than the residual oil fraction, then the WTPO was selected as the raw material for upgrading via the HDS process.

2.3. Characterization of the waste tire powder and its derived WTPO

The level of moisture (0.80 wt%), volatile matter (57.5 wt%), ash (17.0 wt%) and fixed carbon (24.7 wt%) of the dried waste tire

powder and WTPO were evaluated following ASTM D3173-D3175. The elemental analysis was performed using a CHN analyzer (Perkin Elmer, PE-2400) following ASTM D3176-89 to detect the total carbon, hydrogen and nitrogen contents. The total sulfur content in the waste tire powder was determined using a LECO SC-132 Sulfur Determinator (LECO Corporation, St Joseph, Michigan). The oxygen content was then indirectly calculated from the percentage difference. The heating value was evaluated following ASTM D2015 using a bomb calorimeter (Parr-6200). The water contents in the WTPO before and after HDS were examined by using the Karl Fischer titration (Mettler Toledo-V20). The elemental composition of the waste tire powder used and the WTPO including the water content in the obtained WTPO are summarized in Table 1.

The heating value of the obtained WTPO (42 MJ/kg) was 1.3-fold higher than that of the waste tire powder, which is due to its higher carbon content. Since the heating value of the WTPO was similar to that of conventional diesel fuel (42.7 MJ/kg) [13], WTPO has the potential to replace conventional crude oil feedstock. However, the WTPO fraction still had a high sulfur content of 1.15 wt%, which would limit its application as an alternative liquid fuel for combustion engines. Moreover, the small amount of water (0.44 wt%) was observed in the WTPO sample possibly due to the dehydration of some vulcanizing agents such as fatty acids during pyrolysis. This result was similar to the previous literatures reported by Martínez et al. [14] and Siva et al. [1].

2.4. Catalyst preparation

For preparation of the Mo/γ-Al_2O_3 catalyst, the γ-Al_2O_3 powder was dried in an oven at 100 °C for 24 h. Without the sulfidation process, 0.77 M ATTM dissolved in de-ionized water was used as the Mo-catalyst precursor [8] and impregnated onto the dried γ-Al_2O_3. The obtained product was dried in an oven at 60 °C for 12 h and calcined at 250 °C for 3 h. For the NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 catalysts, the above Mo/γ-Al_2O_3 was then further successively impregnated with 1.02 M of $Ni(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ solution to produce the NiMo/γ-Al_2O_3 or CoMo/γ-Al_2O_3 catalyst, respectively [15]. The resulting products were dried as described above and calcined in air at 500 °C for 3 h.

2.5. Catalyst characterization

The surface area, total pore volume and average pore diameter of the prepared catalysts were evaluated using an Autosorb-1, Quantachrom. The surface area was calculated from the N_2 physisorption using the Brunauer–Emmet–Teller (BET) equation, whilst the average pore size was obtained by the Barrett–Joyner–Halenda (BJH) method in the desorption stage. The surface morphology of catalysts after calcination was investigated using scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) on a JEOL JSM-6400 instrument operated at an accelerating voltage of 15 kV. Before analysis, the catalysts were sputter-coated with gold to increase their conductivity.

Table 1
Elemental composition (ash-free basis), heating value and water content of waste tire powder and WTPO.

	Waste tire powder	WTPO
Elemental analysis (wt%)		
• Carbon	70.0	80.5
• Hydrogen	6.79	7.90
• Nitrogen	0.28	0.52
• Sulfur	1.53	1.15
• Oxygen	21.4	9.93
Heating value (MJ/kg)	32.3	42.0
Water content (wt%)	–	0.44