

Article

## Photocatalytic Desulfurization of Waste Tire Pyrolysis Oil

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**Abstract:** Waste tire pyrolysis oil has high potential to replace conventional fossil liquid fuels due to its high calorific heating value. However, the large amounts of sulfurous compounds in this oil hinders its application. Thus, the aim of this research was to investigate the possibility to apply the photo-assisted oxidation catalyzed by titanium dioxide (TiO<sub>2</sub>, Degussa P-25) to partially remove sulfurous compounds in the waste tire pyrolysis oil under milder reaction conditions without hydrogen consumption. A waste tire pyrolysis oil with 0.84% (w/w) of sulfurous content containing suspended TiO<sub>2</sub> was irradiated by using a high-pressure mercury lamp for 7 h. The oxidized sulfur compounds were then migrated into the solvent-extraction phase. A maximum % sulfur removal of 43.6% was achieved when 7 g/L of TiO<sub>2</sub> was loaded into a 1/4 (v/v) mixture of pyrolysis waste tire oil/acetonitrile at 50 °C in the presence of air. Chromatographic analysis confirmed that the photo-oxidized sulfurous compounds presented in the waste tire pyrolysis oil had higher polarity, which were readily dissolved and separated in distilled water. The properties of the photooxidized product were also reported and compared to those of crude oil.

**Keywords:** photooxidation; desulfurization; waste tire; pyrolysis; titanium dioxide

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## 1. Introduction

The growth in the human population size, with the corresponding higher demands for commercial and personal transportation to support daily activities has led to an increasingly huge production of waste tires. For example, consumers and industry in the United States generated some 4.6 million tons of waste tires or 303.2 million scrap tires in 2007 [1]. The two simplest and methods to dispose of the waste tires are landfill and incineration, but these techniques are limited by the availability of landfill space, the possibility of large fires at the stockpiles and the formation of excellent breeding grounds for disease vectors, such as mosquitoes. The toxic exhaust gases and dense black smoke produced during the incineration are also serious air pollutants [2,3]. Although there have been attempts to encourage the recycling of waste tires for use in various applications, they have been deemed as a “hard-to-recycle” material, largely resulting from the crosslinking obtained from the vulcanization process to promote their thermosetting properties, which also makes them largely non-biodegradable [4].

Since the major components in tires are natural and synthetic rubbers, both having long hydrocarbon chains, waste tires have higher heating value (39.1 MJ/kg) [5] compared to waste biomass, such as palm (18–20 MJ/kg) [6] or rice husk (15 MJ/kg) [7]. Thus, waste tires have a high potential for use as a supplemental energy resource aimed at partially or totally replacing conventional fossil fuels. To convert waste tires into fuels, their thermal decomposition in an oxygen-starved atmosphere, which is called a pyrolysis process, is normally applied to transform them into a solid char [ca. 40% (w/w)] and low molecular weight liquids or gases [ca. 60% (w/w)] [8]. However, the main drawback of the waste tire-derived fuels that limits their wider application in real combustion processes is the high sulfur content [1.0–1.4% (w/w)] [9]. In the oil refinery industry, the hydrodesulfurization (HDS) process removes organosulfur compounds from fossil liquid fuels with high efficiency, but this process is costly to refiners due to the requirement of a high reaction temperature (>300 °C) and a high hydrogen pressure (>2 MPa) in the presence of a precious metal catalysts operated in the large reactor volume to convert sulfur compounds to hydrogen sulfide [10,11]. Thus, the options for directly applying this process for reducing sulfur contents to waste tire pyrolysis oil, which is generally produced on the small and medium enterprises (SME) scale, are limited. Moreover, the waste tire pyrolysis oil with large amounts of sulfur compounds might not be appropriate for the conventional HDS process due to the high hydrogen consumption with reduction of the catalyst efficiency. For upgrading the waste tire pyrolysis oil in a small scale process before treating with the HDS, a pre-treatment step operating under milder reaction conditions without the hydrogen requirement for partially reducing some sulfurous compounds in the waste tire pyrolysis oil is proposed. A well-known reaction for sulfur removal operated under non-severe conditions is oxidative desulfurization (ODS), which is carried out at low reaction temperatures with the addition of some oxidants [11]. In our previous research work, ODS in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), formic acid and waste tire pyrolysis char at 60 °C has been applied to decrease the sulfur content in the waste tire pyrolysis naphtha to achieve 72% of sulfur removal [12].

As one of ODS processes, the utilization of UV-light for pollutant removal via photocatalytic oxidation has been extensively studied. Over the past decade, the use of titanium dioxide ( $\text{TiO}_2$ )-based photocatalysis in environmental purification to decompose organic compounds in air and wastewater has increased since this method can be conducted under mild reaction conditions [13,14]. Moreover,  $\text{TiO}_2$  is inert to chemical corrosion, has a strong oxidizing power (with UV light) and is cost effective [15]. Like the ODS process, the photocatalytic desulfurization consists of two main stages. In the first stage, the sulfur-containing compounds are subjected to photocatalytic oxidation to produce sulfoxides or sulfones via oxygen donation to the sulfurous compounds. Then, the higher polarity oxidized products are extracted by exposure to a polar solvent-extracting phase. The application of photocatalysis for deep desulfurization to successfully remove thiophenes and derivatives of benzo-thiophene and dibenzothiophene, which are the models of sulfur compounds in gasoline [16], light oil [17,18] and diesel [19], respectively, has been reported in previous literatures. The results indicated that the photodesulfurization had more reactivity than the conventional HDS to decompose steric dibenzothiophene derivatives such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) [17]. However, the application of photo-assisted oxidation to decompose more complicated organic sulfur compounds found in the waste tire pyrolysis oil has not been studied. Thus, the aim of this research was to examine the possibility of applying  $\text{TiO}_2$ -based photocatalytic desulfurization process for upgrading the quality of waste tire pyrolysis oil. The effects of the  $\text{TiO}_2$  loading, reaction temperature, type and amount of the extracting solvent and sources of oxygen donor on the degree of photodesulfurization of waste tire pyrolysis oil were investigated. The change of sulfurous compounds in the waste tire pyrolysis oil was also monitored by using a gas chromatograph equipped with a flame photometric detector (GC-FPD) and high performance liquid chromatography (HPLC). Moreover, the properties of waste tire pyrolysis oil were reported and compared to those of crude oil.

## 2. Experimental

### 2.1. Materials

The waste tire powder ( $\phi = 355\text{--}425\ \mu\text{m}$ ) was received from Union Commercial Development Co., Ltd. (Samutprakarn, Thailand).  $\text{TiO}_2$  (commercial grade Degussa P-25), with BET surface area of *ca.*  $65\ \text{m}^2/\text{g}$  was obtained from J.J. Degussa Hüls Co., Ltd. (Singapore). Analytical grade methanol ( $\text{CH}_3\text{OH}$ ) from QRëC (New Zealand), acetonitrile ( $\text{CH}_3\text{CN}$ ) and tetrahydrofuran (THF) from Fisher Scientific (Leicestershire, UK) and 30% (w/w) of  $\text{H}_2\text{O}_2$  from Merck (Germany) were all used as received. Tetradecane ( $\text{C}_{14}\text{H}_{30}$ ), thiophene ( $\text{C}_4\text{H}_4\text{S}$ ), benzothiophene ( $\text{C}_8\text{H}_6\text{S}$ ) and dibenzothiophene ( $\text{C}_{12}\text{H}_8\text{S}$ ) were purchased from Sigma-Aldrich, Co., Ltd. (USA). Air at 99.98% purity was obtained from Praxair Co., Ltd. (Samutprakarn, Thailand).

### 2.2. Proximate and Ultimate Analysis of the Waste Tire Powder Composition

The proximate analysis of the waste tire powder was evaluated following ASTM D3173-D3175 to detect the levels of moisture, volatile matter, ash and fixed carbon. The total carbon, hydrogen and nitrogen contents of the waste tire powder were determined by dry combustion using a LECO

CHN-2000 analyzer. The total sulfur content was measured using a sulfur analyzer (LECO SC-132 Sulfur Determinator). The oxygen content was then calculated by the percentage difference. The gross calorific value of the waste tire powder was also investigated following ASTM D2015.

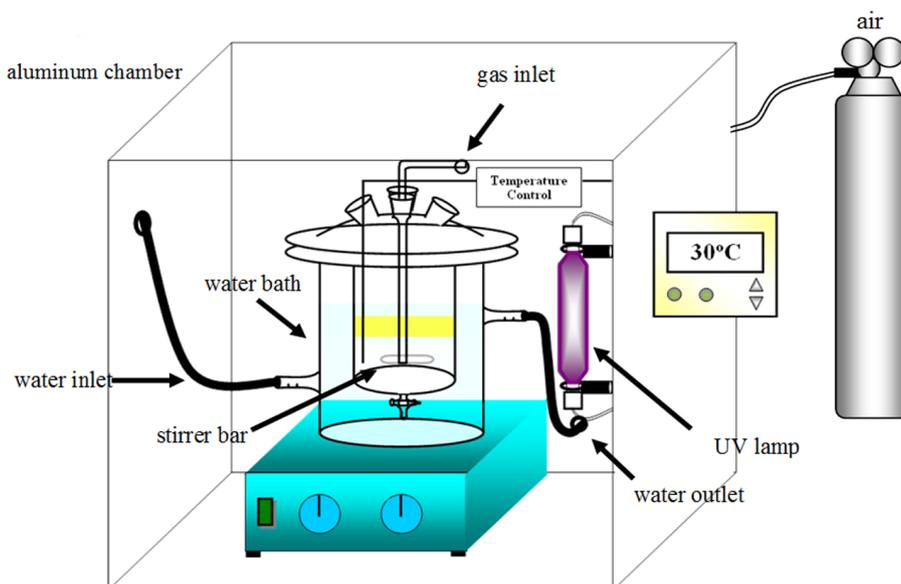
### 2.3. Pyrolysis of the Waste Tire Powder and Yields of the Resultant Components

The waste tire powder (100 g/batch) was pyrolyzed in a stainless steel tubular fixed bed reactor at 400 °C under a nitrogen atmosphere at a flow rate of 0.1 L/min, starting with a heating rate of 20–25 °C/min for 15 min or until no further significant release of oil was observed. The light fraction of the waste tire pyrolysis oil was obtained from vapor condensation during pyrolysis in a series of Erlenmeyer flasks immersed in an ice bath. The heavy fraction, which was trapped in the pyrolysis char and the reactor, was collected by washing with THF. The gas fraction was then calculated by the percentage difference in weight. The heating value of the pyrolysis light oil was also determined by using bomb calorimeter following ASTM D2015.

### 2.4. Photocatalytic Desulfurization of the Waste Tire Pyrolysis Oil

Figure 1 shows a schematic diagram of the experimental apparatus used for the photocatalytic desulfurization of the waste tire pyrolysis oil. A Pyrex glass photoreactor (max. volume = 100 mL) was placed in a water bath on a magnetic stirrer in an aluminum box. A 400 W high-pressure mercury lamp was used as the light source for inducing photocatalytic desulfurization, at a bulb to approximate surface distance of 20 cm. The reaction temperature was controlled using a water-cooling system. Air was introduced into the reaction solution from a gas cylinder at the desired flow rate.

**Figure 1.** Schematic diagram of the experimental apparatus used for the photocatalytic desulfurization of the waste tire pyrolysis oil.



Distilled water was used as the main extracting solvent. The waste tire pyrolysis oil (10 mL) was mixed with distilled water at 1/1–4/1 (v/v) (distilled water/waste tire pyrolysis oil) and then transferred into the photo-reactor. The specific amount of TiO<sub>2</sub> (1–10 g/L of waste tire pyrolysis oil) was then

added into the reaction mixture under the specified air flow rates (0–150 mL/min) and the reaction temperature was varied in the range of 30–70 °C for 7 h. It was observed that the most of TiO<sub>2</sub> was at the interface between the pyrolysis oil and the water. When the reaction was terminated, the TiO<sub>2</sub> particles and distilled water were completely removed from the oxidized waste tire pyrolysis oil by centrifugation at 3000 rpm for 10 min, with harvesting of the upper oil phase.

When methanol or acetonitrile were used as the extracting solvent for comparison with distilled water, the procedure was as above except for the final extraction. The oxidized waste tire pyrolysis oil in the presence of methanol or acetonitrile was further charged into the distilled water to separate the oxidized sulfurous compounds from the fraction of the hydrocarbon fuel.

### *2.5. Determination of Sulfurous Compounds in the Waste Tire Pyrolysis Oil*

Since GC-FPD has higher sensitivity (100,000 times) to sulfurous and phosphorous compounds than hydrocarbons [20], the sulfurous compounds in the waste tire pyrolysis oil before and after photocatalytic desulfurization were detected by this technique (Agilent 6890N). The oil samples were diluted in acetonitrile to 1% (w/w) and then injected into the GC-FPD at 250 °C. An HP-5 capillary column (30 m long × 0.32 mm inner diameter (ID), 0.52 µm film thickness) coated with 5% (w/w) of phenylmethylsilicone was used for separation of the sulfur compounds. The GC oven temperature was programmed to rise from 35 °C (held for 10 min) to 130 °C at a heating rate of 15 °C/min, and thereafter to 220 °C at a heating rate of 10 °C/min. The carrier gas was nitrogen (45.7 mL/min). The detector operated at 250 °C with an air/hydrogen flame, for which the air and hydrogen gas pressures were 0.74 and 0.98 bar, respectively.

The pyrolysis oil and its oxidized products from the photocatalytic desulfurization in the presence of acetonitrile used as the extracting solvent were also analyzed by using HPLC (Agilent 1100). This could detect the conversion of sulfurous compounds in the waste tire pyrolysis oil by comparison of the pyrolysis oil polarity before and after the photochemical oxidation. The standard sulfur compounds used for calibration and comparison were thiophene, benzothiophene and dibenzothiophene. The HPLC was equipped with a Lichrosphere C-18 bonded packing and UV detector at 245 nm. A 9:1 (v/v) ratio of acetonitrile/distilled water was used as the mobile phase at a flow rate of 0.8 mL/min. Each 20 µL aliquot of the sample solution was injected into the HPLC by using an injection loop.

### *2.6. Properties of Waste Tire Pyrolysis Oil*

The properties of waste tire pyrolysis oil before and after photoirradiation were analyzed in terms of kinematic viscosity and the copper strip corrosion following ASTM D 445 and ASTM D 130, respectively.

## **3. Results and Discussion**

### *3.1. Composition of the Waste Tire Powder and Its Pyrolysis Products*

The composition of waste tire powder is summarized in Table 1. The results from the ultimate analysis showed that the waste tire powder had a large amount of carbon (80.1% w/w) with high hydrogen content (7.48% w/w) resulting in the higher calorific value (35.7 MJ/kg) than biomass containing lower hydrogen/carbon ratios [5]. However, it was found that the waste tire powder

contained a sulfur content of 1.54% (w/w), which resulted from vulcanizing agents used in the vulcanization process of tire production.

Pyrolysis, as described in Section 2.3, yielded light oil, heavy oil, char and gas fractions at 39.6, 14.0, 38.2 and 8.12% (w/w), respectively. Due to the highest yield of light oil fraction with a high gross calorific value (43 MJ/kg), which is close to that of crude oil (45.5 MJ/kg), low-sulfur diesel (45.6 MJ/kg) and conventional gasoline (46.5 MJ/kg) [21], this fraction was used as the raw material for the photocatalytic desulfurization. The total sulfur content in this pyrolysis oil fraction, as evaluated using a sulfur analyzer, was some 1.83-fold lower than that in the waste tire powder before pyrolysis (0.84% vs. 1.54%, w/w).

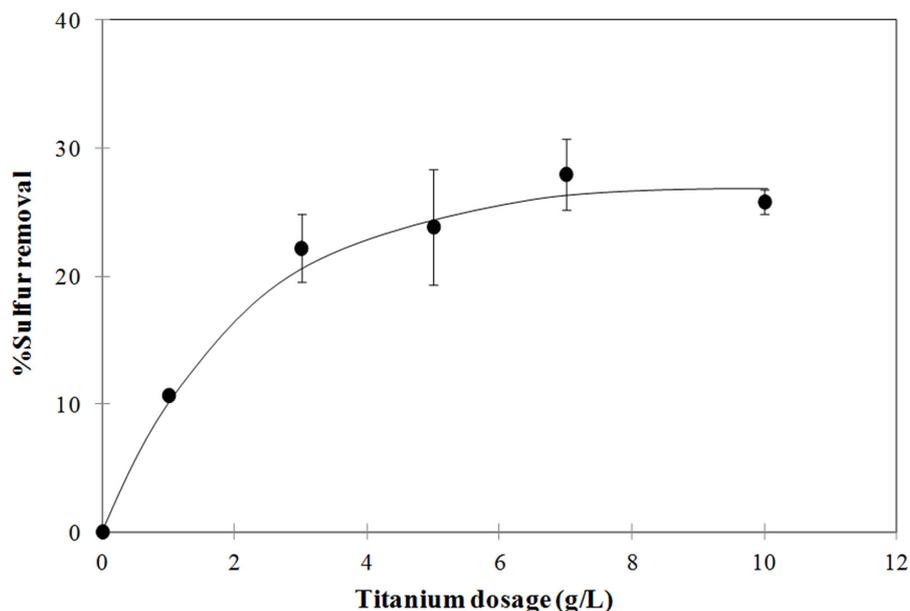
**Table 1.** Composition of the waste tire powder used as feedstock.

<b>Analytical</b>	<b>% (w/w)</b>
<u>Proximate Analysis</u>	
Volatiles	62.4
Fixed carbon	27.6
Ash	8.73
Moisture	1.22
<u>Ultimate Analysis</u>	
Carbon	80.1
Hydrogen	7.48
Nitrogen	0.42
Sulfur	1.54
Oxygen	10.5
Calorific heating value (MJ/kg)	35.7

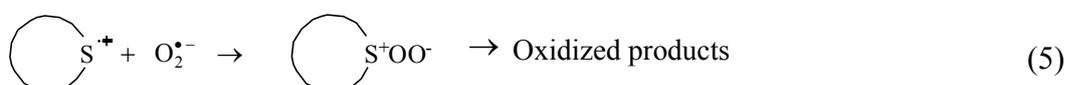
### 3.2. Influence of the TiO<sub>2</sub> Dosage on the Degree of Sulfur Removal

The effect of the concentration of the TiO<sub>2</sub> suspension on the level of sulfur reduction of the waste tire pyrolysis oil is presented in Figure 2. When the dosage of TiO<sub>2</sub> was increased from 0–10 g of TiO<sub>2</sub>/L of waste tire pyrolysis oil and the photocatalytic reaction was carried out at 30 °C for 7 h and 1/1 (v/v) of distilled water/waste tire pyrolysis oil, the % sulfur removal increased up to the maximal level (27.9%) at a TiO<sub>2</sub> loading of 6–7 g/L of waste tire pyrolysis oil, and then leveled off when the TiO<sub>2</sub> concentration increased up to 10 g/L of pyrolysis oil. The increase in the TiO<sub>2</sub> content likely promoted a higher level of the photo-assisted reaction in the presence of water and air to generate active oxygen species, such as hydroxyl radicals (<sup>•</sup>OH), superoxide radical anion or peroxy ion (O<sub>2</sub><sup>•-</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which could then further react with the organic substances under photocatalytic oxidation [22].

**Figure 2.** Effect of TiO<sub>2</sub> dosage on % sulfur removal of waste tire pyrolysis oil (distilled water/waste tire pyrolysis oil (v/v) = 1/1; air flow rate = 150 mL/min; T = 30 °C for 7 h).



Since most sulfurous compounds in the pyrolysis oil derived from waste tire are polycyclic aromatic sulfur hydrocarbons (PASH) [23], the proposed mechanism for photocatalytic degradation of these sulfurous compounds has been reported as shown in Equations 1–5 [24,25]. In this scenario, under UV light and oxygen, the electron from the valence band of TiO<sub>2</sub> is activated to the conduction band to form a hole in the valence band ( $h_{\text{VB}}^+$ ) and an electron in the conduction band ( $e_{\text{CB}}^-$ ) (Equation 1). The  $h_{\text{VB}}^+$  then reacts with either sulfurous compounds in the waste tire pyrolysis oil to form the photogenerated sulfur radical cation (Equation 2) [24] or with water to generate  $\cdot\text{OH}$  and proton ( $\text{H}^+$ ) (Equation 3) [25]. The  $e_{\text{CB}}^-$  can react with oxygen molecules ( $\text{O}_2$ ) adsorbed on the TiO<sub>2</sub> surface to produce the superoxide anion ( $\text{O}_2^{\cdot-}$ ) (Equation 4) [24]. Consequently, it interacts with the photogenerated sulfur radical cation to obtain the intermediate persulfoxide as shown in Equation (5) [24,26]. For the case of the oxidation of sulfides, it has been reported that the intermediate persulfoxide can directly react with sulfoxides, which are possibly produced from the photooxidation of sulfurous compounds [27], to generate sulfones [28,29]. The oxidized sulfurous compounds with higher polarity are readily migrated from the pyrolysis oil into the distilled water phase [30]:

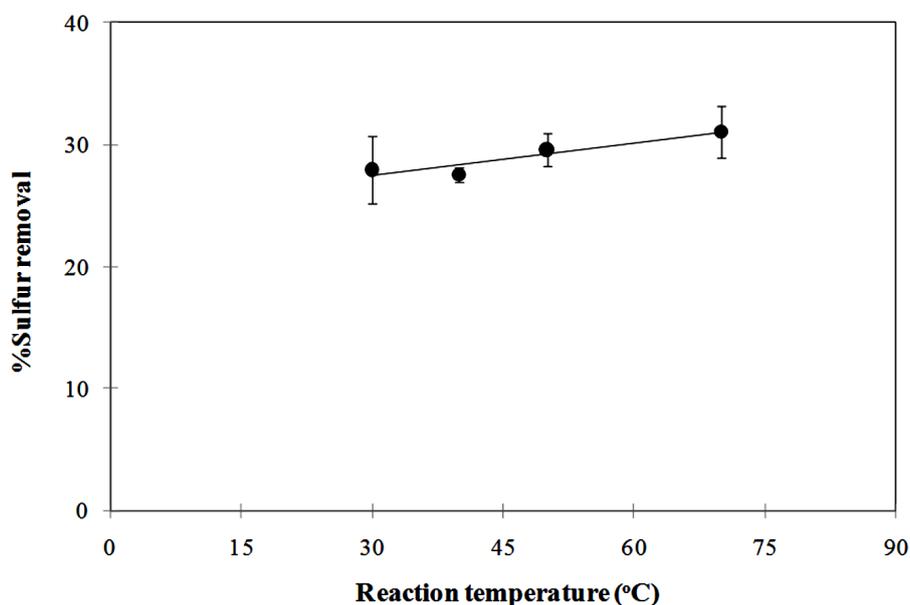


Although the increase in the level of the  $\text{TiO}_2$  suspension resulted in more active sites for the photo-assisted reaction, the addition of  $\text{TiO}_2$  at levels higher than 6–7 g of  $\text{TiO}_2/\text{L}$  of pyrolysis oil either caused no further increase. This can be explained as a result of the increase in the amount of the  $\text{TiO}_2$  suspension increased the greater level of scattered UV light in the system resulting in a reduction of the light penetration [31].

### 3.3. Influence of the Photoreaction Temperature on the Degree of Sulfur Removal

The effect of the photoreaction temperature (30–70 °C) on the level of sulfur reduction in the waste tire pyrolysis oil is shown in Figure 3. The reaction was performed in the presence of a 1/1 (v/v) ratio of distilled water/waste tire pyrolysis oil and 7 g of  $\text{TiO}_2/\text{L}$  of waste tire pyrolysis oil for 7 h. As the reaction temperature was increased from 30 to 70 °C, the % sulfur removal increased slightly from 27.9 to 31.0%. Indeed, the photo-induced catalytic reaction does not require activation from heating, and can be operated at room temperature due to the photonic activation [13]. However, the increase in the reaction temperature still improved the interfacial electron-transfer kinetics and so resulted in the typically observed slight increase in the catalytic activity of  $\text{TiO}_2$  [32]. Higher reaction temperatures (>80 °C) might simply promote water evaporation and desorption of sulfurous compounds deposited on the  $\text{TiO}_2$  surface to possibly decrease the sulfur removal efficiency. Thus, the reaction temperature at 50 °C was chosen for further experiments.

**Figure 3.** Effect of reaction temperature on % sulfur removal of waste tire pyrolysis oil ( $\text{TiO}_2$  dosage = 7 g/L; distilled water/waste tire pyrolysis oil (v/v) = 1/1; air flow rate = 150 mL/min for 7 h).

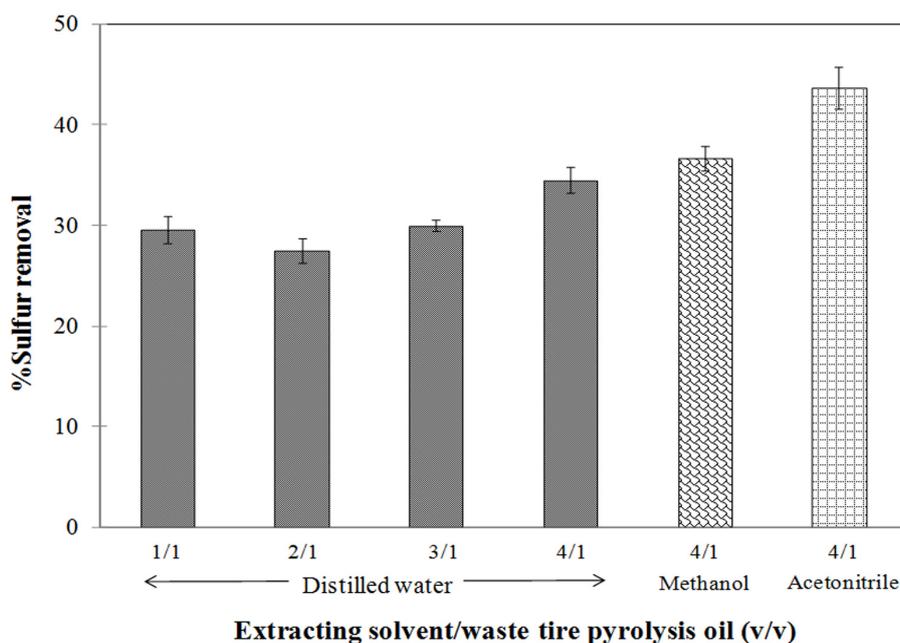


### 3.4. Influence of the Extracting Solvents on the Degree of Sulfur Removal

The proportion (v/v) and type of the extracting solvents likely affected the ability to remove the oxidized sulfurous compounds produced during the photocatalytic desulfurization. In this study, distilled water was selected as the major extracting solvent due to its low cost and practicability.

Methanol and acetonitrile, which have different polarities to distilled water, were used for comparison. The effect of these different types and proportions of the extracting solvents on the degree of photocatalytic desulfurization are shown in Figure 4.

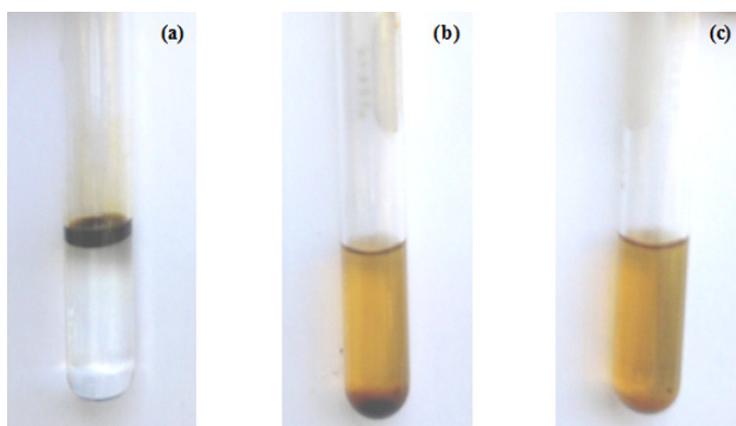
**Figure 4.** Effect of the proportion and type of the extracting solvents on the obtained % sulfur removal from waste tire pyrolysis oil ( $\text{TiO}_2$  dosage = 7 g/L; air flow rate = 150 mL/min,  $T = 50\text{ }^\circ\text{C}$  and reaction time = 7 h).



With distilled water used as the extracting solvent, the increase in the water/waste tire pyrolysis oil (v/v) ratio from 1/1 to 4/1, whilst maintaining the reaction with 7 g of  $\text{TiO}_2/\text{L}$  of waste tire pyrolysis oil at  $50\text{ }^\circ\text{C}$  for 7 h, enhanced the % sulfur removal and reached a maximum of 34.5% at the highest tested water/waste tire pyrolysis oil ratio (4/1). The lower efficiency of the removal of oxidized sulfur compounds from the waste tire pyrolysis oil after photocatalytic desulfurization at lower extracting solvent/waste tire pyrolysis oil ratios was possibly due to the saturation of oxidized sulfurous compounds in the extracting phase. When the extracting solvent was changed from distilled water to methanol at an extracting solvent/waste tire pyrolysis oil (v/v) ratio of 4/1 and under the same reaction conditions, it caused only a slight numerical increase in the % sulfur removal. However, the use of acetonitrile gave a significantly higher % sulfur removal, with a maximum of 43.6%. Considering the polarity of these extracting solvents, they can be ranked in the order distilled water (10.2) > acetonitrile (5.8) > methanol (5.1) [33]. Before photocatalytic desulfurization, the appearance of the pyrolysis oil in the presence of each extracting solvent (Figure 5) revealed the highest level of homogeneity was found with acetonitrile, indicating that the polarity of the waste tire pyrolysis oil was most similar to that of acetonitrile. The color of the waste tire pyrolysis oil in the presence of acetonitrile was also paler, and so it would be easier for UV light penetration to reach the  $\text{TiO}_2$  for oxidizing the sulfurous compounds to have higher polarity, which was then easily removed from the photo-oxidized pyrolysis oil by distilled water in the next step. Moreover, the solubility of oxygen, used for oxidizing the sulfurous compounds, also increases with decreasing solvent polarity [34]. Therefore, it implied that

acetonitrile with the lower polarity than distilled water contained the higher amount of oxygen resulting to the greater sulfur removal efficiency.

**Figure 5.** Appearance of the waste tire pyrolysis oil in the presence of (a) distilled water, (b) methanol and (c) acetonitrile (extracting solvent/waste tire pyrolysis oil (v/v) = 4/1).



### 3.5. Influence of Oxidizing Agents on the Degree of Sulfur Removal

The oxidizing agents applied for the photocatalytic desulfurization of the waste tire pyrolysis oil were air flow rate and the  $\text{H}_2\text{O}_2$  concentration. The reaction was carried out with keeping the ratio of distilled water/pyrolysis oil at 4/1 (v/v) and 7 g of  $\text{TiO}_2$ /L of waste tire pyrolysis oil at 50 °C for 7 h. The results shown in Table 2 indicated that without either of these two oxidizing agents, the degree of photo-assisted desulfurization of waste tire pyrolysis light oil was very low at only 3.22%. This implied that the sulfur compounds in the waste tire pyrolysis oil were not oxidized by irradiation in the presence of the only  $\text{TiO}_2$ . The level of photocatalytic desulfurization of the waste tire pyrolysis oil was significantly increased when either the air flow rate or the  $\text{H}_2\text{O}_2$  concentration was increased, and in a dose-dependent manner in both cases, reaching the maximum observed level at the highest tested air flow rate (150 mL/min) or  $\text{H}_2\text{O}_2$  concentration [30% (v/v)]. Higher air flow rates were not evaluated, but might actually reduce the sulfur removal efficiency due to the enhancement of volatilization of the waste tire pyrolysis oil or extracting solvent at any given reaction temperature [16]. Furthermore, the higher air flow rates could induce bubble formation, which was reported to inhibit UV light absorption by  $\text{TiO}_2$  and so resulted in the reduction of sulfur removal efficiency [35].

**Table 2.** Effect of oxidizing agents on % sulfur removal of waste tire pyrolysis oil.

Oxidizing Agent	Quantity	% Sulfur Removal
No addition		3.22 (2.79) *
Air	50 mL/min	22.3 (0.17)
	100 mL/min	32.5 (0.76)
	150 mL/min	34.5 (1.26)
$\text{H}_2\text{O}_2$	3% (w/w)	11.9 (2.10)
	10% (w/w)	17.7 (0.90)
	30% (w/w)	32.7 (1.20)

\* The number in the parenthesis is the standard deviation; Conditions:  $\text{TiO}_2$  dosage = 7 g/L; distilled water/pyrolysis oil (v/v) = 4/1; T = 50 °C and reaction time = 7 h.

H<sub>2</sub>O<sub>2</sub> was normally selected as an additional oxidant due to its commercial availability, infinite solubility in water, high cost effectiveness for •OH production and simple operation for attacking most organic substances [36]. The concentration of H<sub>2</sub>O<sub>2</sub> in distilled water used as the extracting solvent was varied in the range of 0–30% (w/w). Without the introduction of air into the system, H<sub>2</sub>O<sub>2</sub> also increased the photocatalytic efficiency of TiO<sub>2</sub> to decompose sulfur compounds in the pyrolysis oil in a dose-dependent manner, increasing some ten-fold as the H<sub>2</sub>O<sub>2</sub> concentration was increased from 0 to 30% (w/w). This could be explained as that H<sub>2</sub>O<sub>2</sub> was the source of hydroxyl free radicals (•OH), which have strong oxidizing properties. Thus, the increase in the H<sub>2</sub>O<sub>2</sub> concentration increased the number of •OH radicals via H<sub>2</sub>O<sub>2</sub> photodissociation (Equation 6) [37,38] and the reaction between H<sub>2</sub>O<sub>2</sub> and electrons photogenerated on the TiO<sub>2</sub> surface (e<sup>-</sup><sub>cb</sub>) (Equation 7) [39] to enhance the % sulfur removal:

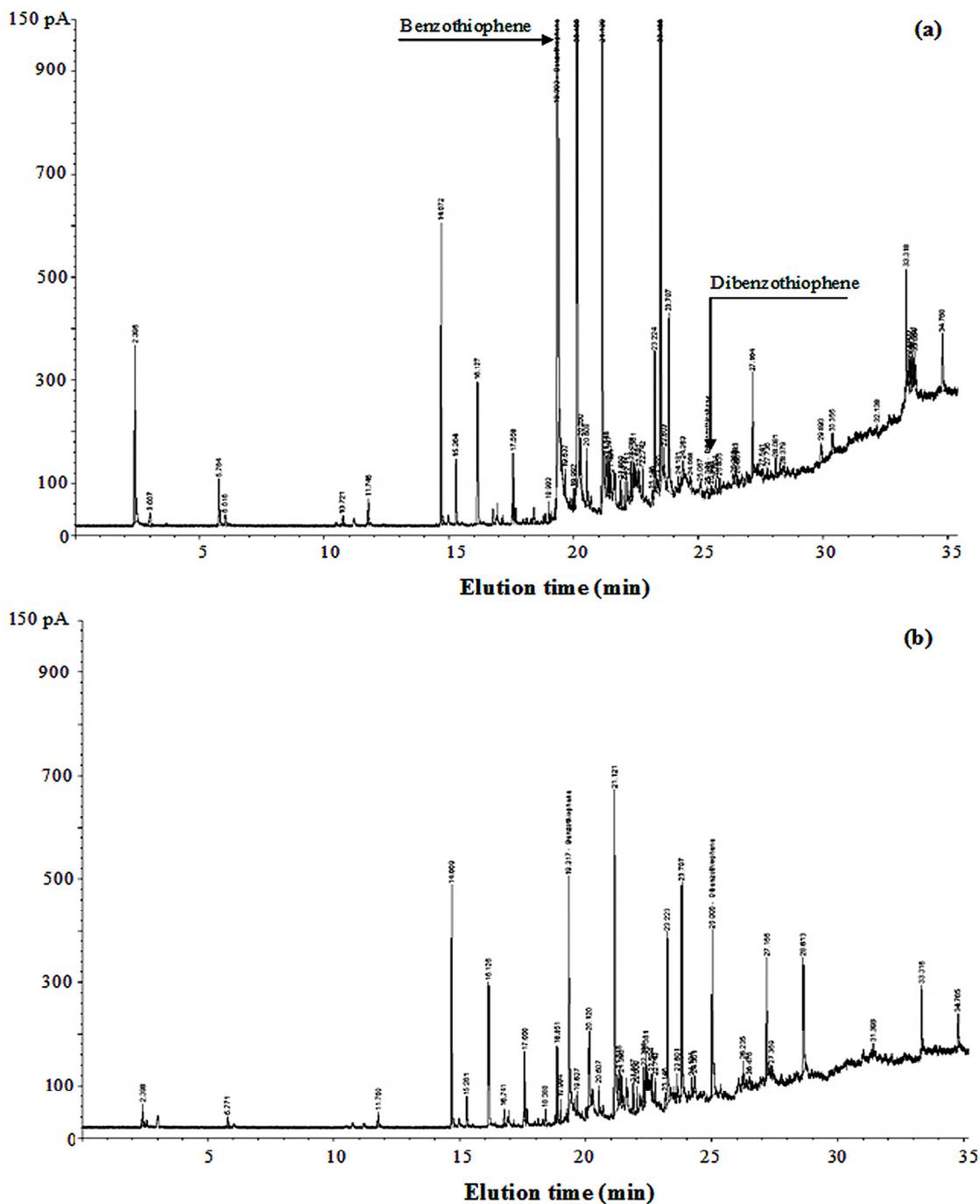


### 3.6. Characterization of Sulfurous Compounds Containing in Waste Tire Pyrolysis Oil

The types of sulfurous compounds in the waste tire pyrolysis oil before and after photocatalytic desulfurization using TiO<sub>2</sub> were characterized using GC-FPD, with representative chromatograms shown in Figure 6. Since a large diversity of sulfurous compounds (GC-FPD peaks) was observed in the waste tire pyrolysis oil (Figure 6a), the pure sulfurous compounds, thiophene, benzothiophene and dibenzothiophene, were used for comparison. The peaks obtained from GC-FPD of these compounds appeared at elution times of 3.67, 18.9 and 25.0 min, respectively. When they were compared to the GC-FPD chromatogram of the waste tire pyrolysis oil (Figure 6a), it was found that the main sulfurous compounds (amongst the large array) in the waste tire pyrolysis oil might be benzothiophene, dibenzothiophene and their large molecular size derivatives. The peaks appearing at a lower retention time (<18.9 min), might be the sulfurous compounds with smaller molecular structures.

After photocatalytic desulfurization in the presence of acetonitrile used as the extracting solvent, followed by washing with distilled water to extract the oxidized sulfurous compounds and separate the waste tire pyrolysis oil product from acetonitrile, a reduced peak intensity and the number of peaks in the spectra was seen (Figure 6b). It was found that the peaks appearing in the 18–23 min range tended decrease after photocatalytic desulfurization. This implied that benzothiophene and its derivatives appeared to be the most reduced components, and thus were the most favorable for photooxidation. However, this technique had low efficiency for the reduction of some sulfurous compounds with larger chemical structures, such as dibenzothiophene derivatives, since their steric hindrance effect might limit the adsorption onto the surface of TiO<sub>2</sub> resulting in their lower reactivity. This phenomenon has also been postulated for the adsorption of 4,6-dimethyldibenzothiophene on zirconia [40] and the photo-oxidation of kerosene [10]. Moreover, the new signals at 18.9 and 28.6 min were found in the oxidized pyrolysis oil after isolating by using distilled water (Figure 6b). These might be the remaining oxidized sulfur compounds generated from the photo-oxidation of benzothiophenes or dibenzothiophenes which their larger molecules showed GC-FPD signals at longer elution time [10,18,41].

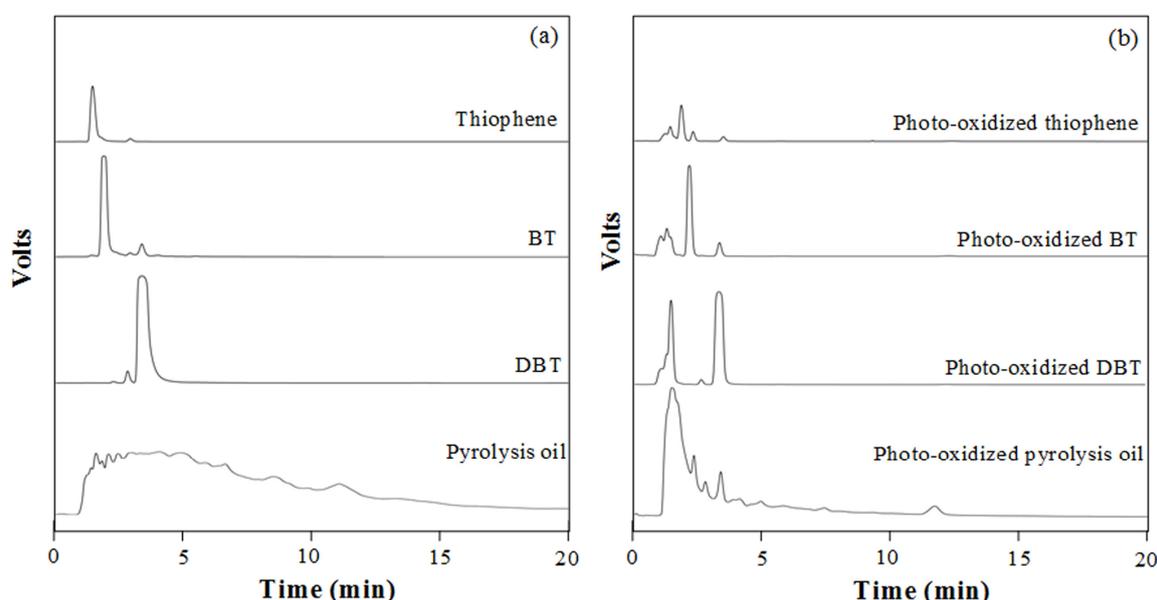
**Figure 6.** GC-FPD chromatograms of the waste tire pyrolysis oil (a) before and (b) after being photo-oxidized in the presence of acetonitrile and isolated by using distilled water.



To monitor the conversion of the sulfurous compounds by photoirradiation, the oxidized waste tire pyrolysis oil obtained from the photocatalytic desulfurization in the presence of acetonitrile for 7 h was subjected to HPLC separation (monitored at 245 nm wavelength) before washing with distilled water. The results were compared against the standards (thiophene, benzothiophene and dibenzothiophene), which were photo-oxidized under the same conditions. Before photocatalytic desulfurization (Figure 7a), the HPLC signals of the standard sulfurous compounds were eluted at 1.99, 2.47 and 4.26 min for thiophene, benzothiophene and dibenzothiophene, respectively, while the waste tire pyrolysis oil indicated a much more complex (broader) signal, reflecting the diversity of sizes of the sulfurous

compounds in the waste tire pyrolysis oil, in accord with that seen in the GC-FPD based analysis. After photocatalytic desulfurization (Figure 7b), the new signals of the oxidized standard sulfurous compounds appeared at an earlier elution time (1.2–1.9 min), indicating their higher polarity as sulfone, sulfoxide, sultine or other anionic compounds [42]. For the oxidized waste tire pyrolysis oil, the HPLC spectra was much narrower with sharper peaks that also appeared at an earlier elution time, similar to the results obtained from the oxidized standard sulfurous compounds. Thus, most of the sulfurous compounds in the waste tire pyrolysis oil were likely to have been converted to oxidized sulfurous substances with a higher polarity after photocatalytic desulfurization.

**Figure 7.** Comparison of the representative HPLC chromatograms of thiophene, benzothiophene, dibenzothiophene and waste tire pyrolysis oil: (a) before and (b) after photocatalytic desulfurization.



### 3.7. Properties Consideration of Waste Tire Pyrolysis Oil

Table 3 shows the properties such as viscosity (ASTM D 445), corrosive properties (ASTM D 130) and gross calorific heating value (ASTM D 2015) of waste tire pyrolysis oil before and after photo-irradiation and compared to those of Murban crude oil, of which Thailand imported 11,989 million litres from the United Arab Emirates in 2009 [43]. This table indicates that the viscosity of waste tire pyrolysis oil (2.66 cSt) was slightly increased to 2.85 cSt after treating by photodesulfurization possibly due to the polymerization of some organic free radicals generated during operation. The gross calorific heating value of the photo-oxidized waste tire pyrolysis oil was 43 MJ/kg, which was not different from the untreated one and close to that of the crude oil (45.5 MJ/kg) [21]. This means that this process did not affect the gross calorific heating value of product. Moreover, the sulfur content of photo-oxidized waste tire pyrolysis oil was 2.22-fold lower than that of Murban crude oil with no indication of the corrosion and the color change of copper strips in the corrosive properties testing. Thus, it implies that the photo-oxidized waste tire pyrolysis oil can possibly be used as an alternative crude oil or for blending with petroleum feedstock before treating by HDS process in the general refineries for producing commercial petroleum products.

**Table 3.** Viscosity, ability of corrosion and gross calorific heating values of oils.

Products	Viscosity @ 100 °F (cSt)	Gross Calorific Heating Value (MJ/kg)	Sulfur Content (% w/w)
Murban crude oil	2.94 ([44])	45.5 ([21]) *	0.82 ([44])
Waste tire pyrolysis oil	2.66	43	0.84
Photo-oxidized waste tire pyrolysis oil **	2.85	43	0.37

\* General heating value of crude oil; \*\* Photodesulfurization condition: 7 g/L; air flow rate = 150 mL/min, T = 50 °C, extracting solvent = acetonitrile and reaction time = 7 h.

#### 4. Conclusions

The photocatalytic desulfurization of waste tire pyrolysis oil was carried out using TiO<sub>2</sub> as the photocatalyst. It was found that the maximum % sulfur removal of 43.6% was achieved when 7 g of TiO<sub>2</sub>/L of waste tire pyrolysis oil was loaded into the system containing 1/4 (v/v) of waste tire pyrolysis oil/acetonitrile at 50 °C for 7 h. The conversion of sulfurous compounds in the waste tire pyrolysis oil after photoirradiation was monitored using GC-FPD and HPLC. The results indicated that the raw waste tire pyrolysis oil consisted of sulfurous compounds with large molecular structures. The results from HPLC showed that the photo-oxidized sulfurous compounds had higher polarity, which made them easily separable from the oxidized pyrolysis oil product by using distilled water. From the properties testing, the gross calorific heating value and viscosity of the photo-oxidized waste tire pyrolysis oil were similar to those of Murban crude oil. However, the sulfur content in the photo-oxidized waste tire pyrolysis oil was lower. Thus, it is possible to apply the photo-oxidized waste tire pyrolysis oil as the alternative source of crude oil feedstock for refining to further the commercial petroleum products.

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