Desulphurisation of a Spent Tyre Pyrolysis Oil and Its Distillate via Combined Catalytic Oxidation using H₂O₂ with Formic Acid and Selective Adsorption over Al₂O₃

Qian Zhang¹,²,³, Mingming Zhu*², Isabelle Jones², Zhezi Zhang², Dongke Zhang¹,²

¹Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
²Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
³University of Chinese Academy of Sciences, Beijing 10049, China

(A manuscript accepted by “Energy & Fuels”)

* Corresponding author:
Mingming Zhu
Email: mingming.zhu@uwa.edu.au
Phone: +61 8 6488 5528
Fax: +61 8 6488 7622
Abstract

This paper reports an experimental investigation into the desulphurisation of a spent tyre pyrolysis oil and its distillate using a combined catalytic oxidative and selective adsorption method. The oxidative desulphurisation (ODS) experiments were carried out in a batch reactor using H$_2$O$_2$-formic acid as oxidant. The effect of reaction temperature, time, and oil to H$_2$O$_2$-formic acid ratio on the percentage of sulphur removal was studied. The oil samples after ODS were treated using Al$_2$O$_3$ as an adsorbent in a batch reactor at 25 °C and atmospheric pressure. The oil samples were analysed using ICP-OES for sulphur content, GC-MS and GC-SCD for chemical compositions and sulphur species. The ODS successfully converted the sulphur compounds to sulphoxides and sulphones but only exhibited moderate sulphur removal efficiency because sulphoxides and sulphones were dissolved in the oil and cannot be easily extracted by water. Al$_2$O$_3$ was effective in adsorbing sulphoxides and sulphones. A maximum of 81% and 84% sulphur removal were achieved for the raw pyrolysis oil and distillate, respectively, using combined ODS and Al$_2$O$_3$ adsorption. After three desulphurisation cycles, the sulphur adsorption capacity of Al$_2$O$_3$ decreased from 0.31 to 0.22 mg S g$^{-1}$ Al$_2$O$_3$, still exhibiting high sulphur removal ability.

Keywords: Oxidative desulphurisation; Pyrolysis oil; Selective Adsorption; Spent tyre
1. Introduction

Approximately 17 million tonnes of spent tyres join the waste stream globally each year and this number is predicted to increase year-on-year. While there has been continuous effort to recycle and reuse spent tyres, many of these spent tyres are simply landfilled and stockpiled posing serious health and environmental risks. Pyrolysis plays a crucial role in the clean conversion and utilization of carbonaceous material, including coal, organics, plastics and tyres, into oil, gas and solid carbon materials. Spent tyre pyrolysis oil has been proposed to have great potential as a fuel or petroleum refinery feedstock. However, it typically has a high sulphur content derived from the vulcanising agents used for tyre production. The sulphur compounds can be problematic as they release highly toxic SO₂ gas emission during combustion or produce an extremely unpleasant odour.

Oxidative desulphurisation (ODS) has shown a great promise to remove sulphur from petroleum fuel oils. ODS involves two processes, which are the oxidation of sulphur compounds and the removal of the oxidised sulphur products. With the presence of oxidant and catalyst, organic sulphur-containing compounds in oil can be oxidised into high polarity compounds that can be easily removed from the oil phase by solvent extraction or adsorption. The most common oxidant used in ODS is H₂O₂ because of its strong oxidation capacity, environmentally friendly and commercially availability. Studies of H₂O₂ with various catalysts, such as organic acids (e.g. formic acid and acetic acid), heteropolyacid (e.g. phosphotungstic acid) and heterogeneous catalysts (e.g. transition metals based catalysts) have been reported. Formic acid has been found to have a high catalytic activity in ODS of fuel oils. Formic acid first reacts with H₂O₂ to form performic acid. The performic acid oxidises the sulphur-containing compounds and restores formic acid which is available to start a new oxidising cycle. De Filippis et al. studied the oxidation of benzo-, dibenzo-, 4-methylbenzo-, and 4,6-dimethyldibenzothiophene using H₂O₂ and formic acid in the temperature range of 20 - 65 °C and found that the sulphur compounds were completely oxidised into sulphoxides and sulphones. The highly polar sulphoxides and sulphones
from the nonpolar constituents of the oxidised oil can be extracted by solvent such as acetonitrile \(^{16}\), methanol \(^{17,30}\), ethanol \(^{31}\) and water \(^{30,32}\). Ali et al. found that ODS of diesel fuel using \(\text{H}_2\text{O}_2\) and formic acid followed by extraction of the oxidised sulphur compounds using acetonitrile achieved up to 92% of sulphur at low temperature (50 °C) and atmospheric pressure \(^{16}\).

There are a few studies that use ODS in \(\text{H}_2\text{O}_2\)-formic acid system to remove sulphur from spent tyre pyrolysis oils \(^{17,32}\). Al-Lal et al. studied the ODS of a fraction of spent tyre pyrolysis oil with a sulphur content of 0.87 wt% using \(\text{H}_2\text{O}_2\) and formic acid, followed by methanol extraction. A maximum of 53% desulphurisation was obtained \(^{17}\). Aydın et al. investigated desulphurisation of a spent tyre pyrolysis oil with sulphur content of 0.906% by ODS using \(\text{H}_2\text{O}_2\) and formic acid followed by washing with distilled water, but only reached a maximum 64% of sulphur removal \(^{32}\).

The limited literature data suggest that combined ODS and the conventional solvent extraction widely used for sulphur removal in petroleum oils seems not effective for spent tyres pyrolysis oil \(^{17,29-32}\). This may be because the oxidised sulphur species are miscible with spent tyre pyrolysis oil and cannot be easily removed by solvents such as water and methanol.

Solid adsorption \(^{14}\) is an alternative method for sulphur removal from ODS treated oil. Etemadi and Yen \(^{33,34}\) reported that organic sulphone compounds can be selectively removed by solid adsorption on alumina oxide. The solid adsorption of oxidised sulphur compounds has also been successfully applied to jet fuel and diesel fuel after ultrasound-assisted oxidative desulphurisation \(^{35}\). The application of the selective adsorption method to remove oxidised sulphur compounds from spent tyre pyrolysis oil is an innovative and novel alternative method that has, as of yet, not been reported in the literature.

This paper reports an experimental investigation into the ODS in \(\text{H}_2\text{O}_2\)-formic acid system combining with selective \(\text{Al}_2\text{O}_3\) adsorption desulphurisation of a spent tyre pyrolysis oil and its distillate. The effect of reaction temperatures, time, and oil to oxidant ratio on the sulphur removal using ODS was studied. The sulphur removal percentage, sulphur removal capacity and regeneration performance of \(\text{Al}_2\text{O}_3\) adsorption after ODS were investigated. To better understand
the processes of ODS and adsorption desulphurisation of spent tyre pyrolysis oil and its distillate, GC-SCD analysis was used to determine the speciation and quantification of sulphur-containing compounds. The present study is novel as it is the first to (1) demonstrate that combining ODS and selective adsorption can achieve high sulphur removal in spent tyre pyrolysis oil, (2) examine changes in the broad chemical composition of the oil after ODS process, and (3) use GC-SCD analysis in the speciation and quantification of sulphur-containing compounds of a spent tyre pyrolysis oil before and after desulphurisation.

2. Experimental

2.1 Materials

A raw pyrolysis oil produced from an industrial scale retort process and its distillate (solvent fraction) were used. The physicochemical characteristics of the raw pyrolysis oil are summarised in Table 1. The solvent fraction was obtained by distillation of the raw pyrolysis oil in a packed-bed distillation column at temperatures between 105 and 210 °C. The oxidant and catalyst used were aqueous hydrogen peroxide solution (H$_2$O$_2$, 30 wt%) and formic acid (HCOOH, 85 wt%), respectively, purchased from Chem-Supply. Laboratory grade toluene, used as a diluent, was purchased from Asia Pacific Specialty Chemicals Limited. Sodium sulphate (Na$_2$SO$_4$, anhydrous) and aluminium oxide (Al$_2$O$_3$, activity stage I) were purchased from Merck Chemical Company,

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m$^{-3}$)</td>
<td>915</td>
<td>ISO 3675</td>
</tr>
<tr>
<td>Kinematic viscosity (cSt @293K)</td>
<td>4.77</td>
<td>ISO 3104</td>
</tr>
<tr>
<td>Cetane index</td>
<td>29</td>
<td>ISO 3675</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>14.8</td>
<td>ISO 2719</td>
</tr>
<tr>
<td>Distillation temperature for 10% distilled amount (°C)</td>
<td>144</td>
<td>ISO3405</td>
</tr>
<tr>
<td>Distillation temperature for 90% distilled amount (°C)</td>
<td>360</td>
<td>ISO3405</td>
</tr>
</tbody>
</table>
USA. Surface physical properties of Al₂O₃ are shown in Table 2. Standard sulphur compounds, thiophene (99%), benzothiophene (98%), and dibenzothiophene (98%) were supplied by Sigma-Aldrich Chemical Company.

2.2 Oxidation experiments

Figure 1 A schematic of the ODS experimental setup

The literature data 36, 37 and our preliminary tests showed that the ODS reaction using H₂O₂ and formic acid is highly exothermic. The heat released during the oxidation reaction can increase the temperature of the reaction system and lead to violent decomposition of oxidant producing large quantities of gas 27. In order to systematically examine the effect of reaction temperature on the desulphurisation efficiency, both the solvent fraction and raw pyrolysis oil were diluted with non-reactive toluene (1:49 volume ratio) before ODS. Under this dilution factor, the temperature of the system remained unchanged from our experiments. It is worth mentioning that there would be no need for dilution in a practical industrial application because the oxidant can be slowly added to the oil with heat recovery. The ODS experiments were conducted in a round-bottomed flask, equipped with a magnetic stirrer, oil bath heating, a thermometer and a reflux condenser, as shown in Figure 1. The diluted raw pyrolysis oil or solvent fraction was added to the flask and heated to the reaction temperature (50 - 80 °C), which was continuously monitored throughout the experiment by a thermometer. H₂O₂ and formic acid (1:1 v/v) were then added to the oil with different oil to H₂O₂
volume ratio (1:2 and 1:4 v/v) and the reaction started. 10 mL of liquid sample was withdrawn from
the reaction system at 10, 20, 30, 60, 120 and 240 min, respectively. The samples were then washed
with DI water, centrifuged and separated into two layers. The upper layer was dried with anhydrous
Na$_2$SO$_4$ and filtered through filter paper (Whatman No. 1) to obtain oxidised oil samples for further
analysis and selective adsorption experiments.

Table 2 Surface physical properties of Al$_2$O$_3$ obtained from BET

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>136.55 m$^2$ g$^{-1}$</td>
</tr>
<tr>
<td>External surface area</td>
<td>134.88 m$^2$ g$^{-1}$</td>
</tr>
<tr>
<td>Micropore surface area</td>
<td>1.67 m$^2$ g$^{-1}$</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.25 cm$^3$ g$^{-1}$</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>5.48 nm</td>
</tr>
</tbody>
</table>

2.3 Batch selective adsorption experiments

The oxidised oil samples were treated by using Al$_2$O$_3$ adsorption. The Al$_2$O$_3$ was activated
overnight at 200 °C before use. For each experimental run, a predetermined amount (0.5 - 8 g) of
Al$_2$O$_3$ was added to 10 mL oxidised oil in a conical flask. The flask was stirred under 25 °C and
atmospheric pressure for 12 h in order to ensure that the adsorption equilibrium is reached. This
long adsorption time of 12 h was chosen based on a set of preliminary tests to provide a common
basis for comparison of the performance of different amounts of adsorbents. The liquid samples,
after adsorption, were analysed for sulphur concentration and sulphur-containing species using ICP-
OES and GC-SCD, respectively. The used Al$_2$O$_3$ adsorbent was calcined at 550 °C in air in a muffle
furnace for 4 h to remove chemicals adsorbed. The calcined Al$_2$O$_3$ was reused for a new adsorption
experiment in a regeneration performance test.

The percentage of sulphur removal was calculated using the following equations:

\[
\% \text{ Sulphur removal} = \frac{C_0 - C_t}{C_0} \times 100
\]
where $C_0$ (ppm) is the initial sulphur content; $C_t$ (ppm) is the sulphur content after desulphurisation.

The equilibrium adsorption capacity of $\text{Al}_2\text{O}_3$ was determined:

$$q_e = \frac{m_{\text{oil}}(C_b - C_e)}{1000m_{\text{ads}}}$$

(2)

where $q_e$ is the equilibrium adsorption capacity (mg S g$^{-1}$ $\text{Al}_2\text{O}_3$); $m_{\text{oil}}$ and $m_{\text{ads}}$ the initial mass of the oil (g) and adsorbent (g), respectively; $C_b$ and $C_e$ the sulphur content at beginning and end of the adsorption experiment (ppm), respectively.

2.4 Analysis and Characterisation

The concentrations of sulphur in all the samples were determined using a Thermo Scientific iCAP 7400 Duo Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipped with a baffled cyclonic spray chamber and a V-Groove nebuliser. An online 5 ppm internal standard prepared from a Conostan® Y single element (1000 ppm) in white oil standard diluted with Premisolv® was used to correct for matrix effects. Experimental conditions were run with RF power 1220 Hz, auxiliary gas flow of 1.5 L min$^{-1}$, nebuliser gas flow of 0.3 L min$^{-1}$ and pump speed of 20 rpm to minimise carbon deposition during analysis. Calibration standards and the calibration check standard were prepared from a Conostan® S in Crude Oil (10000 ppm) stock standard by dilution with toluene to better mimic the sample matrix and adequately covered the range of approximate sample concentrations. Duplicates and replicates of select samples were run within and between runs to assess precision and stability. In most cases, precision was <3% relative standard deviation.

The qualitative analyses of sulphur-containing compounds in the samples were carried out by an Agilent 7890A gas chromatograph (GC) equipped with an Agilent 8355S sulphur chemiluminescence detector (SCD). The compounds were separated by an HP-5MS column (30 m x 250 µm x 0.25 µm). The GC oven temperature was initially set at 32 °C and held for 8 min, ramped from 32 °C to 90 °C at 2 °C min$^{-1}$ and held at 90 °C for 5 min, then ramped at 5 °C min$^{-1}$ to a final temperature of 300 °C for raw pyrolysis oil, or 200 °C for the solvent fraction, and held for 1 min.
The hydrocarbon compositions of the samples were analysed using a gas chromatograph-mass spectrometry (GC-MS, Agilent 7890A and Agilent 5975C). Separation was carried out with a HP-5MS column (30 m x 250 µm x 0.25 µm) with helium carrier gas at 0.5 mL min\(^{-1}\). The injection temperature was 300 °C. The transfer line was kept at 300 °C. The heating program of GC was the same as described above for GC-SCD. Mass range was from 40 to 550 m/z. A mass spectral library (NIST) was used for the qualitative analysis.

The surface area and pore properties of the Al\(_2\)O\(_3\) adsorbent were measured by nitrogen adsorption at -196 °C using Micromeritics TriStar II. Before the analysis, the sample was degassed at 200 °C overnight. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume (V\(_{\text{total}}\)) was determined by single point adsorption of pores <60 nm at P/P\(_0\)=0.97. The pore size distribution was calculated from adsorption isotherms using the Barrett-Joyner-Halenda (BJH) approach.

The Al\(_2\)O\(_3\) adsorbents before and after adsorption experiments were characterised using a Fourier transform infrared spectrophotometer (FTIR, Thermo Nicolet 6700) operated at wavenumbers of 400 to 4000 cm\(^{-1}\). The samples were homogenized using KBr loaded with 0.5 wt% of Al\(_2\)O\(_3\).

3. Results and Discussion

3.1 Sulphur speciation

![GC-MS chromatograms of (a) raw pyrolysis oil and (b) solvent fraction](image)

Figure 2  GC-MS chromatograms of (a) raw pyrolysis oil and (b) solvent fraction
The pyrolysis oil from spent tyres is a dark, dense liquid made of a complex mixture of hydrocarbons consisting of saturated and unsaturated linear and cyclic hydrocarbons and heterocyclic compounds, such as sulphur, nitrogen and oxygen compounds. The most abundant compounds identified by GC-MS chromatograms of the raw pyrolysis oil and solvent fraction were toluene, ethylbenzene, xylene, styrene, 1,3,5-trimethyl-benzene, 1-methyl-2-(1-methylethyl)-benzene and limonene (Figure 2; Table 3). The full list of hydrocarbons identified with GC-MS analysis was provided as supplementary material. The abundance of hydrocarbon compositions, in particular, makes spent tyre pyrolysis oil an attractive feedstock for the production of solvents.

Table 3  GC-MS analysis of raw pyrolysis oil and solvent fraction

<table>
<thead>
<tr>
<th>Peak number</th>
<th>Retention time (min)</th>
<th>Identification</th>
<th>Formula</th>
<th>CAS number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.044</td>
<td>Benzene</td>
<td>C₆H₆</td>
<td>71-43-2</td>
</tr>
<tr>
<td>2</td>
<td>7.820</td>
<td>Toluene</td>
<td>C₇H₈</td>
<td>108-88-3</td>
</tr>
<tr>
<td>3</td>
<td>14.353</td>
<td>Ethylbenzene</td>
<td>C₈H₁₀</td>
<td>100-41-4</td>
</tr>
<tr>
<td>4</td>
<td>15.021</td>
<td>p-Xylene</td>
<td>C₈H₁₀</td>
<td>106-42-3</td>
</tr>
<tr>
<td>5</td>
<td>16.709</td>
<td>Styrene</td>
<td>C₈H₈</td>
<td>100-42-5</td>
</tr>
<tr>
<td>6</td>
<td>16.822</td>
<td>o-Xylene</td>
<td>C₈H₁₀</td>
<td>95-47-6</td>
</tr>
<tr>
<td>7</td>
<td>22.529</td>
<td>Benzene, 1-ethyl-4-methyl-</td>
<td>C₀H₁₂</td>
<td>622-96-8</td>
</tr>
<tr>
<td>8</td>
<td>25.042</td>
<td>Benzene, 1,3,5-trimethyl-</td>
<td>C₀H₁₂</td>
<td>108-67-8</td>
</tr>
<tr>
<td>9</td>
<td>27.296</td>
<td>Benzene, 1,3,5-trimethyl-</td>
<td>C₀H₁₂</td>
<td>108-67-8</td>
</tr>
<tr>
<td>10</td>
<td>27.635</td>
<td>Benzene, 1-methyl-2-(1-methylethyl)-</td>
<td>C₁₀H₁₄</td>
<td>527-84-4</td>
</tr>
<tr>
<td>11</td>
<td>27.896</td>
<td>D-Limonene</td>
<td>C₁₀H₁₆</td>
<td>5989-27-5</td>
</tr>
<tr>
<td>12</td>
<td>53.022</td>
<td>Naphthalene, 1,7-dimethyl-</td>
<td>C₁₂H₁₂</td>
<td>575-37-1</td>
</tr>
<tr>
<td>13</td>
<td>56.351</td>
<td>Naphthalene, 1,6,7-trimethyl-</td>
<td>C₁₃H₁₄</td>
<td>2245-38-7</td>
</tr>
</tbody>
</table>

However, the high sulphur content (1.44 wt%) in pyrolysis oil prevents its use in many cases. The
GC-MS data, as shown in the Supplementary Materials, identified a very limited number of sulphur-containing compounds in both the raw pyrolysis oil and solvent fraction. This is because both the raw pyrolysis oil and solvent fraction are extremely complex mixtures. The concentration of a single compound is very low. Compared with the concentrations of individual hydrocarbons, the concentrations of sulphur-containing compounds are even much lower. Therefore, the abundance of sulphur-containing compounds in GC-MS is extremely low and usually obscured by the signal of hydrocarbons. Only a very limited number of sulphur-containing compounds with relatively high concentrations were identifiable by using GC-MS. In order to comprehensively understand the speciation of sulphur-containing compounds, GC-SCD technique was adopted and used for both the raw pyrolysis oil and solvent fraction. The SCD is a dedicated sulphur-selective detector. Therefore, the sulphur-containing compounds can be easily identified using it, not affected by the presence of hydrocarbons.

Figure 3  GC-SCD chromatograms of (a) standard organic sulphur compounds (b) raw pyrolysis oil and (c) solvent fraction
Figure 3 shows the GC-SCD chromatograms of standard organic sulphur compounds (thiophene, benzothiophene and dibenzothiophene), raw pyrolysis oil and solvent fraction. According to the identification of standard organic sulphur compounds, the sulphur compounds on the GC-SCD chromatograms were identified as the thiophene group (<42.5 min), the benzothiophene group (42.5-62.8 min), and the dibenzothiophene group (>62.8 min). The major organic sulphur compounds in the raw pyrolysis oil were mainly composed of a wide range of derivatives of thiophene, benzothiophene, and dibenzothiophene. There was a wider variety of sulphur-containing species in the raw pyrolysis oil than in the solvent fraction. In the solvent fraction, the thiophene and benzothiophene groups were predominant. However, it appeared that some of the benzothiophene group and all of the dibenzothiophene groups that were present in raw pyrolysis oil (retention time >48 min) were removed.

3.2 Sulphur removal by ODS

![Graph](image)

Figure 4 Effect of reaction temperature and time on the percentage of sulphur removal of (a) solvent fraction and (b) raw pyrolysis oil by catalytic oxidation desulphurisation.

Reaction conditions: $V_{oil}/V_{H_2O_2}=1:2$, $V_{H_2O_2}/V_{HCOOH}=1:1$

The percentage of sulphur removal from solvent fraction and raw pyrolysis oil at 50, 60, 70 and 80 °C with $V_{pyrolysis\,oil}/V_{H_2O_2}=1:2$ is shown in Figure 4. Initially, the total sulphur content in the raw pyrolysis oil and solvent fractions were 1.44 wt% and 1.27 wt%, respectively. Sulphur removal increased with time before plateauing at a maximum of 57% for the solvent fraction and 31% for
the raw pyrolysis oil. While maximum sulphur removal was reached within 240 min and was the same for the same feedstock at all temperatures, the plateaus were reached faster at higher temperatures.

Figure 5  Pseudo-first order correlations of (a) solvent fraction and (b) raw pyrolysis oil by catalytic oxidation desulphurisation at various temperatures. Reaction conditions: $V_{\text{oil}}/V_{\text{H}_2\text{O}_2}=1:2$, $V_{\text{H}_2\text{O}_2}/V_{\text{HCOOH}}=1:1$

Table 4  The pseudo-first order kinetic rate constants of ODS for solvent fraction and raw pyrolysis oil at different reaction temperatures

<table>
<thead>
<tr>
<th>Oil types</th>
<th>Temperature</th>
<th>k  (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent fraction</td>
<td>50</td>
<td>0.0088</td>
<td>0.9741</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.0132</td>
<td>0.9788</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0174</td>
<td>0.9729</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0211</td>
<td>0.9524</td>
</tr>
<tr>
<td>Raw pyrolysis oil</td>
<td>60</td>
<td>0.0103</td>
<td>0.9926</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.0145</td>
<td>0.9791</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0317</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 5 shows the relationship between $\ln(C_0/C_t)$ and the reaction time at different temperatures for...
the solvent fraction and raw pyrolysis oil. The results demonstrate a linear relationship, suggesting that both the solvent fraction and raw pyrolysis oil ODS reaction follows a pseudo-first order reaction rate\textsuperscript{38-41}. This may be expected given the excess H\textsubscript{2}O\textsubscript{2} present during the ODS reaction. The kinetic rate constant $k$ (min$^{-1}$) can be determined using the following pseudo-first order equations:

$$\frac{dC_t}{dt} = kC_t$$  \hspace{1cm} (3)

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$  \hspace{1cm} (4)

$$k = A e^{-\frac{E_a}{RT}}$$  \hspace{1cm} (5)

$$\ln k = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (6)

where $A$ is the pre-exponential factor, $E_a$ the apparent activation energy (kJ mol$^{-1}$), $R$ and $T$ are universal gas constant (8.314×10$^{-3}$ kJ mol$^{-1}$ K$^{-1}$) and the reaction temperature (K), respectively. The values of the pseudo-first order rate constants for the different temperatures are summarised in Table 4. The Arrhenius plot of the rate kinetic constants (Figure 6) gives apparent activation energies of 27.69 kJ mol$^{-1}$ and 54.93 kJ mol$^{-1}$ for solvent fraction and raw pyrolysis oil, respectively. These data are similar to the activation energy of dibenzothiophene (59.8 kJ mol$^{-1}$) ODS using H\textsubscript{2}O\textsubscript{2} with formic acid reported in literature\textsuperscript{40,41}.

Figure 6  Arrhenius activation energies for ODS of (a) solvent fraction and (b) raw pyrolysis oil at various temperatures. Reaction conditions: $V_{oil}/V_{H2O2}=1:2$, $V_{H2O2}/V_{HCOOH}=1:1$
Figure 7 Effect of oxidant loading ratio on the percentage of sulphur removal of both solvent fraction and raw pyrolysis oil by catalytic oxidation desulphurisation. Reaction conditions: \( \frac{V_{H_2O_2}}{V_{HCOOH}} = 1:1 \), \( T=80 \, ^{\circ}C \)

Figure 7 shows the percentage of sulphur removal from solvent fraction and raw pyrolysis oil with different \( \frac{V_{oil}}{V_{H_2O_2}} \) ratios. In both cases, neither the solvent fraction nor raw pyrolysis oil had 100% sulphur removal, despite excessive oxidant. Doubling the oxidant concentration only increased the sulphur removal by ca. 9%, from 57% to 66% in the solvent fraction and 31% to 40% in raw pyrolysis oil. According to the concentration of sulphur in the raw pyrolysis oil and solvent fraction, the required molar ratio of \( H_2O_2/S \) was estimated to be approximately 50:1 with \( \frac{V_{oil}}{V_{H_2O_2}} = 1:2 \), which is much higher than the theoretical value (2:1). This may be due to the competing reactions between the oxidation of sulphur-containing compounds by \( H_2O_2 \), and the epoxidation of unsaturated hydrocarbons. The required amount of oxidant for our pyrolysis oil was, therefore, higher than some literature data \(^{17,32} \). The difference between the results of this study and literature results may relate to variations in the sulphur and hydrocarbon chemical composition between different feedstock.
Figure 8 GC-MS chromatograms of (a) solvent fraction before catalytic oxidation desulphurisation, (b) solvent fraction after catalytic oxidation desulphurisation, (c) raw pyrolysis oil before catalytic oxidation desulphurisation and (d) raw pyrolysis oil after catalytic oxidation desulphurisation. Reaction conditions: $V_{\text{oil}}/V_{\text{H}_2\text{O}_2}=1:4$, $V_{\text{H}_2\text{O}_2}/V_{\text{HCOOH}}=1:1$, $T=80 ^\circ \text{C}$, reaction time=240 min

The GC-MS chromatograms of the pyrolysis oils before and after ODS are shown in Figure 8. The figures show that many unsaturated hydrocarbons, with carbon-carbon double bonds and triple bonds, in the raw pyrolysis oil and solvent fraction disappeared after ODS. Unsaturated hydrocarbons can react with hydrogen peroxide and performic acid to form epoxides in the epoxidation reaction \(^{36}\). The epoxidation reaction was confirmed by the detection of the products (limonene oxide, trans-, $C_{10}H_{16}O$, CAS No. 6909-30-4) of limonene epoxidation in a separate study using limonene as a model fuel. Epoxidation reactions are highly exothermic processes, driving the
temperature of the reaction uncontrollably upward as observed during preliminary trials. The need for such an excess of oxidant may be due to competing reactions among the oxidation of sulphur-containing compounds, the non-productive decomposition of H₂O₂ itself to produce H₂O and O₂, and the epoxidation of these unsaturated hydrocarbons.

Figure 9  GC-SCD chromatograms of (a) solvent fraction before desulphurisation, (b) solvent fraction after Al₂O₃ adsorption desulphurisation, (c) solvent fraction after oxidative desulphurisation and (d) solvent fraction after oxidative and Al₂O₃ adsorption desulphurisation. Catalytic oxidation desulphurisation conditions: V_{oil}/V_{H₂O₂}=1:4, V_{H₂O₂}/V_{HCOOH}=1:1, T=80 °C, reaction time=240 min. Al₂O₃ dosage of adsorption desulphurisation is 8 g.

The comparison of GC-SCD chromatograms of the solvent fraction and raw pyrolysis oil before and after ODS are shown in Figure 9 (a) (c) and Figure 10 (a) (c), respectively. Following ODS, almost all of the sulphur-containing species detected in both oil samples disappeared. The remaining sulphur compounds in the oil were thiophene derivatives, which were not been completely oxidised.
by the ODS treatment because of their low reactivity. However, new sulphur-containing species, sulfoxides and sulphones, were formed (Figure 9 (c) and Figure 10 (c)). Approximately 66% of the total sulphur for solvent fraction and 40% for raw pyrolysis oil was dissolved in the aqueous phase and removed by subsequent phase separation. The remaining sulphur compounds had strong solubility in the oil and could not be successfully separated by aqueous phase extraction.

![GC-SCD chromatograms](image)

Figure 10 GC-SCD chromatograms of (a) raw pyrolysis oil before desulphurisation, (b) raw pyrolysis oil after Al₂O₃ adsorption desulphurisation, (c) raw pyrolysis oil after oxidative desulphurisation and (d) raw pyrolysis oil after oxidative and Al₂O₃ adsorption desulphurisation. Catalytic oxidation desulphurisation conditions: \( V_{oil}/V_{H₂O₂}=1:4, V_{H₂O₂}/V_{HCOOH}=1:1, \) T=80 °C, reaction time=240 min. Al₂O₃ dosage of adsorption desulphurisation is 8 g

### 3.3 Sulphur Removal by ODS Combined with Adsorption Desulphurisation

Several studies have also proposed the use of Al₂O₃ adsorption in oil, either in conjunction with ODS or as a method in and of itself. To test the effectiveness of Al₂O₃ adsorption for
sulphur removal in this particular feedstock, the sulphur content of the raw pyrolysis oil and solvent fractions in Al₂O₃ adsorption was compared to combined ODS-Al₂O₃ adsorption. Figure 11 shows the comparisons of sulphur removal efficiency of the three different desulphurisation processes. The Al₂O₃-only adsorption used 8 g per 10 mL of oil and removed a maximum of 20% and 14% sulphur from the raw pyrolysis oil and solvent fraction, respectively, which was substantially lower than ODS alone. At the same absorbent to oil ratio, combined ODS-Al₂O₃ adsorption showed dramatically improved sulphur removal efficiency over both ODS and Al₂O₃-only adsorption, reaching 81% and 84% for the raw pyrolysis oil and solvent fraction, respectively. Al₂O₃ shows significantly different adsorption behaviour to the original sulphur species and sulphur species after ODS.

Figure 11 Comparison of different desulphurisation processes: (a) Al₂O₃ adsorption desulphurisation, (b) catalytic oxidation desulphurisation and (c) combined oxidation and adsorption desulphurisation for solvent fraction and raw pyrolysis oil. Catalytic oxidation desulphurisation conditions: V_{oil}/V_{H₂O₂}=1:4, V_{H₂O₂}/V_{HCOOH}=1:1, T=80 °C, reaction time=240 min. Al₂O₃ dosage of adsorption desulphurisation is 8 g.

Figure 9 (d) and Figure 10 (d) show the GC-SCD chromatograms of pyrolysis oil after combined ODS oxidation and selective adsorption using Al₂O₃. After ODS, the dipole magnitude increased due to the presence of the S=O group. A much higher negative electrostatic potential was found.
on oxidative sulphur species, which was located in the one or two oxygen atoms. The significantly increased molecules polarity of oxidised sulphur species was one possible reason that made them more effectively adsorbed by Al$_2$O$_3$. It is evident that the adsorbent is capable of removing almost all types of oxidised sulphur species from the pyrolysis oil after ODS to achieve a deep desulphurisation.

![Figure 12](image)

**Figure 12** Effect of Al$_2$O$_3$ adsorbent dosages on the total percentage of sulphur removal for both solvent fraction and raw pyrolysis oil after catalytic oxidation desulphurisation.

Catalytic oxidation desulphurisation conditions: $V_{\text{oil}}/V_{\text{H}_2\text{O}_2}=1:4$, $V_{\text{H}_2\text{O}_2}/V_{\text{HCOOH}}=1:1$, $T=80$ °C, reaction time=240 min

The dosage of adsorbent is a fundamental cardinal factor in all adsorption studies that directly affects the percentage of sulphur removal. The results of the adsorption desulphurisation of the oxidised solvent fraction and raw pyrolysis oil over different Al$_2$O$_3$ dosages are shown in Figure 12. Sulphur removal was improved from 40% to 75% for the raw pyrolysis oil, and 66% to 80% for the solvent fraction when the dosage of Al$_2$O$_3$ was increased from 0.5 to 3 g. At an adsorbent mass of less than 3 g, Al$_2$O$_3$ became saturated with sulphur compounds. Further increasing the adsorbents dosage from 3 to 8 g only slightly increased the sulphur removal to 81% and 84% for raw pyrolysis oil and solvent fraction, respectively. The increase in sulphur removal with the increase in Al$_2$O$_3$
dosage is attributable to an increase in the available adsorption sites for sulphur compounds. However, there appears to be no advantage to using Al$_2$O$_3$ adsorbent dosages greater than 3 g, as there may be too little of the effective sulphur molecules (sulphur oxides and sulphones) remaining to bind onto the per unit mass of adsorbent. Consequently, the sulphur capacity for the Al$_2$O$_3$ in the solvent fraction and raw pyrolysis oil was 0.08 mg S g$^{-1}$ Al$_2$O$_3$ and 0.31 mg S g$^{-1}$ Al$_2$O$_3$, respectively.

Figure 13 FTIR analysis for (a) fresh Al$_2$O$_3$, (b) Al$_2$O$_3$ after adsorption desulphurisation of the oxidised raw pyrolysis oil and (c) Al$_2$O$_3$ after adsorption desulphurisation of the oxidised solvent fraction. Al$_2$O$_3$ dosage of adsorption desulphurisation is 1 g. Catalytic oxidation desulphurisation conditions: $V_{\text{oil}}/V_{\text{H}_2\text{O}_2}=1:4$, $V_{\text{H}_2\text{O}_2}/V_{\text{HCOOH}}=1:1$, $T=80$ °C, reaction time=240 min.

The FTIR transmittance spectra of the Al$_2$O$_3$ samples before and after adsorption are shown in Figure 13. The broad peak centred at 3433 cm$^{-1}$ is the -OH stretching vibration and the peak at 1640 cm$^{-1}$ is attributed to the H-O-H bonds. Before adsorption, the -OH and H-O-H peaks of the Al$_2$O$_3$ were identified in the spectra but had low transmittance intensities, suggesting the presence of -OH functional group and H-O-H bonds on the surface of Al$_2$O$_3$. The samples after adsorption of raw pyrolysis oil and solvent fraction displayed similar FTIR spectra, suggesting they contained similar functional groups. However, the peaks corresponding to the -OH and H-O-H bonds were
found to increase after adsorption, indicating that the presence of strong hydrogen bonds, and the –OH groups were also adsorbed that would inhibit the adsorption of sulphur compounds because of a part of the active site on Al₂O₃ surface were occupied. The peak observed at 2927 cm⁻¹ is ascribed to C-H stretching vibrations in aliphatic CH, CH₂, and CH₃ groups. The new emerging C-H functional groups after desulphurisation proved the presence of adsorbed organic compounds on the adsorbents. However, the weak intensity indicated that the content of organic compounds was low. No peaks relating to S=O of sulfoxides and SO₂ of sulphones in the FTIR spectra were observed, which was probably due to the extremely low concentration of sulphur adsorbed onto the surface of the Al₂O₃.

![FTIR spectra](image)

**Figure 14** Regeneration performance of Al₂O₃ for raw pyrolysis oil after catalytic oxidation desulphurisation. Al₂O₃ dosage of adsorption desulphurisation is 1 g. Catalytic oxidation desulphurisation conditions: Voil/VH₂O₂=1:4, VH₂O₂/VHCOOH=1:1, T=80 °C, reaction time=240 min. The % S removal is total sulphur removal combined catalytic oxidation and adsorption desulphurisation.

The regeneration performance of Al₂O₃ was tested using 1 g Al₂O₃ dosage for 10 mL of the raw pyrolysis oil after ODS and the results of three desulphurisation-regeneration cycles for Al₂O₃ are shown in Figure 14. The sulphur adsorption capacity of Al₂O₃ decreased from 0.31 mg S g⁻¹ Al₂O₃ to 0.22 mg S g⁻¹ Al₂O₃ after three regeneration cycles, resulting in only a slight decreased in sulphur.
removal by combined ODS-Al₂O₃ adsorption from 57% to 54%. These results demonstrate the applicability of Al₂O₃ adsorption after the ODS process to remove sulphur from spent tyre pyrolysis oil.

4. Conclusions

The combined catalytic oxidative and selective adsorption desulphurisation of a spent tyre pyrolysis oil and its distillate using H₂O₂ as oxidant, formic acid as catalyst and Al₂O₃ as adsorbent was experimentally studied. The percentage of sulphur removal increased with increasing the temperature, time, and amount of oxidant (H₂O₂-formic acid). The H₂O₂-formic acid itself exhibited moderated sulphur removal efficiency, with 40% sulphur removal for the raw pyrolysis oil and 66% for the solvent fraction. The unsaturated hydrocarbons in the raw pyrolysis oil and solvent fraction competed with sulphur-containing compounds for the H₂O₂-formic acid via the epoxidation reaction, reducing sulphur removal percentage and changing the compositions of the raw pyrolysis oil and solvent fraction. Despite this, it was found that the sulphur-containing species were oxidised into sulphoxides and sulphones, which can be effectively removed by Al₂O₃ adsorption. A maximum of 81% and 84% sulphur removal were achieved for the raw pyrolysis oil and the solvent fraction, respectively, using the combined catalytic oxidation and selective adsorption. After three desulphurisation-regeneration cycles, the Al₂O₃ still exhibited a high sulphur removal ability.

Supporting Information

GC-MS analysis of chemical compositions of the raw pyrolysis oil and solvent fraction

Acknowledgement

The authors wish to acknowledge the financial support for this research received from the Australian Research Council under the ARC Linkage Projects scheme (LP160100035) and Keshi Technologies Pty Ltd. Miss Qian Zhang received a living stipend from the Centre for Energy at The University of Western Australia.
References


