

DESULFURIZATION OF WASTE TIRE PYROLYTIC OIL (TPO) USING ADSORPTION AND OXIDATION TECHNIQUES



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Declaration

I Moshe Mello hereby declare that I'm the sole author of this dissertation. All the work in this dissertation was compiled by me and it is because of my efforts with the help from respected parties mentioned in the acknowledgement. I declare that no plagiarism was committed, with the knowledge of the consequence resulting from plagiarism and therefore I will take full responsibility.

A handwritten signature in blue ink, appearing to be 'M. Mello', enclosed within a light gray rectangular box.

18 Jan 2017

Signature (Moshe Mello)

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Abstract

The presence of tires in open fields, households and landfills is a great threat to the wellbeing of the ecosystem around them. Tire creates an ideal breeding ground for disease carrying vermins and their possible ignition threatens the surrounding air quality due to the harmful gases produced during combustion. Pyrolysis of tires produces four valuable products namely; char, steel, tire pyrolytic oil (TPO) and non-condensable gases. TPO has been reported to have similar properties to commercial diesel fuel. The biggest challenge faced by TPO to be used directly in combustion engines is the available sulfur content of about 1.0% wt. Considering the stringent regulations globally for allowable sulfur content in liquid fuels, TPO therefore, requires deep desulfurization before commercialization.

In this study, different desulfurization techniques were applied to reduce the sulfur content in TPO. A novel study on combination of adsorptive and air-assisted oxidative desulfurization (AAOD) was developed for desulfurization of TPO. Different carbon materials were employed as catalyst and/or adsorbent for the AAOD system. The effect of operating conditions; catalyst/adsorbent dosage, $\text{H}_2\text{O}_2/\text{HCOOH}$ ratio, reaction time, temperature and air flowrate were studied. Oxidation equilibrium was reached at 80 °C for both commercial activated carbon (CAC) and activated tire char (ATC) at a reaction time of 50 min. With a total oil recovery of more than 90% and the initial sulfur content of 7767.7 ppmw, the presence of air at a flow rate of 60 l/hr increased oxidation from 59.2% to 64.2% and 47.4% to 53% for CAC and ATC, respectively.

The use π -complexation sorbent was also applied to study the selectivity of such sorbents to organosulfur compounds (OSC) found in liquid fuels. The π -complexation-based adsorbent was obtained by ion exchanging Y-zeolite with Cu^+ cation using liquid phase ion exchange (LPIE). Batch adsorption experiments were carried out in borosilicate beakers filled with modified Cu(I)-Y zeolite for both TPO and synthesized model fuels. For model fuels (MF), the selectivity for adsorption of sulfur compounds followed the order dibenzothiophene (DBT) > benzothiophene (BT) > Thiophene.

Key words: Adsorption, Desulfurization, Dibenzothiophene, Tire pyrolytic oil

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Symbols and Abbreviations

Symbols

C_o	- Initial concentration (mg/L)
C_t	- Concentration at time t (mg/L)
C_e	- Equilibrium concentration (mg/L)
C	- Final concentration (mg/L)
t	- Reaction time (min)
q_e	- Amount of adsorbate ions adsorbed on the adsorbent at equilibrium (mg/g)
q_t	- Amount of adsorbate ions adsorbed on the adsorbent at time t (mg/g)
K_f	- Freundlich model constant related to the adsorption capacity (mg/g)
n	- Freundlich model constant related to intensity of adsorption (g/L)
q_m	- Langmuir model constant related to maximum adsorption capacity (mg/g)
k_L	- Langmuir model constant related to energy of adsorption (L/g)
k_1	- Pseudo first-order rate constant (L/min)
k_2	- Pseudo second-order rate constant (g/mg.min)

Abbreviations

AAOD	- Air-assisted oxidative desulfurization
ASTM	- American society for testing and materials
ATC	- Activated tire char
BiCh	- Bicyclohexyl
BiPh	- Biphenyl
CAC	- Commercial activated carbon
CHB	- Cyclohexylbenzene
CI	- Compression ignition
DBT	- Dibenzothiophene
DTC	- Demineralized tire char
FTIR	- Fourier Transform Infrared
GC-MS	- Gas chromatography mass spectroscopy
GC-FPD	- Gas chromatography flame photometric detector
GVC	- Gross calorific value

HDS	- Hydrodesulphurization
HHDBT	- Hexahydrodibenzothiophene
HPLC	- High performance liquid chromatography
HYD	- Hydrogenation desulfurization
H NMR	- Hydrogen nuclear magnetic resonance
MO	- Molecular orbital
ODS	- Oxidative desulfurization
PAH	- Polycyclic aromatic hydrocarbons
PASH	- Polycyclic aromatic sulfur hydrocarbons
Ppmw	- Parts per million by weight
SBR	- Styrene butadiene rubber
SEM	- Scanning electron microscope
TC	- Tire char
TGA	- Thermogravimetric analysis
THDBT	- tetrahydrodibenzothiophene
TPO	- Tire pyrolytic oil
XRF	- X-ray fluorescence
4-MDBT	- 4-Methyldibenzothiophene
4,6-DMDBT	- 4,6-Dimethyldibemzothiophene

CHAPTER 1

1. Introduction

1.1 Background

The number of people who rely on public transport is declining. It is true that almost all of us want to own a car. Busy highways are also considered to be a sign of a developed economy. However, an increase in the usage of private cars is not exactly a positive trend. The growing population of private cars have multiple drawbacks, mainly related to environmental contamination. The exhaustion of gases from combustion engines contaminates the air and will eventually lead to global warming. Disposal of most exhausted car parts or utilities such as tires, batteries and waste engine oil are hazardous to the environment. Open dumping of tires pollutes the soil, contaminates underground water and provides ideal breeding grounds for disease carrying vermin such as mosquitos and rats (Uçar et al., 2005). Therefore, the recycle and reuse of such materials are desirable for turning waste into worthy products.

Tires are extremely challenging to recycle due to the available chemically cross-linked polymer which constitutes their nature and, therefore, they are neither fusible nor soluble and, consequently, cannot be remoulded into other shapes without serious degradation (Trongkaew et al., 2011). There are various methods reported for the recycling of waste tires such as grinding, retreading, incineration and pyrolysis, although these methods can solve the above-mentioned problem, they also have their own drawbacks (de Marco Rodriguez et al., 2001). The benefits of pyrolysis in comparison with the disadvantageous open field dumping to produce low cost fuel and other valuable products is an appetizing research field to turn waste into energy (Pilusa et al., 2013). Pyrolysis is the heating system of matter in the absence of oxygen; this technology is normally practiced for the thermochemical decomposition of organic compounds. There are various uses of pyrolysis such as turning wood into charcoal, which is an ancient method of charcoal production on an industrial scale. The thermal decomposition of tires by pyrolysis produce char, steel, non-condensable gases and tire pyrolytic oil (TPO) (Laresgoiti et al., 2004).

Murugan et al. (2008) reported that TPO can be used in compression ignition (CI) engines, thus justifying the almost similar properties to commercial diesel fuel as suggested by (Cunliffe and Williams, 1998; Huang and Tang, 2009; Abdul-Raouf et al., 2010). The challenge facing commercialization or direct use of TPO in CI engines is the presence of sulfur content greater than 1.0% wt. Therefore, this drawback calls for desulfurization of TPO before use in CI engines.

There are technologies in place for desulfurization of liquid hydrocarbons. Hydrodesulfurization (HDS) is the industrially applied technology for removal of sulfur compounds and operates at high temperatures and pressure in the presence of a catalyst (Moses et al., 2009; Srivastava, 2012; Jantaraksa et al., 2015). The problem associated with this technology is its inability to remove complex organosulfur compounds (OSC) such as dibenzothiophene (DBT) and its derivatives; 4-Methyldibenzothiophene (4-MDBT) and 4,6-Dimethyldibenzothiophene (4,6-DMDBT) (Williams and Bottrill, 1995). There are other technologies that have received tremendous attention to supplement the conventional HDS technique. These technologies include; oxidative desulfurization, adsorptive desulfurization, photocatalytic desulfurization and bio-desulfurization. Some of these technologies have proven to have potential in removal of complex and non-complex OSC in liquid hydrocarbons. Industrially produced liquid fuels can therefore undergo a two-stage desulfurization process whereby they are first treated using the conventional HDS and later with either oxidative desulfurization, adsorptive desulfurization, photocatalytic desulfurization or bio-desulfurization technique depending on the nature of fuel and desired end properties.

This study focuses on desulfurization of TPO using adsorption and oxidation techniques. A review study on the current studies for pyrolysis of waste tire and multiple desulfurization technologies used for treating TPO and other liquid fuels globally was compiled. This also included details specification on operating conditions of a pyrolysis reactor in achieving desirable products in terms of composition and ratios. Co-adsorptive and oxidative desulfurization experiments were carried out using commercial activated carbon and activated tire char in the presence of air for assistance using hydrogen

peroxide and formic acid as the main oxidizing agent and catalyst, respectively. Modified Cu(I)-Y zeolite π -complexation-based adsorbent was used for desulfurization of TPO and synthesized model fuel comprising of thiophene, benzothiophene (BT) and DBT prepared in n-octane solution.

1.2 Problem Statement

Disposal of waste tires is a huge global crisis which poses a threat to the environment and living organisms. Pyrolysis is a step towards solving this environmental issue. Pyrolysis is a process by which waste tires are being thermally degraded in the absence of oxygen gas to produce oil, char, steel and non-condensable gases. The oil produced in this process contains traces of sulfur, which is an undesirable species in the oil due to its environmental hazards that it poses during combustion of the oil in car engines and industrial equipment. There are various technologies available for the desulphurization of oil derived from waste tires. Hydrodesulphurization (HDS) is the commonly practiced technique for the removal of sulfur species in liquid hydrocarbons. This technology operates at high temperatures and pressure for the effective removal of the sulfur species. However, the HDS technique fails in the presence of complex sulfur species such as dibenzothiophene (DBT). This study will investigate the viability of oxidation and adsorptive desulphurization technologies for efficient removal of complex and non-complex sulfur species in TPO.

1.3 Main Objective

The main aim of this project is to develop and optimise a process for the desulphurization of waste tyre pyrolytic oil (TPO) using adsorption and oxidation techniques.

1.4 Specific Objectives

- a) To characterize carbon adsorbents tire char (TC), Demineralized tire char (DTC), activated tire char (ATC) and commercial activated carbon (CAC) using Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM)

- b) To determine the effect of adsorbent dosage, time and temperature on adsorptive desulfurization of TPO and fit the data to Freundlich isotherm model, Langmuir isotherm model, pseudo-first order kinetic model and pseudo-second order kinetic model.
- c) To determine the effect of air-assisted oxidation for desulfurization of TPO using performic acid system catalyzed by ATC and CAC
- d) To determine the effectiveness of π -complexation sorbent for desulfurization of TPO and model fuel using Cu(I) – Y zeolite

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CHAPTER 2

2. WASTE TIRE PYROLYSIS AND DESULFURIZATION OF TIRE PYROLYTIC OIL (TPO) – A REVIEW

2.1 Abstract

Solid waste management is one of the major difficulties facing the world at large. The presence of tire waste on open field or household creates an ideal breeding ground for disease carrying vermin which pose a threat to humans. There are various technologies studied for efficient use of waste tires such as pyrolysis which results in char, oil and non-condensable gases. The tire pyrolytic oil (TPO) has been reported to have similar properties to commercial diesel fuel. The current hurdle for use of TPO in commercial diesel engines is the available sulfur content (>1.0 wt%). Disadvantages of sulfur in liquid fuels are its ability to reduce the life of the engine due to corrosion and the undesirable emission of SO_x that subsequently damages public health and property. There is rising need for development of efficient technologies for desulfurization of such liquid fuels. Beside the conventional hydrodesulfurization, there are other emerging technologies such as; adsorption, oxidation, photocatalytic degradation and biological desulfurization. This chapter reviews the status quo on pyrolysis of waste tires and desulfurization technologies for TPO and other liquid fuels.

2.2 Introduction

The nature of tires makes them extremely challenging to recycle due to the available chemically cross-linked polymer and, therefore, they are neither fusible nor soluble and, consequently, cannot be remoulded into other shapes without serious degradation (Trongkaew et al., 2011). Open dumping of tires pollutes the soil, contaminates underground water and provides ideal breeding grounds for disease carrying vermin such as mosquitos and rats (Uçar et al., 2005). There are various methods reported for the recycling of waste tires such as grinding, retreading, incineration and pyrolysis, although these methods can solve the above-mentioned problem, they also have their own drawbacks (de Marco Rodriguez et al., 2001). Pyrolysis is the heating system of matter in the absence of oxygen, this technology is normally practiced for the thermochemical decomposition of organic compounds. There are various uses of pyrolysis such as turning wood into charcoal, which is an ancient method of charcoal production on an industrial scale. The thermal decomposition of tires by pyrolysis produces char, steel, non-condensable gases and oil

(Laresgoiti et al., 2004).

The percentage yield and composition of TPO obtained from pyrolysis of scrap tires is strongly dependent on the rubber composition and operating conditions; temperature, heating rate, pressure and residence time in the conventional fixed bed pyrolysis reactor (Huang and Tang, 2009; Abdul-Raouf et al., 2010). The yield of TPO increases with a decrease in the reactor temperature while inversely, the gas yield increases with an increase in the reactor temperature. Pyrolysis of waste tires is normally carried out at a temperature and pressure of 480 – 520 °C and 10 kPa, respectively (Roy et al., 1999). These operating conditions are all dependent on the desired products outcome (oil, char and gas ratio). The composition of oils derived from waste tires has common properties to commercial diesel fuel (Cunliffe and Williams, 1998). The problem associated with the light oil derived from pyrolysis of waste tires is that it has a high sulfur content (>1.0 wt.%). This high sulfur content is attributed by the vulcanization stage during tire manufacturing and therefore this emits harmful sulfur oxide (SO_x) gases to the atmosphere when combusted in diesel engines. These gases react with water in the atmosphere to form sulfates and acid rain which damages buildings, acidifies soil, and ultimately leads to loss of forests and the ecosystems (Shiraishi et al., 2002). The above-mentioned hurdle calls for pre-desulfurization treatment of TPO before use in diesel engines.

Table 2.1: Typical composition of a scrap tire (Williams and Bottrill, 1995).

Elemental composition (wt%)		Proximate analysis (wt%)		Gross Calorific value (MJ/kg)
C	85.9	Volatiles	66.5	40.0
H	8.0	Fixed Carbon	30.3	
N	0.4	Ash	2.4	
S	1.0	Moisture	0.8	
O	2.3			
<i>Ash 2.4</i>				

Desulfurization of TPO is necessary due to the increasing stringent environmental regulations worldwide. Hydrodesulfurization (HDS) is the commonly practiced technique for the removal of sulfur species in liquid hydrocarbons. During HDS technique, the high pressurized inlet hydrogen gas reacts with the sulfur species in the liquid hydrocarbons to form a hydrogen sulphide (H₂S) product (Jantaraksa et al., 2015). The formation of H₂S from

this reaction operates at very high pressure (30 – 130 atm) and temperature (300 – 400 °C). HDS is a catalyst supported process for the effective removal of sulfur compounds, and therefore there is a range of catalysts studied (Moses et al., 2009). TPO contains species of sulfur in a form of cyclic compounds (sulfur-polycyclic aromatic hydrocarbons) such as dibenzothiophene (DBT) and its derivatives (Williams and Bottrill, 1995). Thus, this pose a huge drawback as HDS technique struggles in efficient removal of this complex sulfur compounds. Moreover, the production of liquid hydrocarbons from waste tires is normally practiced on a small-scale production, therefore unlike in big oil refineries where hydrogen is supplied as a by-product from other processes, this will be much costlier as it should be purchased elsewhere.

Oxidative desulfurization (ODS) is the most promising technique for efficient reduction of sulfur compounds in liquid hydrocarbons due to its low energy consumption, temperature (~ 50 °C) and atmospheric pressure (Srivastava, 2012). In the previous years, most researchers focused on reducing the available sulfur species in TPO by adjusting the operating conditions within the system than coming up with a post treatment process (Unapumnuk et al., 2008). The most commonly known oxidant for the ODS technique is H₂O₂ (hydrogen peroxide). This is due it its friendliness to the environment as compared to other oxidising agents such as HNO₃ (nitiric acid) and H₂SO₄ (sulfuric acid). The efficiency of H₂O₂ for ODS is dependent on various catalyst such as HCOOH (formic acid), CCl₃COOH (trichloroacetic acid), CF₃COOH (trifluoroacetic acid) and methyltrioxorhenium (Shiraishi et al., 2002). The oxidised sulfur species present in the liquid hydrocarbons become more polarized as compared to the rest of the liquid, and therefore this enhances its removal by either solvent extraction or adsorption technique (Ukkirapandian et al., 2008).

Photocatalytic desulfurization of oil is normally conducted under the presence of UV irradiation because sulfur species cannot be degraded under the presence of visible light (Li et al., 2012). The above-mentioned statement is supported by the principle of bend gaps. Most published photo-catalysis studies use TiO₂ as a catalyst due to its high reactivity nature, and on that note, TiO₂ can only absorb UV light ($\lambda < 387\text{nm}$). This wavelength only accounts 3 – 5% of the total energy from the sun because of its wide band gaps of 3.2eV, therefore this hampers with the convenience of using natural sunlight (Zhang et al., 2010; Mishra et al., 2011). The use of UV light for the removal of sulfur-polycyclic aromatic hydrocarbons found in TPO is a promising technology and this is not only for TPO but also for the liquid hydrocarbons industry.

Adsorptive desulfurization is another promising technique for desulfurization of liquid hydrocarbons. There are numerous adsorbents available (zeolite, alumina, zinc oxide, activated carbon etc.) for the adsorption of sulfur compounds from liquid hydrocarbon fuels (Lee et al., 2002). It is known that only a few special adsorbents are capable of efficiently removing complex sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) species from liquid hydrocarbon fuels (Kim et al., 2006). Activated carbon is the most widely used adsorbent for the removal of heavy metals and other organic/inorganic pollutants found in waste water. Properties of activated carbon which makes it highly favourable in various industries include good porosity and high surface area, and subsequently high adsorption of the desired compound species depending on its application (Tao et al., 2009; Demirbas et al., 2009). Development of new sorbents for π -complexation have been exploited in recent years (Yang, 2003). Commercialization of such sorbents has already been employed in numerous industries and they promise tremendous potential for future applications in separation and purification processes for both chemical and petrochemical industries. This is due to the suggestion that chemical complexation bonds are much stronger than those van der Waals and electrostatic forces, thus resulting in higher selectivity (King, 1987). Most hydrocarbon separation such as olefin/paraffin separation and purification employed solutions containing silver (Ag^+) and cuprous (Cu^+) ions (Takahashi et al., 2002; Takahashi et al., 2001)

Using biotechnology as one of the methods for the removal of sulfur compounds in liquid hydrocarbons has long been proposed and has been given revived attention by current researcher's due to the idea of greener technology applicable to most petroleum industries (Monticello, 2000). The greener technology idea resulting from the use of bio-desulfurization in liquid hydrocarbons is because of researcher's knowledge of enzymology and genetics. This knowledge strongly assists in the bioprocessing of bacterial metabolic pathway which connects into viable commercial products. The most utilized bacterial species for desulfurization of liquid hydrocarbon is *Rhodococcus*, this bacterium has been exploited by various researchers due to its ability to catabolize an extensive range of compound found in liquid hydrocarbons (Maghsoudi et al., 2001; Monticello, 2000). During the metabolism of aromatic compounds found in liquid hydrocarbons such as TPO by *Rhodococcus* bacterial species, the aromatic compounds are firstly oxygenated to form a diol (two alcohol groups).

Thereafter the oxidized ring is chopped with intra/extradiol mechanisms, therefore opening the ring and exposing the substrate to further metabolism.

The current environmental regulations are applying stringent forces to petroleum industries concerning the allowable sulfur content in liquid fuels. These regulations are working towards 0% sulfur content in future, therefore it is a great motivation for researchers and industries to collaborate and make the 0% sulfur content in liquid fuels a reality. This paper reviews the current studies for pyrolysis of waste tire and multiple desulfurization technologies used for treating TPO globally. This will also include detailed specification on operating conditions of a pyrolysis reactor in achieving desirable products in terms of composition and ratios.

2.3 Effects of sulfur on the ecosystem

The anthropogenic emission of sulfur dioxide (SO_2) and other harmful gases such as carbon dioxide (CO_2) and nitrous oxides (NO_x) have a tremendous negative impact to the ecosystem. Although some of the natural and physical actions such as volcano and fire do cause air pollution, anthropogenic emission is the main basis of air pollution worldwide. Human kind, marine species and all animals' species in general are directly affected by the emission of this harmful gases (Pope III et al., 2007). These harmful pollutants found in the environment differ by their chemical composition, reaction properties, their rate of acceleration from one point to another within a given time, and ultimately their impact on human beings, animals and plants health (Schell et al., 2006). The presence of sulfur dioxide found in the atmosphere is normally because of combustion of fossil fuels which are known to contain a certain percentage of sulfurous compounds. Combustion of this sulfurous compounds in the atmosphere can lead to reaction with oxygen to form sulfur dioxide and this eventually leads to acid rain (Koch et al., 1996). Acid rain is not the only known drawback for combustion related pollutants, Shiraishi et al. (1998) reported that smog, global warming and water pollution are environmental pollution hurdles caused by the combustion of fossil fuels. Current standards and regulations for the allowable emission of sulfur dioxide are becoming more and more stringent globally.

The inhalation of this gases by human beings has been reported to cause tremendous health instabilities. The presence of this harmful particles in the atmosphere because of engine exhaustions are known to cause short term and chronic diseases ranging from minor upper

respiratory irritation, heart disease, acute respiratory infections in children, lung cancer, asthmatic attacks, bronchitis in adults and aggravating pre-existing heart and lung diseases (Kampa and Castanas, 2008). All the stated diseases are very well known to reduce the life expectancy of human beings.

The availability of this toxic material within the atmosphere also find its way to the food chain and the plantation system. Chemical compounds such as dioxins are emitted to the atmosphere because of incomplete combustion of materials containing chlorine (e.g. tires) and whenever these materials are burned within an open environment. On emission to the open environment, this dioxin species tends to be deposited to the soil and water. The mechanism used by dioxins species to enter the plants and the food chain it is through air and dust or pesticides, this occurs due to bio-accumulation mechanism and the bound stability of dioxins to lipids (Schechter et al., 2006). Therefore, desulfurization and other detoxing technologies are of vital importance for the removal of chemical species which may cause harm to the environment during post application of that material or product.

2.4 Waste tires vacuum pyrolysis

Vacuum pyrolysis operating conditions have a tremendous impact on the distribution of compounds in the composition and the yield of TPO. Numerous researchers have reported the effect of tire pyrolysis temperature and heating rate on the elemental composition, oil yield and type of compound found in TPO. Results published by (de Marco Rodriguez et al., 2001) indicates that pyrolysis temperature (300 – 700 °C) has no significant impact on the elemental composition, H/C ratio and the Gross Calorific Value (GCV) of the TPO. Although the effect of temperature from 300 – 700 °C (with 100 °C difference) showed a much substantial impact on the TPO yield and the chemical compound in TPO. Tables 2.2 and 2.3 represent the effect of temperature reported by (de Marco Rodriguez et al., 2001) on TPO yield and type of compounds found in TPO, respectively.

Table 2.2: Tire pyrolysis yield (wt%) at different temperatures

Pyrolysis temperature (°C)	300	400	500	600	700
Solid yield	87.6	55.9	44.8	44.2	43.7
Liquid yield	4.8	24.8	38.0	38.2	38.5
Gas yield	7.7	19.3	17.2	17.5	17.8

Table 2.3: TPO types of compounds (analyzed using GC-MS)

Pyrolysis temperature (°C)	300	400	500	600	700
Aromatics	34.7	59.3	62.4	75.6	57.4
Aliphatics	59.2	34.9	31.6	19.8	37.0
Nitrogenated	4.5	3.7	4.2	2.6	3.8
Benzothiazol	1.6	2.1	1.8	2.0	1.8

Table 2.2 shows that an increase in the reaction temperature decreases the solid yield while increasing the liquid yield. At 500 °C, there is no major change in the three materials and this temperature can be regarded as the optimum temperature. Table 2.3 above shows that TPO consist of mainly aliphatic and aromatic compounds. This is due to the mother converter styrene butadiene rubber (SBR). It has been reported that SBR typically comprises of 25% styrene and 75% butadiene (Benallal et al., 1995). Benallal et al. (1995) reported tire pyrolysis oil yield and types of compound under 510 °C pyrolysis temperature. The TPO naphtha contained high concentrations of aromatics, olefins and iso-alkanes (45, 22 and 15 vol. % respectively). Since SBR contains three quarters of butadiene which is an aliphatic compound, it is expected that the composition of TPO contain high concentration of aliphatic compounds to aromatic compounds. The high concentration of aromatic compounds in TPO is due to the suggested secondary reactions of compounds such as ethylene, propylene and butadiene which gives aromatic and polyaromatic products such as benzene and naphthalene at high reaction temperatures (Wolfson et al., 1969). From table 3 above it can be stated that, waste tire pyrolysis temperature is directly proportional to aromatic compounds concentration and inversely proportional to the aliphatic compounds concentration, until a temperature of 600 °C. This trend shows high concentrations of aliphatic compounds at low temperatures and lower concentrations at higher temperatures, with aromatic showing a contrary behaviour and it has been reported by other researchers as well (Wolfson et al., 1969; Williams et al., 1990). The suggested mechanisms which occurs within the batch reactor is firstly cracking of the long chain polymers found in the SBR to small chain mostly conjugated and non-conjugated double bonded hydrocarbons. Cyclization of the conjugated double bond hydrocarbons results in formation of aromatic compounds; thus, this is a justification of high aromatic hydrocarbons concentration in TPO.

The non-conjugated hydrocarbons tend to form olefinic compounds (Katheklakis et al., 1990). The very simplest and well-known cyclization mechanism of the conjugated double bonded reaction is the Diels-Alder reaction, see figure 2.1.

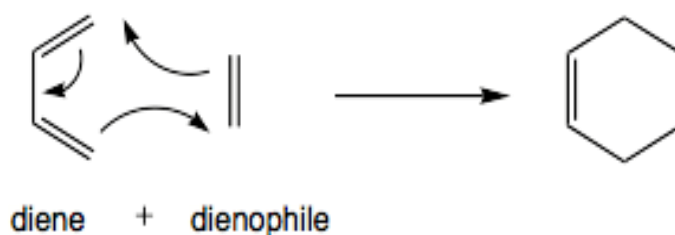


Figure 2.1: The Diels-Alder cycloaddition reaction for the formation of cyclohexene (substituted) from diene (substituted) and olefin (substituted)

2.5 TPO distillation

Raw TPO straight from the pyrolysis reactor is not suitable for direct use due to the available impurities such as suspended solids and the undesirable hydrocarbons for use as a diesel fuel. There are various researchers who reported the use of distillation practice to purify raw TPO before further use, mostly as a substitute for diesel fuel in internal combustion engines. (de Marco Rodriguez et al., 2001) reported that about 30 wt% of raw TPO is easily distillable by simple distillation between the boiling temperature range of 70 – 210 °C. This boiling point range is said to be like that of commercially produced petrol fuel from crude oil. Subsequently further distillation of the same oil produces about 60 wt% liquid fuels with the boiling point range (150 – 370 °C) of commercially produced diesel from crude oil. This fraction was distilled using an automatic distillation test at atmospheric pressure in comparison with commercial diesel fuel, see table 2.4 for their results.

Table 2.4: TPO 150–370 °C fractional distillation data (pyrolysis carried out at 500 °C)

Temperature (°C)	Distilled (vol%)	
	TPO	Commercial diesel
157.5	1.0	0.0
160	2.2	0.2
170	7.5	2.0
180	13.3	6.5
190	19.8	10.3

200	24.3	14.8
210	27.5	18.8
220	31.4	22.3
230	35.0	26.4
240	37.7	31.6
250	40.9	35.1
260	44.6	39.9
270	47.8	45.3
280	51.2	51.6
290	54.8	59.4
300	59.3	66.3
310	63.6	71.6
320	67.8	79.9
330	72.5	84.3
340	78.0	89.4
350	84.4	91.5
360	91.7	94.8
370	99.7	94.8

de Marco Rodriguez et al. (2001) suggested that the two TPO products (petrol and diesel like distillates) obtained at the two temperature ranges must be further analyzed to quantify their possible potential. This will include analysis on the induction time, corrosion properties, octane and cetane number etc. Based on the analysis results, a clear indication will be set on whether to use TPO product as direct substitutes to commercially known products or maybe use this TPO products as feed stock/blending for production of already commercialized products.

2.6 TPO characterization

It has been reported by various researchers that TPO has the same properties as diesel engine oil (Cunliffe and Williams, 1998; Banar et al., 2012). The percentage yield and composition of TPO obtained from pyrolysis of scrap tires is strongly dependent on the rubber composition and operating conditions; temperature, heating rate, pressure and residence time in the conventional fixed bed pyrolysis reactor (Huang and Tang, 2009; Abdul-Raouf et al., 2010). The yield of TPO increases with a decrease in the reactor temperature

while contrariwise, the gas yield increases with an increase in the reactor temperature (Islam et al., 2008; Laresgoiti et al., 2004). (Banar et al., 2012) reported characteristics of pyrolytic oil obtained at different temperatures (350 – 600 °C) and heating rates (5 and 35 °C/min). The maximum oil yield of 38.8% (solid – 34% and gas – 27.2%) was achieved at a heating rate of 5 °C/min and a temperature of 400 °C. Using mainly the American Society for Testing and Materials (ASTM) methods; ASTM D-93, ASTM D-1298, ASTM D-88, ASTM D-86, CHNS-O Elemental Vario EL III and C200 calorimeter (ASTM D-5865), the general fuel properties of TPO that is; the flash point, density, viscosity, distillation, elemental composition and GCV were determined respectively. The same oil was characterized using the instruments listed on Table 2.5 below. Almost all researchers in this field have used these characterization techniques to quantify different components found in TPO. This is mainly because TPO comprise of several and diverse components.

Table 2.5: Characterization of techniques and their functions

Characterization technique	Function
FT-IR – Fourier transform infrared spectrometer	to determine the functional groups, present in the TPO
GC-MS – gas chromatography -mass spectroscopy	to determine the different chemical compounds found in TPO
H NMR – hydrogen nuclear magnetic resonance	to determine molecular structures available in TPO

For environmental purposes, the availability and number of toxic species such as polychlorinated dibenzodioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) were determined (Banar et al., 2012).

Results obtained by various researchers using some of the mentioned characterization techniques indicated that there is only a slight difference in properties of TPO and the commercial diesel fuel and gasoline, see Table 2.6 for comparison. Properties of commercial diesel and gasoline where obtained from the following authors (Chung et al., 1999) and (Arpa and Yumrutas, 2010), respectively.

Table 2.6: Properties of TPO reported by different authors in comparison with commercial diesel and gasoline

Parameters/ Element (wt%)	Authors						Commercial products	
	Banar et al., 2012		Islam et al., 2008	Cao et al., 2009	Laresgoiti et al., 2004	Cunliffe and Williams 1998	Diesel	Gasoline
	5 °C/min (400 °C)	35 °C/min (400 °C)	475 °C		400 °C	450 °C		
C	68.91	79.61	85.86	84.35	85.9	85.6	87.4	85.4
H	9.6	10.04	9.15	6.73	10.6	10.4	12.1	14.1
N	2.05	0.94	0.65	0.39	0.3	0.5	370 ppm	200 ppm
S	1.07	0.11	1.25	1.6	1.1	1.4	1.39	280 ppm
O	18.37	9.3	2.87	2.58	2.1	2	2.1	
H/C	1.67	1.51	1.27	0.96	1.49		1.76 - 2.24	1.98
GCV (MJ/kg)	42.61	42.66	42	39.1	42.6	42.6	45.5	43.9
Density (kg/m³)	820	830	957	962			838	780
Viscosity cSt	0.95 ^a	1.01 ^a	4.75 ^b	6.38			2.1 ^a	
Flash point °C	61	65	≤ 32			14	54	43

^a at a temperature of 50 °C

^b at a temperature of 30 °

GVC - Gross Calorific Value

The general elemental analysis of the TPO from all the authors are consistently within the same range. These results were obtained at reaction temperatures ranging from 400 – 475 °C, which too consistently produces the highest percentage oil yield. The only unusual results on the elemental analysis from the table above are reported by (Banar et al., 2012), at a heating rate of 5 °C/min. This indicates that the heating rate has an impact on the elemental composition of the TPO, and therefore for (Banar et al., 2012), 35 °C/min was the optimum heating rate to achieve the elemental properties which are like those of commercial diesel. Other factors which may hamper with the elemental alignment of TPO includes; reactor type and capacity, residence time, shape and type of tires. The GCVs of TPO from all the above studies are close to that of commercial diesel oil and gasoline. The GCV is not affected by the reactor operating conditions and other factors which have shown to have an impact on the elemental outline. The densities reported by (Islam et al., 2008) and (Cao et al., 2009) are much higher than that of commercial diesel. (Banar et al., 2012) reported densities which are like those of commercial diesel density range (820 – 860 kg/m³) for both heating rates of 5 and 35 °C/min, resulting in densities 820 and 830 kg/m³, respectively. Viscosity is one of the most important quantity for any fluid. Diesel engines design specifications consider the viscosity of diesel, and therefore it is of vital importance for TPO to be within the required range for it to be commercialized and applicable in diesel engines. The viscosities on table 6 are within the acceptable range to be used in diesel engines. It is also important to quantify the flash point of liquid hydrocarbons, so as identify the conditions or maybe in some occasions design the storage equipment. (Banar et al., 2012) reported the flash points of 61 and 65 °C for heating rates 5 and 35 °C/min, respectively. These results indicate that both fluids can easily be stored under room temperature and they are also close to the flash point temperature of commercial diesel oil which is 54 °C. (Cunliffe and Williams, 1998) reported the lowest flash point temperature of 14 °C, which means that the storage facility for their TPO should be tailored to avoid potential heat sources such as the sun, furnace etc.

The functional groups found in TPO are quantified using the FT IR analyzing spectroscopy. The available functional groups found n TPO includes; alkanes, ketones or aldehydes, alkenes and aromatics chemical class (Banar et al., 2012). Table 2.7 summarizes some of the FT IR results reported by multiple authors for TPO.

Table 2.7: The FT-IR functional groups and the indicated compounds of TPO

Frequency range (cm ⁻¹)	Authors				Functional groups	Class of compounds
	Islam et al., (2008)	Banar et al., (2012)	(González et al., 2001; Williams et al., 1990)	Williams et al., (1990)		
3600 – 3250					O-H stretching	Alcohol, phenols or carboxylic acids
3250 – 3100					C-H stretching	Aromatic compounds
3100 – 3000					C=C stretching	Alkenes
3000 – 2800					C-H stretching	Alkanes
1750 – 1650					C=O stretching	Aldehydes or ketones
1650 – 1605					C=C stretching	Alkenes
1600 – 1545					C-C stretching	Aromatic compounds
1520 – 1115					C-H bending	Alkanes
1115 – 1000					C-H in-plane bending	Aromatic compounds
1000 – 845					C=C stretching	Alkenes
810 – 660					C-H out-of-plane bending	Aromatic compounds

The shaded areas are within the specified frequency range

From Table 2.7 above it can be suggested that all tire produced fuels should contain alkanes, alkenes and aromatic compounds, despite the type of tire used to produce the fuel. This is due to the common stretching vibrations and bend at $3000 - 2800\text{ cm}^{-1}$, $1650 - 1605\text{ cm}^{-1}$, $1600 - 1545\text{ cm}^{-1}$ and $1520 - 1115\text{ cm}^{-1}$ found by all authors cited in table 7 which represents the functional groups C-H stretching, C=C stretching, C-C stretching and C-H bend falling under a class compounds alkanes, alkenes, aromatics and alkanes, respectively. Other class of compounds are also found in TPO as reported by various researchers. Although it should be known that in most cases these compounds are present in very low concentrations. For example, the presence of ketones or aldehydes reported by (Banar et al. 2012; Williams et al.1990) represented by the C=O stretching between 1650 and 1750 cm^{-1} , had no much intense transmittance which indicates low concentration of these species.

The H NMR analysis reported by (Banar et al., 2012) and (Islam et al., 2008) are represented on Table 2.8.

Table 2.8: H NMR results of TPO from different authors

Type of hydrogen	Chemical shift (ppm)	Percentage of total hydrogen (mol%)		
		Banar et al., 2012		Islam et al., 2008
		5 °C/min	35 °C/min	
Aromatics	9.0 - 6.5	9.43	12.95	13.31
Phenolic (OH) or olefinic proton	6.5 - 4.5	1.02	2.91	9.74
Aliphatic adjustment to oxygen/hydroxyl group	4.5 - 3.3	0.98	1.53	-
Aliphatic adjustment to aromatic/alkane group	3.3 - 1.8	19.26	15.62	17.55
Other aliphatic (bonded to aliphatic only)	1.8 - 0.4	69.31	66.99	59.4

GC-MS analysis has been performed by many researchers to quantify the concentration of aliphatic and aromatic hydrocarbons found in TPO. The TPO naphtha-like fraction contains high percentages of benzene, toluene and xylene fraction (Pakdel et al., 1991).

The most dominant chemical species reported by numerous researchers from the GC-MS analysis is Limonene, with a concentration range of 70 – 85% purity (Islam et al., 2008; Banar et al., 2012; Cunliffe and Williams, 1998; Laresgoiti et al., 2004). Depending on the rubber composition within the tire and the pyrolysis process conditions, the composition of TPO can either be dominated by aromatic or aliphatic compound species, this is mainly because tire rubbers are composed of SBR which is made of both aromatic and aliphatic compounds (Laresgoiti et al., 2004). (Banar et al., 2012; Islam et al., 2008) reported that aliphatic compound are the most dominant chemical species from their TPO. Whereas on contrary, other researchers found aromatic compounds in abundance as compared to aliphatic compound species (Cunliffe and Williams, 1998; de Marco Rodriguez et al., 2001; Kyari et al., 2005). There is an endless and complex number of alkanes, alkenes and polycyclic aromatic hydrocarbons (PAH) present in TPO. This fact makes it difficult to tabulate the GC-MS analysis results obtained by various researchers around the globe. Reference for GC-MS results can be found on the already mentioned authors within this section (2.6 TPO characterization).

2.7 Studies on desulfurization of TPO and other liquid fuels

2.7.1 Hydrodesulfurization (HDS)

Studies have been reported for desulfurization of liquid fuels using HDS and it can be noted that the HDS technique is strongly dependent on a catalyst and hydrogen to convert the sulfurous compounds to H_2S . (Jantaraksa et al., 2015) studied the removal of sulfur species from TPO through HDS in the presence of a solid catalyst. Jantaraksa et al., (2015) evaluated the removal efficiency of sulfur species using three catalysts supported on a γ -alumina ($\gamma-Al_2O_3$) refractory, these catalysts are namely molybdenum ($Mo/\gamma-Al_2O_3$), cobalt-molybdenum ($CoMo/\gamma-Al_2O_3$) and nickel-molybdenum ($NiMo/\gamma-Al_2O_3$). As it has been entailed in the introduction that the two most vital parameters in HDS process are temperature and pressure; therefore, the effect of H_2 pressure, temperature and time were also evaluated at different catalyst loading to evaluate the percentage removal of sulfur from TPO. The quality of TPO before and after HDS treatment in terms of its heating value, and iodine value for evaluation of saturation was also comparatively evaluated. HDS retains the physical properties of the fuel after treatment. Chemical properties are

mostly affected under harsh conditions (300 – 450 °C and 3.0 – 5.0 MPa). Under such conditions, a loss of octane rating is experienced as result of hydrogenation of olefins. Another drawback encountered in HDS technique is the reaction of H₂S with olefins which results in the regeneration of simplest sulfur compounds such as mercaptans.

2.7.1.1 HDS: reaction conditions and mechanisms

HDS reaction is ideally carried out in a trickle-bed reactor with the liquid fuel running down the column in counter-current with hydrogen gas taking an upward flow. The common operating conditions for such reactors range from 300 – 450 °C and 3.0 – 5 MPa hydrogen gas pressure in the presence of a solid catalyst.

The most common and generally accepted reaction mechanism followed during HDS process is that one proposed by (Houalla et al., 1978; Houalla et al., 1980). There are two main reaction mechanism pathways suggested for desulfurization of DBT and 4,6-DMDBT using the conventional HDS technique:

- Pathway 1: this pathway allows sulfur to be removed without abetting the aromatic rings. The reaction occurs through direct desulfurization or hydrogenolysis where carbon–sulfur single bond is cleaved by hydrogen.
- Pathway 2: this pathway follows hydrogenation process whereby aromatic rings of DBT containing compounds are hydrogenated to 4*H*-or 6*H*-DBT intermediates and are subsequently desulfurized.

The two described pathways are represented in Figure 2.2 as suggested by (Houalla et al., 1978). Pathway 1 which involves direct desulfurization shows that C-S bond hydrogenolysis of DBT gives biphenyl (BiPh). The subsequent reaction involves hydrogenation of the BiPh compound which produces cyclohexylbenzene (CHB). Pathway 2 represents a hydrogenation desulfurization (HYD). This reaction mechanism is said to be HYD because the DBT compound is hydrogenated prior to desulfurization. The two reversible compounds produced from direct hydrogenation of DBT in pathway 2

are tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT). The two compounds THDBT and HHDBT are further hydrogenated, thus desulfurized and form CHB. Further hydrogenation of the products CHB results in a secondary product bicyclohexyl (BiCh).

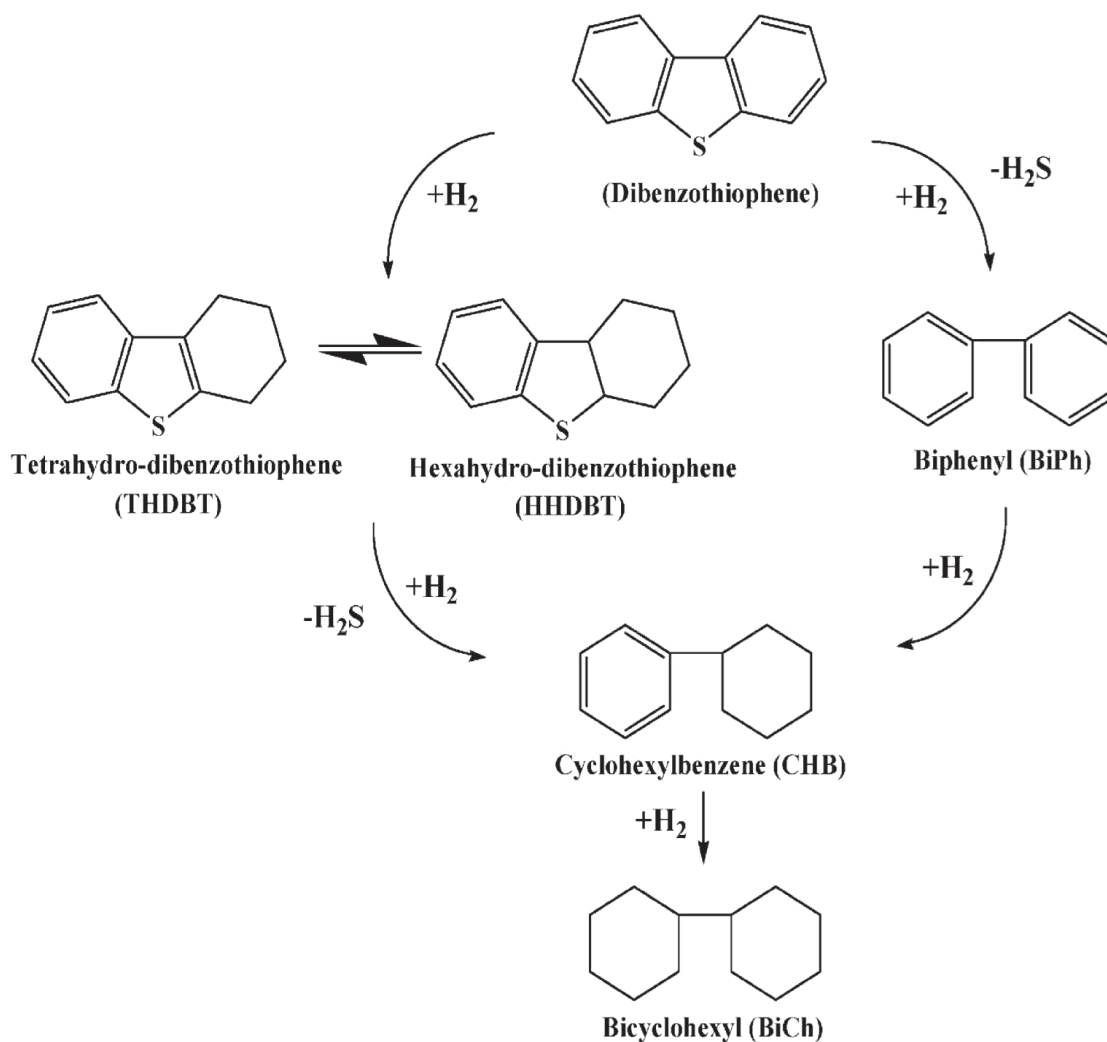


Figure 2.2: Pathways for HDS of DBT at 300 °C and 102 atm in the presence of CoMo/Al₂O₃ catalyst (Houalla et al., 1978).

Pathway 1 reaction is faster than pathway 2. But, through continued studies by Houalla and peers, it has been reported that pathway 2 is the better route for increasing desulfurization extent of the catalyst. This is after a study showing that the yield of CHB at a certain conversion was three times higher with NiMo/Al₂O₃ catalyst

than with CoMo/Al₂O₃. Pathway 2 allows the sulfur atoms to reach the surface of the catalyst more easily as compared to pathway 1, with subsequent easily removal of the sulfur atoms through pathway 2.

2.7.2 Oxidative desulfurization (ODS)

Al-Shahrani et al. (2007) reported an oxidative desulfurization catalytic system making use of 30% H₂O₂ (hydrogen peroxide), CH₃COOH (acetic acid) and Na₂WO₄ (sodium tungstate) catalyst for the removal of sulfur species in diesel. Complete conversion of the sulfur species Dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) to sulfones was achieved at 70 °C in less than 60 minutes. The catalytic process operates at atmospheric pressure and room temperature, and it has proven to remove traces of sulfur species which remained during the HDS process from a few hundred ppm to a minimum limit.

Shiraishi et al. (2001) reported an efficient study of up to less than 0.05 wt% desulfurization of light oil using hydrogen peroxide and acetic acid. Lanju et al. (2007) evaluated ODS of simulated gasoline containing multiple sulfur species of thiophene (TH) and 3-methylthiophene dissolved in n-heptane in hydrogen peroxide (H₂O₂) and formic acid (HCOOH) process system which consisted of metal oxide molecular sieve. The percentage removal sulfur from the mixture was more favourable to the H₂O₂/organic acid reaction as compared to that one of the H₂O₂/inorganic acid reaction mixture (Lanju et al., 2007).

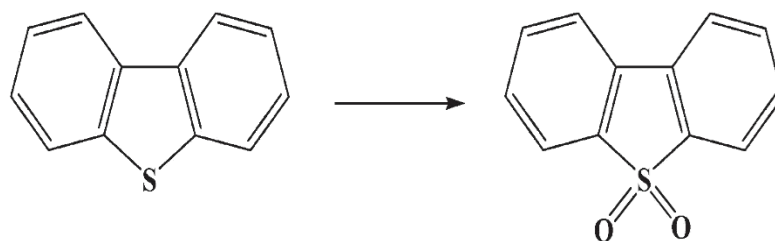
Cedeño-Caero et al. (2008) studied oxidative desulfurization of DBTs using V₂O₅ catalyst supported by alumina, ceria, niobia, titania and silica refractory. Results showed that conversion of sulfur species to their respective sulfones is indirectly proportional to the textural properties or Vanadium content. The sulfur removal reached almost 99% using vanadium on titania catalyst, the trend showed a decrease in total sulfur removal for other support systems in the order: alumina> titania> niobia> Al-Ti mixed oxide> SBS-15. The oxidation process of DBTs for vanadium catalyst supported with niobia or alumina base refractory showed high catalytic performance than all other catalysts (niobia> alumina>

SBA-15> titania> ceria> Al-Ti mixed oxide). However, the best performing catalysed system was observed when using titania-supported catalyst in the presence of an N-compound such as indole (Cedeno-Caero et al., 2008).

Radiation assisted oxidation is another practised method for ODS of hydrocarbon fuels. Irradiation techniques are applied to minimise sulfur species in a known liquid by using radiation induced reaction mechanism of hydrogenation in which hydrogen is a product of radiation-induced hydrocarbon destruction. (Zaykina et al., 2002) justified that radiation is an efficient method for the conversion of sulfur species such as mercaptans and other light compounds to sulfones, sulfuric oxides and acids.

2.7.2.1 ODS: reaction conditions and mechanisms

ODS reactions are normally ran under mild conditions, mostly at atmospheric pressure and temperatures below 50 °C. During the mechanistic behaviour of oxidation, the sulfurous compounds found in the liquid hydrocarbon bonds with one or two atoms of oxygen found in the liquid, this reactive mechanism occurs without breaking any carbon-sulfur bond existing within the liquid, thus yielding sulfoxide and sulfone. The oxidised sulfur compounds are then more polar than other hydrocarbons within the liquid and therefore, can be easily extracted using an extracting solvent such as acetonitrile. Therefore, the representation in oxidation of DBT to sulfone can be presented as: (Srivastava, 2012; Liu et al., 2001; Otsuki et al., 2000; Zannikos et al., 1995)



The reaction mechanisms and kinetics for ODS of liquid hydrocarbons has been studied by various researchers around the globe. (Heimlich and Wallace, 1966) studied the

reaction mechanisms and kinetics of ODS of solution containing dibenzothiopenes (DBT) using hydrogen peroxide and acetic acid as oxidising agents. Their study was held under atmospheric pressure and temperature range of 50 – 100 °C. Under these mild reaction conditions, ODS of DBT showed that acetic acid demonstrated a first order reaction, while hydrogen peroxide gives a second order reaction. The activation energy of the reaction was recorded to be 14 kcal/mol in 64.5% acetic acid and it was also found that the monoxide is oxidised 1.4 times quicker than DBT. Figure 2.3 shows a representative of the oxidation mechanism reported by (Heimlich and Wallace, 1966).

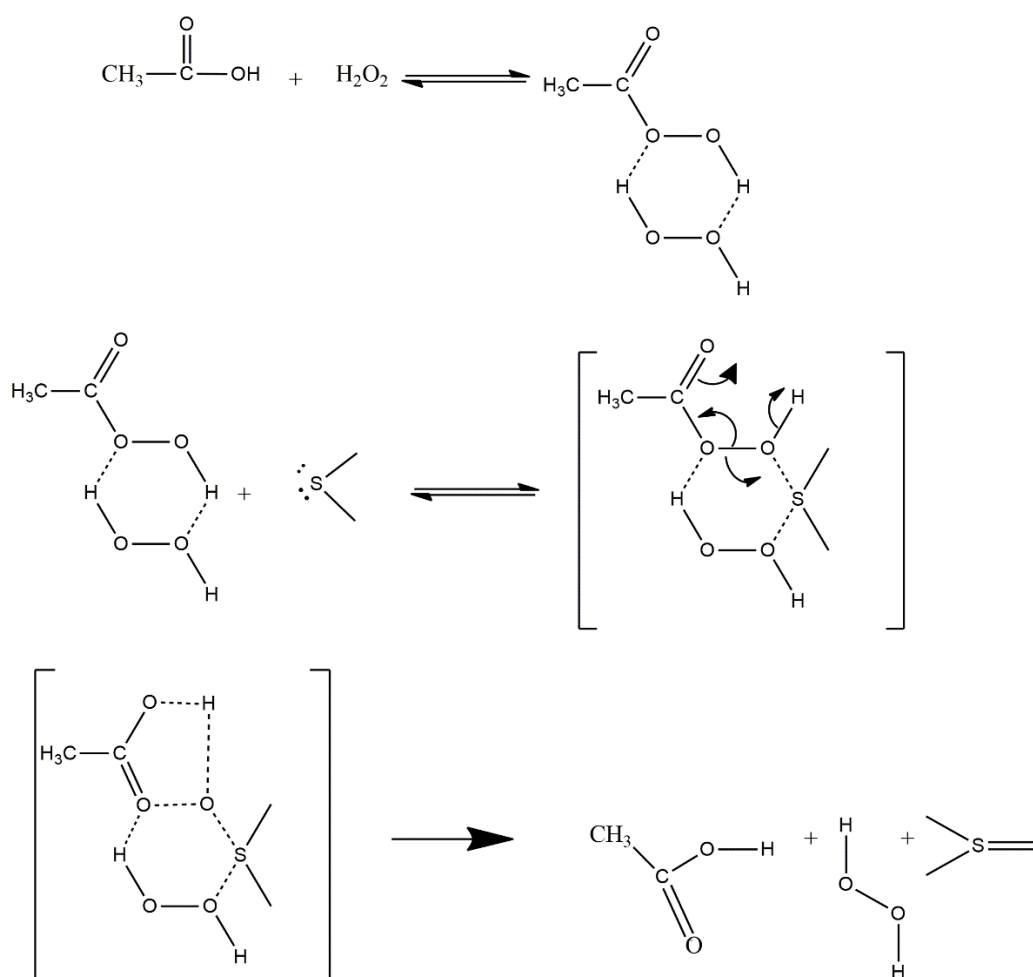


Figure 2.3: Mechanism for oxidation of DBT (Heimlich and Wallace, 1966).

2.7.3 Photocatalytic desulfurization

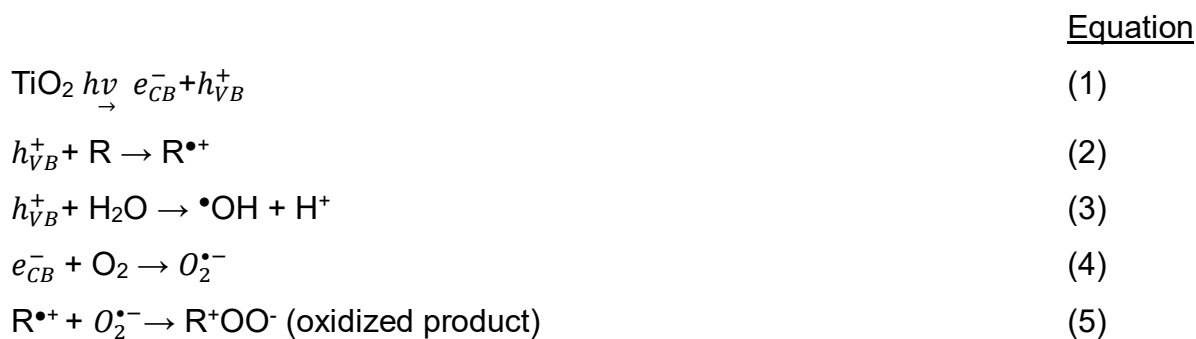
Photocatalytic desulfurization technique is to a certain extent a type of ODS technique. Most studies reported involve the use of irradiation to assist the oxidation process, thus falling under photo-oxidative desulfurization. Photo-oxidative desulfurization of compounds such as DBTs have been studied by various researchers whereby the photo-decomposition using UV light and subsequent removal of the resulting sulfur species by water or acetonitrile is achieved (Pawelec et al., 2011). Hirai et al. (1996) used high pressure mercury lamp ($\lambda=280$ nm) to study the photodecomposition of DBTs dissolved in tetradecane. This practice indicates that the decomposed products were eliminated from the aqueous solution as SO_4^{2-} at ambient temperature and atmospheric pressure. The rate conversion and order of reactivity by different DBTs sulfur species showed the trend $\text{DBT} < 4\text{-MDBT} < 4,6\text{-DMDBT}$.

Trongkaew et al. (2011) investigated the possible removal of sulfurous compound in TPO using photo-assisted oxidative desulfurization technology in the presence of a catalyst (TiO_2 , Degussa P-25). TiO_2 as a catalyst has been exploited by a lot of researchers in different fields such as photocatalysis application in wastewater treatment research field for decomposition of organic compounds found in water (Herrmann, 1999; Chong et al., 2010). This considerable attention given to TiO_2 as a catalyst is due to its environmental friendliness and besides, TiO_2 has a strong oxidising ability (in the presence of UV irradiation), it is cost efficient and is inert to chemical corrosion (Yu et al., 2007). Trongkaew et al. (2011) achieved a total of 43.6% (w/w) removal of sulfurous compounds from an initial concentration of 0.84% (w/w) under the following reaction conditions; dosage of 7 g/L TiO_2 catalyst, $\frac{1}{4}$ (v/v) blend of TPO/acetonitrile under atmospheric pressure at 50 °C in the presence of bubbled air. Analysis obtained using gas chromatography – flame photometric detector (GC-FPD) and high-performance liquid chromatography (HPLC) indicated that the oxidised sulfurous compounds in the TPO had higher polarity because of photo assisted oxidation and therefore this mobilized their ability to dissolve and be easily separated using distilled water.

2.7.3.1 Photocatalytic desulfurization: reaction conditions and mechanisms

The rate of any chemical reaction is affected by several operating conditions, specifically operating parameters. In photocatalysis the rate of disappearance of a species to form another species is affected by the presence and adjustment of the following parameters; solvent, catalyst type and dosage, oxygen flow, pH, reaction temperature and source of light (Habibi and Vosooghian, 2005). The general trend for the effect of catalyst dosage in photocatalytic desulfurization for removal of polycyclic sulfurous compounds in liquid hydrocarbons is normally represented by a steady increase in percentage removal until equilibrium is reached and thereafter a sudden slightly fall. (Habibi and Vosooghian, 2005) indicated that an increase in TiO_2 dosage creates more surface area for photo-assisted reaction in the presence of water and air (for oxygen supply) to produce active oxygen species. This oxygen species generated include; hydroxide anion ($\bullet\text{OH}$), peroxy ion ($\text{O}_2^{\bullet-}$) and hydrogen peroxide (H_2O_2). The presence of this oxygen species in the solution subsequently react with organic materials under the principle of photocatalytic oxidation.

The suggested mechanism of photocatalytic degradation of polycyclic sulfur compounds using TiO_2 as a catalyst have been reported by numerous researchers for desulfurization purposes (Trongkaew et al., 2011; Vargas and Núñez, 2010; Abdel-Wahab and Gaber, 1998). During this mechanism, all researchers came up with 5 equations represented below.



The reaction conditions including TiO_2 and UV light generates an electron from the valence band of TiO_2 and this electron is transported to the conduction band (equation 1), therefore generating a hole in the valence band (h_{VB}^+) and an electron in the conductive

band (e_{CB}^-). The holes therefore subsequently react with organic substrates (sulfurous compounds in TPO) which generates free radicals (equation 2) of the desired chemical species. The hole correspondingly reacts with water molecules to generate hydroxide anion ($\bullet\text{OH}$) and proton (H^+) (equation 3). The generated electron (e_{CB}^-) from equation 1 reacts with dissolved oxygen to produce superoxide radicals ($\text{O}_2^{\bullet-}$) (equation 4) which subsequently reacts with the free sulfurous radicals to form an oxidized product (equation 5) which is highly polarized as compared to the rest of the solution (Gaya and Abdullah, 2008; Hoffmann et al., 1995; Clennan, 2001).

2.7.4 Adsorptive desulfurization

Adsorption of sulfurous compounds from liquid hydrocarbons is conventionally studied under a two-stage process, which firstly includes oxidation and thereafter adsorption of the oxidised sulfur species (de Luna, Mark Daniel G et al., 2014). Therefore, with that noted, it can be agreed that this type of adsorption falls under other methods of ODS technique. (Tsietzi et al., 2014) developed a process system for the removal of sulfur species found in TPO using molecular sieves (crystalline alumina-silicates) to enhance the gas-liquid phase oxidative adsorption performance. A simple distillation was setup to generate vapours of TPO at 300 °C, thereafter the gas phase was promoted to the oxidative adsorption bulb with packed iron oxide and molecular sieve (stage 1). On completion, the gas phase product was condensed and thereafter transported to the liquid phase adsorption tube with activated carbon black for final adsorption reaction (stage 2). During the first stage of this process, a total sulfur removal of 19.6% was achieved. Stage 2 indicated that a further 3.6% sulfur removal can be achieved by using activated carbon black. It has also been reported that 23.6% of the total initial sulfur was removed during the dehydration stage as low boiling point mercaptants, sulphides and disulphides.

2.7.4.1 Adsorptive desulfurization: reaction conditions and mechanisms

The behaviour and rate of adsorption process is studied using various models such as kinetics and isotherms. Adsorption kinetics basically describes the rate of adsorption and they show the uptake rate of adsorbate, and controls the residual time of the whole process. Adsorption isotherms are used to describe the mechanism of how adsorbate

ions interact on the surface of the adsorbent (Ania and Bandosz, 2005). (Wen et al., 2010) reported desulfurization isotherms and kinetics of heterocyclic sulfur compounds onto activated carbon. The isotherm model indicated that activated carbon used in their study presents a highly heterogeneous surface for adsorption of DBT. An increase in adsorption capacity with an increase in temperature was experience and therefore this indicates chemisorption mechanism (Wen et al., 2010).

2.7.4.2 Adsorption isotherms

Adsorption isotherms are basically developed to evaluate the capacity of any adsorbent for the adsorption of molecules, ions or atoms. They constitute the first experimental information, which is generally used as a tool to differentiate among different adsorbents and thereby choose the most appropriate one for an application. The shape of the isotherms is the first experimental tool to identify the nature of a specific adsorption phenomenon, and it is convenient to classify the most common type's phenomenon (Moreno-Castilla, 2004).

Adsorption equilibrium is often formulated by two empirical models, the Langmuir and Freundlich equations. These two models have been widely used because they are simple and only two parameters are needed in the calculations (Chen et al., 1996).

For the Freundlich isotherm

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

K_f and n are the constants for the Freundlich model related to the adsorption capacity and intensity of adsorption, respectively (Yu et al., 2003). This isotherm describes equilibrium on heterogeneous surfaces (Günay et al., 2007) i.e. the energy of adsorption is not equivalent for all adsorption sites, which is a more realistic assumption than the Langmuir isotherm.

For the linear traditional Langmuir isotherm,

$$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \left(\frac{1}{q_m} \right)$$

This empirical isotherm is based on four hypotheses:

- i. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal
- i. Adsorbed molecules do not interact
- ii. All adsorption occurs through the same mechanism
- iii. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not bond with other molecules which are already bonded to the surface of the adsorbent (Günay et al., 2007).

The empirical constants q_m and k_L for the Langmuir model are related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/g) respectively (Yu et al., 2003; Ören and Kaya, 2006).

2.7.4.3 Adsorption kinetics

Kinetic study is important to adsorption process because it shows the uptake rate of adsorbate, and controls the residual time of the whole adsorption process (Demirbas et al., 2009). There two most widely used kinetic models for adsorption and those are pseudo first-order and pseudo second-order kinetics.

The pseudo first-order equation can be expressed in the linear form as,

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_e and q_t are the amount of adsorbate ions adsorbed (mg g⁻¹) on the adsorbent at the equilibrium and at time t , respectively, and k_1 is the rate constant of adsorption (L min⁻¹). Values of k_1 can be calculated from the plots of $\log(q_e - q_t)$ versus t for different concentrations of the adsorbate.

The pseudo second-order equation can be expressed as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$$

Where k_2 is the rate constant of pseudo second-order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$). The constants can be obtained from plotting $\frac{t}{q_t}$ versus t .

(Muzic et al., 2008) represented kinetic and statistical study for desulfurization of diesel using three types of commercially produced activated carbon materials. In their study, both discussed adsorption isotherms and kinetics were covered. Pseudo-second kinetic model showed best fit in all three adsorbents indicating that adsorption taking place does not involve interparticle diffusion. For equilibrium studies, the better fit was achieved using Freundlich isotherm model which justifies physical adsorption for all three carbon materials. The lowest achieved sulfur concentration for this study was found to be 9.1 mg/kg.

2.7.5 π -Complexation Sorbents and Applications

π -Complexation sorbents have attracted tremendous attention recently due to their selective nature of adsorption. The bond between the sorbent and sorbate is very strong, however their strong nature leads to possible reversible reaction in through mechanical operating conditions such as increased pressure and temperature. This interaction between the sorbate and sorbent depends on the following; as reported by (Yang, 2003).

- The emptiness of the outer-shell s-orbital of the cation found on the sorbent surface;
- The amount of π electrons available on the adsorbate ready to interact with the s-orbital of the cation found on the sorbent surface;
- The number of d-orbital electrons of the cation and their ability to effortlessly get donated to the adsorbate molecules.

The molecular orbital (MO) theory is the known theorem used to study π -complexation and has been applied by multiple researchers in designing specific sorbents for π -

complexation for any given target adsorbate molecule (Chen and Yang, 1996; Huang et al., 1999; Yang et al., 2001; Takahashi et al., 2002).

2.7.5.1 Preparation of Cu^+ -Y and Ag^+ -Y zeolites

There is a variety of cations of the *d*-block metals which can be used for π -complexation adsorption, but the most employed ones are Ag^+ and Cu^+ . It has been reported that there are three types of π -complexation sorbents (Yang, 2003):

- a) Monolayer or near-monolayer salts supported on porous substrates;
- b) Ion-exchange resins; and
- c) Ion-exchange zeolites.

Type (a) and (b) are known to be used for bulk separation, while type (c) is used for purification purposes.

The use of Ag-Y zeolite for commercial purposes has already been employed in multiple purification processes/industries. Ag^+ cation has shown good selectivity for zeolite and the exchange is readily at ambient temperature and pressure conditions and low concentrations. Takahashi et al. (2001) prepared four types of Ag-Y zeolites with different Si/Al ratios. The four used as received zeolites in Takahashi's study were; Na-type Y-zeolite (Si/Al=2.43, or 56 Al atoms/unit cell), NH_4 -type Y-zeolite (Si/Al=6, or 27.4 Al atoms/u.c.), H-type Y-zeolite (Si/Al=15, 12 Al atoms/u.c.), and H-type ultra-stable Y-zeolite (H-USY, Si/Al=95, 0.98 Al atoms/u.c.). All four powder form samples were prepared using the same procedure which involved ion-exchanging the zeolite samples with excess amount (five-fold cation-exchange-capacity) of 0.1M AgNO_3 at room temperature for 24 hours. Na-Y zeolite showed 100% exchange because Ag^+ has a higher selectivity compared to Na^+ (Padin et al., 1999).

Unlike the modest direct preparation of Ag-Y zeolite, preparation of Cu(I)-Y zeolite is not possible with direct ion exchange with Cu^+ because the cuprous salts are water insoluble and mostly readily oxidized to cupric compounds in solution. There are two methods employed for preparation of Cu(I)-Y zeolite through reduction of Cu^{2+} to Cu^+ . First method involves the reduction of Cu^{2+} to Cu^+ through a reducing gas medium and the second one

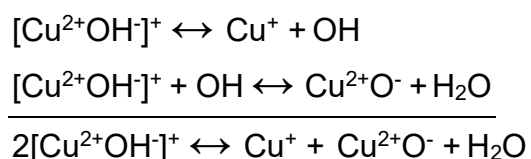
is auto-reduction without a reducing gas.

Multiple studies have been published for reduction of Cu(II) Y zeolite to Cu(I) Y zeolite using CO as the main reducing gas. Following the first study of (Naccache and Taarit, 1971) which involved reducing of Cu(II) Y zeolite to Cu(I) Y zeolite using CO at 400 °C, more researches used the same procedure to study Cu(I) based π -complexation sorbents (Chao and Lunsford, 1972; Huang and Vansant, 1973; Takahashi et al., 2001). In correlation to using CO as the main reducing gas, some authors furthered this study by introducing pre-treatment measures to try and optimize the procedure. (Huang, 1973) reported that treatment of the sorbent by first adsorbing ammonia could help establish a more efficient way of reducing Cu(II) Y zeolite to Cu(I) Y zeolite at a low temperature of 100 °C. Takahashi et al. (2001) used 75% CO in helium gas at 450 °C for 12 hours to completely reduce Cu(II) Y zeolite to Cu(I) Y zeolite. In another study, ethylene at 1 atm and 150 °C was used to reduce Cu(II) Y zeolite to Cu(I) Y zeolite (Cen and Yang, 1989).

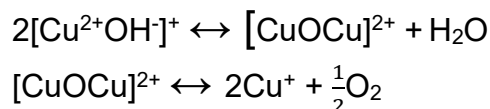
The use of auto-reduction has also drawn attention for the reduction of Cu(II) Y zeolite to Cu(I) Y zeolite. This follows a series of mechanisms that are achieved in an inert environment without the use of a reducing gas. (Takahashi et al., 2000 and Takahashi et al., 2001) prepared Y-zeolite using the known liquid-phase ion-exchange technique (LPIE). The LPIE technique was achieved by first ion exchanging Na-Y with a $\text{Cu}(\text{NO}_3)_2$ solution of 0.5M for 48 hours followed by an auto-reduction of Cu^{2+} to Cu^+ . Helium at 450 °C for 18 hours was used to auto-reduce Cu^{2+} to Cu^+ . Quantification of the copper within the ion exchange solution was found to be equivalent to 5- to 10- fold cation exchange capacity.

There are two main mechanism proposed for auto-reduction of Cu^{2+} in zeolites.

Mechanism 1: (Larsen et al., 1994).



Mechanism 2: (Iwamoto and Hamada, 1991; Sárkány et al., 1992; Valyon and Hall, 1993).



2.7.5.2 Application of Ag⁺-Y and Cu⁺-Y zeolites for desulfurization of liquid fuels

The use of π -complexation sorbents for desulfurization of liquid fuels have been studied extensively in the past years. Hernandez-Maldonado and Yang have completed a series of multiple studies for desulfurization of liquid fuels using π -complexation sorbents prepared using metals such as copper, nickel, zinc and silver. (Hernández-Maldonado and Yang, 2003) studied four π -complexation adsorbents for removal of low concentrate thiophene in either benzene and/or n-octane solution at ambient temperature and pressure. The four adsorbents were namely; Cu(I)-Y, Ag-Y, H-Y and Na-Y zeolites. In this study Cu(I)-Y zeolite have shown good selectivity of thiophene compounds in n-octane solution (760 ppmw sulfur or 2000 ppmw thiophene) for both breakthrough and saturation adsorption following the order Cu(I)-Y > Ag-Y > H-Y > Na-Y and Cu(I)-Y > H-Y > Na-Y > Ag-Y, respectively. In another study (Hernandez-Maldonado and Yang, 2003) used commercial gasoline and diesel to study the selectivity of Cu(I)-Y zeolite for desulfurization of thiophene and its derivatives in commercial fuels. GC-FPD results displayed that the use of π -complexation sorbents is far much better than the conventional HDS technique for desulfurization of thiophene and its derivatives (benzothiophene and DBT). MO theory have shown that π -complexation bond between cations Cu⁺ or Ag⁺ and thiophene compounds are considerably stronger than that with benzene (Yang et al., 2001).

2.7.6 Bio-desulfurization

Intense research has been conducted to study microbiology and molecular biology of competent strains to increase their desulfurization activity. To date even the highest activity reached is not good enough to suggest industrialization of the activity. Schilling et al. (2002) described a method of desulfurization using *Rhodochrous* bacteria. This bacterium has a very advantageous reaction mechanism for desulfurization of liquid

hydrocarbons in a sense that, it can convert DBT into 2-dihydroxybiphenyl (HBP) with subsequent creation of sulphite while the mother structure present in the liquid hydrocarbon remains the same.

Li et al. (2007) exploited *Mycobacterium goodii* X7B facultative thermophilic bacterium for desulfurization of DBT in tetradecane solution. Almost total desulfurization was reached with 99% of sulfur removed, from 200 ppm to 2 ppm. The operating conditions were 40 °C for 24 hours. The use of thermophilic biodesulfurization could be advantageous for industrialization because conventional HDS operates at higher temperatures and therefore such bacteria could handle the harsh conditions. (Le Borgne and Quintero, 2003) further emphasised that thermophilic biodesulfurization reduces the viscosity of crude oil, which makes this process more practicable for industrial application than others.

Kodama enzymatic pathway on DBT is a well-known mechanism for desulfurization of DBT using microbial technology. Unfortunately, the Kodama mechanism is regarded as a destructive enzymatic pathway because it is not specific in removing the sulfur from DBT thiophene ring (Soleimani et al., 2007). Multiple attempts have been made to try and isolate types of aerobic and anaerobic strains that could possibly remove sulfur non-destructively. Regrettably, despite the multiple attempts, all trials were unsuccessful and gave rise to the isolation of more strains with carbon-destructive pathway (Stevens Jr and Burgess, 1987). As a form of ODS, (Kilbane, 1989) proposed a pathway which involves a series of oxidation reactions from DBT to hydroxybiphenyl (HBP). This mechanism is famously known as the 4S pathway as shown in figure 2.4.

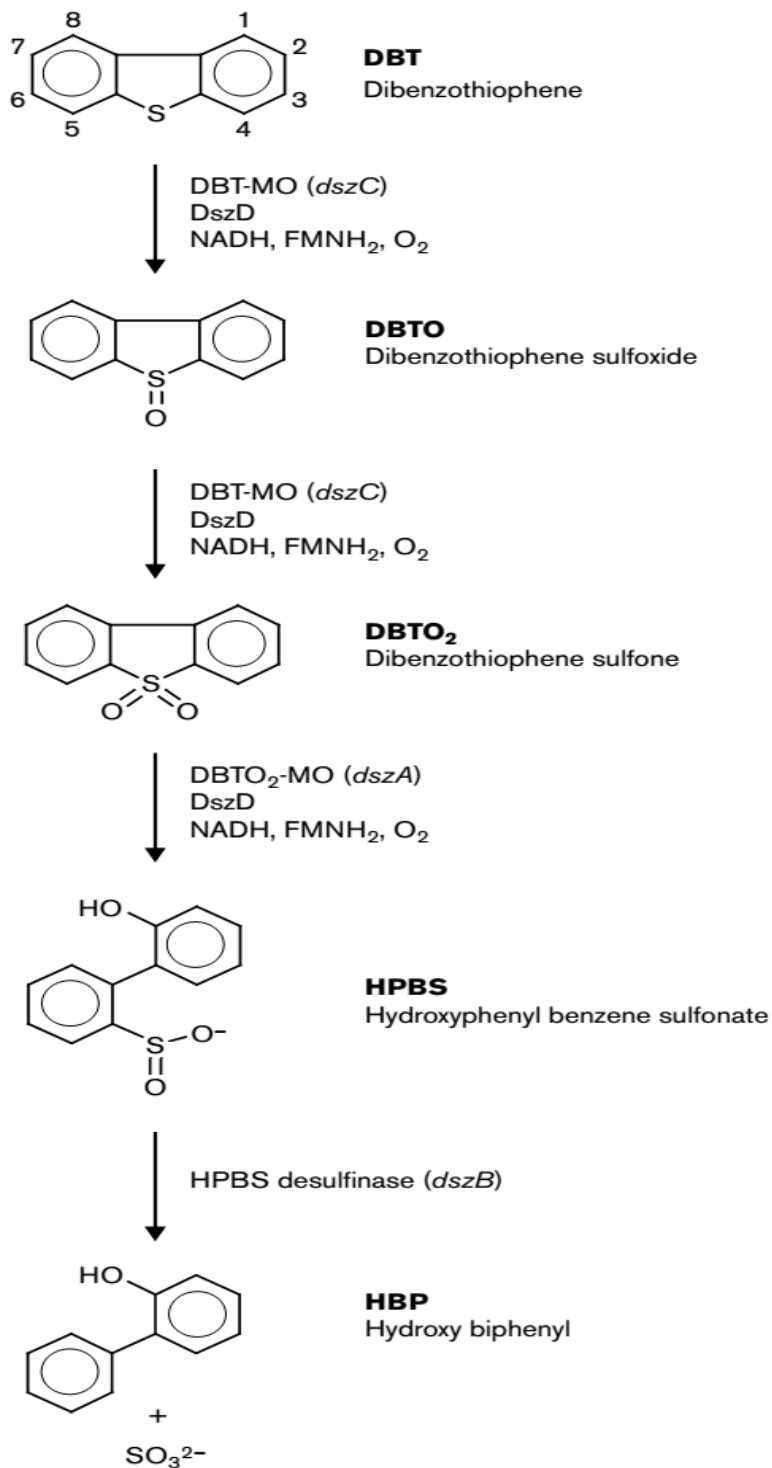


Figure 2.4: The '4S' pathway for the biological desulfurization of DBT and its derivatives.

The key enzymes in the pathway are dibenzothiophene monooxygenase (DBT-MO), a

tetramer encoded by the *dszC* gene, dibenzothiophene sulfone monooxygenase (DBTO₂-MO), a dimer encoded by the *dszA* gene, HPBS desulfonase, encoded by the *dszB* gene, and the NADH: FMNH₂ oxidoreductase encoded by the *dszD* gene (Folsom et al., 1999; Monticello, 2000).

2.8 Conclusion

There is still a great deal of work needed to be done by researchers around the world to enhance innovation of liquid fuels desulfurization technologies to cater for the future stringent regulations. Despite the conventional HDS technique, researchers in the field of desulfurization of liquid fuels have also focused on ODS, adsorptive desulfurization, photocatalytic desulfurization and bio-desulfurization techniques. It can be stated that although HDS struggles in desulfurization of complex sulfur compounds such as DBT, it is still of great importance to study and understand the mechanisms and catalysts involved in the conventional HDS technique. Industrially produced liquid fuels can therefore undergo a two-stage desulfurization process whereby they are first treated using the conventional HDS and later with either ODS, adsorptive desulfurization, photocatalytic desulfurization or bio-desulfurization technique depending on the nature of fuel and desired end properties. This will allow HDS to reduce the sulfur content of the fuel to a few hundred ppmw comprising mainly of the complex sulfur compounds and subsequent desulfurization by the mentioned techniques to a possible complete desulfurization. Fuel properties (GCV, Octane and cetane number, viscosity, flash point etc) are of paramount importance in the petroleum industry. Therefore, as researchers continue searching for new alternative desulfurization techniques, much work still need to be done in retaining the desired fuel properties whilst accomplishing deep desulfurization of the fuel. Some of the extracting solvents are known to partially dissolve in the fuel and thus such an event hampers with the fuel properties. The use of H₂O₂ for industrial purposed is still an economical challenge and therefore, other oxidising agents should be given attention in ODS. For adsorptive desulfurization, π -complexation sorbents have shown better selectivity of complex and non-complex sulfur compound in liquid fuels. Further studies must be carried out to study their reusability and a more economical way of regenerating of the sorbents at lower temperatures.

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CHAPTER 3

3. ADSORPTIVE DESULFURIZATION OF TIRE PYROLYTIC OIL USING ACTIVATED TIRE CHAR

3.1 Abstract

The adsorptive ability of different carbon materials tire char (TC), demineralized tire char (DTC), activated tire char (ATC) and Aldrich supplied commercial activated carbon (CAC) was studied for desulfurization of tire pyrolytic oil (TPO). TPO with initial sulfur content of 7767.7 ppmw was used in this present study. Preparation of ATC was achieved by chemical treatment of raw TC using a potassium hydroxide (KOH) solution and subsequent activation at 800°C in the presence of nitrogen. The thermal behavior, surface microstructure and surface functional groups of the carbon materials (TC, DTC, ATC and CAC) were investigated using thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), respectively. Adsorptive desulfurization of TPO using the carbon materials was performed and they perform in the order CAC>ATC>DTC>TC. Adsorption kinetics were studied and pseudo-first order kinetic model displayed a better fit compared to pseudo-second order model. For isotherm studies, Freundlich isotherm model fitted to the equilibrium data better than the Langmuir isotherm model.

3.2 Introduction

Countries worldwide are exponentially tightening their regulations regarding the allowable sulfur content in liquid transportation fuels such as diesel. This is mostly experienced in developed and developing countries. In the past years the regulations have brought down the level of sulfur in diesel fuel from 500 ppm (parts per million) to 50 ppm. This has really caused a great stir to the petroleum refineries and thus questioning the future and long-term economics of the petroleum refineries. Tire pyrolytic oil (TPO) as a possible alternative to the liquid fuel industry, specifically as a substitute for diesel fuel must also comply with the specified regulations. Currently Asian countries like Japan and the entire European Union (EU) are producing ultra-low sulfur diesel fuel of less than 50 ppm since 2005 (Bu et al., 2011). The EU and US have recently updated their sulfur content limits

to less than 10 and 15 ppm, respectively (Khan and Jhung, 2012; Rabarihoela-Rakotovao et al., 2006). The major driving force for these stringent regulations is the fast-changing climate conditions.

The conventional desulfurization method used by petroleum refineries around the globe is hydrodesulfurization (HDS). HDS only manages to reduce the sulfur content to around 500 ppm. Further deep HDS to achieve ultra-low sulfur fuels is required and consequently comes at a higher cost due to the high pressure and temperature conditions needed to achieve less than 15 ppm sulfur content (Rabarihoela-Rakotovao et al., 2006; Song et al., 2006). This fact has given rise to a search for alternative technologies for desulfurization of liquid fuels. Various methods such as adsorption (Song and Ma, 2003; Song et al., 2006; Fallah and Azizian, 2012; Seredych and Bandosz, 2009), oxidation (Ali et al., 2006; Matsuzawa et al., 2002), bio-desulfurization (Monticello, 2000) and photocatalytic desulfurization (Matsuzawa et al., 2002) have been intensively studied. Among the mentioned technologies, adsorption is regarded as one of the most competitive technology due ambient operating conditions.

The use of adsorption for desulfurization of liquid fuels have been extensively investigated over a range of different adsorbents (Takahashi et al., 2002; Hernández-Maldonado et al., 2005; Dai et al., 2006; Hernandez-Maldonado and Yang, 2003; Yang et al., 2002; Padin et al., 1999). The most exploited adsorbents includes activated carbon (Song and Ma, 2003; Fallah and Azizian, 2012; Zhou et al., 2006; Seredych and Bandosz, 2009; Zhou et al., 2009) and zeolite (Xiao et al., 2008). Activated carbon is the most desirable adsorbent in most processes due to its microstructure, high adsorption capacity and the possible introduction of surface functional groups on the material. Precursors and the process used for preparation of activated carbon have a significant impact on the surface area, microstructure and surface functional groups. The main challenge faced by adsorptive desulfurization of liquid hydrocarbon fuels is selectivity of sulfur compounds of low polarity from non-polar fluid phase (Zhou et al., 2006).

In this present work, we investigated the efficiency of different carbon materials derived from tire char in comparison with commercial activated carbon for the removal of sulfur

compounds found in TPO. Various Kinetics and isotherm models were also fitted to study the type of adsorption taking place.

3.3 Experimental methodology

3.3.1 Materials

TPO with a sulfur content of 7767.7 ppmw and TC with particle size (250 – 850 μm) were purchased from a local pyrolysis plant in Gauteng province, South Africa. A fixed bed pyrolysis reactor charged with automobile tires was used and the reactor is operated under the following conditions; Temperature 600 °C and heating rate 35 °C/min. CAC was purchased at Sigma Aldrich. Nitric acid (HNO_3), potassium hydroxide (KOH), potassium bromide (KBr) and hydrochloric acid (HCl) of analytical-grade reagents (AR) were purchased at Merck Chemicals. Nitrogen gas (N_2) cylinder was supplied by Air Liquide (Pty) Ltd, a local air separation company.

3.3.2 Methods

3.3.2.1 Tire char (TC) activation

TC obtained from the pyrolysis plant was initially washed with distilled water several times and dried at 110°C for 24h in a drying oven. The char was then subjected to demineralization stage where minerals such as zinc (Zn), calcium (Ca), copper (Cu), titanium (Ti) and magnesium (Mg) were removed. The demineralization process was achieved by mixing 20g of tire char in 16 ml HNO_3 (65% pure) for 24hrs and later 1L of water was added to the mixture and stirred for 2hrs. The demineralized tire char (DTC) was filtered from the solution using a 10 μm filter paper and it was subsequently rinsed several times with deionized water until the pH of the tire char containing water was equal the pH of demineralized water. The sample char was then dried at 110 °C for 24h in a drying oven and stored for characterization/adsorption studies and for a further chemical activation stage. DTC was activated by chemical means using KOH solution. Equal amounts by weight of 1M KOH and DTC (100g of DTC and 100g of KOH) was mixed and placed into an Elite TSH12 horizontal tube furnace. The sample was heated to 800 °C at 20 °C/min heating rate and was kept constant at this temperature for 60 min. The activation was performed in a furnace using nitrogen gas (N_2) at 100 ml/min. The sample

was left to cool in the same N₂ atmosphere and after cooling several rinsing of the sample was performed to remove the excess KOH attached to the sample. The activated tire char (ATC) was then mixed and stirred with 50ml HCl for 24hrs and subsequently rinsed with deionized water until the pH between 5.6 - 6.0 was achieved. Finally, the ATC was scattered in a widespread crucible and dried at 110°C for 24h in a drying oven and stored for adsorption studies.

3.3.2.2 Characterization of TC, DTC, ATC and CAC

3.3.2.2.1 Thermogravimetric analysis (TGA)

The thermogravimetric carbonization experiment of TC and KOH impregnated DTC was conducted using a PerkinElmer Thermogravimetric Analyzer (Pyris 1 TGA). A sample of ± 10 mg material was heated at 20 °C/min from 25°C to 800°C and the temperature was kept constant at 800 °C for 60 min before cooling. N₂ at a flow rate of 100 ml/min was used as an inert gas.

3.3.2.2.2 Fourier transform infrared spectroscopy (FT-IR)

The spectra were recorded using PerkinElmer Spectrum 400 FT-IR/FT-NIR Spectrometer. The carbon samples were free of moisture or any oily material. The equipment was loaded with anhydrous KBr pellets which mixes with the loaded carbon materials. The mixture was pressed under vacuum to obtain pellets which are analyzed between the spectra 400 – 4500 cm⁻¹. All the samples CAC, TC, DTC and ATC were investigated using the same procedure.

3.3.2.2.3 Scanning electron microscopy (SEM)

Scanning electron microscope (SEM, FEI Quanta 250 FEG ESEM with integrated Oxford X-Max 20 EDX system) was used to depict images and to provide the surface morphology of TC, DTC and ATC samples. The samples were initially subjected to gold palladium spray, which subsequently created a layer on top of the carbon sample to give out visible images.

3.3.2.3 Adsorptive desulfurization of TPO

The adsorption capacity of different carbon materials (TC, DTC, ATC and CAC) was determined. TPO with initial sulfur content of 7767.7 ppmw was used in this present work. For each typical experiment, 100ml TPO was poured in a 3neck 250ml flat bottom flask mounted with a condenser and temperature control probe. The effect of multiple operating parameters was studied to find optimum operating conditions and were varied as follows; adsorbent dosage (0.5 – 2.5 g/ 100ml), reaction time (10 – 50 min) and temperature (25 – 75 °C). At the end of each reaction, the liquid mixture was separated from the solids by vacuum filtration using WHATMAN grade 1 filter paper, a Buchner funnel and a vacuum pump. Sulfur analysis of the samples was performed using Rigaku NEX QC+ Energy Dispersive X-ray fluorescence spectrometer.

Sulfur percentage removal was calculated using the formula:

$$\% \text{removal of sulfur} = \frac{C_o - C}{C_o} \times 100$$

Where C_o is the initial sulfur concentration (mg L^{-1}) and C is the sulfur concentration remaining in the TPO (mg L^{-1}).

3.3.2.3.1 Adsorption Kinetic studies

The study of adsorption kinetics is one way of gaining an intense understanding of the process of adsorption. There are various kinetic models implemented but for this study only pseudo-first order and pseudo-second order kinetics were employed.

The pseudo-first order equation can be expressed in the linear form as,

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where q_e and q_t are the amount of adsorbate ions adsorbed (mg g^{-1}) on the adsorbent at the equilibrium and at time t , respectively, and k_1 is the rate constant of adsorption (min^{-1}). Values of k_1 are calculated from the plots of $\log(q_e - q_t)$ versus t for different concentrations of the adsorbate.

The pseudo-second order equation can be expressed as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$$

Where k_2 is the rate constant of pseudo-second order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). The constants are obtained from plotting $\frac{t}{q_t}$ versus t .

3.3.2.3.2 Adsorption Isotherms

To further understand the design and operation of the adsorption system, equilibrium characterization was performed by fitting experimental data to Freundlich and Langmuir isotherms.

The equilibrium expression of Freundlich isotherm is given by,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

$K_f (\text{mg g}^{-1})$ and $n (\text{g L}^{-1})$ are the constants for the Freundlich model related to the adsorption capacity and intensity of adsorption, respectively (Yu et al., 2003). This isotherm describes equilibrium on heterogeneous surfaces (Günay et al., 2007) i.e. the energy of adsorption is not equivalent for all adsorption sites, which is a more realistic assumption than the Langmuir isotherm.

For the linear traditional Langmuir isotherm,

$$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \left(\frac{1}{q_m}\right)$$

The empirical constants q_m and k_L for the Langmuir model are related to the maximum adsorption capacity (mg g^{-1}) and energy of adsorption (L g^{-1}) respectively (Yu et al., 2003).

3.4 Results and discussion

3.4.1 Tire Char (TC) Activation

During the last stage of activation when DTC was mixed with 5M HCl, two separate colors were visible after 24hrs of stirring the mixture. The black sediment ATC settled at the bottom of the beaker and the colorless acid on top. These two phases were easily separated by decanting the acid from the solid ATC. This behavior is attributed by the available pores created during activation. This allows water or low viscous liquids to penetrate through the pores of the ATC, thus providing settling of the material instead of floating which is normally experienced with TC. Another visible factor which justified the availability of pores created during activation is filtrating of both materials, TC and ATC. ATC filtration rate was much greater than that of TC filtration, hence indicating the presence of pores which allowed the liquid to flow more rapidly through the ATC as compared to the TC.

3.4.2 Characterization of TC, ATC and CAC

3.4.2.1 Thermogravimetric analysis (TGA)

Characteristic TGA results for TC and KOH chemically impregnated DTC are shown in Figure 3.1 and 3.2, respectively. Observing both Figures, there is a huge difference in the thermal decomposition pattern between the two samples. This is mainly because the impregnated sample comprises of too much moisture content since impregnation was achieved with equal amounts of DTC and KOH solution. As shown on Figure 3.1, the decomposition behavior of TC gives almost a linear relation with a minor weight loss of 0.92 mg from 30 to 750 °C. This is because most of the volatiles are lost during pyrolysis of the tires. The minor weight loss might be contributed by moisture content because of the TC storage conditions and the remaining volatiles which were present after pyrolysis. The thermogravimetric results of KOH impregnated DTC shown in Figure 3.2 indicate that the sample contains a lot of moisture content as justified by the rapid weight loss of 4.0 mg between 22 to 50 °C. The weight loss which resulted in the major turning point of the plot is experienced between 30 and 110 °C. This is due to evaporating moisture that was

absorbed by the carbon material, and therefore, the remaining weight of 5 mg at 110 °C is attributed by the dry DTC and KOH solids compounds. The weight loss between 110 to 750 °C is 0.4 mg and this corresponds to the thermal degradation of TC on Figure 3.1. The degradation is resulted from volatile compounds on the carbon material which remained after pyrolysis.

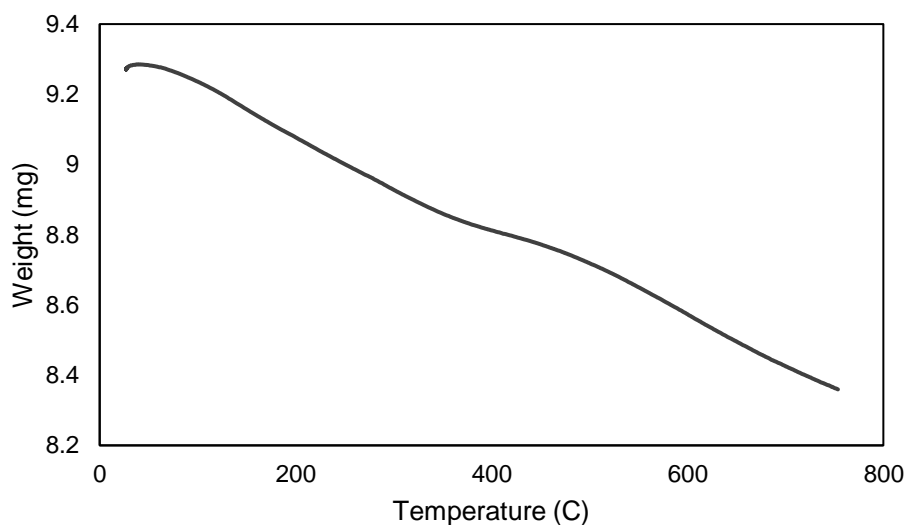


Figure 3.1: Thermogravimetric results of TC at heating rate 20 °C/min from 30 °C to 800 °C

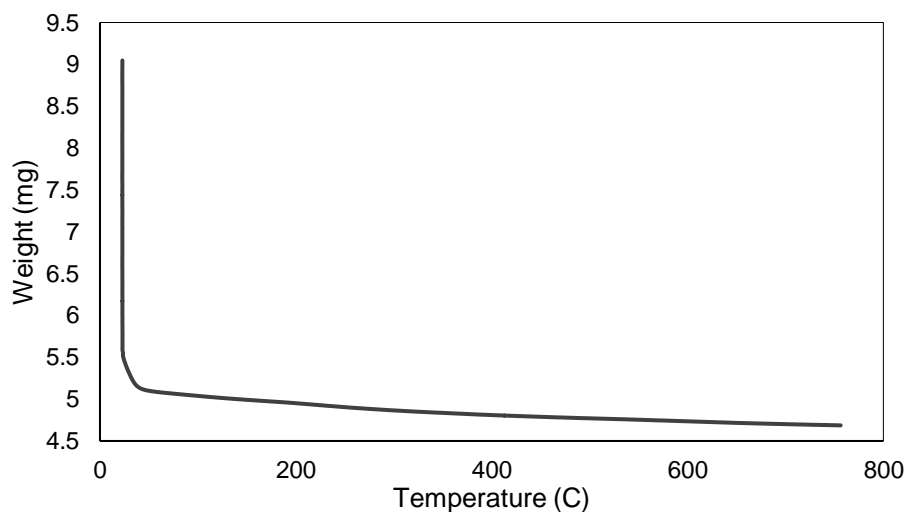


Figure 3.2: Thermogravimetric results of KOH impregnated DTC at heating rate 20 °C/min from 30 °C to 800 °C

3.4.2.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy is widely used for characterization of multiple adsorbents and catalysts due to its ability to provide finger printing in the structural interpretation of multiple functional groups present on the surface of the solid material. The FT-IR spectrum of TC, DTC and ATC are shown in Figure 3.3. Oxygen containing functional groups on to carbon materials are desirable for both adsorption and oxidative process.

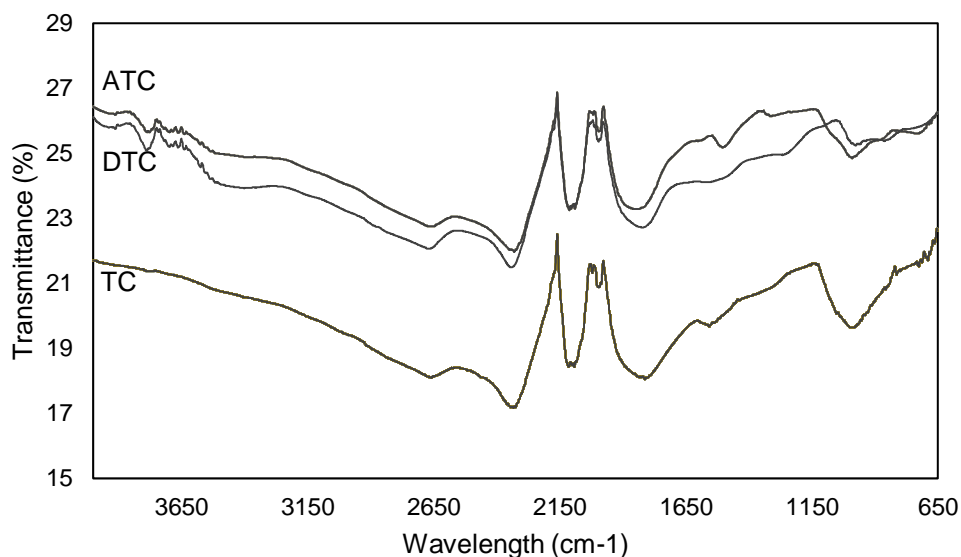


Fig. 3.3. FTIR spectra for TC and its derivatives DTC and ATC

It can be observed on Figure 3.3 that there are two bands for DTC and ATC at 3772 cm^{-1} and 3642 cm^{-1} respectively. These are relatively high frequency $>3500\text{ cm}^{-1}$ attributed by the OH stretching vibration in the hydroxyl groups. The same bands can still be attributed by the vibration in alkyl or aryl groups (El-Hendawy, 2006; El-Hendawy, 2009). These peaks are not visible on TC and therefore this suggests that both demineralization and chemical activation of TC enhances the oxygen containing sites on the material as desired for this current study. DTC has an un-similar band at 1515 cm^{-1} in comparison with TC and ATC which is attributed by the N-O asymmetric stretch in the nitro compounds. This suggest that there was some excess HNO_3 which remained on the surface of the material during demineralization stage. Those similar bands assignments

found on the three carbon materials on Figure 3.3 are summarized in Table 3.1, in reference to multiple studies by other authors.

Table 3.1: the assignment of FTIR vibrations for TC, DTC and ATC shown on Fig.4 in comparison with vibrations reported in literature

Peak (cm-1)			Surface group	Assignment	Activated carbon prepared from	Reference
Current study	Solid material	In reference				
3772, 3642	DTC, ATC	>3500	OH	Vibration in alkyl or aryl	Date pits, Maize stalks	(El-Hendawy, 2006; El-Hendawy, 2009)
2666	T-D-A*	2920-2600			Date pits	(El-Hendawy, 2006)
2325	T-D-A*	2332	C≡C	Vibration in alkyne group C≡C	CAC D43/1	(Biniak et al., 1997)
2108	T-D-A*	2132	C≡C	Vibration in alkyne group C≡C	CAC D43/1	(Biniak et al., 1997)
1556	TC	1558	C=O	Vibration of C=O	CAC D43/1	(Terzyk, 2001)
1501	ATC	1505	C=C	Vibration in aromatic groups C=C	CAC D43/1	(Biniak et al., 1997)
991,983	T-D-A*	1300-900	C–O	Vibration in esters, ether or phenol groups C–O		

*T-D-A (TC, DTC and ATC)

* CAC D43/1 (Commercial activated carbon D43/1)

3.4.2.3 Scanning electron microscope (SEM)

Scanning electron microscope was used to examine the surface characteristics of TC, DTC and ATC. Figure 3.4 shows topographical SEM images of (A) TC, (B) DTC and (C) ATC at 1215 and 60000 magnifications, respectively. The effect of chemical activation by KOH can be clearly seen in Figure 3.4. Images 1A and 1B show that TC and DTC have spherical shapes at 1215 magnification. At the same magnification, ATC portrays more like cubical shapes. Therefore, this justifies that demineralization of tire char has no effect on the shape of the material while chemical activation using KOH changes the shape from spherical to cubical shape as seen at 1215 magnification. Taking a closer look at the carbon materials using 60000 magnifications, TC has undesirable morphology in terms of porosity, image 2A. Image 2B also shows that demineralization of TC has no effect on the morphology of the carbon material. Images 2C and 3C which are captured at 60000 magnifications from different locations of the ATC shows that activation with KOH improved the surface morphology of the adsorbent. Both images show some pores which are formed on the surface of the ATC because of the chemical activation process. Furthermore, a huge crack can be observed on image 2C which justifies the rupturing of the carbon material during activation at higher temperatures thus creating pores.

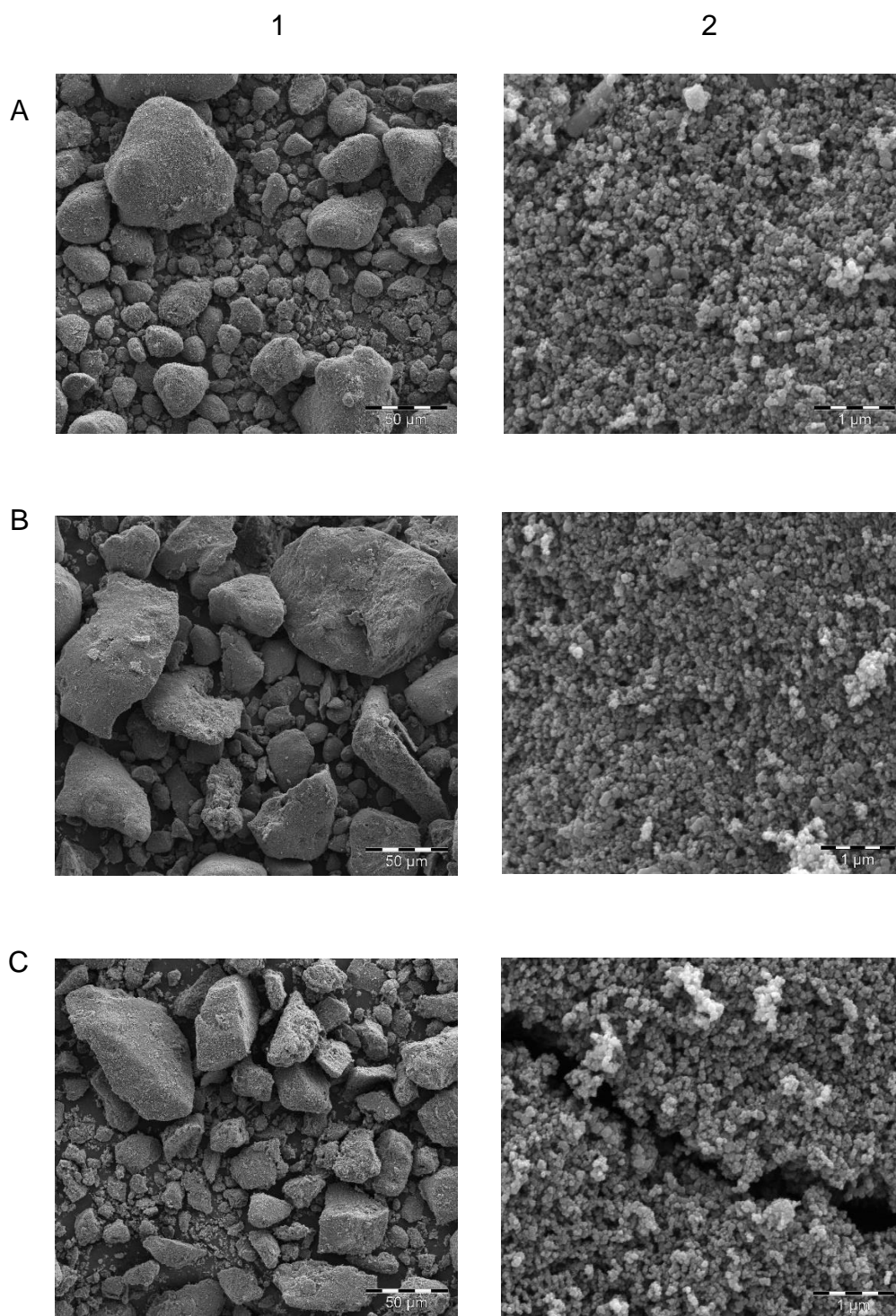


Figure 3.4. Topographical SEM images of (A) TC, (B) DTC and (C) ATC at 1215 and 60000 magnifications, respectively.

3.4.3 Adsorptive desulfurization of TPO

3.4.3.1 Adsorption of organosulfur compounds onto TC, DTC, ATC and CAC

The nature of carbon materials and specifically activated carbon is that they have well developed porous structure, huge surface area and have multiple oxygen containing functional groups on their surface. This makes activated carbon a desirable material to act as an adsorbent and catalyst for oxidative desulfurization of liquid fuels. To determine the effect of activated carbon on desulfurization of TPO as a liquid fuel, four adsorbents namely, TC, DTC, ATC and CAC were prepared and used for adsorption studies. The effect of time was studied under adsorption process to understand the kinetics of adsorption. Figure 3.5 represent the effect of time on different adsorbents. The optimum adsorption time was found to occur at 50 min.

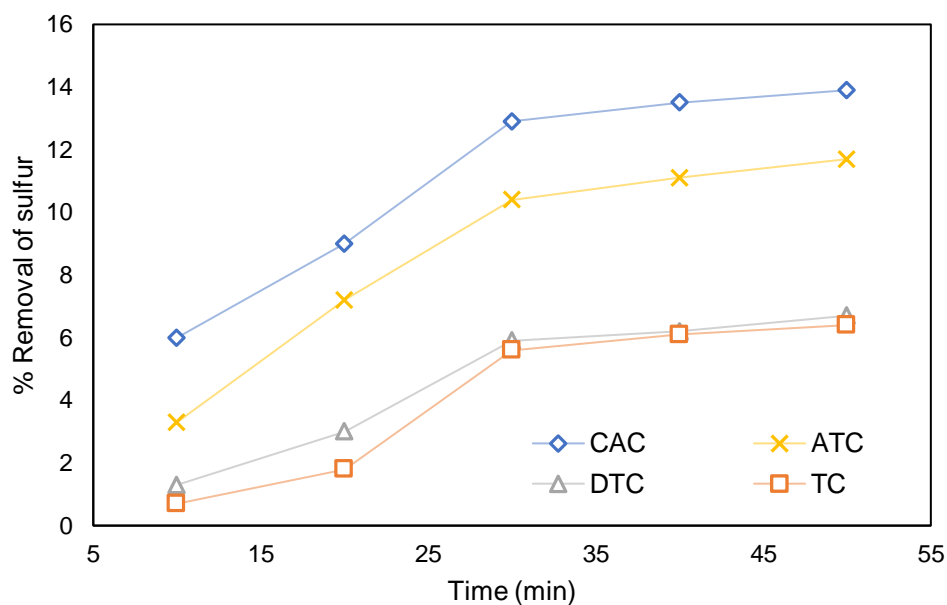


Figure 3.5: The effect of reaction time for adsorption process. Reaction conditions were kept constant at; Temperature 25°C, Adsorbent dosage 2 g/100 ml, Stirring speed 250 rpm.

The relationship between percentage removal of OSC and adsorbent dosage of different carbon materials is represented by Figure 3.6. The adsorption efficiency of the different carbon materials decreases in the order CAC > ATC > DTC > TC.

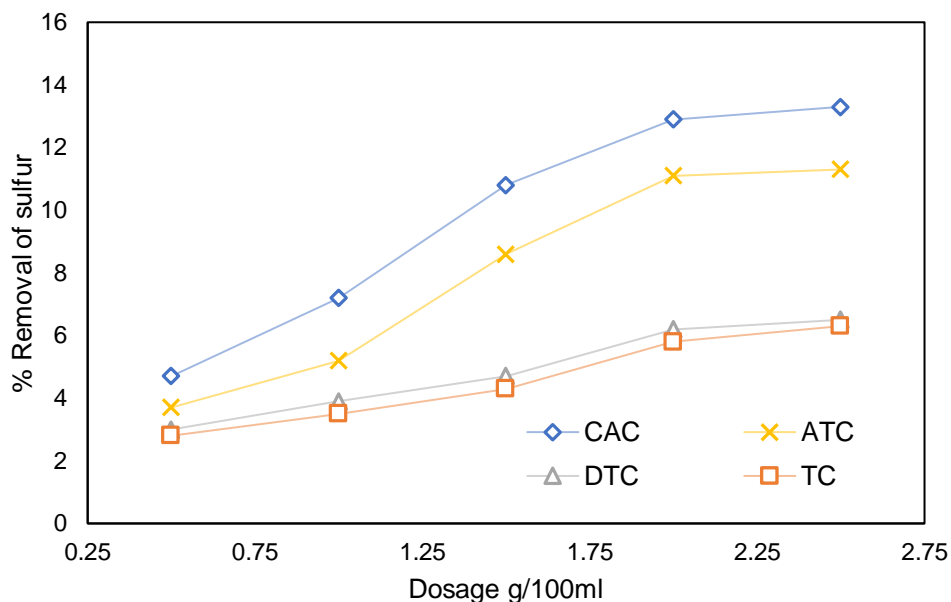


Figure 3.6: Variation of adsorbent dosage per 100ml of oil. Reaction conditions were kept constant at; Temperature 25°C, time 50 min, Stirring speed 250 rpm.

The represented similar trends on Figure 3.6 indicate that the uptake of OSC on the different carbon materials is consistent until equilibrium is reached at a dosage of 2 g/100ml of oil. The adsorption capacity of CAC is greater than that of tire char and its derivatives. This is because CAC have larger surface area and higher mesoporous volume percentage. It has been reported that the efficiency of adsorptive desulfurization of OSC in liquid hydrocarbons is primarily determined by the pore structure of carbons (Yu et al., 2005). The highest percentage removal reached by CAC is 13.3% with a very low increase of 0.4% from 12.9% at the optimum dosage of 2 g/100ml. Further adsorption could not take place since TPO consist of numerous types of OSC and therefore this suggests that a specific species of OSC based on their molecular weight and shape was

compatible with the pore size and structure of carbons used in this study (Davis and Gloor, 1981).

Figure 3.7 shows the effect of temperature on the percentage removal of OSC. It is evident that this process is temperature dependent. As the temperature is increased from 25°C to 75°C there is a decrease in the percentage removal of OSC for all carbon materials. From this behavior, it can be said that the adsorption of OSC onto the different carbon adsorbents is an exothermic process. Temperature increases the attractive forces between the adsorption sites on the surface of the carbon materials and the OSC in solution weakens which causes a decrease in the removal of OSC as the temperature is increased. Possible desorption of OSC on the surface of the carbon could also be occurring. The optimum adsorption temperature was at 25°C for all adsorbents (TC, DTC, ATC and CAC) used for this study.

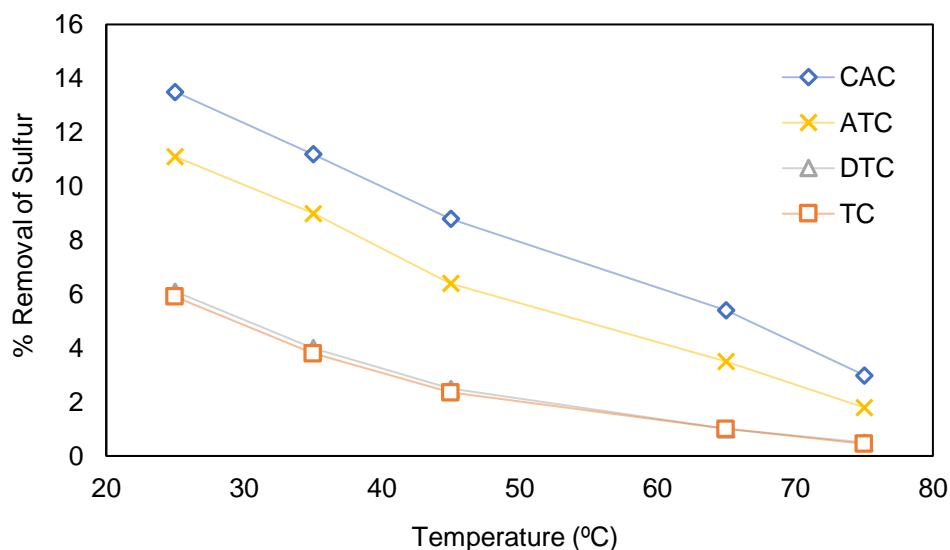


Figure 3.7: The effect of temperature for adsorption process. Reaction conditions were kept constant at; Time 50 min, Adsorbent dosage 2 g/100 ml, Stirring speed 250 rpm.

3.4.3.2 Adsorption Kinetic studies

Kinetics studies were applied on two carbon materials, CAC and ATC. The applicability of pseudo-first order and pseudo-second order kinetic models were tested for the adsorption of OSC in TPO onto CAC and ATC. The graphical representation of the two kinetic studies is shown in Figures 3.8 and 3.9 for pseudo-first order and pseudo-second order kinetic models, respectively. The correlation coefficient, R^2 , values for both kinetic models, equilibrium sorption uptake and their respective rate constants, k , are represented in Table 3.2. The correlation coefficient of CAC is 0.96 for both pseudo-first order and pseudo-second order kinetic models suggested that the overall adsorption might be controlled by more steps: external diffusion, pore diffusion, and adsorption on the sorbent surface (Vimonses et al., 2009; Alkan et al., 2004). On the other hand, the correlation coefficient of >0.98 for ATC showed adequate fit for pseudo-first order model indicating that the reaction is more inclined towards physical adsorption.

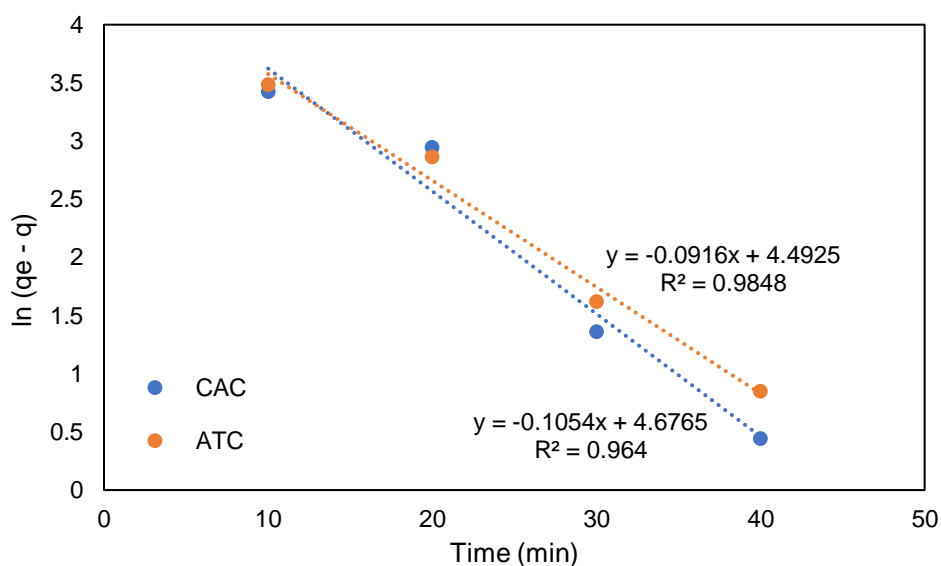


Figure 3.8: Results on pseudo-first order kinetic model for CAC and ATC

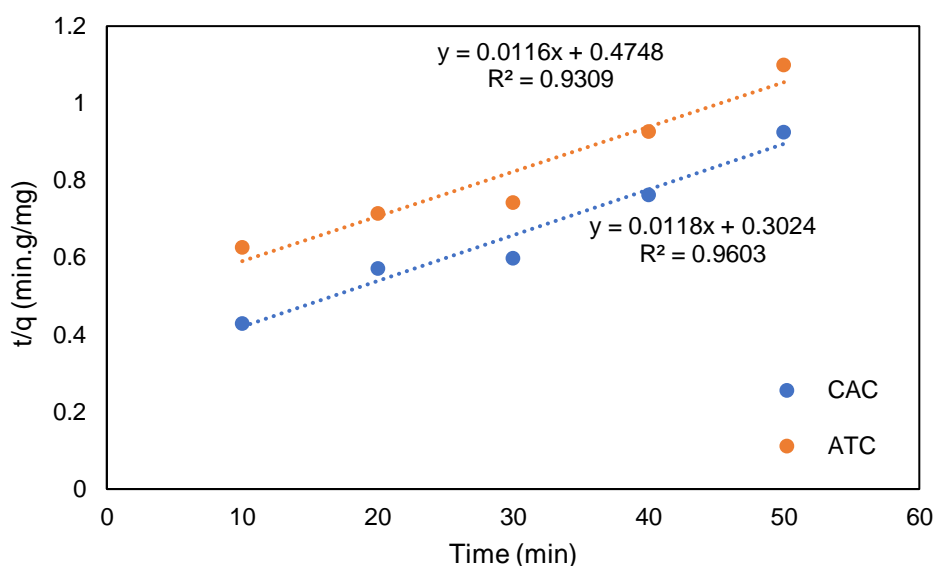


Figure 3.9: Results on pseudo-second order kinetic model for CAC and ATC

Table 3.2: Rate constants, equilibrium sorption uptake and correlation coefficients results for pseudo-first order and pseudo-second order kinetic models

Pseudo-first order model			
Adsorbent	k_1 (min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2
CAC	0.1054	107.39	0.9640
ATC	0.0916	89.34	0.9848
Pseudo-second order model			
Adsorbent	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2
CAC	0.00046	84.75	0.9603
ATC	0.00028	86.21	0.9309

3.4.3.3 Adsorption Isotherm studies

Langmuir and Freundlich isotherm models were used to study equilibrium adsorption data and the results can be seen in Figure 3.10 and 3.11, respectively. Results show that Freundlich model describes the adsorption of OSC onto the carbon materials better than the Langmuir model, with their correlation coefficient R^2 values of 0.9871 and 0.9814 for

CAC and ACT, respectively. These results further justify that this adsorption falls under physical adsorption for both CAC and ATC (Do, 1998; Jung et al., 2001; Jarvie et al., 2005; Aktaş and Çeçen, 2006). Both carbon materials present a heterogenous surface and only a monolayer is formed, that is OSC do not bond with other OSC which are already bonded to the surface of the adsorbent (Günay et al., 2007). The K_F and n constants show that the adsorption capacity is low. This agrees with the assumption that OSC in liquid fuels are well represented by the amount of sulfur found in the fuel (Muzic et al., 2008), and in this case TPO contains a massive 7767.7 ppmw. Isotherm parameters for both Langmuir and Freundlich models are presented in Table 3.3.

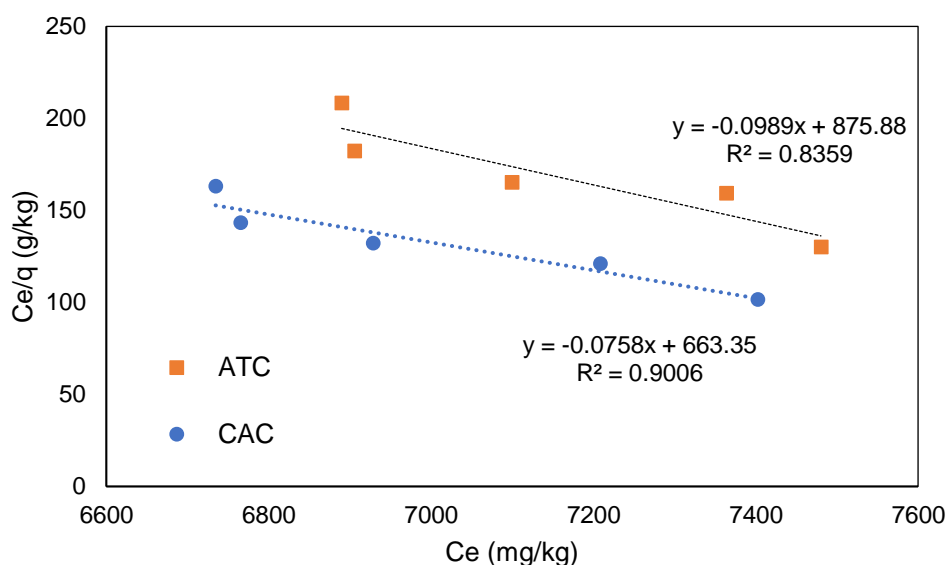


Figure 3.10: Results on Langmuir isotherm model for CAC and ATC

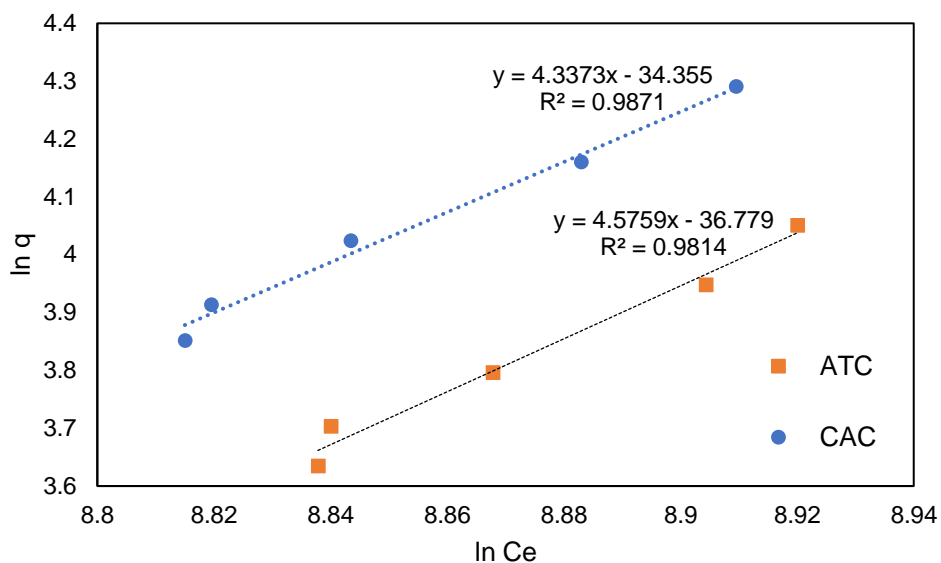


Figure 3.11: Results on Freundlich isotherm model for CAC and ATC

Table 3.3: Langmuir and Freundlich isotherm constant and R^2 values for CAC and ATC

Langmuir isotherm			
Adsorbent	K_L (kg mg ⁻¹)	Q_m (mg g ⁻¹)	R^2
CAC	0.00011	13.1326	0.9006
ATC	0.00011	10.1112	0.8359
Freundlich isotherm			
Adsorbent	K_F	n	R^2
CAC	1.2×10^{-15}	0.23064	0.9871
ATC	1.1×10^{-16}	0.21855	0.9814

3.5 Conclusion

ATC is a competitive adsorbent for desulfurization of OSC in TPO. Treatment of TC through demineralization and chemical activation with KOH enhances the oxygen containing sites on the material as shown by FTIR. Modification of DTC by chemical activation improves the surface morphology of the material as shown by SEM images. A kinetic study on adsorption showed that the best fit is achieved when pseudo-first order kinetic model is applied with correlation coefficients (R^2) of 0.964 and 0.985 for ATC and CAC, respectively. The isotherm results showed that both carbon materials ATC and CAC presents a heterogeneous surface in the adsorption of OSC in TPO by following the Freundlich isotherm model with correlation coefficients (R^2) of 0.981 and 0.987 for ATC and CAC, respectively. The two carbon materials show that carboxylic group content on the surface of the material plays a vital role for adsorption. The optimum adsorbent dosage, time and temperature were found to be 2g/100ml of TPO, 50 min and 25 °C, respectively.

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CHAPTER 4

4. AIR-ASSISTED OXIDATIVE DESULFURIZATION OF WASTE TIRE PYROLYTIC OIL (TPO) CATALYZED BY ACTIVATED TIRE CHAR

4.1 Abstract

The catalytic ability of different carbon materials activated tire char (ATC) and Aldrich supplied commercial activated carbon (CAC) was studied for air-assisted oxidative desulfurization (AAOD) of TPO in the presence of performic acid. TPO with initial sulfur content of 7767.7 ppmw was used in this present study. The effect of operating conditions; $\text{H}_2\text{O}_2/\text{HCOOH}$ ratio, reaction time, temperature and air flowrate were studied. Oxidation equilibrium was reached at 80 °C for both ATC and CAC at a reaction time of 50 min. The presence of air at a flow rate of 60 l/hr increased oxidation from 59.2% to 64.2% and 47.4% to 53% for CAC and ATC, respectively. CAC and ATC are two competitive catalysts for oxidative desulfurization of TPO with a total oil recovery of more than 90%.

4.2 Introduction

Waste tire pollution has become a worldwide problem due to its environmental devastation which threatens human life and the ecosystem. These contaminations are of great concern and therefore, present humanity have become increasingly concerned with environmental issues related to disposal of this matter. Recycling and reuse of scrap tires are important processes to reduce pollution caused by this waste tires. The current huddle is the nature of tires which makes them extremely challenging to recycle due to the available chemically cross-linked polymer and, therefore, they are neither fusible nor soluble and, consequently, cannot be remolded into other shapes without serious degradation (Trongkaew et al., 2011). The disposal of this non-biodegradable material in the landfills creates breeding ground for disease carrying mosquitos and other vermin such as mice, rats and bugs (Uçar et al., 2005). The same pile of tires might cause great damage to the environment if ignited by lightning or any other source. There are many methods reported for the recycling of waste tires such as grinding, retreading, incineration and pyrolysis, although these methods can solve the above-mentioned problem, they also

have their own drawbacks (de Marco Rodriguez et al., 2001). Recycling of waste tires by pyrolysis process results in four products, namely char, oil, steel and non-condensable gases. Cunliffe and Williams (1998) investigated the composition of TPO and discovered common properties to commercial diesel fuel. The problem associated with the light oil derived from pyrolysis of waste tires is that it has a high sulfur content and therefore emits harmful sulfur oxide gases to the atmosphere when combusted in diesel engines. These gases react with water in the atmosphere to form sulfates and acid rain which damages buildings, acidifies soil, and ultimately leads to loss of forests and various other community of interacting organisms (Shiraishi et al., 2002). The present hurdle calls for pre-desulfurization treatment of TPO before using it in diesel engines. The available sulfur content in tire pyrolytic oil is because of the vulcanization process entailed in the manufacturing of tires (de Marco Rodriguez et al., 2001).

Hydrodesulfurization (HDS) is the commonly practiced technique for the removal of sulfur species in liquid hydrocarbons. During HDS technique, the high pressurized inlet hydrogen gas reacts with the sulfur species in the liquid hydrocarbons to form a hydrogen sulfide (H_2S) product (Jantaraksa et al., 2015). The formation of H_2S from this reaction operates at very high pressure (30 – 130 atm) and temperature (300 – 400 °C) (Jantaraksa et al., 2015). HDS is a catalyst supported process for the effective removal of sulfur compounds, and therefore there is a range of catalysts studied such as Co-Mo/ Al_2O_3 or Ni-Mo/ Al_2O_3 . However, the HDS technique fails in the presence of complex sulfur species such as dibenzothiophene (DBT). It has been reported that unlike conventional liquid hydrocarbon fuels such as diesel and gasoline, TPO contains species of sulfur in a form of cyclic compounds (sulfur-polycyclic aromatic hydrocarbons) such as DBT and its derivatives (Williams and Bottrill, 1995; Pakdel and Roy, 1994). Thus, this pose a huge drawback as HDS technique struggles in efficient removal of this complex sulfur compounds. Moreover, the production of liquid hydrocarbons from waste tires is normally practiced on a small-scale production, therefore unlike in big oil refineries where hydrogen is supplied as a byproduct from other processes, this will be much costlier as it must be purchased elsewhere.

The char obtained from the pyrolysis of waste tires can be modified to produce activated carbon. There are two known activation processes namely the physical and chemical activation process (Davis and Gloor, 1981; Alkan et al., 2004; Günay et al., 2007). In physical activation, the pyrolysis char undergoes thermal treatment inside a reactor with the heat supplied by superheated steam at temperatures above 800 °C for 2 to 3 hours or carbon dioxide at temperatures above 900 °C for more than three hours (Biniak et al., 1997; Aktaş, and Çeçen, 2006; Antoniou et al., 2014). For the physical activation step, it has been reported that physical activation of the pyrolysis char using superheated steam results in the production of activated carbon having narrow micro pores, large BET surface areas and large micro pore volumes in comparison with the one activated using carbon dioxide (San Miguel et al., 2003; Hofman and Pietrzak, 2011). Chemical activation involves impregnation of the carbon material with certain chemicals, typically an acid, a strong base or a salt (generally phosphoric acid or zinc chloride) (Jung et al., 2001; Jarvie et al., 2005; López et al., 2013). The impregnated material is later carbonized at a lower temperature as compared to physical activation, usually 450 °C – 900 °C (Terzyk, 2001; Lua and Yang, 2004). During carbonization, the impregnating chemical acts as a supporting medium and does not allow the carbon material to shrink. The latter is dehydration of the material resulting in rupturing of the material, thus creating a porous and an extended surface area.

Oxidative desulfurization is the most promising technique for efficient reduction of sulfur compounds in liquid hydrocarbons due to its low energy consumption, temperature (~ 50 °C) and atmospheric pressure (Srivastava, 2012). In the previous years, most researchers focused on adjusting the operating conditions such as heating rate and temperature within the pyrolysis system to produce low sulfur TPO without coming up with a post treatment process to reduce the sulfur content in the already produced TPO (Unapumnuk et al., 2008). The most commonly known oxidant for the ODS technique is hydrogen peroxide (H₂O₂). This is due to its friendliness to the environment as compared to other oxidising agents such as nitric acid (HNO₃) and sulfuric acid (H₂SO₄). The efficiency of H₂O₂ for ODS is dependent on various catalyst such as formic acid (HCOOH), trichloroacetic acid (CCl₃COOH), trifluoroacetic acid (CF₃COOH) and methyltrioxorhenium (Shiraishi et al., 2002). The oxidised sulfur species present in the liquid hydrocarbons becomes more

polarized as compared to the rest of the liquid, and therefore this enhances its removal by either solvent extraction or adsorption technique (Ukkirapandian et al., 2008).

In the present work, air assisted oxidative desulfurization (AAOD) of organosulfur compounds (OSC) present in TPO were investigated using different carbon materials derived from tire char as catalysts for AAOD. Tire char was demineralized with nitric acid (HNO_3) and then activated by chemical means using KOH solution. Performic acid yielded by the reaction of H_2O_2 and HCOOH was the main oxidising agent in this work. The extraction of oxidised sulfur species was performed using acetonitrile/water mixture as an extraction solvent.

4.3 Experimental methodology

4.3.1 Materials

TPO with a sulfur content of 7767.7 ppmw and TC with particle size (250 – 850 μm) were purchased from a local pyrolysis plant in Gauteng province, South Africa. The feed stock to the fixed bed pyrolysis reactor mainly comprises of private car tires and the reactor is operated under the conditions; Temperature 600 $^\circ\text{C}$ and heating rate 35 $^\circ\text{C}/\text{min}$. CAC was purchased at Sigma Aldrich. All chemicals were of analytical-grade reagents (AR) and were purchased at Merck Chemicals; hydrogen peroxide 30 wt% (H_2O_2), formic acid 90 wt% (HCOOH), nitric acid (HNO_3), potassium hydroxide (KOH), hydrochloric acid (HCl) and Acetonitrile. Nitrogen gas (N_2) cylinder was supplied by Air Liquide (Pty) Ltd, a local air separation company.

4.3.2 Methods

4.3.2.1 Tire char (TC) activation

TC obtained from the pyrolysis plant was initially washed with distilled water several times and dried at 110 $^\circ\text{C}$ for 24h in a drying oven. The char was then subjected to demineralization stage where minerals such as zinc (Zn), calcium (Ca), copper (Cu), titanium (Ti) and magnesium (Mg) were removed. The demineralization process was achieved by mixing 20g of tire char in 16 ml HNO_3 (65% pure) for 24hrs and later 1L of water was added to the mixture and stirred for 2hrs. The demineralized tire char (DTC)

was filtered from the solution using a 10 μm filter paper and it was subsequently rinsed several times with deionized water until the pH of the tire char containing water was like that of pure deionized water. The sample char was then dried at 110 °C for 24h in a drying oven and stored for characterization/adsorption studies and for a further chemical activation stage. DTC was activated by chemical means using KOH solution. Equal amounts by weight of 1M KOH and DTC (100g of DTC and 100g of KOH) was mixed and placed into an Elite TSH12 horizontal tube furnace. The sample was heated to 800 °C at 20 °C/min heating rate and kept constant at 800 °C for 60 min. The activation was performed in a furnace using nitrogen gas (N_2) at 100 ml/min. The sample was left to cool in the same N_2 atmosphere and after cooling the sample was rinsed to remove the excess KOH attached to the sample. The now activated tire char (ATC) was then mixed and stirred with 50ml HCl for 24hrs and subsequently rinsed with deionized water until the pH between 5.6 to 6.0 was achieved. Finally, the ATC was dried at 110 °C for 24h in a drying oven and stored for adsorption and co-catalysis studies (El-Hendawy, 2006; El-Hendawy, 2009).

4.3.2.2 Air-assisted oxidative desulfurization (AAOD) of TPO

The catalytic ability of ATC and CAC was exploited for AAOD process. TPO with initial sulfur content of 7767.7 ppmw was used in this present work. For each typical experiment, 100ml TPO was poured in a 3neck 250ml flat bottom flask mounted with a condenser, temperature control probe and inlet air stainless-steel tube. The effect of multiple operating parameters was studied to find optimum operating conditions and were varied as follows; $\text{H}_2\text{O}_2/\text{HCOOH}$ ratio, reaction time (10 – 50 min), temperature (25 – 80 °C) and air flowrate (20 – 100 l/hr). Catalyst dosage was maintained at 2g/100ml of TPO as was found to be the optimum dosage in the previous study in chapter 3. The mixture was bubbled with dried and purified air by inserting a stainless-steel pipe inside the mixture and compressing air through to the reaction mixture using a Jun-Air compressor with a maximum pressure of 8 bar. At the end of each reaction, the liquid mixture was separated from the solids by vacuum filtration using WHATMAN grade 1 filter paper, a Buchner funnel and a vacuum pump. Thereafter the oil/performic acid mixture was easily separated by decanting the top layer oil since the two liquids are immiscible. The oxidized

oil was mixed with equal amount by volume of acetonitrile/water (80%/20%) and stirred at 600rpm for 15min using a magnetic stirrer. The sample mixture was then left for 24hr to form two layers before decanting the desulfurized oil which was on the top layer. Sulfur analysis of the samples was performed using Rigaku NEX QC+ Energy Dispersive X-ray fluorescence spectrometer. See Figure 4.1 for the schematic representation of this process used for air-assisted oxidative desulfurization.

Sulfur percentage removal was calculated using the formula:

$$\% \text{removal of sulfur} = \frac{C_o - C}{C_o} \times 100$$

Where C_o is the initial sulfur concentration (mg L^{-1}) and C is the sulfur concentration remaining in the TPO (mg L^{-1}).

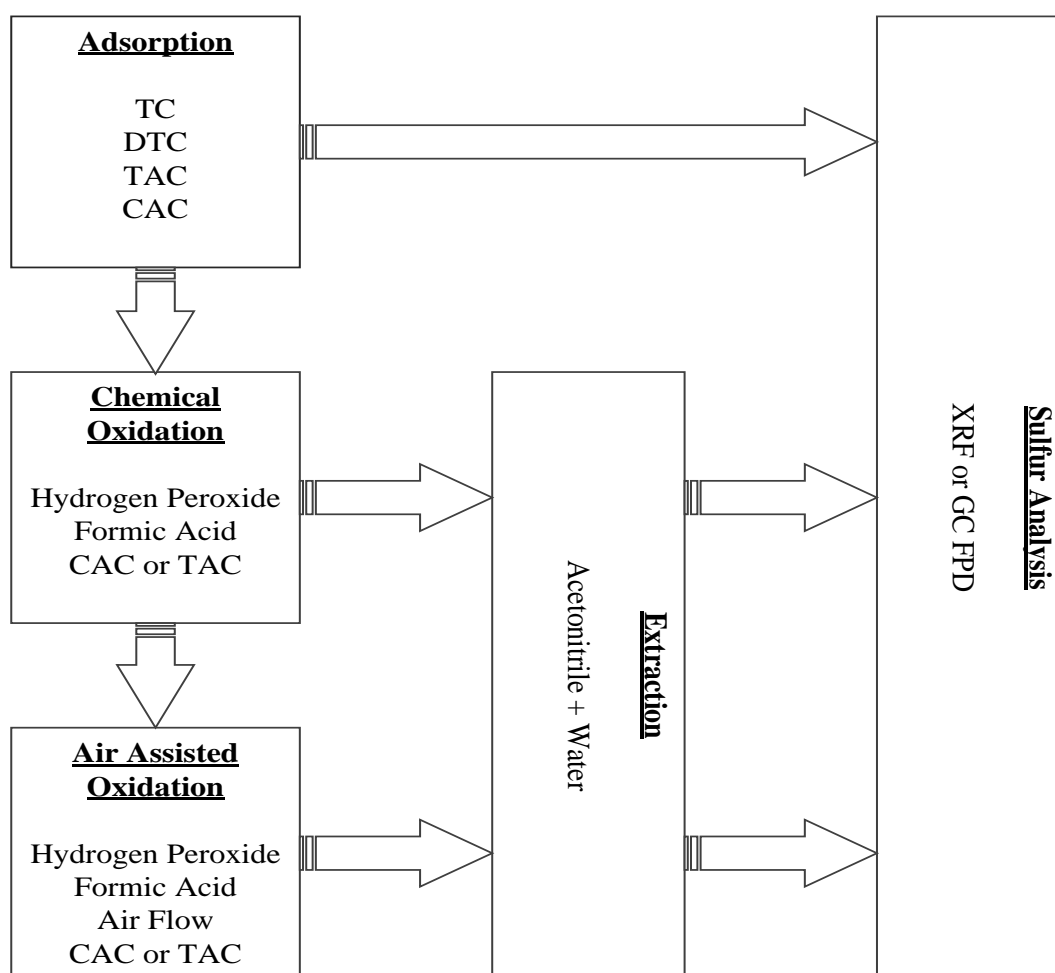


Figure 4.1: Schematic flow diagram of AAOD procedure (TAC=ATC)

4.4 Results and discussion

4.4.1 Tire Char (TC) Activation

During the last step of activation when DTC was mixed with 5M HCl, two separate colors were visible after 24hrs of stirring the mixture. The black sediment ATC settled at the bottom of the beaker and the colorless acid on top. These two phases were easily separated by decanting the acid from the solid ATC. This behavior is attributed by the available pores created during activation. This allows water or low viscous liquids to penetrate through the pores of the ATC, thus providing settling of the material instead of floating which is normally experienced with TC. Another visible factor which justified the availability of pores created during activation is filtrating of both materials, TC and ATC. ATC filtration rate was much greater than that of TC filtration, hence indicating the presence of pores which allowed the liquid to flow through the ATC then through the filter.

4.4.2 Air-assisted oxidative desulfurization (AAOD) of TPO

4.4.2.1 Oxidative desulfurization using H_2O_2 and $HCOOH$

This step involves the introduction of H_2O_2 and $HCOOH$ for oxidation purposes. The desulfurization reaction mechanisms were catalyzed by CAC and ATC which also acted as an adsorbent for the oxidized sulfur compounds in TPO. For this study since no direct analysis of oxidized OSC was performed, it was therefore assumed that 100% extraction of oxidized OSC takes place during the extraction stage with acetonitrile and water. Hydrogen peroxide reacts with formic acid to form performic acid, which is a strong oxidizing agent. The performic acid oxidizes the OSC present in TPO. Figure 4.2 represents the effect of H_2O_2 and $HCOOH$ at different ratios for oxidation OSC which were later removed by extraction with acetonitrile-water solution.

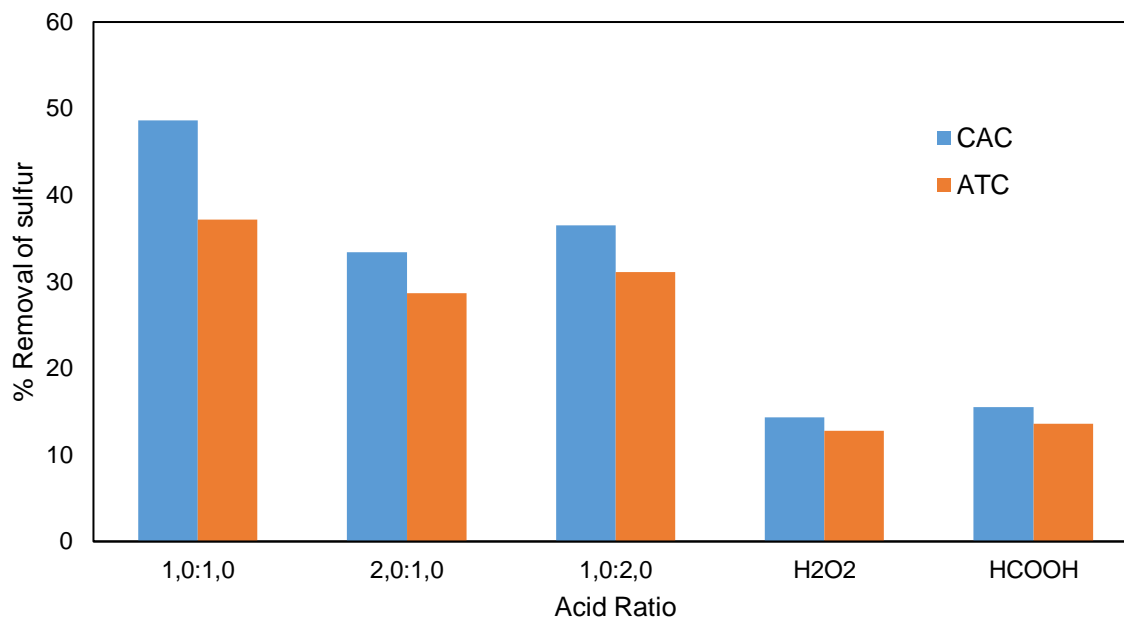
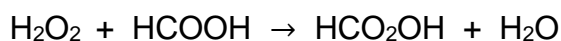


Figure 4.2: The effect of H₂O₂/HCOOH ratios on oxidative desulfurization catalyzed by CAC and ATC. Reaction conditions were kept constant at; Temperature 25 °C, Adsorbent dosage 2 g/100 ml, Stirring speed 250 rpm, Time 40 min.

The higher the adsorption capacity of carbon materials results in better catalytic performance for the oxidation procedure since CAC performs better than ATC. Both CAC and ATC reached a maximum percentage removal of 48.6% and 37.2%, respectively at ratio 1:1. These carbon materials also increase the collision chances between the available OSC and active oxygen compounds ready to oxidize, thus propelling the overall oxidation reaction. Both H₂O₂ and HCOOH were first introduced to the system individually for oxidation and it can be grasped from Figure 4.2 that HCOOH performs better than H₂O₂. This is because H₂O₂ is a weak oxidizing agent. Although the presence of carbons in a H₂O₂ system results in hydroxyl radical through decomposition, H₂O₂ performs better at lower pH values of less than 2, thus an acid is required to reduce the solution's pH value. Therefore, the introduction of formic acid into the system has two major roles: firstly, to reduce the solution pH which results in better performance of H₂O₂ in the

presence of carbon for oxidation purposes; secondly to react with H₂O₂ to form performic acid which oxidizes OSC.

To investigate the effect of performic acid oxidation, different H₂O₂/HCOOH ratios were employed. Performic acid is a strong oxidizing agent and it performs better than the pure H₂O₂ and HCOOH as shown of Figure 4.2. The reaction of H₂O₂ and HCOOH to produce performic acid is given bellow



The reaction must be kept below 85 °C to avoid explosion. This reaction can produce around 90% by weight of performic acid if the reactants are 70 – 98 wt% of HCOOH and 35 – 50 wt% of H₂O₂ (Yu et al., 2005). Therefore, based on the results obtained in Figure 4.2, ratio 1:1 performance was more efficient than 1:2 and 2:1. This is because during 1:1 ratio there was major conversion of both hydrogen peroxide and formic acid to form performic acid which is a stronger oxidizing agent as compared to the individual reactants. Figure 4.2 also shows that formic acid is a better oxidizing agent in comparison with hydrogen peroxide (Yu et al., 2003). Therefore, based on the nature of formic acid being a better oxidizing agent, it is realized that ratio 1:2 performs better than 2:1 and this is because some of the unreacted formic acid remains in the solution and acts concurrently with performic acid to oxidize OSC in TPO.

4.4.2.2 Temperature effect on oxidative desulfurization

The effects of temperature and reaction time were studied for oxidation of OSC in TPO. The effect of temperature was studied between 25 to 80 °C to avoid explosion possibilities of performic acid over 80 °C. The results on Figure 4.3 and 4.4 shows that an increase in temperature increases the oxidation rate and thus the removal percentage of OSC in TPO. A maximum percentage removal of 59.2% for CAC is experienced for both temperatures 60 °C and 80 °C. ATC shows a maximum percentage removal of 47.4% for 80 °C and a slightly lower percentage removal of 45.8% for 60 °C. Therefore, it can be suggested that oxidation equilibrium of OSC for TPO is reached at 80 °C. This behavior

can be driven by the fact that H_2O_2 decomposes at higher temperatures and the possibility of catalyst deactivation (García-Gutiérrez et al., 2008). Furthermore, beside the decomposition of H_2O_2 as a drawback, the undesirable side products affect the quality of liquid fuels (Haw et al., 2010). Ali et al., (2006) reported that oxidation of liquid fuels at a temperature of greater than 70 °C poses a risk of oxidizing valuable compounds within the fuel.

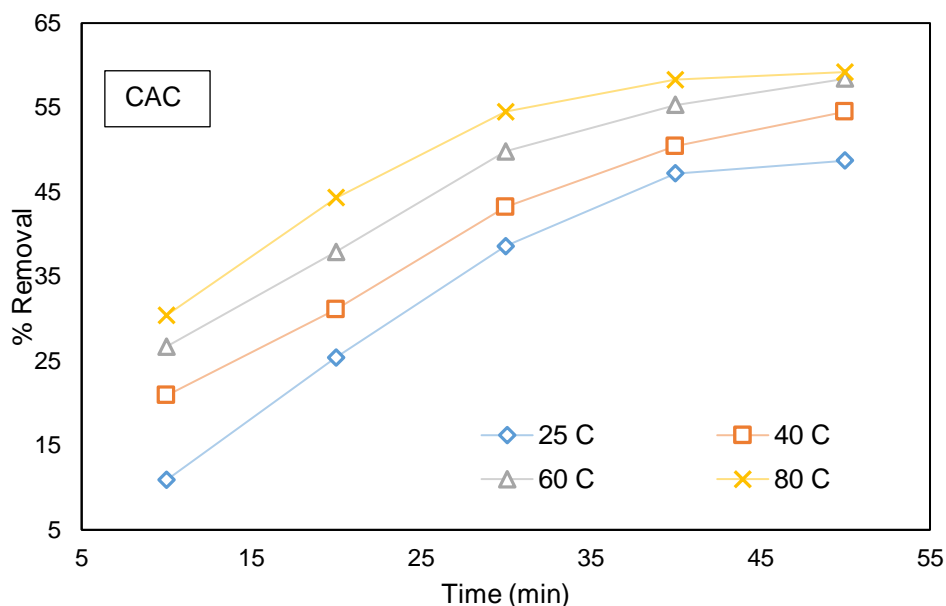


Figure 4.3: Effect of temperature on oxidative desulfurization of TPO catalyzed by CAC. Reaction conditions were kept constant at; $\text{H}_2\text{O}_2/\text{HCOOH}$ ratios 1:1, Catalyst dosage 2 g/100 ml, Stirring speed 250 rpm.

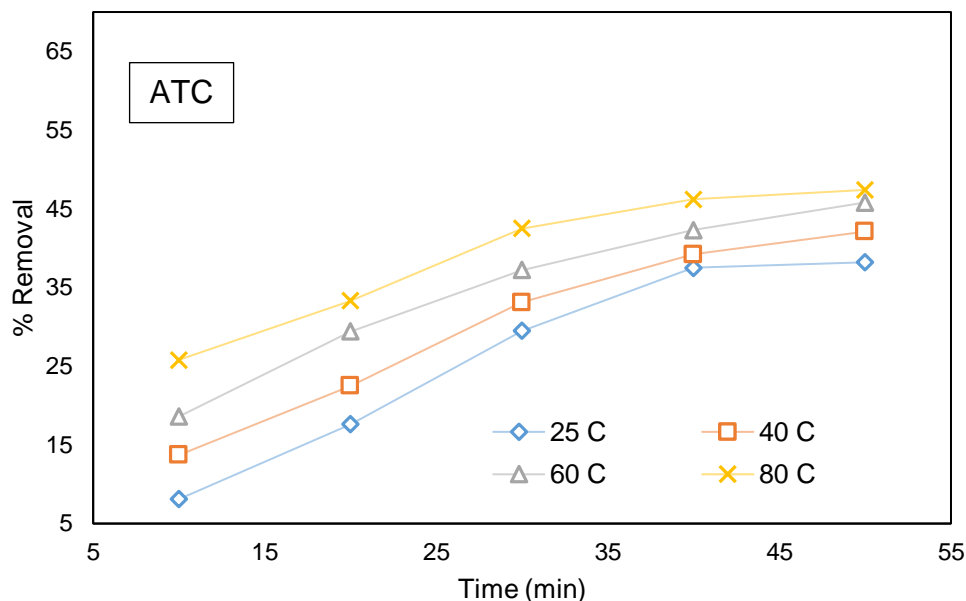


Figure 4.4: Effect of temperature on oxidative desulfurization of TPO catalyzed by ATC. Reaction conditions were kept constant at; $\text{H}_2\text{O}_2/\text{HCOOH}$ ratios 1:1, Catalyst dosage 2 g/100 ml, Stirring speed 250 rpm.

Oxidation kinetics of OSC in TPO were studied for both ATC and CAC. For both CAC and ATC, the plot of $\ln(C_0/C_t)$ against time t (Figure 4.5 and 4.6) shows a linear relationship, thus indicating that the oxidation reaction followed first order kinetics. Imtiaz et al. (2013) reported kinetic studies for oxidation of thiophenes, DBTs and 4-MDBTs and all these OSC followed the first order kinetics. The correlation coefficients for all three temperatures are greater than 0.9 and therefore this represent a strong relationship between temperature and time for oxidation of OSC in TPO. Temperatures 25 °C and 40 °C showed a perfect fit with correlation coefficients greater than 0.99 for both catalytic systems. A slightly lesser correlation coefficient of greater than 0.97 was experienced for both catalytic systems (ATC and CAC) under 60 °C temperature.

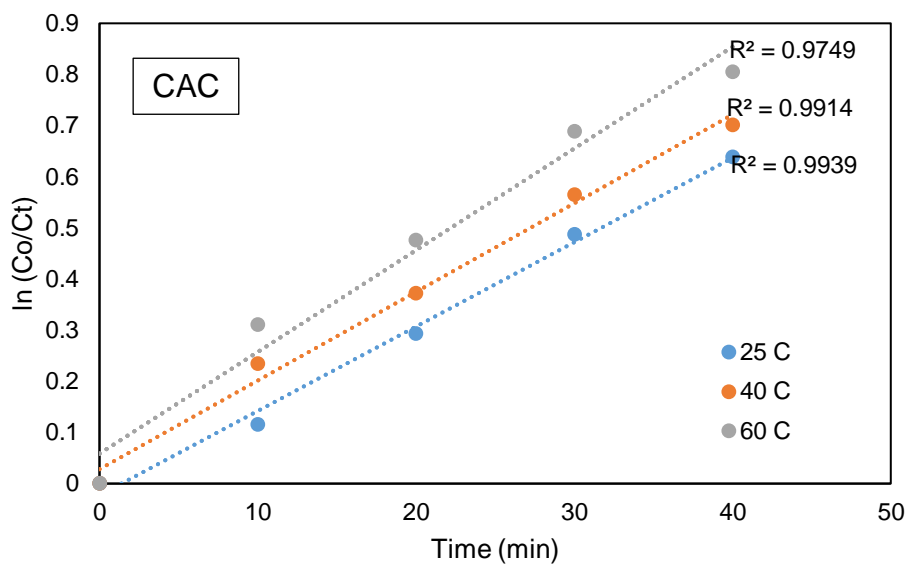


Fig. 4.5: First order kinetics of oxidation of TPO at different temperatures using CAC

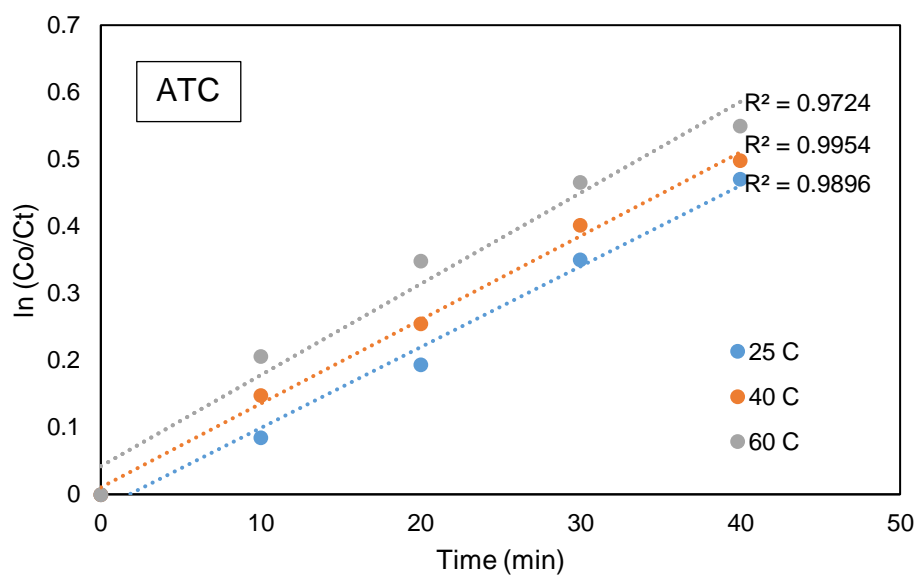


Fig. 4.6: First order kinetics of oxidation of TPO at different temperatures using ATC

4.4.2.3 Air assisted oxidative desulfurization (AAOD)

Multiple studies have been conducted to remove OSC from liquid fuels using air oxidation, but it has been reported that air alone has no ability to oxidize the sulfur compounds directly (LaCount and Friedman, 1977; Pasiuk-Bronikowska et al., 1992). Therefore, air can be used as an assisting agent to improve oxidation of the OSC in liquid hydrocarbons to their respective sulfoxide and sulfones. The effect of air flow rate was studied for desulfurization of OSC in TPO using optimum operating conditions from previous systems; catalyst, $\text{H}_2\text{O}_2/\text{HCOOH}$ ratio, temperature and time effects. The reaction conditions were; $\text{H}_2\text{O}_2/\text{HCOOH}$ ratios 1:1, Catalyst dosage 2 g/100 ml, stirring speed 250 rpm, Time 50 min. Results represented on Table 4.1 shows that an increase in air flow rate increases the oxidation reaction until 60 l/hr. A sudden decrease in %removal of OSC is experienced from 80 l/h to 100 l/h. This behavior is because of the inefficient condenser deployed in this study. TPO contains more complex OSC such as DBT and its derivatives as compared to the simplest OSC such mercaptans. Therefore, at this higher air flow rates of 80 to 100 l/hr, more simple hydrocarbons such as methane and mercaptans sulfur compounds escape the process with the vented air before they can be condensed thus concentrating the complex OSC within the oil. Therefore, a more effective and efficient condenser can be suggested for further exploitation of air assisted oxidation studies for desulfurization of liquid fuels.

Table 4.1: Effect of air flow rate on the desulfurization of TPO using different catalysts

Air Flow (l/hr)	%Removal	
	CAC	ATC
No air	59.2	47.4
20	62.4	51.1
40	63.9	53.6
60	66.7	55.9
80	64.2	53
100	61.9	49.8

From 20 l/h to 60 l/hr air acts as a co-oxidizing agent which regenerates the peroxyacid formed during the reaction (Imtiaz et al., 2013). Compressed air enhances collision probabilities between the catalyst and the binary phase liquid mixture thus creating a heterogeneous emulsion (as seen during the experiment) which enhances the oxidation rate.

4.5 Conclusion

ATC in comparison with CAC is a competitive catalyst for desulfurization of OSC in TPO. The effect of $\text{H}_2\text{O}_2/\text{HCOOH}$ ratio (1:1) shows that performic acid is a strong oxidizing agent and it performs better than pure H_2O_2 and HCOOH for oxidation of OSC in TPO. The effect of temperature was studied, and it was found that oxidation equilibrium is reached at 80 °C for both ATC and CAC. This behavior is driven by the fact that hydrogen peroxide decomposes at higher temperatures and the possibility of catalyst deactivation. A plot of $\ln(C_0/C_t)$ against time t presented a linear relationship at three different temperatures, thus indicating that the oxidation reaction followed first order kinetics. The correlation coefficients for all three temperatures are greater than 0.97 and therefore this represent a good agreement on the relationship between temperature and time for oxidation. Air alone has no ability to oxidize the sulfur compounds directly and therefore, air is used as an assisting agent to improve oxidation of the OSC in liquid hydrocarbons to their respective sulfoxide and sulfones. The presence of air at a flow rate of 60 l/hr increased oxidation from 59.2% to 64.2% and 47.4% to 53% for CAC and ATC, respectively.

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CHAPTER 5

5. ADSORPTIVE DESULFURIZATION OF TIRE PYROLYTIC OIL (TPO) USING Cu(I) – Y ZEOLITE VIA π -COMPLEXATION

5.1 Abstract

The accelerating requirement to reach 0% sulfur content in liquid fuels demands researchers to seek efficient alternative technologies to challenge the predicament. In this current study, the adsorption capabilities of modified Cu(I)-Y zeolite were tested for removal of organosulfur compounds (OSC) present in TPO. The π -complexation-based adsorbent was obtained by ion exchanging Y-zeolite with Cu^+ cation using liquid phase ion exchange (LPIE). Preparation of the adsorbent involved firstly ion-exchange between Na-Y zeolite with a $\text{Cu}(\text{NO}_3)_2$ aqueous solution of 0.5M for 48 hours followed by reduction of Cu^{2+} to Cu^+ . Fixed-bed breakthrough studies for TPO in comparison with model diesel comprising of sulfur compounds such as thiophene, benzothiophene (BT) and dibenzothiophene (DBT) showed that modified Cu(I)-Y zeolite is an effective adsorbent for removal of OSC in liquid fuels. The effect of operating conditions such as adsorbent dosage and reaction time were studied to optimize the adsorptive desulfurization process. For model diesel fuel, the selectivity for adsorption of sulfur compounds followed the order $\text{DBT} > \text{BT} > \text{Thiophene}$. The Cu(I)-Y zeolite is fully regeneratable and this is achieved by a simple procedure of blowing the adsorbent with air at 350 °C, followed by reactivation at 450 °C in a rich helium surrounding.

5.2 Introduction

The need for sighting alternative and renewable energy is of great importance in the present century due to the depletion of fossil fuels and the negative impact they impose to the environment during consumption. Turning a non-environmentally friendly waste such as tires to a worthy alternative energy such as diesel fuel is an important process which still needs great attention from researchers around the globe. Pyrolysis of waste tires produces four valuable products namely; char, steel, non-condensable gases and

oil (Laresgoiti et al., 2004). The char is used in water treatment facilities for adsorption of heavy metals, the steel can be taken for recycling and the non-condensable gases are used within the plant for heating the pyrolysis reactor. It has been reported by multiple authors that TPO have the same properties as commercial diesel fuel (Cunliffe and Williams, 1998; Benallal et al., 1995; de Marco Rodriguez et al., 2001). Therefore, this makes TPO a possible substitute for commercial diesel. The greatest hurdle faced by TPO is the presence of OSC such as thiophene and thiophene derivatives which are much more sophisticated as compared to those OSC found in crude oil. Therefore, due to the nature of OSC found in TPO, conventional desulfurization technologies such as hydrodesulfurization (HDS) struggle to effectively remove the OSC compounds. The removal of sulfur species in liquid fuels is of great importance in the petrochemical industry. This is because the production of SO_x by automobiles during combustion leads to many problems including poisoning of the catalytic converter by binding to and deactivating the metal catalyst as well as corrosion of internal combustion engines (Shiraishi et al., 2001). Moreover, the SO_x containing smoke emitted by these combustion engines reacts with water in the atmosphere and subsequently cause acid rain which is harmful to the ecosystem (Shiraishi et al., 2002). Desulfurization of liquid fuels is therefore of great importance before they can be used. There are various desulfurization technologies currently being employed and potential technologies being studied around the globe.

HDS in combination with carbon rejection technologies, such as coking and fluid catalytic cracking, are the main technologies industrially employed for the desulfurization of heavy oil (Rayo et al., 2008). The HDS process employs Co- Mo/ Al_2O_3 or Ni-Mo/ Al_2O_3 catalyst at high temperatures $>300^\circ\text{C}$ and pressures between 20 – 100 atm of H_2 (Gates et al., 1979) . Although these technologies are quite capable of removing lighter sulfur compounds in the heavy oil, their carbon footprints are substantial. Furthermore, HDS struggles greatly with removing dibenzothiopenes with methyl groups positioned at 4- and 6- (Hernández-Maldonado et al., 2005). Therefore, this makes HDS an incompetent desulfurization technology for TPO.

There is a continuous effort given to adsorptive desulfurization as a promising technology for substitution of conventional methods. The greatest advantage for the use of adsorbent in desulfurization of liquid fuels would be ambient operating conditions that is pressure and temperature. Multiple adsorbents such as activated carbon, activated alumina and nickel-based adsorbent have been employed to explore their effectiveness (Kim et al., 2006). Unfortunately, most available commercial adsorbents tested for desulfurization of commercial liquid fuels have proven to be ineffective. De Luna, Mark Daniel G et al. (2014) reported that most adsorptive desulfurization studies involves two stages, which first include oxidation and thereafter adsorption of the oxidized sulfur compounds. This is due to the properties of sulfur compounds being slightly more polar than hydrocarbons of the same nature. The greatest obstacle faced by adsorptive desulfurization is selective adsorption of the OSC in liquid fuels. This is because sulfur compounds in this liquid hydrocarbons or petroleum individually vary in their reactivity. In recent years, the use of π -complexation adsorbents have proven to selectively adsorb thiophenic compounds and its derivatives and not valuable hydrocarbon compounds such as benzene as found in liquid fuels (Yang et al., 2001; Takahashi et al., 2002; Yang et al., 2002). Because of the selectivity, this makes π -complexation sorbent much more superior than other adsorbents for desulfurization of liquid fuels. The use of this selective adsorbent has not been utilized on industrial scale since π -complexation bonds are also weak at higher temperatures and pressure (King, 1987).

The aim of this current study is to exploit the removal capacity of modified Cu(I)-Y zeolite π -complexation-based adsorbent for desulfurization of OSC in TPO and synthesized model fuel comprising of thiophene, BT and DBT prepared in n-octane solution. The importance of model fuel is to understand the individual behavior/reactivity of the sulfur compounds. The competitiveness of aromatic compounds through the introduction of benzene has been studied too to understand the selectivity of Cu(I)-Y zeolite to OSC in comparison with aromatic compounds as mostly found in liquid fuels.

5.3 Experimental Methodology

5.3.1 Materials

TPO with a sulfur content of 7767.7 ppmw was purchased at a local pyrolysis plant located at Alrode industrial complex, Gauteng province, South Africa. Sodium type (Na) Y zeolite, copper(II) nitrate $[\text{Cu}(\text{NO}_3)_2]$, anhydrous n-octane and benzene solution were purchased at Sigma-Aldrich. All standards thiophene, benzothiophenes (BT) and dibenzothiophene (DBT) were purchased from Merck Chemicals and no further purification was performed before use in the experiments. Helium gas (He) cylinder was supplied by Air Liquide (Pty) Ltd, a local air separation company.

5.3.2 Adsorbent preparation

The adsorbent used in this study is modified Y-zeolite prepared by using the known liquid-phase ion-exchange technique (LPIE). The LPIE technique was achieved by first ion exchanging Na-Y zeolite with a $\text{Cu}(\text{NO}_3)_2$ solution of 0.5M for 48 hours followed by an auto-reduction of Cu^{2+} to Cu^+ . Helium at 450 °C for 18 hours was used to auto-reduce Cu^{2+} to Cu^+ . Auto-reduction of cupric ions to cuprous has been reported by multiple authors specifically for zeolite synthesis (Takahashi et al., 2000; Takahashi et al., 2001).

5.3.3 Model Fuel

Four model fuels were prepared in this work to study the effect of different refractory sulfur compounds and the presence of aromatic compound on desulfurization. Table 5.1 represent the four synthesized model fuels (MF1 – MF4) at different concentrations of benzene, thiophene, BT and DBT. MF1 to MF3 has no aromatic compounds and were used to study the effect of individual sulfur compound, thiophene, BT and DBT at different concentrations (100 and 200 ppmw S). MF4 introduces the presence of aromatic compounds at a concentration of 20 wt% and all other sulfur compounds are kept at the same concentration of 100 ppmw S to study the presence of aromatic compounds.

Table 5.1: Compositions of model fuels (MF1 to MF4) prepared in anhydrous n-octane solution

Name	Benzene (wt%)	Thiophene (ppmw S)	BT (ppmw S)	DBT (ppmw S)
MF1	-	100	100	200
MF2	-	100	200	100
MF3	-	200	100	100
MF4	20	100	100	100

5.3.4 Batch adsorption studies

All batch adsorptive experiments were carried out in a borosilicate glass beaker. The nature of zeolite is that it can absorb moisture, and therefore because of this hygroscopic nature, it was ensured that dehydration of the zeolite and beakers was performed before each experiment. This was achieved by blowing helium gas in the beaker packed with modified Cu(I)-Y zeolite. Before any experiment, pure n-octane (sulfur free) solvent was used to wash the zeolite and beaker to remove the trapped helium gases, as suggested by (Yang et al., 2001; Yang et al., 2003). Although, (Bhandari et al., 2006) reported that no considerable difference is found when running the experiments with or without sulfur free solvent wash. The now moisture and gas free zeolite was used in batch experiments for both TPO and model fuels (MF1 – MF4). The effect of operating conditions were varied as follows; adsorbent dosage (0.5 – 3.0 g) and reaction time (10 – 50 min) were studied to optimize the process per 100 ml of MF or TPO. At the end of each reaction, the liquid mixture was separated from the solids by vacuum filtration using WHATMAN grade 1 filter paper, a Buchner funnel and a vacuum pump. Sulfur analysis of the samples was performed using Rigaku NEX QC+ Energy Dispersive X-ray fluorescence spectrometer.

Sulfur percentage removal was calculated using the formula:

$$\% \text{removal of sulfur} = \frac{C_o - C}{C_o} \times 100$$

Where C_o is the initial sulfur concentration (mg L^{-1}) and C is the sulfur concentration remaining in the TPO (mg L^{-1}).

5.4 Results and Discussion

5.4.1 Effect of adsorbent dosage and time on the percentage removal of sulfur for model fuels

Figure 5.1 shows the effect of adsorbent dosage on the percentage removal of sulfur from model fuels (MF1 – MF4). From Figure 5.1, it is seen that the percentage removal of sulfur increases gradually with an increase in the adsorbent dosage from 0.5 g/100 ml to 2.0 g/100 ml and thereafter the removal percentage slightly increases from 2.0 g/100 ml to 2.5 g/100 ml and finally remains unchanged with an increase in the adsorbent dosage from 2.5 g/100 ml to 3 g/100 ml. These results evidence the performance of modified Cu(I)-Y zeolite for desulfurization of OSC present in the prepared model fuels. The increase in the percentage removal of OSC as the adsorbent dosage is increased from 0.5 g/100 ml to 2.5g /100ml takes place due to the availability of adsorption sites on the surface of the modified Cu(I)-Y zeolite leading to OSC being adsorbed onto the adsorption sites of the adsorbent. However, increasing the adsorbent dosage from an adsorbent dosage beyond 2.5 g/100 ml does not result in any further increase in the percentage removal of modified Cu(I)-Y zeolite form all model fuels. This behavior takes place because at an adsorbent dosage of 2.5 g/100 ml to 3 g/100 ml equilibrium between the adsorption sites on the surface of the adsorbent and the OSC in the model fuels has been reached and at this point the rate of adsorption is equal to the rate of desorption from the adsorption sites of the adsorbent which results in a constant percentage removal of OSC.

Figure 5.1 also shows that modified Cu(I)-Y zeolite has a higher selectivity towards more complex OSC such as DBT. Through molecular orbital calculations, Yang et al. (2002) showed that methyl groups in the substituted thiophenic compounds can enhance the electron back-donation process during π -complexation and, thus, results in higher energies of adsorption. This agrees well with the results shown in Figure 5.1. The effect of aromatic compound was also studied by introducing benzene at 20% for MF4. The results show that MF4 at the lowest sulfur concentration of 300 ppmw S does not have the highest desulfurization percentage because of the presence of aromatic compounds present. Therefore, it is evident from the results that aromatic compounds can also get adsorbed since they can compete through interaction of their π -electron cloud.

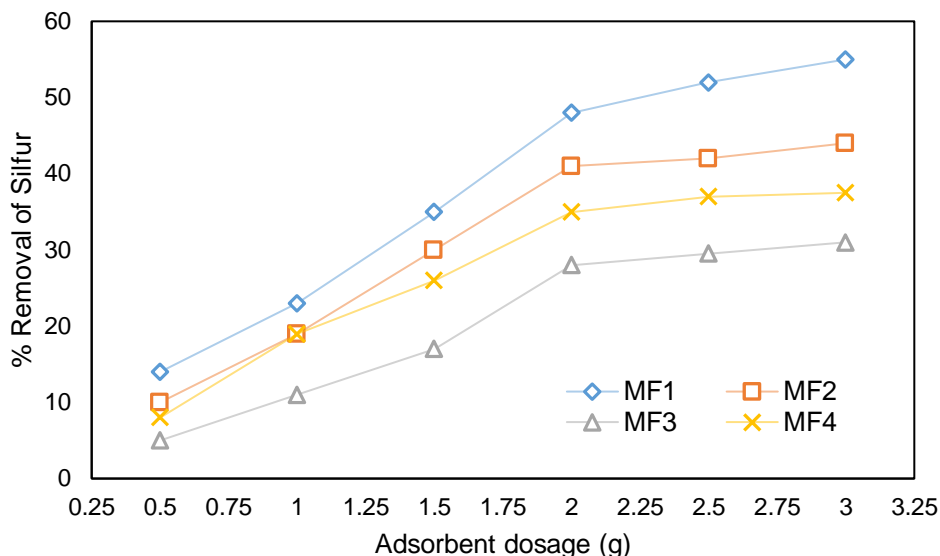


Figure 5.1: Variation of adsorbent dosage per 100ml of MF. Reaction conditions were held constant as follows; Temperature 25 °C, time 40 min, Stirring speed 250 rpm.

The effect of contact time on the percentage removal of OSC is shown in Figure 5.2. The percentage removal of sulfur increases with an increase in the contact time for all model fuels (MF1 -MF4) using modified Cu(I)-Y zeolite. The percentage removal of sulfur increases gradually from 10 – 30 min and thereafter there is a slight increase from 30 – 40 min. It is notable that the intake of OSC onto the modified Cu(I)-Y zeolite reaches equilibrium after 40 min for all model fuels. Correspondingly, it is still evident from the effect of time that modified Cu(I)-Y zeolite has a higher selectivity towards more complex OSC as seen on the effect of adsorbent dosage. The effect of time also suggests that the adsorption of OSC onto modified Cu(I)-Y zeolite is a faster reaction since equilibrium was reached within 40 min.

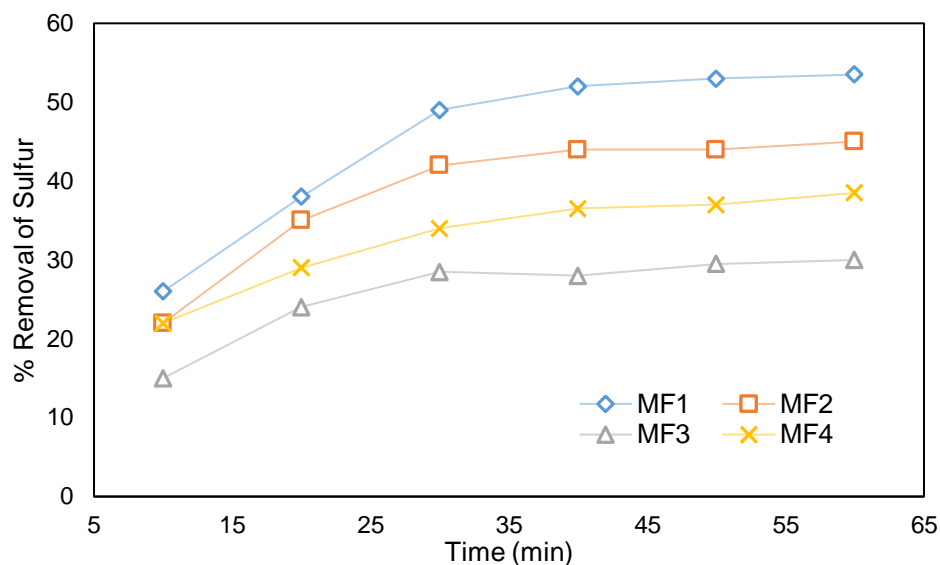


Figure 5.2: The effect of reaction time for adsorption process. Reaction conditions were held constant as follows; Temperature 25 °C, Adsorbent dosage 2.5 g/100 ml MF, Stirring speed 250 rpm.

5.4.2 Effect of adsorbent dosage and time on the percentage removal of sulfur for TPO

Figure 5.3 and 5.4 shows the effect of adsorbent dosage and contact time on the adsorption capacity of modified Cu(I)-Y zeolite for the removal of OSC present in TPO, respectively. From both Figures, it is evident that an increase in both the adsorbent dosage and contact time results in the increase in the adsorption capacity of the modified Cu(I)-Y zeolite. The increase in the adsorption capacity with an increase in the adsorbent dosage is due to an increase in the adsorption sites available for the adsorption of OSC as the adsorbent dosage is increased. Similarly, an increase in the adsorption capacity as the contact time is increased is due to the increased amount of time for the adsorbent to be in contact with the OSC which results in adsorption and hence higher adsorption capacities at an increasing contact time.

A general comparison between the prepared model fuels and TPO suggests that higher percentage removal of OSC are experienced with model fuels as compared to TPO. These results are mainly due to the initial OSC concentrations found in both fuels,

whereby TPO has a much higher concentration 7767.7 ppmw as compared to the prepared model fuels ranging between 300 – 400 ppmw. Furthermore, the presence of aromatic compounds proved that they can also get adsorbed since they can compete through interaction of their π -electron cloud. TPO have been reported to have high concentrations of aromatic compound based on the pyrolysis reactor conditions. Table 5.2 below represent the effect of temperature reported by (de Marco Rodriguez et al., 2001) on TPO yield and type of compounds found in TPO. The results as reported by (de Marco Rodriguez et al., 2001) suggests that the TPO used in this study contains around 62.4% aromatic compounds. therefore, this further justifies the lower percentage removal of OSC for TPO.

Table 5.2: TPO types of compounds (analyzed using GC-MS)

Pyrolysis temperature (°C)	300	400	500	600	700
Aromatics	34.7	59.3	62.4	75.6	57.4
Aliphatics	59.2	34.9	31.6	19.8	37.0
Nitrogenated	4.5	3.7	4.2	2.6	3.8
Benzothiazol	1.6	2.1	1.8	2.0	1.8

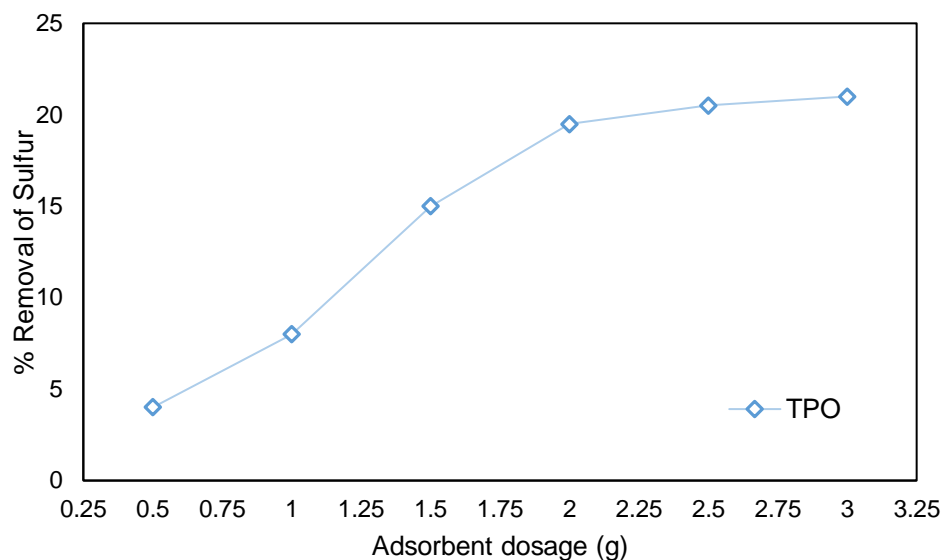


Figure 5.3: Variation of adsorbent dosage per 100ml of TPO. Reaction conditions were held constant as follows; Temperature 25 °C, time 60 min, Stirring speed 250 rpm.

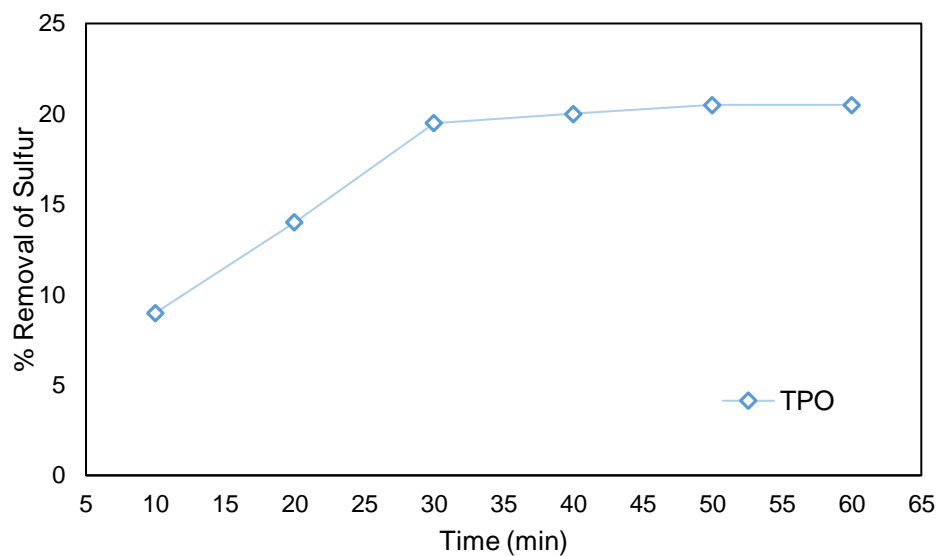


Figure 5.4: The effect of reaction time for adsorption process. Reaction conditions were held constant as follows; Temperature 25 °C, Adsorbent dosage 2.5 g/100 ml TPO, Stirring speed 250 rpm.

5.5 Conclusion

Desulfurization of liquid fuels such as the prepared model fuels and TPO can be accomplished at ambient temperature and conditions using modified Cu(I)-Y zeolite through π -complexation adsorption. An increase in both the adsorbent dosage and contact time results in the increase in the adsorption capacity of the modified Cu(I)-Y zeolite because of an increase in the adsorption sites available until equilibrium is reached. Based on the batch adsorption studies, the selectivity of OSC by of modified Cu(I)-Y zeolite decreases as follows: DBT > BT > Thiophene. The aromatic content in the model fuel (MF4) was found to have a negative impact on the desulfurization capacity of the adsorbent. The effect of initial sulfur concentration also proved to have a drastic impact on the adsorption capacity. This effect is seen when the adsorption capacity of modified Cu(I)-Y zeolite was higher for TPO than model fuels. The modified Cu(I)-Y zeolite is fully regeneratable and this is achieved by a simple procedure of blowing the adsorbent with air at 350 °C, followed by reactivation at 450 °C in a rich helium surrounding.

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CONCLUSION

This study presents findings on the desulfurization of TPO using adsorption and oxidation techniques. Preparation and characterization of carbon adsorbents TC, DTC, ATC and CAC was achieved using Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscope (SEM). Treatment of TC through demineralization and chemical activation with KOH enhances the oxygen containing sites on the material as shown by FTIR. Modification of DTC by chemical activation improves the surface morphology of the material as shown by SEM images. TGA analysis confirmed that more volatile matter and ash was removed from the ATC during the activation process. Adsorption experiments revealed that CAC achieves higher removal percentages of OSC compared to ATC. The adsorption experiments further showed the effect of process variables affecting the adsorption of OSC onto CAC and ATC, and the optimum operating conditions were obtained. Pseudo-first order kinetic model provided a better fit for both CAC and ATC. Furthermore, both adsorbents present a heterogeneous surface by following the Freundlich isotherm model.

The presence of carboxylic group content on the surface of the material plays a vital role for adsorption and qualifies them as catalysts for oxidative desulfurization processes. CAC and ATC were exploited as catalysts for air-assisted oxidative desulfurization of TPO using performic acid as the main oxidizing agent. The effect of $\text{H}_2\text{O}_2/\text{HCOOH}$ ratios showed that performic acid is a strong oxidizing agent and it performs better than its individual precursors H_2O_2 and HCOOH for oxidation of OSC in TPO. Air alone has no ability to oxidize the sulfur compounds directly and therefore, air is used as an assisting agent to improve oxidation of OSC in liquid hydrocarbons to their respective sulfoxide and sulfones.

Preparation of π -complexation adsorbent was achieved by ion exchanging Y-zeolite with Cu^+ cation using liquid phase ion exchange (LPIE). Based on the batch adsorption studies, the selectivity of OSC by of modified Cu(I)-Y zeolite decreases as follows: DBT > BT > Thiophene. The aromatic content in the model fuel (MF4) was found to have a negative impact on the desulfurization capacity of the adsorbent. The effect of initial sulfur concentration also proved to have a drastic impact on the adsorption capacity. Modified

Cu(I)-Y zeolite have proven to be a better adsorbent as compared to carbon derived adsorbents as used in this study.