



Original Research Article

Upgrading of Tire-Derived Oil Quality Using Two-Stage Ultrasound-Assisted Oxidative Desulfurization and Adsorption

*¹Abubakar, A., ¹Gaiya, J.D. and ²Ahmed, U.O.

¹Department of Chemical Engineering, Ahmadu Bello University, Zaria, Nigeria.

²Department of Chemical and Petroleum Engineering, Bayero University, Kano, Nigeria.

*abubakara@abu.edu.ng

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ABSTRACT

Waste tire-derive oil has attracted considerable attention as an alternative fuel due to the similarity in its properties with diesel oil. Unfortunately, the tire-derived oil is usually associated with high amount of undesirable sulfur that is by far higher than the allowable limit. This necessitates its treatment before it can be suitable for use in engines. Having been adjudged to be the most efficient and the most environmentally friendly method because of its mild operating conditions, oxidative desulfurization of the tire-derived oil was adopted in this study with the assistance of ultrasound energy to further enhance its efficiency. Having optimized the process conditions oxidative desulfurization, attempt was made to further reduce the sulfur content and improve other oil properties by subjecting to selective adsorption. The results revealed sulfur removal of 76.1 % during the oxidative desulfurization at optimum temperature, time, and oxidant-to-oil ratio of 51.4 °C, 46.2 min., and 1, respectively. The further treatment by adsorption brought about additional 58.4 % sulfur removal resulting to a combined sulfur removal of 90.1%. There were also decreases in viscosity (34.5 %), flash point (23.4 %), and acid value (93.4%) while increases were recorded in heating value (14.9 %) and cetane number (23.5%). Overall, there is a substantial improvement in the tire-derived oil quality using a combined ultrasound-assisted oxidative desulfurization and adsorption making more suitable to serve as an alternative to diesel.

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1. INTRODUCTION

According to Rowhani and Rainey (2016), there were roughly 1.5 billion of scrap tires being added annually to the already existing 4 billion due to the continuous increase in the production of cheaper cars that are now easily accessible by developing countries. Without strict wastes management laws in place, especially by the developing countries, these tires, after being used or expired, are likely discarded into the environment, and

then ended up being accumulated in dumping sites. This problem is now rampant in cities as evidenced by the percentage of the landfill occupied by waste tires.

The use of the expired tires as fuel, as it was the case in the past, is now considered detrimental to the environment due to the release of various harmful gases such as CO₂, CO, SO_x, and NO_x (Glushankova *et al.*, 2019). Other problems associated with burning of waste tires include damage to human health caused by other pollutant emissions such as polyaromatic hydrocarbons (PAHs), benzene, styrene, butadiene, and phenol-like substances (Glushankova *et al.*, 2019). Therefore, open dumping seems to be most convenient option of scrap tires disposal and about 65.5% of scrap tires are dumped in the open air or landfills according to Ahmad *et al.* (2016). However, the fact that tires are inherently nonbiodegradable also cause safety concerns and health-related problems as the dump sites constitute a suitable ground for breeding of insect and mosquitos as well as accidental fires (Williams, 2013; Debek and Walendziewski, 2015; Islam and Nahian, 2016). Alternative usage options of the used tires that are devoid of the highlighted challenges include: (1) tire reconstruction where structurally sound tires are rethreaded for reuse, (2) recovery of materials where tires are shredded to produce rubber chips that can be used as noise barriers in sports facility flooring, roofing materials etc., and (3) recovery of energy from waste tires that can be achieved through thermal processes such as pyrolysis, combustion and gasification (Zhang *et al.*, 2008; Rowhani and Rainey, 2016; Islam and Nahian, 2016; Namchot and Jitkarnka, 2016; Alvarez *et al.*, 2017; Wang *et al.*, 2019; Sathiskumara and Karthikeyan, 2019).

Pyrolysis is most common method for recovery of energy from waste tires. The process is a thermal decomposition of the waste tires in absence of air or oxygen to produce gases, oil, and char (Chorazy *et al.*, 2020; Xu *et al.*, 2021). The oil, also known as tire-derived oil (TDO), is the most important product as it can serve as an alternative fuel for diesel engine replacing the usual petroleum diesel (Mangesh *et al.*, 2020; Wang *et al.*, 2020; Yaqoob *et al.*, 2021). In addition, the TDO can even be blended with gasoline to improve the performance of electric generator (Odejobi *et al.*, 2020). However, the presence of high amount of sulfur, which comes from the rubber vulcanization stage during the production of the tires, constitute a major setback as its combustion in engines results to the production and release of sulfur oxides into the atmosphere (Banar *et al.*, 2012; Rowhani and Rainey, 2016; Islam and Nahian, 2016). Thus, ensuring the usage of the oil within the sulfur emission limit (e.g. 10 ppm by European countries) will require efficient desulfurization approach (Al-Lal *et al.*, 2015). Different desulfurization approaches and technologies such as hydrodesulfurization, oxidative desulfurization, extractive desulfurization, adsorptive desulfurization etc. have been employed to reduce the level of sulfur in the TDO (Serefontse *et al.*, 2019).

In hydrodesulfurization process, the severe operating conditions such as high temperature (350-450 °C) and pressure (20-200 bar), and the requirement of expensive catalysts constitute a major setback. Fortunately, oxidative desulfurization (ODS) does not require these stringent and expensive conditions. Rather, it requires mild conditions (temperature of not more than 100 °C) and a suitable oxidant that can selectively convert the sulfur-containing compounds in the oil to their respective sulfoxides and sulfones by denoting one oxygen atom and two oxygen atoms to the sulfur atoms in the oil, respectively as illustrated in Figure 1 (Hossain *et al.*, 2019; Kaur, 2021; Kaur *et al.*, 2021). In contrast to the original sulfur-containing compounds, the sulfones produced from this oxidation process are polar with lower C-S bond energy and therefore, can be easily removed from the oil by adsorption, extraction, distillation, or decomposition (Hossain *et al.*, 2021). Besides its mild operating conditions, ODS also has advantage of offering superdeep fuel oil desulfurization efficiency (Rezvani *et al.*, 2018; Kang *et al.*, 2018; Dizaji *et al.*, 2019; Zhang *et al.*, 2021).

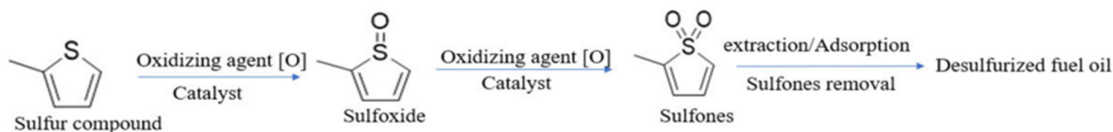


Figure 1: Mechanism involved in the oxidative desulfurization of fuel oil (Hossain *et al.*, 2021)

Although the mild operating conditions of the oxidative desulfurization is one of the reasons that makes this approach the most attractive, great care must be taken on the choice of the oxidizing agent as some of the

oxidants are not quite selective and tend to cause side reactions, which alter the quality and quantity of the oil (Ahmad *et al.*, 2016). There are several oxidizing agents that have been successfully tested for the ODS. They include H_2O_2 , O_2 , K_2FO_4 , cumin hydroperoxide (CHP), and tert-butyl hydroperoxide (TBHP) etc. Among these oxidizing agents, H_2O_2 have been used by most researchers because of its commercial availability, low cost, non-polluting, and comparatively less corrosive (Andevary *et al.*, 2019).

Another non-conventional desulfurization approach is the extractive desulfurization, which takes advantage of the fact that some of organo-sulfur compounds are more readily soluble in polar solvents than hydrocarbons. Because of the applicability at low temperatures and pressure, this liquid-liquid separation process is also attractive as it is carried out at relatively low conditions. Meanwhile, this method is better appreciated after subjecting the oil to oxidative desulfurization since the sulfur removal rate is low when used alone as revealed by Ali *et al.* (2006). The success of the adsorptive desulfurization process depends on how well the organo-sulfur compounds in the oil can be selectively adsorbed by a solid adsorbent. This can be achieved through either physical adsorption or reactive adsorption, also known as chemisorption. Like the liquid-liquid extraction method, the performance of this solid-liquid extraction method in terms of the sulfur removal is also appreciated when it is carried out after the oxidation of TDO. It also has the advantage of being carried out at low temperature and pressure (Javadli and de Klerk, 2012; Omar and Verma, 2022).

Ultrasound-Assisted oxidative desulfurization (UAOD), an advancement of the ODS process is a method used to achieve an oxidation reaction with sulfur compounds under mild reaction conditions with the help of ultrasound energy. This innovative UAOD technology was introduced to improve the desulfurization efficiency of conventional ODS processes (Jalali and Sobati, 2017). The additional cavitation process introduced into oxidation reaction by the ultrasound energy makes the UAOD more effective at removing sulfur than ordinary ODS. Cavitation is a phenomenon that is attributed to the formation, growth, and collision of microbubbles in the liquid medium, and it generates excessive heat energy and pressure in the reaction medium. The physical and chemical effects of the cavitation phenomena improve the oxidation reaction rate in the UAOD process by increasing the interfacial mass transfer rate between the hydrocarbon and oxidant phases (Choi *et al.*, 2016; Sinhmar and Gogate, 2019; Lin *et al.*, 2020; Dana *et al.*, 2020).

It can be adduced from foregoing that the oxidative desulfurization (ODS) offered the best performance among these different approaches in terms of sulfur removal efficiency, operating conditions, and environmental friendliness. However, the stringent environmental regulation on the allowable sulfur content in engine fuels is still not met by even the best performance the ODS can provide. Besides, the presence of other unwanted polar compounds such oxygenates limit the usage of the oil as an alternative to diesel (Mohan *et al.*, 2019; Uguz *et al.*, 2021). Therefore, there is need to further find ways of improving the desulfurization process and one way this may be achieved is to subject the oxidation process of the conventional ODS to ultrasound agitation, as already been done for fossil fuels. The ultrasound introduces cavitation, which is the formation, growth and collision of microbubbles that results to increased mixing, heat energy and pressure in the system.

Therefore, the aim of this work was to upgrade TDO using two-stage approach of ultrasound-assisted oxidative desulfurization (UAOD) and adsorption processes. The UAOD process is to substantially reduce the sulfur content of the tire-derived oil while the adsorption process is to further reduce the sulfur content of the tire-derived oil to acceptable level and improve other properties of the oil. The essence of carrying out the desulfurization in the presence of the ultrasound is to help in achieving the target limit of sulfur content in the oil at less stricter operating conditions. The process parameters of the oxidation process were also optimized using central composite design (CCD). The choice of the adsorption process in reducing other unwanted polar compounds was based on its mild operating conditions (and hence low energy consumption) as compared with conventional distillation process. Based on the literature available to us, this adopted approach of upgrading TDO has not been reported.

2. MATERIALS AND METHODS

2.1. Materials

The raw TDO were purchased from El-Hyatt Pyrolysis Company, along Zaria-Kano Express way, Zaria, Kaduna State, Nigeria. All the chemicals used such as the oxidant (hydrogen peroxide, 30 wt.%), catalyst (acetic acid, 90 wt. %), diluent (toluene), extraction solvent (N,N-dimethylformamide), drying agent (anhydrous sodium sulphate), Silica gel (60–120 mesh), petroleum ether (60–80 °C) were of analytical grade produced by Sigma Andrich company. Design-Expert version 13.0 was used for the optimization of the UAOD process parameters. Ultrasonic Lab Homogenizer (Model No.: JH1000W-20) manufactured by Hangzhou Precision Machinery Ltd, China was used to achieve the UAOD process.

2.2. Ultrasound-Assisted Oxidative Desulfurization of TDO

The optimization of the oxidation (UAOD) process was carried out the help of Design Expert® software version 13.0. Precisely, Central Composite Design (CCD) was adopted to investigate the effects of three process parameters such as temperature (T), time (t), and oxidant-to-TDO ratio (R) on the percentage of sulfur removal, S_R (wt. %). Table 1 presents the design ranges of the three parameters or factors. Meanwhile, the relationship between coded factors (X_i) and actual factors (x_i) is given in Equation (1).

$$X_i = (x_i - x_o) / \Delta x \quad (1)$$

where x_o denotes value of x_i at the center point and Δx denotes step change.

Table 1: Design ranges of the operating parameters

Parameter	Symbol		Units	Type	Low	High
	Actual	Coded				
Temperature	T	X_1	°C	Factor	30	80
Time	t	X_2	min.	Factor	30	100
Oxidant-to-Oil Ratio	R	X_3	v/v	Factor	1	3

Now, UAOD experiment began by adding 25 mL of the raw tire-derived oil (R-TDO) into 250 mL 3-neck round bottom flask. Depending on the TDO-to-oxidant ratio under consideration, an appropriate amount of the hydrogen peroxide was added into the flask followed by the addition of the catalyst (acetic acid) and diluent (toluene). The oxidant-to-acid ratio was kept constant at 1:1 (v/v) while the TDO-to-diluent ratio was kept constant at 1:2 (v/v). The diluent is non-reactive, and its presence is to prevent (or at least drastically reduce) the possible heat generated by the exothermic oxidation reaction so that the temperature of the reacting system can be controlled. The ultrasonicator set at constant frequency of 20 kHz to provide the required ultrasound energy was then inserted into the central neck of the flask while a thermometer and a reflux condenser were inserted into the side necks of the flask. Heat was supplied into flask by a temperature-controlled water bath, which ensured uniform distribution of the heat. After the UAOD process, the desulfurized oil was separated by extraction using N,N-dimethylformamide as the extraction solvent at oil-to-solvent ratio of 1:1 (v/v) in a separating funnel. The separated desulfurized was then washed and separated twice with distilled water at ratio of 1:2 (v/v) using the same separating funnel. To ensure that there was not any trace of water in the extracted oil, anhydrous sodium sulfate was added and then filtered out using filter paper (Whatman No. 1) to obtain the desulfurized tire-derived oil, which was denoted as D-TDO. The percentage of sulfur removal after UAOD of the TDO was calculated using the following equation.

$$S_R(\%) = \frac{C_o - C_d}{C_o} \times 100 \quad (2)$$

where S_R is percentage of sulfur removal, C_o is initial sulfur content (wt. %) in the TDO, and C_d is sulfur content (wt. %) in the desulfurized TDO.

2.3. Upgrading of Desulfurized TDO via Adsorption Process

In order to improve its quality, the desulfurized TDO at optimized conditions was further upgraded using selective adsorption process. In a 500-mL conical flask, 50 mL of the desulfurized TDO was added, then stirred continuously in a magnetic stirrer at room temperature for 10 minutes before petroleum ether (60-80 °C) was added at TDO-to-petroleum ether ratio of 1:3 (v/v) and the stirring continued for another 15 minutes. The supernatant from the solution was transferred into another 500 mL conical flask and then 50g of silica gel (i.e., adsorbent dosage of 1 w/v) was added. The petroleum ether served as a diluent to reduce the physical attachment of the silica gel to the TDO. The mixture was then stirred continuously for 1 hour at room temperature before it was subjected to vacuum filtration to separate the solution. The residue, which was largely the silica gel was washed with fresh petroleum ether at 1:1 (w/v) and then vacuum filtered again to recover more oil. The two filtrates containing the oil and the petroleum ether were thereafter combined and then the petroleum ether was removed by evaporation in a rotary evaporation at 60 °C and reduced pressure of 3 in. Hg to obtain the upgraded oil denoted as U-TDO. Both silica gel and petroleum ether can be regenerated or recovered by calcination and distillation respectively. This procedure was repeated for adsorbent dosage of 2, 3, and 4 w/v to determine the effect of adsorbent dosage on the quality of the TDO in terms of the sulfur content, density, cetane index, thermal stability, viscosity, flash point, acid value, and heating value. Equation (3) was used to calculate the percentage of sulfur removal after the upgrading or adsorption process.

$$S_R(\%) = \frac{C_d - C_u}{C_d} \times 100 \quad (3)$$

where C_d and C_u denote the sulfur contents (wt. %) before and after upgrading the desulfurized TDO respectively.

2.4. Characterization of Upgraded TDO

The sulfur contents (wt. %) of both raw and upgraded TDO were determined from ultimate (elemental) analysis using Series II CHNS/O Analyzer (Model No: 2400, Serial No: 241N9022721) manufactured by Perkin Elmer. The density, viscosity, flash point, cetane number, heating value, and acid value of the TDO were determined according to ASTM D4052, ASTM D445, ASTM D93, ASTM D613, ASTM D4868, and ASTM D664, respectively.

3. RESULTS AND DISCUSSION

Table 2 presents the experimental and predicted results of the CCD design. It is observed that all the three factors (temperature, time, and oxidant-to-oil ratio) had considerable effect on the sulfur removal. For instance, the endothermic nature of the desulfurization process was obvious as the increase in the temperature from 13 to 95 °C resulted to a consistent increase in the sulfur removal from 56.6 to 91.9 % at constant time and oxidant-to-oil ratio of 65 min. and 2, respectively. In addition, variation in the time from 6 to 124 min. at constant temperature of 55 °C and oxidant-to-oil ratio of 2 brought also about a consistent increase in the sulfur removal from 60.1 to 90.6 %. Finally, the effect of oxidant-to-oil ratio from 1 to 3 at constant temperature of 80 °C and time of 100 min. on the sulfur removal was found to be moderate as it only increased from 91.1 to 95.0 %. Therefore, the minimum sulfur removal recorded was 47.1 % coinciding with the lowest set of operating conditions (temperature = 30 °C, time = 30 min., and oxidant-to-oil ratio = 1). Similarly, the maximum sulfur removal of 95.0 % coincided with the highest set of operating conditions (temperature = 80 °C, time = 100 min., and oxidant-to-oil ratio = 3). Meanwhile, the comparison between the experimental and

predicted results reveals that the deviations range from 0 to 7.4 %, indicating the high accurate prediction of the model from CCD.

Table 2: CCD matrix with experimental and predicted responses

Std	Run	T (°C)	t (min.)	R (v/v)	Coded Values			S _R (%)	
					X ₁	X ₂	X ₃	Exp.	Predicted
9	1	13	65	2	- α	0	0	52.6	56.5
4	2	80	100	1	1	1	-1	89.2	91.1
7	3	30	100	3	-1	1	1	85.6	85.1
19	4	55	65	2	0	0	0	91.5	91.5
17	5	55	65	2	0	0	0	90.8	91.5
11	6	55	6	2	0	- α	0	55.0	60.1
8	7	80	100	3	1	1	1	93.2	95.0
20	8	55	65	2	0	0	0	92.2	91.5
5	9	30	30	3	-1	-1	1	64.3	60.6
14	10	55	65	3.68	0	0	α	92.5	94.0
2	11	80	30	1	1	-1	-1	80.7	79.4
10	12	97	65	2	α	0	0	93.3	91.9
18	13	55	65	2	0	0	0	91.5	91.5
16	14	55	65	2	0	0	0	92.7	91.5
3	15	30	100	1	-1	1	-1	77.3	77.0
15	16	55	65	2	0	0	0	91.0	91.5
12	17	55	124	2	0	α	0	93.1	90.6
1	18	30	30	1	-1	-1	-1	50.7	47.1
13	19	55	65	0.32	0	0	- α	78.3	79.4
6	20	80	30	3	1	-1	1	90.1	88.6

* $\alpha = 1.682$

Table 3 presents the summary of the models' statistics. Four models (linear, 2FI, quadratic, and cubic) were tested, and quadratic model was found to be the best and therefore suggested based on statistical data such sequential p-value, lack-of-fit p-value, standard deviation, normal R², adjusted R², predicted R², and predicted sum of square (PRESS), which were all within acceptable values. Linear model was the second best as it was only good with respect to its p-values but very poor with respect to its standard deviation and R² values. The next was cubic model which showed good lack-of-fit p-value and standard deviation but very poor with respect to other data. Finally, 2FI model was only good in lack-of-fit value while showing high deficiencies in the remaining statistical data.

Table 3: Model summary

Source	Seq. p-value	L/F* p-value	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	PRESS	
Linear	0.0002	< 0.0001	8.69	0.7049	0.6496	0.5508	1840.16	
2FI	0.5166	< 0.0001	8.86	0.7508	0.6358	0.4557	2230.00	
Quadratic	< 0.0001	0.0007	3.06	0.9772	0.9567	0.8309	692.57	Suggested
Cubic	0.0293	0.0024	1.79	0.9953	0.9852	0.1064	3660.80	Aliased

*L/F = Lack of Fit

The ANOVA results of the selected quadratic model are presented in Table 4. The F-value of 47.64 for the model shows that it is significant and can adequately govern the design space. The adequate precision value of 22.13, which measure the signal-to-noise ratio was found for the quadratic model, signifying that there is an adequate precision as the value was greater than the minimum value of 4 according to Obi *et al.* (2024). All the model terms except three ($T \cdot R$, $T \cdot R$, and R^2) are significant based on their F-values and the p-values of less than 0.05. The coded and actual quadratic models are presented in Equations (4) and (5).

In terms of individual parameter, temperature was found to be the most influencing factor on the sulfur removal because of its lowest p-value, highest F-value as well as its highest coefficient in the actual model. This was followed by time and then oxidant-to-oil ratio, which had the least impact on the sulfur removal. In terms of parameter interaction, the most dominant one was between temperature and time followed by the quadratic self-interactions of temperature, time, and oxidant-to-oil ratio in that order. Figure 2 is a Pareto graph showing the contribution of individual term of the actual model to the sulfur removal. Like the ANOVA results, temperature term contributed the most to the sulfur removal having recorded a lion share of almost 44 %. Time term had the next highest contribution of about 25 % followed by the temperature square term (11.7 %), oxidant-to-oil ratio term (7.1 %), temperature and time interaction term (5.3 %), and time square term (4.7 %) in that order. The least contributed term was oxidant-to-oil ratio term with about 0.76%. Meanwhile, the sulfur removal of 76.1 % was achieved at optimum temperature, time, and oxidant-to-oil ratio of 51.4 °C, 46.2 min., and 1, respectively. This amount of sulfur removal was experimentally validated at the optimum conditions and 75.5 % was achieved indicating a deviation of only 0.8 %.

Table 4: ANOVA for sulfur removal

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	
Model	4003.34	9	444.82	47.64	< 0.0001	Significant
<i>T</i>	1513.07	1	1513.07	162.05	< 0.0001	
<i>t</i>	1118.20	1	1118.20	119.76	< 0.0001	
<i>R</i>	256.46	1	256.46	27.47	0.0004	
<i>T · t</i>	164.71	1	164.71	17.64	0.0018	
<i>T · R</i>	9.03	1	9.03	0.9672	0.3486	
<i>t · R</i>	14.31	1	14.31	1.53	0.2440	
<i>T</i> ²	539.54	1	539.54	57.78	< 0.0001	
<i>t</i> ²	473.13	1	473.13	50.67	< 0.0001	
<i>R</i> ²	42.48	1	42.48	4.55	0.0587	
Residual	93.37	10	9.34			
Lack of Fit	90.78	5	18.16		0.0007	
Pure Error	2.59	5	0.5177			
Cor Total	4096.71	19				

Std. Dev. = 3.06, *Mean* = 82.3, *C.V.* = 3.71 %, *R*² = 0.98, *Adj. R*² = 0.96, *Pred. R*² = 0.83, *Adeq. Precision* = 22.13

$$S_R(\%) = 91.54 + 10.53 \cdot X_1 + 9.05 \cdot X_2 + 4.33 \cdot X_3 - 4.54 \cdot X_1 \cdot X_2 - 1.06 \cdot X_1 \cdot X_3 - 1.34 \cdot X_2 \cdot X_3 - 6.12 \cdot X_1^2 - 5.73 \cdot X_2^2 - 1.72 \cdot X_3^2 \quad (4)$$

$$S_R(\%) = -41.51 + 1.92 \cdot T + 1.23 \cdot t + 16.02 \cdot R - 0.005 \cdot T \cdot t - 0.04 \cdot T \cdot R - 0.04 \cdot t \cdot R - 0.01 \cdot T^2 - 0.005 \cdot t^2 - 1.72 \cdot R^2 \quad (5)$$

The plot of normal probability against studentized residuals is presented in Figure 3. The plot clearly mimics “S-shaped” pattern across the normal or diagonal line. This indicates that the requirement for the transformation of the actual data is not necessary and can be ignored. In Figure 4, the behaviour of externally studentized residual data against run number reveals that the actual data do not also require transformation. In addition, the plot also reveals that the suggested quadratic model was generally fitted by the data as only one data point or outlier was found to be outside the red lines. The accuracy of the model prediction was evaluated using Figure 5, which presents the comparison between predicted responses against actual responses. Based on this plot, all the data can be said to be adequately predicted by the model given the nearness of the data to – and the even distribution of the data across – the diagonal line. This also reinforces the fact that the need for the data transformation to improve the performance of the model can be neglected.

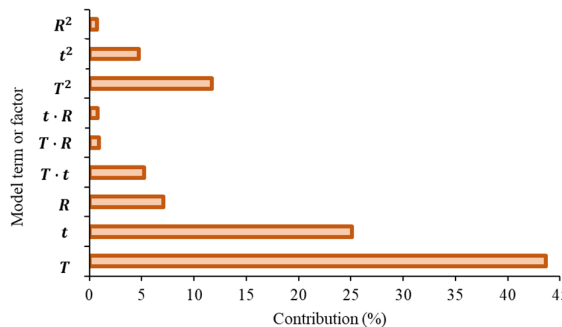


Figure 2: Pareto graph

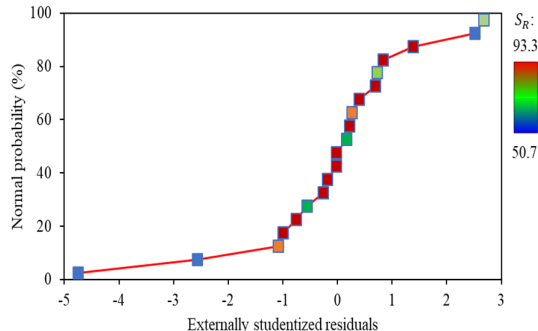


Figure 3: Normal probability against studentized residual plot

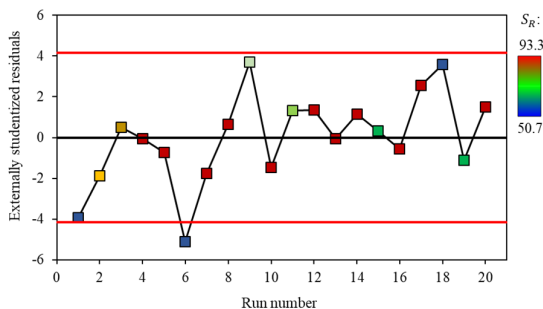


Figure 4: Internally studentized residuals against run number

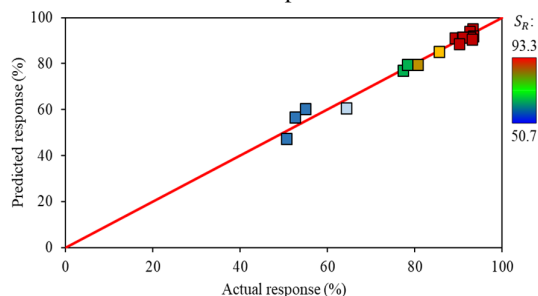


Figure 5: Comparison of predicted responses with actual responses

Figures 6 – 8 are three-dimensional surface plots that present the combined effects of two factors on the sulfur removal while the remaining factor is kept constant. Specifically, the dependence of the sulfur removal on the combined effects of temperature/time at constant oxidant-to-oil ratio of 2, temperature/oxidant-to-oil ratio at constant time of 65 min., and time/oxidant-to-oil ratio at constant temperature of 55 °C are shown in Figures 6, 7, and 8, respectively. The combination of very low temperature and low to moderate time in the desulfurization process (Figure 6) led to moderate sulfur removal. However, the combination of low temperature and high time, low time and high temperature as well as high temperature and high time all led to high performance of the desulfurization process. This indicates that both temperature and time were highly influential though the former was more pronounced than the latter. These trends agree with the findings of Cherop *et al.* (2019). In the case of Figure 7, the combination of low temperature and low to moderate oxidant-to-oil ratio also led to moderate performance of the desulfurization process but at high temperature and low to high oxidant-to-oil ratio, the sulfur removals were very high. This reveals that the oxidant-to-oil ratio posed very little influence on the desulfurization process as compared with temperature. Figure 8 displays very similar trends to those observed in Figure 6 in the sense that oxidant-to-oil ratio offered little to desulfurization process compared with time.

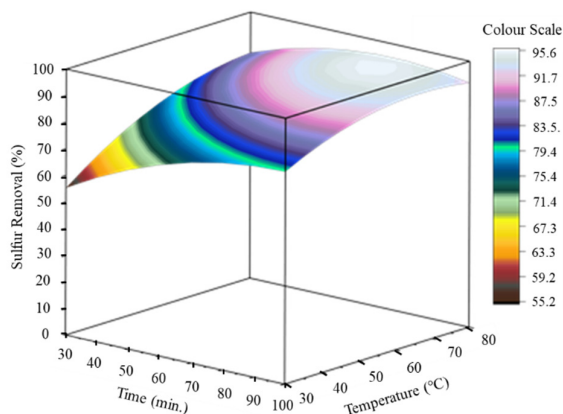


Figure 6: Interacting effects of time and temperature on sulfur removal at constant oxidant-to-oil ratio of 2

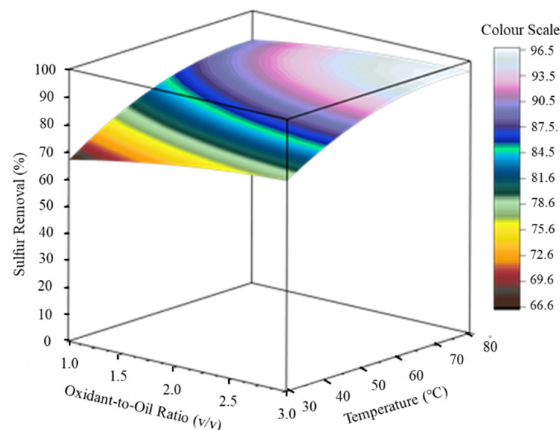


Figure 7: Interacting effects of oxidant-to-oil ratio and temperature on sulfur removal at constant time of 65 min

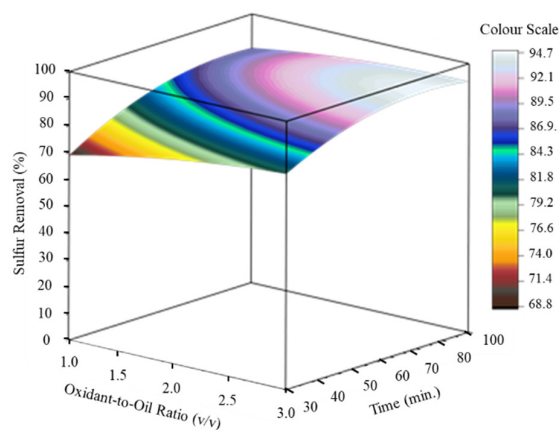


Figure 8: Interacting effects of oxidant-to-oil ratio and time on sulfur removal at constant temperature of 55 °C

Table 5 presents the results of the analyzed physical properties of both the raw and treated TDO while Figures 9 – 11 show the variations of the key properties as a function of adsorbent dosage. It is observed that the sulfur removal was drastically increased with an increase in the adsorbent dosage up to 2 w/v after which further increase in the sulfur removal was not pronounced (Figure 9) indicating that the use of adsorbent dosage above this value did not impact significantly on the sulfur removal. It should be noted that high adsorbent dosage during adsorption process generally results to high performance due to the increase in the available adsorption sites. In Figure 10, both density and viscosity decreased (847 – 838 kg/m³ and 3.18 – 2.34 cSt, respectively) with an increase in the adsorbent dosage signifying that the adsorption process considerably improved the lightness of the oil. This is expected as the adsorbed compounds are usually dominated by high molecular weights polar compounds. Comparing with density (799 kg/m³) and viscosity (2.1 cSt) of a typical diesel (Banar *et al.*, 2012; Moha *et al.*, 2019), the upgraded oil will serve as a better alternative to diesel than the raw oil.

The increase in the adsorbent dosage up to 3 w/v led to a sharp increase in the heating value while further increase in adsorbent dosage produced insignificant increase in the heating value. Overall, the heating value was increased from 36.12 to 41.06 MJ/kg, which is an improvement to the oil quality when compared to the heating value (45.81 MJ/kg) of typical diesel. The improvement in the heating value is an indication of the removal of the low energy-containing polar compounds by the adsorption process. As expected, the heating

value is inversely proportional to H/C mole ratio as more amounts of carbon relative to hydrogen favours high calorific value. In Figure 11, both the acid value and flash point decreased drastically with an increase in the adsorbent dosage up to 2 w/v while the reverse was the case for cetane number. Further increase in the adsorbent dosage did not substantial change the values of these properties. These changes are also an indication of improvement in the oil quality making it more suitable to be used as an alternative to diesel. For instance, a typical diesel has an acid value of 0.5 mg KOH/g oil and a cetane number of 45 (Mohan *et al.*, 2019) compared with the oil which has its acid value reduced from 8.2 to 0.7 mg KOH/g oil and its cetane number increased from 36 to 42 at the highest adsorbent dosage. The decrease in the acid value can be attributed to the removal of oxygen-containing acidic compounds like carboxylic acids by the adsorbent, which is also expected to improve the chemical and thermal stability of the oil.

Table 5: Analysis of raw and treated tire-derived oil

Property	R-TDO	D-TDO ⁺	U-TDO			
			1= ⁼	2	3	4
Elemental (ultimate) analysis (wt. %)						
C	80.253	86.551	86.245	87.035	87.580	87.981
H	7.405	6.749	6.566	6.672	6.148	5.809
N	0.576	0.461	0.487	0.432	0.393	0.380
S	0.975	0.233	0.162	0.115	0.102	0.097
O*	10.791	6.006	6.540	5.746	5.777	5.733
Viscosity (cSt)	3.57	3.18	3.12	2.79	2.43	2.34
Density (kg/m ³)	865	847	845	841	839	838
Heating value (MJ/kg)	35.75	36.12	37.32	38.93	40.86	41.06
Flash point (°C)	47	45	40	37	36	36
Acid value (mg KOH/g oil)	10.6	8.2	2.5	1.1	0.8	0.7
Cetane number	34	36	40	41	42	42
H/C mole ratio	1.11	0.94	0.91	0.92	0.84	0.79

*Determined by taking difference, ⁺At optimum conditions, ⁼adsorbent (silica gel) dosage (w/v)

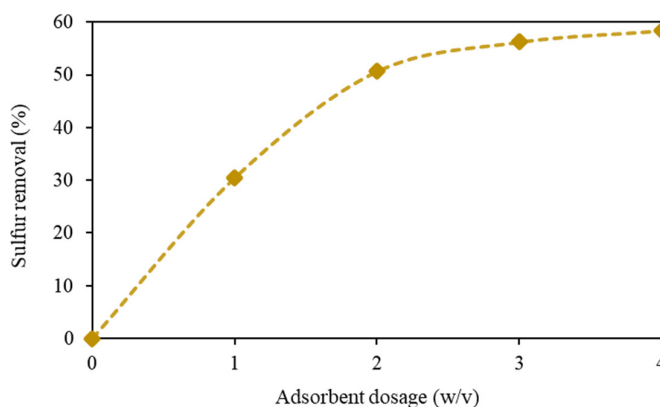


Figure 9: Sulfur removal as a function of adsorbent dosage

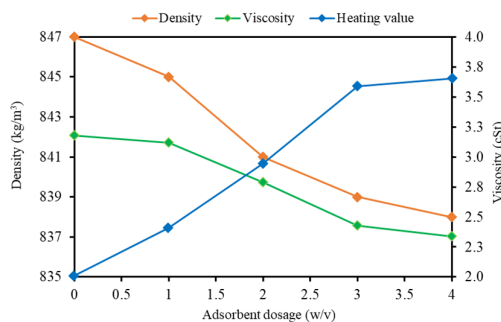


Figure 10: Effects of adsorbent dosage on density, viscosity, and heating value of oil

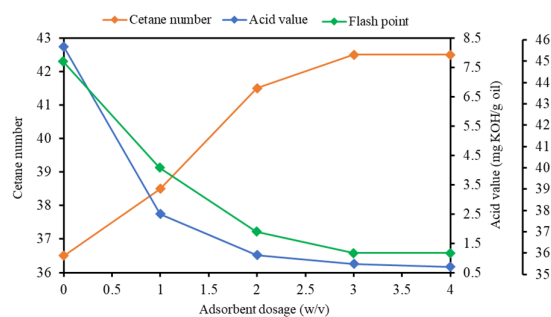


Figure 11: Effects of adsorbent dosage on cetane number, acid value, and flash point of oil

4. CONCLUSION

In this study, the quality of a tire-derived oil was upgraded using two-stage approach of ultrasound-assisted oxidative desulfurization and adsorption processes with the following conclusions drawn from the results.

1. The sulfur removal of 76.1 % was achieved during the ultrasound-assisted oxidative desulfurization (UAOD) at optimum temperature, time, and oxidant-to-oil ratio of 51.4 °C, 46.2 min., and 1, respectively.
2. The UAOD also helped in slightly improving the other key properties of the oil like viscosity (3.57 – 3.18 cSt), density (865 – 847 kg/m³), heating value (35.75 – 36.12 MJ/kg), flash point (47 – 45 °C), acid value (10.6 – 8.2 mg KOH/g oil), and cetane number (34 – 36).
3. The adsorption process on the desulfurized oil produced additional 58.4 % sulfur removal resulting to a combined sulfur removal of 90.1%.
4. The adsorption process led to reductions in viscosity by 34.5 %, flash point by 23.4 %, and acid value by 93.4% while increases in heating value by 14.9 % and cetane number by 23.5% were achieved.
5. The improvement in the oil quality by this treatment makes it more suitable to serve as an alternative to diesel.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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