Study of sulphur removal in waste tyre pyrolysis oil using hybrid design

Peter T. Cherop

Abstract - Waste tyres are very difficult to dispose and there is a growing interest to produce fuel from waste tyres. However, the high sulphur content in the oil obtained from the pyrolysis of waste tyres is a potential obstacle to the utilisation of waste tyre pyrolysis oil in real combustion processes. The aim of this study was to investigate the interaction of parameters during the oxidative desulphurisation of waste tyre pyrolysis oil using a hybrid design approach. The parameters investigated were the temperature (48-62 °C), the amount of acetic acid (5.2-10.8 mL) and the amount of hydrogen peroxide (6-10.8 mL). The stirring speed and the reaction time were kept constant at 300 rpm and 50 minutes respectively. The acetonitrile to the oxidised tyre oil ratio used during all experiments was 1:2. The results showed that the sulphur content was significantly influenced by the three factors investigated during the study. The maximum sulphur reduction was 46 % while the minimum sulphur reduction was 33 %. The model obtained for the prediction of the sulphur removal was of the quadratic nature based on results of the statistical parameters. The high values of the coefficient of determination and the adjusted R^2 was an indication of the accuracy and reliability of the model obtained. Moreover, the p-value of below 0.05 also indicated that the model had a high predictive power.

Key words: waste tyre pyrolysis oil, hybrid design, interaction effect, model

I. INTRODUCTION

Due to increasing population size, the global consumption of tyres has risen in the recent past. This increase in the amount of tyres consumed has come because of the need to meet both personal and commercial transport needs. Approximately 1.5 billion waste tyres are dumped all over the world [1, 2]. With tyres having a high gross calorific value of between 33-35 MJ kg^{-1} and high content of volatile compounds, energy recovery turns out to be an attractive option to recycle waste tyres [3].

Pyrolysis, which is simply the thermal decomposition process in absence of oxygen, is one of the potential ways that can be used to recover energy from waste tyres. The high sulphur content (1.0 - 1.4 wt. %) is the major drawback of utilisation of waste tyre pyrolysis oil (WTPO) in wider range application in real combustion processes [4].

P. T. Cherop, Department of Mechanical and Industrial Engineering, Masinde Muliro University of Science and Technology (phone: +254718357948; e-mail: tumwet2@gmail.com).

Hydrodesulphurisation (HDS), which efficiently removes large sulphur compounds from fossil fuels, is used in the oil refinery. However, due to the need for high reaction temperature (above 300 °C) and high hydrogen pressure (above 20 atm) in presence of an active catalyst in a huge reactor volume to aid conversion of sulphur compounds to hydrogen sulphide, HDS becomes costly for the refinery industry [5, 6].

Oxidative desulphurisation (ODS) has been considered a complementary technology for deep desulphurisation due to the high operating costs associated with HDS [7]. The operating conditions are milder in the ODS process in comparison with HDS. The oxidative desulphurisation process involves two stages. The first stage is the oxidation of organic sulphur compound s to the corresponding polar sulphones, while the second stage involves the extraction of the oxidised sulphur compounds using polar solvents [8-10]. In an ODS process, hydrogen peroxide (H_2O_2) or its mixture with a strong or organic acid is used to boost the efficiency of sulphur removal [11, 12].

The purpose of this study was to investigate the parametric interactions during the oxidative desulphurisation of waste tyre pyrolysis oil by using the hybrid design technique. The hybrid design technique is a component of the response surface methodology. This type of design borrows the columns from the central composite design and it has +/-1 factorial points. The values greater than 1 constitute the axial points. The hybrid design is helpful when budgetary considerations have to be made such that the use of the Box-Behnken, central composite or the factorial designs is prohibited.

II. EXPERIMENTAL

A. Materials

The waste tyre pyrolysis oil used during this study was obtained from FFS Refiners, South Africa. The initial sulphur content of the tyre oil was 12451 mg/kg. Acetic acid (99 wt. %) and H_2O_2 (50 wt. %) were purchased from Shalom Laboratory Supplies, South Africa. Hydrogen peroxide was used as received while acetic acid was diluted further to a concentration of 85 w/w. Acetonitrile (99.8 %) was purchased from Macron Fine Chemicals™ and was used as received. The experimental set up for the oxidation stage of the oxidative desulphurisation experiments comprised of a water bath, a customised mechanical stirrer, a reflux condenser and a round bottom flask. The solvent extraction was carried out using a separation funnel.

B. Oxidative desulphurisation procedure

The oxidative desulphurisation experiments were carried out in a water bath. The stirring speed, reaction time and the amount of waste tyre pyrolysis oil were kept constant in all runs at 300 rpm, 50 minutes and 100 mL respectively. During each run, the required temperature was set on the temperature-controlled water bath. This was followed by the transfer of tyre oil into the round bottom flask. The measured amounts of acetic acid and hydrogen peroxide were then transferred into the round bottom flask. The reflux condenser and the stirrer were connected to the flask and clamped before placing it on the water bath and setting the reaction time. The water bath was switched off at the end of the specified reaction time and the flask removed before solvent extraction.

During the solvent extraction stage of the oxidative desulphurisation, a 1:2 solvent to oxidised tyre oil ratio was used. The mixture was then shaken vigorously for approximately 3 minutes before charging it with 10 mL of deionised water and leaving it to settle for 5 minutes. The oil layer formed at the top while the aqueous layer formed at the bottom. The two layers were separated by opening the stopcock to collect the aqueous phase from the bottom whereas the oil phase was transferred from the top. The sulphur content in the original and desulphurised oils was analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the percentage of sulphur removal in the waste tyre pyrolysis oil was calculated using eq (1):

$$Sulphur\ removal\ (\%) = \frac{S_0 - S_f}{S_0} \times 100 \quad (1)$$

where S_0 is the initial sulphur content in the WTPF and S_f is the final sulphur content.

C. Design of experiments

The design and analysis of experiments was carried out using Design-Expert® Software. The hybrid design was used as the technique to study parametric interaction during the oxidative desulphurisation process. Table I shows the ranges of the three factors considered in this study. The choice of these ranges was partly informed by previous studies on oxidative desulphurisation of waste tyre pyrolysis oil [7, 13, 14]. The total number of runs obtained as per the hybrid design was 13. The runs consisted of three centre points. The centre point aids to calculate the experimental error. According to Montgomery [15], the distance from the centre points to the axial points is a function of the number of factors.

TABLE I
RANGES OF PARAMETERS FOR THE HYBRID DESIGN

Parameter	Ranges				
	$-\alpha\ (-1.414)$	-1	0	$+1$	$+\alpha\ (+1.414)$
A: CH_3COOH (mL)	5.17	6	8	10	10.83
B: H_2O_2 (mL)	5.17	6	8	10	10.83
C: Temperature (°C)	47.93	51.5	55	58.54	62.07

III. RESULTS AND DISCUSSION

A. Results of sulphur removal and process modelling

The results of the sulphur removal for interaction of the three parametric interaction are presented in Table 2. As seen in Table II, the sulphur removal range was between 33 to 46 %.

B. Model analysis

The quadratic model obtained can be expressed in terms of coded factors according to eq (2). This model shows the relationship between the sulphur removal and the four factors considered in the study. Eq (2) can predict the sulphur removal for given ranges of each factor, in which case the low and high levels of the factors are coded as −1 and +1 respectively. In addition, this equation can help to identify the relative impact of the factors by comparing factor coefficients.

$$S\ removal = 36.50 - 0.21A + 0.29B - 0.81C - 2.13AB - 1.30AC - 4.05BC - 3.93A^2 - 0.15B^2 - 0.50C^2 \quad (2)$$

The analysis of variance (ANOVA) showed that p-value of the model was 0.0026 (< 0.05), an indication that the model is significant. The significant terms of the model were C, AB, AC, BC and A^2 since the p-values for each of these terms was less than 0.05. The model terms A, B, B^2 and C^2, on the other hand, were insignificant since the values of p in these cases were greater than 0.1. However, it is important to note that the hierarchical factors A (CH_3COOH) and B (H_2O_2), which are among the insignificant model terms are involved in other significant interactions.

The number of significant model terms are more than the non-hierarchical insignificant terms, which implies that the model fits well the experimental data. Moreover, the lack of fit (LOF) p-value of 0.2965 shows its insignificance relative to pure error. An insignificant LOF is an indicator that the model fits well. The coefficient of determination, R^2 value of 0.9951 indicates that the empirical model could explain the over 99.51 % of the data deviation. In addition, an adjusted R^2 value of 0.9805 shows that the correlation between the observed and predicted responses is high. Finally, the adequate precision of 25.804 (greater than 4) is a desirable value

with an adequate signal, and therefore the model can be used to navigate the design space.

TABLE II
SULPHUR REMOVAL FOR VARIOUS PARAMETRIC INTERACTIONS

Run	CH_3COOH (mL)	H_2O_2 (mL)	Temperature (°C)	% S removal
1	6.00	10.00	58.54	41.10
2	10.83	8.00	51.46	46.00
3	8.00	8.00	62.07	36.00
4	5.17	8.00	51.46	44.00
5	10.00	10.00	58.54	34.60
6	8.00	5.17	51.46	33.00
7	8.00	8.00	55.00	36.00
8	10.00	6.00	58.54	44.00
9	8.00	10.83	51.46	41.90
10	8.00	8.00	55.00	37.00
11	6.00	6.00	58.54	42.00
12	8.00	8.00	55.00	36.50
13	8.00	8.00	47.93	39.00

The plot of externally studentized residuals versus the run number is presented in Fig.1 while Fig.2 shows the normal probability plot of the externally studentized residuals. Figure 1 shows a random dispersal of residuals near the line, which is an indication of the adequacy of the reduced cubic model. Moreover, Figure 2 shows a consistent appearance of the data points obtained on a linear trendline, which is an indication of absence of obvious dispersal and that the residuals follow a normal distribution.

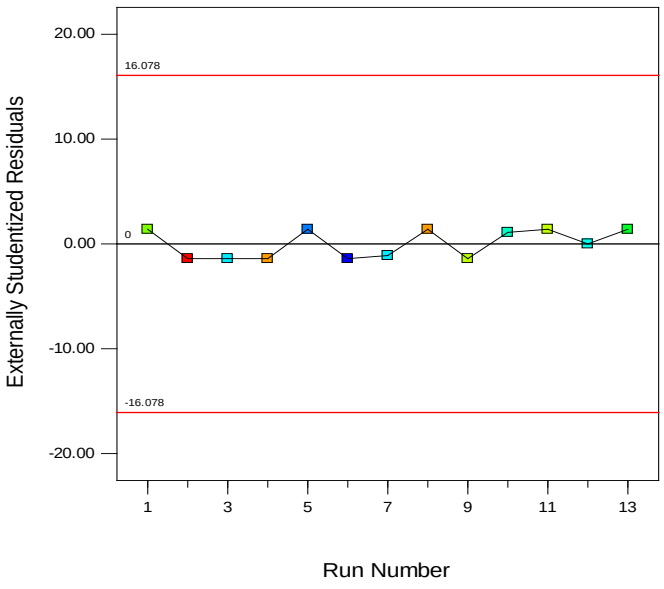

Fig.1. Plot of residuals versus run number

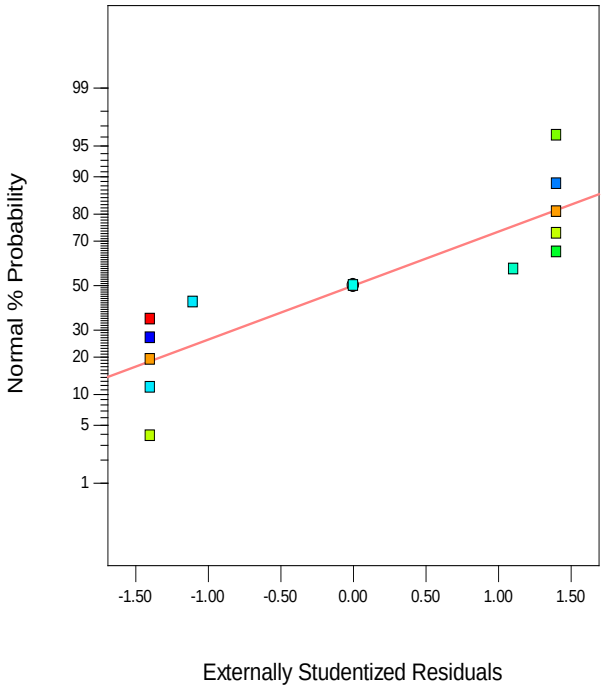

Fig.2. Normal probability of residuals

The plot of predicted sulphur removal versus actual values of sulphur removal is presented in Fig.3. It can be seen that there is a good agreement between the predicted and the experimental sulphur removal. This indicates that the model is adequate and significant, and therefore it can effectively be used to reproduce the experimental data in the range studied.

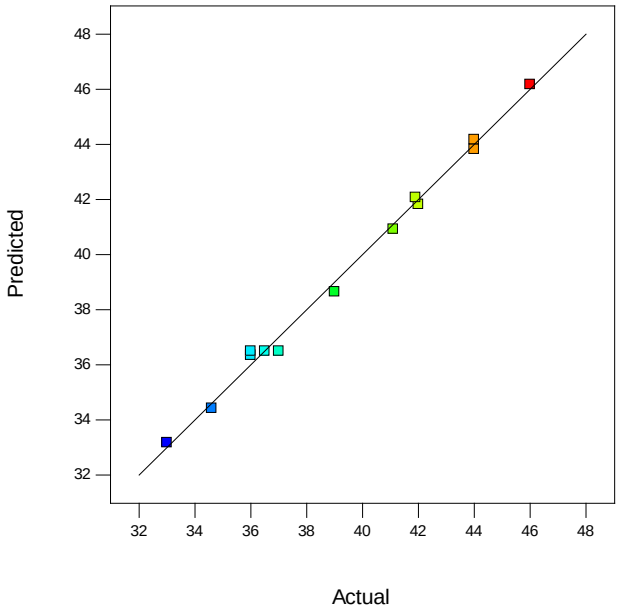

Fig.3. Predicted versus actual sulphur removal

IV. CONCLUSION

This study focused on understanding the interaction of different factors during the oxidative desulphurisation of waste tyre pyrolysis oil. The hybrid design was used as the response surface design technique. The amount of acetic acid, amount of hydrogen peroxide and temperature were the three factors whose interactive effects on sulphur removal were investigated. The maximum and minimum values of sulphur removal achieved were 46 % and 33 % respectively. The ANOVA results (as backed by statistical parameters) indicated that the quadratic model was the best predictor of sulphur removal for the oxidative desulphurisation process.

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