Simultaneous Adsorptive Desulphurization and Denitrogenationin Crude Tire Pyrolysis Oil Refining

ABSTRACT

Pyrolytic oil usually contains high nitrogen and sulphur content which reduces its efficiency in addition to posing crucial environmental and health concerns. Hence the need for desulphurization and denitrogenation of pyrolytic oil obtained from waste tire for efficient application.Freshly prepared Ni-Cr adsorbent impregnated with TiO_2-SiO_2 catalyst was used as the adsorbent in the treatment of the pyrolytic oil through adsorption process.Effect of operating time and catalyst ratio were investigated. The result showed that both operating time and catalyst ratio influenced the percentage removal of sulphur and nitrogen. TiO_2:SiO_2 catalyst ratio of 2:3 gave78.38% sulphur removal while ratio of 5:0 gave 89.80% nitrogen removal. The effect of time indicated that 78.84% and 93.98% removal of sulpur and nitrogen were obtained respectively after 120 minutes. For optimal simultaneous removal of both sulphur and nitrogen, a mixing ratio of 1:4 was obtained. The study showed that Ni-Cr/TiO_2-SiO_2 can be an effective adsorbent in desulphurization and denitrogenation of crude tire pyrolytic oil.

KEYWORDS: Desulphurization; denitrogenation; adsorption; waste tire; pyrolytic oil

1.0INTRODUCTION

Environmental pollution is one of the major challenges facing the contemporary society (Ohale et al. 2020). The extraordinary rise in automobile vehicle worldwide generates stockpile of waste tires which is one of the main causes of environmental pollution.The composition of waste tires which includes a blend of natural and synthetic rubber, embedded steel belts, and textile reinforcements, poses significant challenges for recycling due to difficulty of separating these materials and the presence of various chemical additives(Islam et al. 2016).On account of large number of automobiles, lorries, tricycles, etc in use, an estimate of over 1.0 billion waste tires are being created annually (Zhang et al. 2021).

Additionally, the inherent durability and resistance of tire components, combined with potential contaminants like dirt and oils, complicates the recycling process. As the number of automotive vehicles increase on the roads, the stock pills of waste tires increase after the service life of the tires. These tires will just keep getting accumulated with no further use and pose a threat to the environment and to humans. Researchers are now investigating various ways of converting different waste products into useful forms such as energy that will still meet global standards (Kumar et al. 2022).The best way to tackle the waste tire disposal problem is by using pyrolysis process to convert them to useful products (Karagoza et al. 2020).

Pyrolysis is a process where thermal decomposition occurs at an elevated temperature with the absence of oxygen (Elbaba and Williams, 2012)and the subsequent combustion of the generated gases emit significantly fewer pollutants than burning (Czajczyńska, et al, 2017).The pyrolysis process is widely incorporated in modern industries mostly because it is a source to renewable energy.

The pyrolysis process can be carried out in several types of reactors such as fixed bed (batch), screw kiln, rotary kiln, fluidized and vacuum bed (Islam *et al,* 2011). The pyrolysis of waste tires gives three principle products in the forms of solid (carbon black), liquid (Crude Tire Pyrolysis Oil, CTPO) and gas (pyrolytic gas) respectively (Arya *et al,* 2020). Pyrolysis oil, which is a product from the process, has a lot of industrial applications in today's world, one of which is its use as a fuel for internal combustion engines. In addition, the generated oils can be used as a source of chemicals (Williams, 2013). However, the characteristic high sulphur and nitrogen content of pyrolytic oils are the main disadvantages in the application of the pyrolticoil (Zhang et al. 2021). When used added to diesel engines, it leads to harmful emissions that may result to lung and eye diseases, asthma problems etc (Kumar et al. 2024).Therefore, there is need for the simultaneous denitrogenation and desulphurization of pyrolytic oil so as to ensure better combustion and a safer environment.

Desulphurization is a chemical process for the removal of sulfur from a material. This involves either the removal of sulfur from a molecule (e.g. A=S → A) or the removal of sulfur compounds from a mixture such as oil refinery streams (Badich, 2003). Similarly, denitrogenation can simply be defined as the removal of nitrogen from a material. There are various means by which the desulphurization process can be carried out such as hydrodesulphurization (Mendez *et al,* 2017), biodesulphurization (Boniek *et al,* 2015), pervaporation desulphurization (Fihri *et al,* 2016), extractive desulphurization (Sharma *et al,* 2013), oxidative desulphurization (Otsuki *et al,* 2000) and adsorptive desulphurization (Lee and Valla, 2019). Similarly, we have the hydrodenitrogenation process, extractive means and adsorptive means for denitrogenation. However, most of these methods were found to be expensive and cumbersome therefore preventing industrial application. Adsorptive desulphurization and denitrogenation offers a special route to get rid of these pollutants especially from waste tire pyrolysis oil using cheap and available catalysts.

Adsorptive desulphurization and denitrogenation applies the principle of adsorption in the removal of sulphur and nitrogen. Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. The adsorption process is usually advantageous because of its ease of use, high operational effectiveness, environmental friendliness and operational flexibility (Onu et al. 2021; Ohale et al. 2022; Ohale et al. 2023;Onu et al. 2025).Besides, the adsorption process is cost effective when compared with other methods (Onu et al. 2023).Adsorptive desulphurization and denitrogenation is the process of using physicochemical adsorption techniques to remove organic sulphurand nitrogen molecules from petroleum fractions. This method uses modest temperatures and pressures and doesn’t require costly hydrogen.

Adsorption is typically reliant on the effectiveness of the adsorbents, therefore finding the right adsorbent is crucial. The textural characteristics of the adsorbent mostly determine how well adsorptive desulfurization works. High surface areas as well as strong and stable structure are the advantageous features of an adsorbent (Onu et al. 2022).As a result, numerous research teams are working on adsorptive desulphurization and denitrogenation at the moment, and by adjusting the type of adsorbent in accordance with various requirements and adsorption mechanisms, the outcomes are progressively getting better.

In this work, a novel adsorbent catalyst Ni–Cr/TiO_2–SiO_2, (nickel-chromium/titanium dioxide-silicon dioxide) with special properties for the removal of sulphur and nitrogenous pollutants from waste tire pyrolysis oil was synthesized from local materials. In order to reduce process cost, SiO_2 and TiO_2were synthesized from local kaolin and ilmenite, respectively via thermal and chemical activation. The synthesized adsorbent wasused in removing sulphur and nitrogen from waste tire pyrolytic oil.

2.0 Materials and Methods

2.1 Materials Sourcing and Collection

The waste tire pyrolysis oilwasobtained from an engineering company that offers waste to wealth solutions in Port Harcourt, Rivers state, Nigeria. The oil has a relatively high sulphur and nitrogen content hence it is quite good for the adsorptive simultaneous desulphurization and denitrogenation operation.

Silicon dioxide (SiO_2) and titania (TiO_2) were both locally sourced. Ni^{2+} and Cr^{3+} were synthesized using analytical reagent grade nickel acetate hydrate ($Ni\ (CH_2COOH)_2 \cdot 4H_2O$) and chromium tetra-sulphate($Cr_2(SO_4)_3$) as precursors.

2.2. Ni-Cr / TiO2-SiO2 catalyst Preparation

To prepare the Ni-Cr/TiO_2-SiO_2catalyst, the Ni-Cr were first synthesized. This was done by dissolving 15.55g of ($Ni\ (CH_2COOH)_2 \cdot 4H_2O$) and 41.48g of ($Cr_2(SO_4)_3$) in 500ml distilled water under constant stirring at 60 °C. The constant stirring was to achieve proper dissolution and uniformity. Then different mixing ratios of TiO_2 – SiO_2 each totaling 24g ofTiO_2–SiO_2 was prepared. 50ml of the synthesized Ni-Cr was added to the mixture and stirred continuously for 30mins at room temperature to ensure uniform distribution of the metal ions on the support. 1M solution of NaOH was used to achieve a pH of about 7-8.

Each of the different mixing ratioswere filtered via Wattman filter paper and left to dry overnight in a forced air oven. After drying, each ratio of residue was grinded and kept in a container for storage and usage for the simultaneous desulphurization and denitrogenation process.

2.3 Adsorptive Desulphurization and Denitrogenation Studies

The simultaneous adsorptive desulphurization and denitrogenation studies efficiency was investigated at varying operating time (10, 20, 30, 60, 90, 120 mins) and Ni– Cr/TiO_2–SiO_2composition ratio (0:5, 1:4, 2:3, 3:2, 4:1, 5:0). Table 1 shows the respective parameters and their values. The adsorptive desulphurization and denitrogenation experiment was carried out using a batch process. The process was performed by adding 1g of each of the different mixing ratios of Ni– Cr/TiO_2–SiO_2 adsorbent to various 500 ml beaker containing CTPO solution. The solution was stirred on a magnetic stirrer for 60mins after which the product was filtered out and the filtrate taken for nitrogen and sulfur test.

After varying mixing ratio, the next factor to be varied was operating time. 1g of the 1:4 mixing ratio of TiO_2: SiO_2 was added to a beaker containing CTPO solution. This was stirred for 10mins after which the product was filtered out and the filtrate taken for sulfur and nitrogen test. The same procedure was repeated for reaction time of 20, 30 60, 90 and 120mins.

TABLE 1: Parameters for the simultaneous adsorptive desulphurization and denitrogenation.

Operating time (mins)	10	20	30	60	90	120
Ni–Cr/TiO_2:SiO_2composition ratio	0:5	1:4	2:3	3:2	4:1	5:0

2.4 Determination of Sulphur Content

1.0gm of finely powdered soil was mixed with 5.0g of Na_2CO_3 and $NaNO_3$, in a crucible. The mixture was preheated at 400°C for 30mins in an electric furnance, and fused at 600°C.After the fusion, the crucible was allowed to cool. Deionized water was added and the mixture heated at a temperature until the melt was thoroughly designated. The crucible was then removed and washed with deionized water. At this point 20cm^3 of 6m HCl was added to neutralize the Na_2CO_3 and to make the solution slightly acidic. This was filtered into a 100cm^3 volumetric flask and the volume made up to the mark with deionized water.

The solution was boiled and 10cm^3 of 10% $BaCl_2.2H_2O$ was slowly added to precipitate the sulphate. The solution was allowed to cool and was filtered. The residue was washed with deionized water.

Theashless filter paper was ignited at low temperature (40°C) and the precipitate weighed. The percentage sulphur in the precipitate was calculated from the expression below,

$$\% \boldsymbol{Sulphur} = \frac{\boldsymbol{BaSO4x100}}{\boldsymbol{wt.ofsampleingram}} \quad (1)$$

2.5DeterminationOf Nitrogen Content

Exactly 0.5g of sample was weighed into a 30ml Kjehdal flask (gently to prevent the sample from touching the walls of the side of each) and then the flasks were stoppered and shaken. Then 1g of the Kjedahl catalyst mixture was added. The mixture was heated cautiously in a digestion rack under fire until a clear solution appeared.

The clear solution was then allowed to stand for 30 minutes and allowed to cool. After cooling about 100ml of distilled water was added to avoid caking and then transferred to the Kjedahl distillation apparatus.

A 500ml receiver flask containing 5ml of boric acid indicator was paced under a condenser of the distillation apparatus so that the tap was about 20cm inside the solution. The 10ml of 40% sodium hydroxide was added to the digested sample in the apparatus and distillation commenced immediately until distillation reaches the 10ml mark of the receiver flask. Then it was titrated to pink colour using 0.01N hydrochloric acid.

Calculations

% Nitrogen = Titre value x 0.01 x atomic mass of nitrogen x 4 (2)

Where 0.01 = normality of the acid.

% protein = % nitrogen x 6.25 3

3.0 RESULTS AND DISCUSSION

Tables 2 to5 showed the percentages of both sulphur and nitrogen remaining after the adsorption process. These values were used to calculate the percentage removal of both nitrogen and sulphur using the following formulars;

%removal of Sulphur = C_{OS}-C_{TS}/C_{OS} x 100% 4

%removal of Nitrogen = C_{ON}-C_{TN}/C_{ON} x 100%

Where;

C_{OS} = Initial Conc of Sulphur at 0mins = 2.216

C_{TS} = Cons of Sulphur at Time, T

C_{ON} = = Initial Conc of Nitrogen at 0mins = 2.744

C_{TN} = Conc of Nitrogen at Time, T.

The calculated results were tabulated in Tables 6 and 7. These values were used to make plots depicted in figures 1 and 2.

TABLE 2: Percentage of Sulphur remaining at different TiO_2:SiO_2mixing ratios.

Mixing Ratios (TiO_2:SiO_2)	**Weight of oil**	**Weight of sample**	**% sulphur**
0:5	0.067	10.002	0.669866
1:4	0.054	10.004	0.539784
2:3	0.048	10.020	0.479042
3:2	0.089	10.014	0.888756
4:1	0.080	10.005	0.7996
5:0	0.078	10.010	0.779221

TABLE 3: Percentage Nitrogen remaining at different TiO_2:SiO_2 mixing ratios

Mixing Ratios (TiO_2:SiO_2)	Titre	% Nitrogen
0:5	0.8	0.448
1:4	0.9	0.504
2:3	1.3	0.728
3:2	1	0.56
4:1	0.7	0.392
5:0	0.5	0.28

TABLE 4: PercentageofSulphur remaining at different time

Time (mins)	Weight of oil	Weight of sample	% sulphur
0	0.222	10.019	2.216
10	0.065	10.019	0.649
20	0.062	10.014	0.619
30	0.061	10.012	0.609
60	0.056	10.010	0.559
90	0.052	10.045	0.518
120	0.047	10.025	0.469

TABLE 5: Percentage of Nitrogen remaining at different time

Time (mins)	Titre	% Nitrogen
0	5.9	2.744
10	1.2	0.672
20	0.8	0.448
30	0.6	0.336
60	0.5	0.28
90	0.4	0.224
120	0.3	0.168

3.1 Effect of varying mixing ratios

Table 6 shows the different sulfur and nitrogen % removal at different mixing ratios of TiO_2:SiO_2. As noticed, the highest percentage removal of sulfur was noticed at a mixing ratio of 2:3 with a Sulphur % removal of 78.3826% indicating that Silica favored the removal of sulfur during the adsorption reaction. On the other hand, the % removal of Nitrogen was the highest at TiO_2:SiO_2 mixing ratio of 5:0 with a % removal of 89.796%. It can however be deduced that Titania favors the removal of nitrogen.

Mixing Ratios (TiO_2:SiO_2)	% removal of Sulphur	% removal of Nitrogen
0:5	69.7789	83.6735

1:4	75.6415	81.6327
2:3	78.3826	73.4694
3:2	59.8937	79.5918
4:1	63.917	85.7143
5:0	64.8364	89.7959

TABLE 6: Percentage removal of Both Sulphur and Nitrogen at different mixing ratios of TiO_2:SiO_2

Figure 1 is a plot of the percentage removal of nitrogen and sulfur at the various mixing ratios. From the plot, it was noticed that the percentage removal of nitrogen was always higher than that of sulfur except when the mixing ratio was 2:3. The highest nitrogen removal was at a ratio of 5:0 where there was no silica present. However, although this ratio greatly favored the denitrogenation process, it showed the lowest percentage removal with respect to sulfur.

A further careful analysis was done to determine the best mixing ratio for simultaneous desulphurization and denitrogenation. It was concluded that a mixing ratio of 1:4 was the optimal for simultaneous desulphurization and denitrogenation of CTPO.

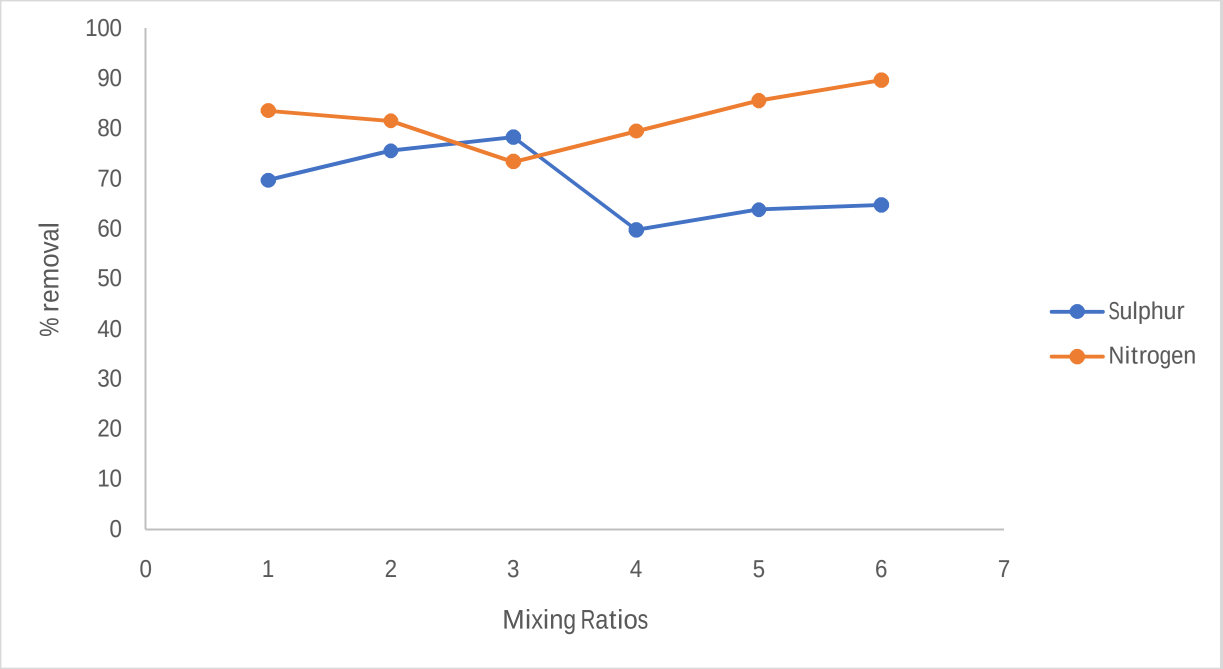

FIGURE 1: Graph Showing % Removal of Sulphur and Nitrogen at Different Mixing Ratios

3.2 Effect Of Time

Table 7 shows the percentage removal of both sulfur and nitrogen at different times. From the table,it was observed that both the percentage removal of sulfur and nitrogen increases with time. The best percentage removal for both sulfur and nitrogen was recorded at 120 minutes with the percentage of sulfur removal being 78.8357% while that of nitrogen was 93.9776%. Increase in reaction time increases the rate of the removal of both sulfur and nitrogen. A direct relationship occurs between time and percentage removal as an increase in time increases the percentage of removal. This is because a longer contact time allows more of the contaminant molecules to interact with the adsorbent material, enhancing the adsorption process (Wu et al., 2009). Therefore, if it is desired to remove more sulfur and nitrogen from the CTPO, the adsorption reaction should be carried out over a longer time.

TABLE 7: Percentage removal of both Sulphur and Nitrogen at different times

Time (mins)	**% removal of Sulphur**	**% removal of Nitrogen**
0	0	0
10	70.713	75.5102
20	72.0668	83.6735
30	72.5181	87.7551
60	74.7744	89.7959
90	76.6245	91.8367
120	78.8357	93.9776

Figure 2 is a diagrammatic representation of table 7. It is a plot of percentage removal against time for both sulfur and nitrogen. From the plot, it is seen that the percentage removal increases with increasing time. From the graph, it was also noticed that the percentage removal had a higher rate of increase at the beginning of the reaction which greatly reduces as the reaction progresses. It can therefore be deduced that the % removal of both sulfur and nitrogen would continue to increase until equilibrium point is reached after which the increase in percentage removal becomes minimal and negligible. Some authors reported similar trend. Ho & McKay (1999) observed that initially the percentage removal often rises quickly as easily accessible sites on the adsorbent surface capture contaminants. However, as the sites become occupied and saturated, the rate of removal slows, eventually reaching equilibrium where additional time results in minimal change in removal percentage.

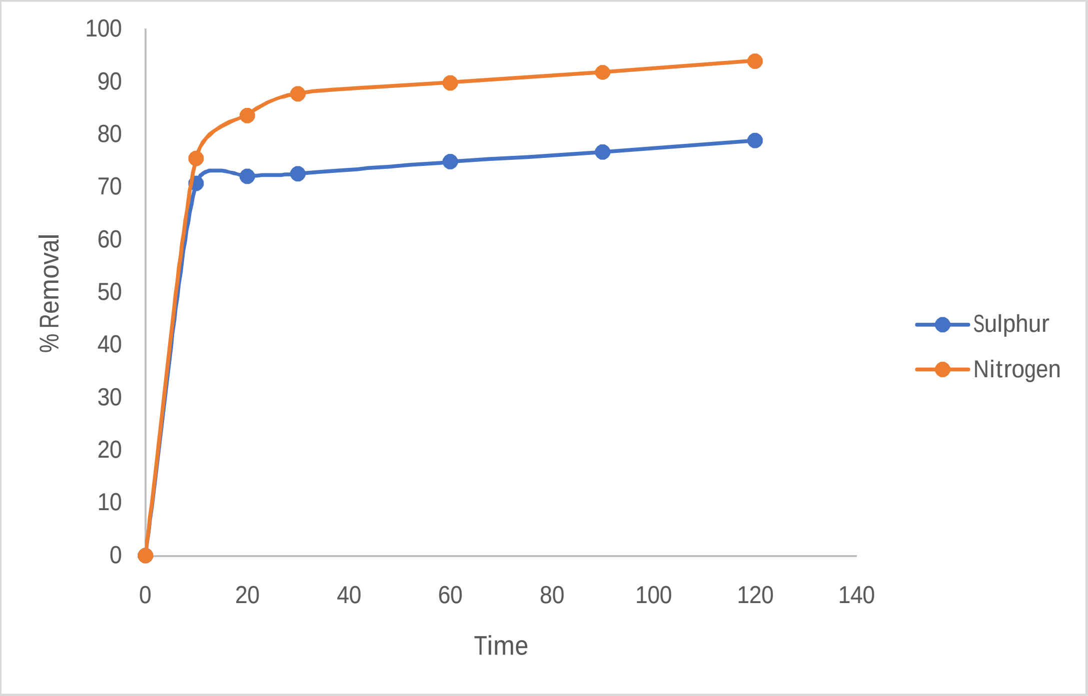

FIGURE 2: Figure Showing a Plot of %removal of Sulphur and Nitrogen Against Time

3.3 Color Change

Figure 3 is a diagram showing an untreated diluted CTPO while Figure4 is a treated diluted CTPO. As observed the untreated compound was darker in color when compared to the treated one. Sulfur and nitrogen compounds typically contribute to darker hues in crude oils, fuels, and other organic mixtures due to the formation of complex aromatic and heterocyclic compounds that have strong color characteristics (Speight, 2014). When sulfur and nitrogen are removed, the color of the solution can become significantly lighter. This is because the removal of these heteroatoms reduces the number of chromophoric (color-producing) groups in the solution (Meindersma et al., 2006).

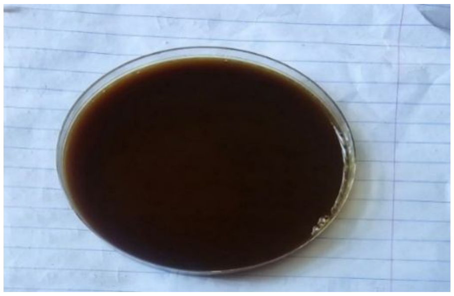

FIGURE 3: Untreated CTPO

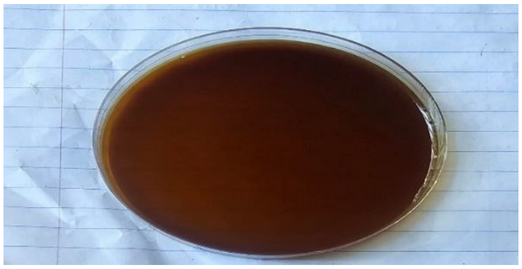

FIGURE 4: Treated CTPO

Pyrolytic oil usually contains high nitrogen and sulphur content which reduces its efficiency in addition to posing grave environmental and health concerns. Hence the need for desulphurization and denitrogenation of pyrolytic oil obtained from waste tire for efficient application. Freshly prepared Ni-Cr adsorbent impregnated with TiO_2-SiO_2 catalyst was used as the adsorbent in the treatment of the pyrolytic oil through adsorption process. Effect of operating time and catalyst ratio was investigated. The result showed that both operating time and catalyst ratio greatly influenced the percentage removal of sulphur and nitrogen. TiO_2:SiO_2 catalyst ratio of 2:3 gave 78.38% sulphur removal while ratio of 5:0 gave 89.80% nitrogen removal. The effect of time indicated that 78.84% and 93.98% removal of sulpur and nitrogen were obtained respectively after 120 minutes. For optimal simultaneous removal of both sulphur and nitrogen, a mixing ratio of 1:4 was obtained. The study showed that Ni-Cr/TiO_2-SiO_2 can be an effective adsorbent in desulphurization and denitrogenation of crude tire pyrolytic oil.

4.0 CONCLUSION

This study successfully synthesized and utilized Ni-Cr/TiO_2-SiO_2adsorbent for the simultaneous desulfurization and denitrogenation of liquid pyrolysis oil obtained from waste tires. Influence of operating time and TiO_2:SiO_2 catalyst ratio were studied.The results show that prolonged operating time enhances the process but becomes less effective after equilibrium is reached. Titania (TiO_2) was more effective in nitrogen removal, while Silica (SiO_2) favored sulfur removal, with an optimal TiO_2:SiO_2 mixing ratio of 1:4. Maximum time of 120 minutes was required for optimum sulfur and nitrogen removal.Sulphur and nitrogen percentage removal of more than 78% was obtained in all cases. The simple, low-cost experimental conditions suggest practical applications for reducing sulfur and nitrogen content in waste tire pyrolytic oil. It is recommended that advanced machine learning techniques be used to model and optimize the desulfurization and denitrogenation process for improved material design.

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