

Desulfurization of Oils; Produced from Pyrolysis of Scrap Tires

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Abstract

The aim of this study is to review the pyrolysis process and the desulfurization of pyrolysis products of scrap tires. Pyrolytic oil obtained in tire pyrolysis is the focussed product in this review. Pyrolytic oils have diesel like fuel properties with high sulfur contents and other contaminants. Treatment of pyrolytic oil for desulfurization and separation of diesel like fuel from pyrolytic oils by distillation has been studied. Use of additives like CaO, CaCO₃, NaHCO₃ and acids like H₂SO₄, H₂O₂ at different operating conditions for the economical desulfurization has been reviewed. This review study is carried out for finding techniques for Pyrolytic oils produced in a local tire pyrolysis plant situated in KPK at Peshawar.

Keywords: Scrap tire pyrolysis, Desulfurization, Distillation, Diesel blending.

Introduction

With the Socio-economic growth of any society the usage of vehicles and thus production of scrap tires increases. The complicated structure of scrap tires doesn't allow its disposal without thermal degradation [1]. On the other hand high calorific value of scrap tire makes sense for its use as a fuel. Until the recent past, use of scrap tires as an alternative fuel in industries like cement was common throughout the world. Due to sulfur presence and hazardous effects of sulfur compounds, the direct use of scrap tires as an alternative fuel is perilous for the environment. The flue gases produced as a result of tire burning is a serious threat to the environment. With the passage of time alternative techniques were developed for disposal of scrap tires.

Pyrolysis is one such approach towards scrap tire disposal and utilization of high percentage of carbon for energy. In pyrolysis of scrap tires, tires are thermally degraded in the absence of oxygen and converted into vapours. The vapours

are then condensed into liquid while the non-condensable vapours are emitted as gases into the environment and the solid residue is left behind in the reactor. A schematic view of pyrolysis process is shown in Fig.1. Pyrolysis of solid fuels like scrap tires provides a potential source of fuel in the form of pyrolytic oils and hot flue gases. Pyrolysis process of solid fuels helps in desulfurization [2,3] because sulfur present in the solid fuels can be easily extracted from solid residue and liquid oils. The gaseous and liquid products of pyrolysis can be used as a fuel or a raw material in the production of other chemicals. Liquid fraction of pyrolysis can be used as a raw feed for extracting benzene, toluene, xylene and limonene [4]. The economic purification via desulfurization of pyrolytic oil is a challenging task and for achieving this task a pile of research work has been done.

This review study also aims to search an economical approach for the purification of pyrolytic oils produced in local tire pyrolysis industry. By doing so not only scrap tires may be disposed easily but also a rich source of energy in

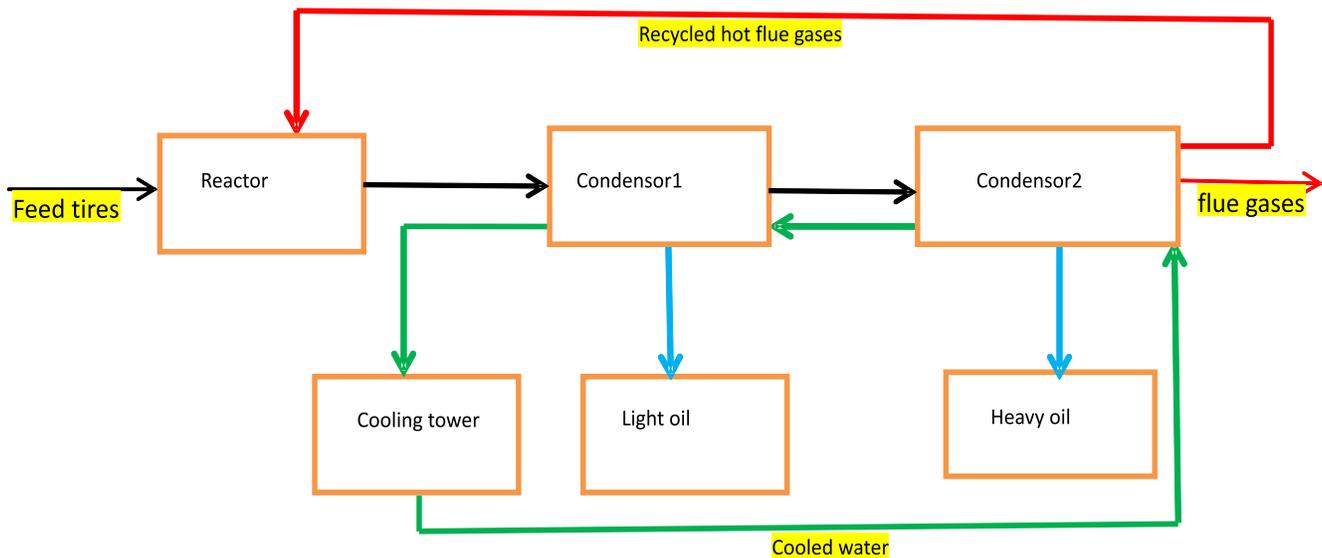


Fig. 1 Process flow diagram of tire pyrolysis

terms of pyrolytic oils will be available and thus environment can be made safe from the hazardous impacts of scrap tires.

Production of Pyrolytic Oil

In pyrolysis of scrap tires, degradation of tires starts at approximately 200°C while completes at 500°C [4]. Pyrolytic oil, solid residue and gases are obtained as pyrolysis products. Solid residue of tire pyrolysis is due to the non-volatile fraction of tires while the liquid and gaseous fractions are contributed by the organic volatile composition of scrap tires. The organic volatile components of tires are about 58.8% of the tire composition [1]. The solid yield remains almost constant while the yield of pyrolytic oil and gases varies with varying operating conditions. Temperature and heating rate are the two important operating parameters affecting the yield and composition of volatile fractions of pyrolysis process [1]. The optimum amount of pyrolytic oil is a function of temperature, heating rate, feed composition and reactor type used for pyrolysis. Different authors have reported different oil yields of pyrolysis process at different experimental conditions as shown in Table 1 [1,5,7].

At the start of the pyrolysis, amount of pyrolytic oil increases with rising temperature while after the completion of the pyrolysis reactions the temperature effect on oil yield vanishes [1]. The oil collected from scrap tire pyrolysis consists of moisture, carbon particles, sulfur compounds and other impurities. The main hurdle in the way of pyrolytic oil to be used as an alternative fuel is the sulfur content of pyrolytic of raw feed composition and the pyrolysis conditions. Composition of different types of tires is shown in Table 2 [5,8]

Table 1: Oil Yield Analysis

Process type	Oil yield (wt. %)	Temperature °C	H _r	Ref
Static batch reactor	56.2	500	5 K/min	(5)
	53.1	600		
Auto clave reactor	24.8	400	15°C/min	(1)
	38.0	500		
	38.2	600		
Batch reactor	30.0	400	12 K/min	(6)
	39.9	500		
	39.1	550		
	42.8	700		
Fixed bed reactor	38.8	400	5°C/min	(7)
	34.2	600	35°C/min	
	31.1	400		
	29.5	600		

Composition of Tire

In market a large number of tire manufacturing industries are operational. Different types of tires are manufactured for different purposes and thus the composition of one type of tire varies from the other. Elemental composition of scrap tires reported by various authors is shown in Table 2. Table 2 shows high amount of carbon content which may be utilized for energy purposes.

Composition of Pyrolytic Oil

The pyrolytic oils consist of paraffins, olefins and aromatic compounds. Composition of pyrolytic oil varies with different tire compositions and operating conditions of pyrolysis. Density, viscosity and flash point of pyrolytic oils are mostly similar to those of diesel and gasoline [9] while the high percentage of sulfur in pyrolytic oils needs to be separate. The analysis of pyrolytic oils reported by different researchers at varying condition is shown in Table 3 and Table 5. In Table 3 and Table 5 the variation of composition and other fuel properties of pyrolytic oils with variation of two important operating parameters (temperature and heating rate) are presented.

Table 2: Composition of Tires [5-8]

Ultimate Analysis (wt. %)				
C	H	N	S	O
74-86	6-8	0.3-1	1.4-2	1-15
Proximate analysis				
Volatiles		58-67		
Fixed carbon		21-30		
Ash		4-18		
Moisture		0.4-1.6		
GCV (MJ/Kg)		31-40		

Rodriguez et al. [1] found that pyrolytic oil is a mixture of organic compounds ranging from C₅ to C₂₀ with a higher proportion of aromatic compounds. The aromatics increase from 34.5 to 75.6% and aliphatics decreases from 59.2 to 19.8% with increasing pyrolysis temperature from 300 to 600°C, while an inverse change in proportions of aromatics and aliphatics has been reported by increasing the pyrolysis temperature from 600 to 700°C [1].

Treatment Of Pyrolytic Oil For Value Addition

Fossil fuel reserves are depleting because of high energy demands, due to which researchers are investigating alternative sources of energy and the conversion of different waste oils into diesel like fuel is one such approach. Ucar et al. [10] have reported that fuel properties such as viscosity, heating value and density of pyrolytic oils are approximately similar to that of diesel fuel. Thus Pyrolytic oils have the potential to be used as an alternative fuel provided desulfurized and purified. The combustion of pyrolytic oils in diesel engine has been investigated by some researchers

[11]. Table 3 and Table 5 show fuel properties of pyrolytic oils reported by different researchers at different operating conditions.

Table 3: Analysis of Pyrolytic Oils at Varying Heating Rate [7]

Parameters	Varying H _r (7)	
	Hr= 15 °C/min	Hr = 35 °C/min
Ultimate analysis %		
C	68.91	79.61
H	9.6	10.04
N	2.05	0.94
S	1.07	0.11
O	18.37	9.3
H/C	1.67	1.51
GCV (MJ/kg)	42.61	42.66
Density (kg/m ³)	820	830
Viscosity, (cSt)	0.95 @ 50 °C	1.01@ 50°C
Flash point (°C)	61	65

The fuel properties of pyrolytic oils produced in a local plant, situated in KPK at Peshawar are shown in TABLE 6. Fuel properties of high speed diesel, LDO and FFO have also shown for comparison TABLE 6. The high sulfur amount of pyrolytic oils is needed to be removed. Therefore, to select an economical approach for desulfurization, the commonly used desulfurization techniques have been reviewed.

Desulfurization by Additives

Different techniques such as extractive desulfurization, oxidative desulfurization, catalytic desulfurization and hydrodesulfurization have been reported for the desulfurization.

Desulfurization of pyrolytic oils can be accomplished by using different additives during pyrolysis or by mixing the additives with the pyrolytic oils after pyrolysis. The latter is called post treatment of pyrolytic oils. The present work also proposes to use the post treatment technique for desulfurization. The commonly used additives are sodium carbonate, zeolite, lime(CaO), and NaOH. Mixing of these additives in different proportions has different desulfurizing effectiveness.

Aydın and İlkılıç [12] have reported that by adding CaO, Ca(OH)₂ and NaOH in different proportions at 500 °C pyrolysis temperature, sulfur content decreases. The maximum decrease (34.25%) in sulfur amount was found by

5% Ca(OH)₂.

Similarly Arpa et al. [13] have used the calcium oxide, sodium bicarbonate and zeolite for converting the used lubricating oils into diesel like fuels. The additives were used in different ratios and it was found that by adding 2 wt% of CaO, the sulfuret contents were decreased by about 3250 mg/Kg. Other fuel properties such as density, flash point, heating value and distillation temperature of used oils were also improved by additives [13].

Oxidative Desulfurization

Oxidative Desulfurization can be carried out at mild operating conditions and have higher efficiency than the hydrodesulfurization. Due to these two reasons, the research in this field of oxidative desulfurization has been stimulated for the last few years. In oxidative desulfurization the solvent is added with liquid fuel to remove sulfur content [14].

Acids or mixture of acids are used in oxidative desulfurization. Hydrogen peroxide (H₂O₂), Acetic acid (CH₃COOH), Formic acid and Sulfuric acids (H₂SO₄) are commonly used in oxidative desulfurization. The use of H₂O₂ in oxidative desulfurization has been reported vigorously because at the completion of conversion H₂O₂ is decomposed into H₂O and O₂, and thus produces no pollutants. The use of acid in combination with hydrogen peroxide (H₂O₂) can increase the desulfurization reactions [(15)].

In a study, sulfur of a fuel was reduced from 1044 ppm to 100 ppm by using formic acid and hydrogen peroxide [16].

Ali et al. [17] have reported 90% desulfurization of petroleum products by hydrogen peroxide and acetic acid using sulfuric acid as a catalyst.

Ahmad et.al [18] have reported the oxidative desulfurization by using air, formic acid (HCOOH) and hydrogen peroxide (H₂O₂) as oxidants. A complete conversion was observed by using H₂O₂- HCOOH-air mixture. The results shown in TABLE-4 reveal that by using air-H₂O₂ and air-HCOOH mixtures, the maximum oxidation of thiophene was 15% and 14% respectively. While the oxidation by H₂O₂- HCOOH mixture was found higher than air- H₂O₂ and air- HCOOH mixtures. From this it was concluded that the conversion was due to performic acid which is formed by H₂O₂- HCOOH reaction [18].

Table 4: effect of air, H₂O₂, and hcooh on the oxidation of model sulfur compounds [18]

Oxidant	Conversion		
	Thiophene	DBT	4,6-DMDBT
Air/H ₂ O ₂ /HCOOH	98.11	97.99	99.31
No HCOOH	13.46	16.11	17.13
No H ₂ O ₂	14.09	12.91	11.18
No air	62.02	79.53	98.69

Aydın and İlkılıç [12] have investigated the effect of pyrolysis temperature along with additives on sulfur content

in pyrolytic oils. At the pyrolysis temperature of 550°C the sulfur amount in pyrolytic oil was minimum while the effect of formic acid-H₂O₂ and acetic acid-H₂O₂ mixtures in a ratio of 1 to 2 was more effective than 1 to 1 molar ratio for desulfurization [12].

Bunthid et al. [9] have tested the effect formic acid, H₂O₂ oxidants with and without adsorbent for desulfurization of pyrolysis oils. The pyrolysis char was used as an adsorbent. The adsorbent alone removed sulfur content up to 47.6%. Similarly oxidizing H₂O₂ alone desulfurized the oils by 41.5% while the char along with H₂O₂ removed the sulfur contents by 57.8% [9].

Nabi et al. [19] have reported the efficacy of H₂SO₄ as a desulfurizing agent. The study suggests to stir 8% H₂SO₄ with Pyrolytic oils for 4 hours and then left for settling. After 40 hours settling time the mixture was separated in two layers, the thin top layer was separated for further treatment while the thick lower layer was separated as sludge [19].

Table 5: Analysis of Pyrolytic Oils at Constant Heating Rate

Parameters	Temperature°C(5)						(8)
	450	475	500	525	560	600	
<i>Ultimate analysis (wt. %)</i>							
C	85.6	84.6	84.9	87.1	86.1	87.9	85.45
H	10.4	11.2	10.2	9.1	10.0	10.1	11.38
N	0.5	0.5	0.5	0.7	0.6	0.5	0.44
S	1.4	1.4	1.3	1.3	1.3	1.3	0.58
O	2.0	2.2	3.1	1.8	2.0	0.1	2.15
Flourene ppm	80	100	140	100	140	100	---
Chlorene ppm	150	270	190	210	90	100	---
GCV (MJ/kg)	42.6	42.9	42.1	42.4	42.1	41.2	43.27
Flash point (°C)	14	15	15	17	18	18	20

Hydrodesulfurization Methods

Hydrodesulfurization method is common in oil refineries for the removal of sulfur contents of the fossil fuels. High temperature (300–400°C), high pressure (30–130atm) and active catalysts are required for hydrodesulfurization [20]. Due to high energy demand, the hydrodesulfurization technique becomes uneconomical for the desulfurization of pyrolytic oils.

Also Pyrolytic oils have Dibenzothiophenes (DBT) in its composition and the effectiveness of Hydrodesulfurization is limited in the treatment of DBT because of their steric hindrance on sulfur atom [21, 22].

Distillation of Pyrolytic Oils

Distillation is useful for separating the liquid fractions.

Distillation of desulfurized pyrolytic oil has been investigated by researchers to separate it into its fractions. In a study [12] it was observed that desulfurized pyrolytic oils contain 50% light hydrocarbons which can be easily burn while the remaining 50% heavier hydrocarbons hardly burns. From the distillation temperatures range of pyrolytic oils it was noted that 85% of the pyrolytic oils can be burn in diesel engines [12].

Rodriguez et al. [1] have reported that more than 30% of pyrolytic oil is distillable in the boiling time temperature range of commercial petrol (70-210°C) while 70% of the pyrolytic oil was found to be distilled below 370°C.

In another research work [23] the desulfurized pyrolytic oil has been distilled into light and heavy fractions of hydrocarbons. Distillation was carried out between 150-200°C and it was observed that 80% of the desulfurized pyrolytic oil was distilled easily while the remaining 20% was left out as pyro gas and sludge [23].

Blending of Pyrolytic Oil with Diesel

Blending of pyrolytic oil with diesel is common to improve the fuel properties of pyrolytic oils and produce diesel like fuel. Fuel properties such as viscosity, density and flash point of pyrolytic oils can be adjusted with diesel blends [23]. In a study [23] it was reported that the engine can be run with 90% distilled tire pyrolysis oil and 10% diesel fuel.

Conclusions

In this paper the research work on pyrolysis process along with techniques of desulfurization and purification of pyrolytic oils is reviewed. Effects of temperature, heating rate, and tire composition on pyrolysis products have been discussed. The optimum yield of pyrolytic oils was found in temperature range of 450-500°C.

Composition and other fuel properties of pyrolytic oil changes with varying operating conditions. The sulfur content of pyrolytic oils may be reduced with the use of additives and acids. In additives the desulfurization efficiency of CaO is better than other additives.

In acids, formic acid and H₂O₂ mixture is effective. The desulfurized pyrolytic oil can be separated into its light and heavy oil fractions by distillation. The desulfurized pyrolytic oil can be used in diesel engine with diesel blend and a mixture of 90% pyrolytic oil and 10% diesel fuel can be burned in diesel engines

Nomenclature

HSD	High speed diesel
LDO	Light diesel oil
FFO	Furnace fuel oil
H _r	Heating rate
DBT	Di-Benzothiophene

Table 6: Properties of Pyrolytic Oils (Attock Oil Refinery)

S/No	Test	Method	Result	PSQCA SPECIFICATION/ARL TYPICAL SPECIFICATION					
				HSD		LDO		FFO	
1	Specific gravity@ 15.6/15.6 °C	ASTM D1298	0.874	Report	0.84-0.850	0.920 Max	0.875-0.890	0.970 Max	0.936-0.945
2	Colour, ASTM	ASTM D1500	D8	3.0 Max	0.5-1.5	3.0 Min	D8	-	-
3	Sulfur, Total, % mass	ASTM D4294	0.48	1.0 Max	0.20-0.35	1.80 Max	-	3.5 Max	0.90-1.2
4	Pour point, °C	ASTM D97	<-18	9 Max	-	14 Max	0-6	24 Max	21-24
5	Flash Point, PMCC, °C	ASTM D93	24	54 Min	58-60	54 Min	60-72	66 Min	68-72
6	Distillation								
	IBP		92.1	-	10-175	-	-	-	-
	5%		140.1	-	18-200	-	-	-	-
	10%		155.7	--	20-215	-	-	-	-
	20%		171.7	-	22-230	-	-	-	-
	50%		203.3	-	27-280	-	-	-	-
	90%		310.5	-	34-354	-	-	-	-
	95%		352.4	-	36-377	-	-	-	-
	FBP		353.0	-	36-380	-	-	-	-
7	Water content, Vol %	ASTM D95	Nil	0.05 Max	Nil	0.25 Max	-	0.5 Max	0.2-0.4
8	Kin. Viscosity@ 30°C	ASTM D445	1.5378	1.5-6.5	2.9-3.5	14 Max	8.5-13.00	180 Max	70.0-115
9	Ash content %wt	ASTM D482	Nil	0.01 Max	0.00-0.003	0.02 Max	-	0.1 Max	0.06-0.07
10	Gross calorific value Btu/lb	ASTM D4868	19359	-	-	-	-	18200 Min	-

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