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Original scientific paper

EVALUATION TIRE PYROLYSIS PRODUCTS

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A b s t r a c t: Generating large amounts of solid hazardous waste, such as scrap motor tires, has raised the question of seeking an appropriate method for their recycling. The pyrolysis of waste tires presents a viable solution not only for addressing environmental challenges, but also for converting discarded tires from landfills into valuable products. This thermochemical process offers an opportunity to produce cost-effective fuel. In this study, waste truck tires were converted into value-added products using the pyrolysis method. The pyrolysis process was carried out in a semi-batch reactor in an oxygen-free environment. A semi-batch reactor was automatically controlled, and three thermostatic separators were used for the pyrolysis of waste rubber. The pyrolysis of waste truck tires yields three main products: solid residue, which constitutes 36.50 %; a liquid fraction known as carbon black, accounting for 51.28 %; and a 12.22 % gas fraction, syngas. The basic characteristics of the obtained liquid and solid products were examined.

Key words: pyrolysis; waste tire; semi-batch reactor; products evaluation

ПРОЦЕНА НА ПРОДУКТИ ДОБИЕНИ СО ПИРОЛИЗА НА ГУМА

А п с т р а к т: Создавањето големи количества цврст опасен отпад како што се отпадни автомобилски гуми, го наметнува прашањето за барање соодветен метод за нивно рециклирање. Пиролизата на отпадните гуми претставува остварливо решение не само за справување со еколошките предизвици туку и за конверзија на отпадните гуми од депониите во вредни производи. Овој термохемиски процес дава можност за производство на економично гориво. Во оваа студија, со примена на методот на пиролиза, отпадните гуми од камиони беа конвертирани во производи со додадена вредност. Процесот на пиролиза беше спроведен во полушаржен реактор во средина без присуство на кислород. Полушаржниот реактор е автоматски контролиран, а за пиролизата на отпадна гума беа користени три термостатирани сепаратори. Со пиролизата на отпадни гуми од камиони се добија три главни производи: цврст остаток, кој сочинува 36,50 %; течна фракција позната како црн јаглен, со 51,28 %; и 12,22 % гасна фракција, сингас. Испитувани се основните карактеристики на добиените течни и цврсти производи.

Клучни зборови: пиролиза; отпадна гума; полушаржен реактор; процена на продукти

1. INTRODUCTION

The automobile industry, a fundamental sector in highly developed nations, generates an increasing volume of waste rubber annually. Tire disposal is growing in importance as an environmental issue that still has to be properly resolved. This waste typically finds its way into urban landfills, posing a significant environmental issue due to its non-biodegradable nature. Consequently, utilizing this waste material as a feedstock for fuel production has become an increasingly pressing challenge for numerous researchers. Alternative energy sources arise with the passage of time because fossil energy sources like coal and crude oil are getting exhausted. Waste tires are not biodegradable, and their reuse or recycling requires mechanical or thermochemical treatment [1].

The thermochemical pyrolysis process is a promising technology for the management of organic solid waste. Pyrolysis has been regarded as the most common and eco-friendly option among waste thermal conversion technologies. This is due to reduced environmental pollution and increased economic advantages [2–5]. The European Tyre & Rubber Manufacturers Association (ETRMA) reports that the annual tire sales in the European Union reach 289 million units, representing merely 20% of the global market, which totals around 1.5 billion tires sold each year worldwide [6, 7]. The pyrolysis method demonstrates its effectiveness by transforming these materials into valuable end products under regulated process conditions. This approach allows for the optimization of specific fractions of interest, particularly the liquid fraction, commonly known as pyrolysis oil, which has a minimal environmental pollution impact [8]. During the pyrolysis process, waste tires are converted into valuable fuel products such as pyrolysis oil, carbon black and syngas. Pyrolysis oil has been derived from polymer materials, used tires, waste textiles, and various biomass compounds. The characteristics of tire pyrolysis oil fuel, such as calorific value (41–44 MJ/kg), density (0.90–98 kg/l), and viscosity (2.5–5.5 mm^2/s), are comparable to those of diesel derived from crude oil [9–13]. Waste rubber, owing to its unique chemical composition, includes 60–65% natural rubber and styrene-butadiene rubber, 25–35% carbon as a filler, 5–7% oil, 1–2% zinc oxide, 1–2% sulfur, along with fatty acids, phenolic resins, stabilizers, antioxidants, petroleum waxes, canvas, and steel wires. It serves as a valuable raw material that can be processed into fuel for use in the automotive sector through refining [14].

The pyrolysis process of waste tires presents a viable solution to address the energy crisis. However, challenges persist regarding the quality of the resulting liquid fraction. These challenges encompass a considerable presence of sulfur, elevated water content, and aromatic compounds, all of which are associated with environmental pollution and health issues [15–17]. The pyrolysis of waste tires serves as an alternative energy source in this world. Diesel fuel can be effectively replaced by waste tire pyrolysis oil. Significant volumes of SOx, NOx, and CO are emitted during tire incineration, making them challenging to handle.

The liquid fuel produced contains significant proportion of aromatic compounds. It exhibits greater viscosity and a higher sulfur content compared to fossil-derived diesel. Consequently, it necessitates further processing either purification or fractional distillation to yield fuels with specific quantities of paraffins, olefins, naphthenes, and aromatic compounds. This additional treatment ensures that the fuel can be utilized safely and complies with the established standards for this category of fuel. Solid residue and gas are produced as by-products, and at times as primary products, each possessing distinct economic value and suitable applications [10, 11, 18].

The pyrolysis of waste rubber is a thermochemical procedure conducted in an oxygen-free environment, frequently utilizing nitrogen, at elevated temperatures ranging from 250 to 550ºC, either under vacuum or atmospheric pressure, with or without a catalyst. This process yields three primary products: approximately 50% liquid fuel, around 40% solid residue, and about 10% gas. The yields of products obtained from the pyrolysis process vary based on the type of waste, which has distinct chemical compositions, as well as the type of reactor and specific conditions applied during the process.

The objective of this study was to assess the pyrolysis products derived from the thermochemical conversion of waste tires. The process parameters were optimized to achieve the highest yield of liquid fuel.

2. MATERIALS AND METHODS

The raw material, consisting of shreds from truck tires with an average particle size of 5 mm, underwent pyrolysis in a semi-batch reactor with a volume of 0.4 dm^3. Between 120 and 170 grams of finely chopped rubber are added to a semi-batch reactor. To ensure an inert atmosphere, nitrogen, as an inert gas, is flown into the reactor for 15 minutes. The pyrolysis process was carried out according to a temperature regime (temperature and heating rate) that was programmed by a PID controller (Unitronics V570). The reactor was heated from ambient room temperature to 505°C at a heating rate of 10 °C/min. The optimal conditions for the pyrolysis process of truck tires in a semi-batch reactor to achieve the highest possible yield of pyrolysis oil are depicted in Table 1. The resulting liquid products were separated using three thermostatically controlled, serially connected separators. The first separator is at a temperature of 90 °C, and the second and third are at 0°C. The collected pyrolysis oil is analyzed and characterized according to standard test methods for examining this type of fuel. The pyrolysis oil is a dark-brown liquid with a strong odor, Figure 1.

T a b l e 1

Optimal conditions of the pyrolysis process

Parameter	Measured values
Pyrolysis temperature, °C	505
Heating rate, °C/min	10
Pyrolysis oil, wt.%	51.28
Carbon black wt.%	36.50
Syngass, wt.%	12.22
Start of pyrolysis, °C	325
End of pyrolysis, °C	505

Fig. 1. Pyrolysis oil

3. RESULTS AND DISCUSSION

The chemical analysis was conducted on the properties of the resulting pyrolysis products, which include the amounts of pyrolysis oil (51.28 %) and carbon black (36.50 %). The generated syngas (12.22 %) was calculated based on the mass balance. The density, viscosity, and sulfur content of the pyrolysis oil were measured at 0.9071 g/cm³, 1.865 mm²/s, and 0.42 %, respectively (Table 2). The fixed carbon and ash content of the carbon black were determined to be 41.06 % and 25.63 %, respectively (Table 3 and Figure 2).

T a b l e 2

Chemical analysis of unrefined pyrolysis oil

c	Measured values	Test method
Appearance (visual)	Opaque liquid	
Color (visual)	Black	
Density at 15 °C, kg/m³	0.9071	ASTM D4052
Kinematic viscosity at 40 °C, mm²/s	1.865	EN ISO 3104
Ignition point, °C	<40	ASTM D 93
pH	9	
Refractive index	1.6893	ASTM D 1218
Distillation at 101.3 kPa*		
Initial boiling point/IBP, °C	45.2	ASTM D 86
Flow temperature, °C	< minus 41	ASTM D 5950
Contain water and sediments, v/v. %	2	ASTM D 2709
Sulfur contents, wt.%	0.42	ASTM D 4294

T a b l e 3

Chemical analysis of carbon black

Parameter	Measured values	Test method
Water content, wt.%	0.35	ISO 589:2008
Volatile substances, wt.%	33.21	ISO 562:2010
Ash content, %	25.63	ISO 1171:2010
Granulometric composition, <500 µm	67.15	ISO 1953:1994
Bulk density, kg/m³	456.87	ASTM D 2854
Fixed coal, wt.%	41.06	Estimated

Fig. 2. Carbon black

Depending on reactor type and catalyst type, process conditions, raw materials and their composition, product yields can vary significantly. During pyrolysis, about 33–39 % of the solid residue is obtained, 34–45 % of the liquid products, and the rest consists of gases [19–22]. The results of the studies indicate that a semi-batch pyrolysis reactor is a good choice for generating pyrolysis oil from solid tire waste. In this study, the pyrolysis process takes place in a temperature interval of 180ºC (from 325ºC to 505ºC) at a heating rate 10°C/min. The properties of the total pyrolysis oil, including density and viscosity, are found to be nearly equivalent to those of automotive diesel fuels and truck pyrolysis oil [23]. The obtained pyrolysis oil was fractionated into light (36.32%) and heavy (30.18%) diesel fuel. The densities of the obtained fractions for light and heavy diesel fuel are 0.8780 g/cm^3 and 0.9381 g/cm^3, respectively. The density of the mixture and the amounts of the two fractions of diesel (0.9071 g/cm^3) show that the pyrolysis oil can be classified as a heavy diesel fraction in which there is a presence of light components. A low initial boiling point (IBP) of 45.2ºC indicates the presence of light components in the pyrolysis oil. The generation of sulfur compounds in the pyrolysis liquid products is attributed to the thermal degradation of the vulcanizing agents incorporated into the rubber [10, 24]. The relatively low sulfur content of pyrolysis oil of 0.42% allows it to be safely used as a heating oil (according to the ASTM standard, the maximum is 0.5%). Therefore, it is within the permissible limits for its safe use. However, fractional distillation and desulfurization are necessary to enable their use as alternative fuels for engines. Certain researchers have determined that liquid oil obtained by pyrolysis of waste automobile tires, when mixed with diesel fuel at concentrations up to 75%, can be effectively used in diesel engines without the need for any modifications to the engine [25, 26]. Research shows that the application of pyrolysis oil mixed with diesel fuel at concentrations of 20%, 40%, 60%, and 75% in a direct injection diesel engine has shown comparable performance and lower emissions to the operation of the same engine when running on pure diesel fuel. They suggest that tire pyrolysis oil could serve as a viable alternative fuel for diesel engines in the future [26–28].

Numerous studies on the pyrolysis of waste tires are focused on obtaining pyrolysis oil and less on obtaining and characterizing solid residue. There are very few studies related to the gas product, pyrolysis gas [29]. The pyrolysis process results in the formation of a huge amount of solid carbonaceous material referred to as solid residue, pyrolysis char, or carbonized residue (commonly known as carbon black). The properties of this solid residue are determined by the specific conditions of the pyrolysis process, as well as the composition of the rubber being processed. It has been established, that part of the organic gaseous products generated during pyrolysis can be adsorbed on the surface of the solid residue. This affects a change in the structural characteristics of the carbon black. To improve these characteristics, increase the diameter of pores, increase the specific surface of the carbon black, demineralization and carbon black activation are required. After that, it can be used in the production of tires, adsorbents, or catalyst carriers [30, 31]. The amount of carbon black obtained during the pyrolysis of truck tires and its characteristics are within the limits of expectations and literature data [6, 15].

4. CONCLUSIONS

The pyrolysis of waste tires serves as a method to generate a substantial quantity of high-quality pyrolysis oil and carbon black. Analysis of the fuel characteristics of tire pyrolysis oil shows similarities with diesel fuel or light fuel oil and can safely be used as a heating oil. Also, because of its relatively low sulfur contents and improving quality, it can be blended with diesel fuel for use in diesel engines. This is of particular importance due to the wide application of diesel engines in the transport sector. The yield of carbon black obtained from the pyrolysis of tires is substantial and exhibits a significant ash content. To enhance the quality of the carbon black, aiming to convert it into higher-grade carbon black, demineralization and activation processes are necessary.

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