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Zastita Materijala 65 (4) 634 – 644 (2024)

# Waste Tyres Pyrolysis Oil (WTPO) as an Alternative Source of Fuel and Chemicals: A Review

### ABSTRACT

Waste tyres are dumped and common kind of abandon solid waste. Almost 3 billion tyres are produced each year and each tyre produced will eventually join the waste products and if not properly handled will become pollutant. In many countries disposal of waste tyres is prohibited; as an alternative they should be recovered and recycled instead. In this review pyrolysis was introduced as an alternative way of recycling waste tyres, Pyrolysis allows the dissolution of the waste and it also produces useful by-products. The products obtained during the process are pyrolysis oil, pyrolysis char and condensable gas. Pyrolysis oil is the major product among them, this paper reviewed pyrolysis oil as an alternative sources of fuel to diesel engines and as well to highlight the chemicals obtained in the waste tyres from the pyrolysis oil which mainly depends on the kind of feedstock (i.e. type of tyres e.g truck, cars, bicycle) used in the pyrolysis process. Most of the compounds obtained are Aliphatic and Aromatic hydrocarbons (especially the Polycyclic Aromatic Hydrocarbon PAHs) such as Naphthalene – NAP, Acenaphthylene – ACY, Acenaphthene – ACE, Fluorene – FLU, Phenanthrene – PHE, Anthracene – ANT, Fluoranthene–FLT, Pyrene–PYR, Benzo[a]anthracene – BAA, Chrysene – CRY, Benzo[b]fluoranthene – BBF, Benzo[k[fluoranthene – BKF, Benzo[a]pyrene - BAP, Dibenzo[a,h]anthracene - DBA, Benzo[g,h,i]perylene - BGP, Indeno[1,2,3-cd]pyrene - IND among others. Consequently the pyrolysis oil obtained need further upgrading via a reaction pathways are hydrodesulfurization (HDS), hydrodearomatization (HDA) and hydrocracking (HC) which can be achieved through a 2-stage hydroprocessing strategy regarding WTPO composition in terms of HDS, HAD and HC. Pyrolysis oil from waste tyres can be used as a substitute for diesel and as well as sources of raw materials and fuel to organic chemical industries.

Keywords: waste tyres, pyrolysis, pyrolysis-oil, chemicals, upgrading.

#### 1. INTRODUCTION

The yearly production of discarded tyres has increased dramatically as a result of the transportation and automotive industries fast development. With an anticipated annual growth in market de-

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Paper accepted: 14.06.2024.

mand of more than 4%, the yearly production of tyres is predicted to be over 3 billion. Additionally, billions of end-of-life tyres will inevitably be created, necessitating trash treatment, disposal, and management. Tyre stockpiling and incorrect disposal harm the environment by creating habitats for insects and rodents, as well as increasing the risk of fire in huge tyre dumps [1] Fig 01.

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Fig 01: Impropoer dumping of waste tyre

Options for recovering materials from scrap tyres include recycling them into rubber and rubber particles for playground and sports field flooring, as well as using them as application materials in civil engineering. In certain nations, disposing of used tyres in a landfill is part of the treatment and disposal process. But because the rubber and sulfur linkages in waste tyres are strongly cross-linked, the rubber in waste tyres does not break down quickly in landfills [2]. As a result, society improperly manages or disposes waste tyres by burning them into ashes on a flat piece of ground (Fig. 2), which pollutes the air, produces unwelcome and toxic smoke, and damages habitats by causing illness. For this reason, there has been a push recently to identify more valuable and sustainable resource recovery methods for handling discarded tyres [1].



Fig 02: Improper handling of waste tyres

# 2. PYROLYSIS AS A WASTE TYRE RECYCLING METHOD

However, because the rubber and sulfur linkages in waste tyres are strongly cross-linked, the rubber in waste tyres does not break down quickly in landfills. For this reason, there has been a push recently to identify more valuable and sustainable resource recovery methods for the process of treating waste tyres which is known as pyrolysis [1].

Pyrolysis is a thermal decomposition process that turns organic molecules into a complicated mixture of solid, liquid, and gaseous components in the absence of oxygen, For many years, this method has been utilized to transform different waste materials—such biomass, plastics, and rubber—like tyres, into useful goods like carbon black, chemicals, and pyro fuels. Pyrolysis is seen as a promising technology because it produces useful goods and minimize waste volume and environmental effect while managing trash and recovering resources [3-4].

Waste tyres are heated to a certain temperature in the absence of oxygen during the pyrolysis process, which yields useful goods like char, gas, and pyrolysis oil. In a pyrolysis reactor, waste tyres are heated to elevated temperatures (usually between 300°C and 700°C). This process releases gas, char, and oil vapours from the tyres as they break down into smaller molecules [5-6].

#### 3. STAGES IN PYROLYSIS PROCESS

The pyrolysis process is be divided into three stages: the initial heating stage, the main pyrolysis stage, and the cooling stage. During the initial heating stage, the temperature of the reactor is raised to the desired temperature. In the main pyrolysis stage, the waste tyres are heated to the desired temperature, and the pyrolysis reactions occur, resulting in the production of pyrolysis oil, gas, and char. Finally, in the cooling stage, the reactor is cooled, and the products are collected [5, 7]

The pyrolysis oil produced from the process can be used as a fuel in boilers, furnaces, and diesel engines after upgrading. The gas produced can be used as a fuel for the pyrolysis process, and the char can be used as a solid fuel or as an additive in rubber products [7].

#### 4. PYROLYSIS APPLICATIONS

Pyrolysis process has been applied in different industries and regions worldwide. In the agriculture

sector, pyrolysis has been used to convert waste agricultural residues into biochar, which can improve crop yields, reduce soil erosion and sequester carbon. In the forestry sector, pyrolysis has been used to convert wood chips and forest residues into biooil, which can serve as a feedstock for further processing to obtain transportation fuels [6,8].

In the municipal solid waste sector, pyrolysis has been used to convert household and commercial waste into biochar and non-condensable gases. The biochar can reduce the amount of waste sent to landfills, while the non-condensable gases can generate electricity or used in heating systems [6,8].

In the industrial sector, pyrolysis has been used to convert manufacturing and processing waste into biochar, which can be used as a fuel or carbon sequestration. The process reduces waste disposal costs and greenhouse gas emissions [6,8].

#### 5. TYPES OF PYROLYSIS

There are three main types of pyrolysis: **fast pyrolysis**, **slow pyrolysis**, **and intermediate py-rolysis**. Each of these types has different operating temperatures, heating rates, and product yields [9,10].

#### 5.1. Fast Pyrolysis

Fast pyrolysis is a high-temperature process that rapidly heats biomass or waste materials at temperatures between 450°C and 600°C in the absence of oxygen. The heating rates in fast pyrolysis are typically in the range of 10°C/s to 50°C/s. The rapid heating and short residence time of the biomass or waste material in the reactor result in the production of a high yield of liquid bio-oil, which contains a mixture of organic compounds. The liquid bio-oil can be used as a fuel for heat and power generation or as a feedstock for the production of chemicals and materials. The remaining solid residue, known as biochar, can be used as a soil amendment or as a carbon sequestration agent [9,10].

#### 5.2. Slow Pyrolysis

Slow pyrolysis is a low-temperature process that heats biomass or waste materials at temperatures between 300°C and 500°C in the absence of oxygen. The heating rates in slow pyrolysis are typically in the range of 0.1°C/min to 10°C/min. The slow heating and long residence time of the biomass or waste material in the reactor result in the production of a low yield of liquid bio-oil, which contains a high proportion of water and oxygenated compounds. The remaining solid residue, known as biochar, has a high fixed carbon content and can be used as a soil amendment or as a carbon sequestration agent [9,10].

#### 5.3. Intermediate Pyrolysis

Intermediate pyrolysis is a moderate-temperature process that heats biomass or waste materials at temperatures between 350°C and 450°C in the absence of oxygen. The heating rates in intermediate pyrolysis are typically in the range of 10°C/min to 100°C/min. The intermediate heating and residence time of the biomass or waste material in the reactor result in the production of a moderate yield of liquid bio-oil, which contains a mixture of organic compounds. The remaining solid residue, known as biochar, can be used as a soil amendment or as a carbon sequestration agent [9,10].

#### 6. PRODUCT TYPES IN PYROLYSIS

The pyrolysis process produces three main end-products, namely **pyro-oil**, **pyro char**, **and non-condensable gases**. Pyro-oil is a dark brown liquid with a high water content and a complex mixture of organic compounds. The pyro-oil requires further processing to remove impurities, such as water, acids, and oxygen compounds (Fig 03). The refined pyro-oil can serve as a feedstock for further processing, such as fractional distillation and hydroprocessing, to obtain transportation fuels [11].

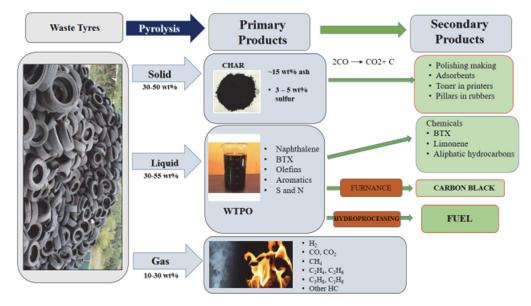


Fig 03: Primary and secondary products from waste tyre pyrolysis.

#### 6.1. Pyrolysis-oil

Pyro-oil is a dark brown liquid that is produced during pyrolysis. It is a complex mixture of organic compounds, such as phenols, ketones, aldehydes, and carboxylic acids. Pyro-oil has a high energy density and can be used as a fuel in various applications, including power generation, heating, and transportation. The main drawback of pyro-oil is its instability, as it degrades rapidly when exposed to air, light and water [12-16]. It contains high water content and requires further processing to remove impurities and obtain transportation fuels. Non-condensable gases can generate electricity or used in heating systems [11].

#### 6.2. Pyro char

Pyro-char is a carbon-rich solid material that is produced during pyrolysis. It is a black porous substance that contains high amounts of carbon, and low amounts of volatiles and ash. Pyro-char can be used as a soil amendment, as it increases soil fertility and water retention, and reduces greenhouse gas emissions. It can also be used as a fuel, as it has a high calorific value and burns cleanly [12-16]. It is a solid residue obtained from pyrolysis that can be used as a soil amendment, carbon sequestration, or fuel. The pyro char has high carbon content and can improve soil fertility, water retention, and reduce greenhouse gas emissions [11].

#### 6.3. Non-condensable gases

Condensable gas is a mixture of various gases, such as methane, ethane, propane, and butane. It is produced during pyrolysis when the organic materials are heated and gasified. Condensable gas can be used as fuel in power generation or as a feedstock for chemical synthesis [12-16].

Non-condensable gases are mainly composed of carbon dioxide, carbon monoxide, and methane. The gases can generate electricity or used in heating systems [6, 8].

#### 7. PYROLYSIS OIL AS A FUEL ENERGY

This is the most abundant as well as the most interesting and economically attractive product of the waste tyres pyrolysis. It is a brownish liquid resembling crude oil (Fig 04) and consists basically of:

(i) The processing liquid as part of the tyre formulation,

(ii) Organic additives, and

(iii) Tyre pyrolysis products [17].



Fig 04: Pyrolysis Oil

The calorific value (CV) of pyrolysis oil (PO) can be as high as 44MJkg<sup>-1</sup>, comparable to valued fuels,

so it requires a separated section to be analyzed in terms of its composition and potential for being used as alternative fuel in diesel engines [17].

#### 7.1. Elemental Composition of Pyrolysis Oil

Despite the different technologies and operational conditions strongly affecting WTPO yield, its composition does not vary as significantly as that of the gaseous fraction (Table1). Sulfur compounds in waste tyre pyrolysis oil (WTPO) have their origin in the thermal degradation of the organic additives used as vulcanization agent sand accelerators in tyre manufacturing [18]. Comparing this data with the elemental analysis of tyres listed in Table 2 which shows the various elemental composition of different kind of tyres: tyres from passenger car tyre (PCT) and truck tyre (TT), bicycle tyre (BT), has higher amounts of C and H are observed in WTPO, together with less oxygen, sulfur and N amount, that has been either removed in the pyrolysis or retained in the solid fraction. The reaction pathways through which sulfur compounds are produced change with pyrolysis conditions (temperature, pressure and residence time) and yield different amounts of sulfurous compounds in WTPO. Some authors have reported values of sulfur in the WTPO of 0.3wt% [18], but the majority of the reported values correspond to ca.1.4wt% [19]. Cleavage of the N-S and C-S bonds of N-N0-caprolactam and benzothiazolic additives in tyres produce caprolactum and benzothiazole in WTPO [20]. Unapumnuk et al., 2008 [21] corroborated the crucial role of temperature on S content in S WTPO, as less S was retained in WTPO removed with increasing temperatures, while heating rate plays no significant role. These authors observed that half of the original sulfur remained in the char.

The amount of O and N present in WTPO is similar to that of S or even higher, with a high H/C ratio representative of aliphatic and aromatic compounds. O and N compounds have their origin in thermal degradation of stearic acid, sulfur compounds, amines and oxygenated oils used in tyre formulation, and should be taken into account when considering WTPO for fuel applications, since pre- treatments are required to remove these elements [18].

Ref	<b>[22]</b> <sup>a</sup>	[ <b>23</b> ] <sup>b</sup>	<b>[24]</b> <sup>c</sup>	<b>[25]</b> ª	<b>[26]</b> <sup>a</sup>	<b>[27]</b> ª	<b>[28]</b> ª
T⁰C	600	550	500	550	550	650	650
Yield, wt%	53.1	44.6	-	38.0	46.1	48.4	56.0
CV, MJkg <sup>-1</sup>	41.2 <sup>d</sup>	41.0	-	40.8 <sup>d</sup>	43.3 <sup>d</sup>	41.6 <sup>d</sup>	42.4 <sup>d</sup>
C, wt%	87.9	85.6	87.2	84.9	85.4	87.6	86.5
H, wt%	10.1	9.6	10.6	9.6	11.4	10.4	11.7
N, wt%	0.5	0.6	0.5	0.1	0.4	< 1	< 1
S, wt%	1.3	1.3	1.2	1.6	0.6	1.4	0.8
O, wt%	0.1	4.0	0.5	3.5	-	-	-
H/C	1.4	1.4	-	1.4	1.6	1.4	1.6

Table 1: Composition of WTPO of various authors as reported in literature

Where: a fixed bed reactor.

<sup>b</sup> Rotary kiln reactor.

<sup>c</sup> Conical spouted bed reactor.

<sup>d</sup> Higher.

Table 2: Elemental analysis of different types of tyres

PCT <sub>1</sub>	PCT <sub>2</sub>	PCT <sub>3</sub>	BT	TT
85.9	82.5	86.4	74.5	83.2
8.0	6.4	8.0	6.5	7.7
2.3	5.7	3.4	16.4	6.2
0.4	0.5	0.5	1.0	1.5
1.0	1.1	1.7	1.6	1.4
2.4	3.8	2.4	-	-
	85.9 8.0 2.3 0.4 1.0	85.9 82.5   8.0 6.4   2.3 5.7   0.4 0.5   1.0 1.1	85.9 82.5 86.4   8.0 6.4 8.0   2.3 5.7 3.4   0.4 0.5 0.5   1.0 1.1 1.7	85.9 82.5 86.4 74.5   8.0 6.4 8.0 6.5   2.3 5.7 3.4 16.4   0.4 0.5 0.5 1.0   1.0 1.1 1.7 1.6

#### 7.2. Molecular Composition of Waste Tyre Pyrolysis Oil

WTPO consists of a very complex mixture of hydrocarbons consisting of :  $C_6-C_{37}$  linear paraffins, particularly  $C_8-C_{13}$ ; low concentration of alkenes, particularly not condensed butadiene, pentenes, pentadienes and isoprene; high amount of aromatics, naphthenes and terpenes (with a total amount of ca. 65wt%), particularly limonene, BTX, alkylated single-ring aromatics and upto 5-ringbenzopyrenes [17].

As a general trend, the amount of aromatics in WTPO increases with pyrolysis temperature, due to their combination reactions that take place among aliphatic and aromatic free radicals and also to the cyclization of aliphatic chains [29]. Several authors [19, 23, 30] have reported that the aromatic content in WTPO is determined by the original amount of aromatics and olefins in rubber. Olefins and diolefins in particular tend to condense through Diels–Alder, cyclization and dehydrogenation reactions to form aromatics. These reactions are favored at high

temperatures so that the amount of aromatics and polycondensed aromatics in WTPO increases with temperature [23]. Increasing the residence time of volatiles in the pyrolysis reactor also results in the increase of aromatics and polycondensed aromatics yield in WTPO [31].

Sulfur in WTPO is in the form of benzothiazole (BTZ) and dibenzothiophene (DBT) and its alkylated forms; methyl, dimethyl, trimethyl and tetramethyldibenzothiophene ( $M_1DBT$ ,  $M_2DBT$ ,  $M_3DBT$ , and  $M_4DBT$ ). Nitrogen in WTPO is in the form of BTZ too, while oxygen appears as hydroxyl compounds such as phenol, 3-methylphenol and 2-ethyl-1-hexanol. As previously mentioned, these hetero atomic molecules represent for a great obstacle for using WTPO in combustion engines or as fuels [17].

# 8. PYROLYSIS OIL AS ALTENATIVE SOURCE FOR CHEMICALS

Some of the mentioned molecules composing WTPO have economic interest. WTPO is an impor-

tant source of d-limonene, a high valued chemical used in the formulation of industrial solvents, resins, adhesives, and fragrances, among others [18]. Limonene is acyclic terpene  $(C_{_{10}}H_{_{16}})$  that exists in its d-and I- form, as d-limonene and I-limonene. Limonene yields are lower at high temperatures due to secondary reactions taking place, mainly dehydrogenation to form aromatics. Arabiourrutia et al., [32] observed a decrease in d-limonene concentration in WTPO with temperature from 23.4wt% at 425 °C to 5.7wt% at 610 °C in a Conical spouted bed reactor (CSBR). Similarly, Li et al., [23] reported a decrease from 5.4 wt% at 450°C to 0.07 wt% at 650°C in d-limonene yield in WTPO obtained in a rotary kiln reactor. Working in vacuum conditions and decreasing gas residence time can partially avoid sequential reactions of d-limonene [18]. López et al., [24] obtained a 60wt% yield of WTPO with a concentration of d-limonene of 26.8wt% working in a CSBR in vacuum conditions, mainly due to the low residence time of volatiles. In the WTPO obtained in a CSBR, the concentration of d,l-limonene is higher (ca.27wt%) than that in the WTPO obtained using other reactors. Various reaction path ways have been reported in literature for d,l-limonene formation [18], many of them agreeing on poly-isoprene (in the NR) cracking through  $\beta$ -scission and intra molecular cyclization. In parallel, isoprene could dimerize through a Diels-Alder path way. Finally, and if temperature and/or residence time are high enough, d,l-limonene further dehydrogenates to aromatics [33]. Stanciulescu and Ikura [34] used a two-stage distillation to obtain naphtha in the first stage, and d-limonene enriched naphtha in the second one. Then, they used the d-limonene enriched mixture to obtain ethers by alkyl oxidation [32].

WTPO is also a potential source of light aromatics such as benzene, toluene and xylene (BTX, which are valued commodities [18], The BTX com-

position in WTPO is inversely proportional to that of d-limonene, as BTX is formed through d-limonene dehydrogenation. Li et al., [23] have proposed optimal pyrolysis conditions for obtaining high yields of BTX: benzene, 2.09wt%; toluene, 7.05wt%; and xylene 2.01wt%. Furthermore, post pyrolysis selective condensation, distillation, and catalytic pyrolysis can further increase the yields of BTX. Another approach for increasing the BTX proportion in WTPO is using a catalyst in the pyrolysis [17], which is known as catalytic pyrolysis or catalytic cracking. Williams and Brindle [35] used HY and HZSM-5 zeolites in a twostage pyrolysis process (pyrolysis reactor followed by a catalytic reactor for the gaseous products) and found that generally, increasing the catalyst/feed ratio had a positive effect on BTX yields, with maxima of 5wt% benzene, 24 wt% toluene, 20wt% m- and p-xylenes, and 7wt% o-xylene. The HY zeolite catalyst gave way to higher concentrations of BTX compared to HZSM-5[17]. Olazar et al., [36] observed the following in aromatic yields: 20.2wt%, without catalyst; 32.5wt%, HZSM-5 zeolite catalyst; and 40.5wt%, HY zeolite catalyst; with BTX maximum yields of 4.15 wt% of benzene, 7.39 wt% of toluene, and 6.59 wt% of xylene using HY zeolite.

Even though different waste tyres combination (i.e being tyre of bicycle, car, trucks among others) produced different variety of fuel according to Neoklis and Zorpas, 2019 [37]. Also WTPO can have a lot of polycyclic Aromatic Hydrocarbons (PAHs) as such as Naphthalene – NAP, Acenaphthylene – ACY, Acenaphthene – ACE, Fluorene – FLU, Phenanthrene – PHE, Anthracene – ANT, Fluoranthene – FLT, Pyrene – PYR, Benzo[a]anthracene – BAA, Chrysene – CRY, Benzo[b]fluoranthene – BBF, Benzo[k[fluoranthene – BKF, Benzo[a]pyrene – BAP, Dibenzo[a,h] anthracene – DBA, Benzo[g,h,i]perylene – BGP, Indeno[1,2,3-cd]pyrene – IND were all found in his pyrolysis oil.

S/N	Property	Characteristics	Issues
1	Sulfur Content	Usually between 0.6 and 1.4 wt%. Sulfur is added to tyres in the vulcanization process. Up to 70% of initial sulfur in tyres remains in recovered carbon black after pyrolysis. The remaining fraction is distributed into pyrolytic gas and TPO. Sulfur compounds in TPO are in the form of thiophene, benzothiazole, ben- zothiophene, etc.	Sulfur containing compounds are environmen- tal pollutants. During oxidation, SOx are produced and released as gas products. SOx also reaches the lubricant oil, causing corrosion problems in combus- tion systems like internal combustion engines.

### 9. MAJOR CHARACTERISTICS OF WTPO AND RELATED CHALLENGES

2	Nitrogen Content	Usually in the range of 0.4–1.05 wt %, depending on initial tyre composition and attributable to thermal degradation of accelerators such as N,N-di-iso- propyl-2-benzothiazole-sulfenamide, 2-(4- morpholinylthio)-benzothiazole, N,N caprolactamdisulphide, and 2- mercaptobenzothiazole incorporated into tyres during formulation. Nitrogen in TPO is commonly found in the form of benzothiazole, also containing sulfur.	High nitrogen levels in the fuel lead to fuel NOx formation during combustion, which may cause acid rain.
3	Flash Point	Usually lower than 30ºC, this low flash point is due to high fraction of volatile compounds in TPO.	High flash point of a liquid fuel is beneficial for storage. A lower flash point is easier for igniting the fuel/air mixture; liquid is considered flammable if its flash point is<60 °C.
4	Aromatic Content	As much as 65 wt% of TPO could be represented by aromatic hydrocarbons, associated with the aromatic nature of rubber (one aromatic ring in the styrene butadiene rubber monomer) and the cyclisation of olefin structures, followed by dehydration and Diels- Alder reac- tions, favored at high temperature in the pyrolysis process.	Aromatic hydrocarbons are associated with incomplete combustion (due to long IDT) and the tendency to form particulate matter (PM) (act as PM precursors).
5	Final Distillation Point	Final distillation point is usually higher than 550°C., associated with the pres- ence of high molecular weight com- pounds like polycyclic aromatic hydro- carbons (PAH) and polycyclic aromatic sulfur hydrocarbon (PASH).	Fuel's boiling point affects its vaporization and combustion process. A high final boiling point may decrease the vaporization rate, resulting in incom- plete combustion and PM formation.
6	Ignition Delay Time (IDT)	Significant presence of light aromatic (benzene, toluene, and xylene) and <i>iso</i> -paraffinic (limonene) hydrocarbons tends to increase the IDT of TPO, resulting in a low cetane number. These compounds have stable molecular struc- tures, requiring high temperatures and pressures to ignite.	In diesel engines, fuels with high IDTs may increase particulate matter emissions, since combustion be- gins in the final stage of the expansion cycle when the temperature inside the chamber decreases. Oxidation rate decreases here, leading to increased concentration of unburned hydrocarbons condens- ing on the surface and increasing the mass of PM

Table as reported by Campuzano et al [38]

#### 10. UPGRADING OF WTPO

Among all the processes comprised within are finery, hydroprocessing is the only one that allows for simultaneously solving the main compositional barriers of WTPO for increasing the value of the feedstock and allow its direct application as a fuel. These barriers can be summarized as: (i) high sulfur content, (ii) high content of aromatics, and (iii) great proportion of molecules within the gas oil boiling point (BP) range. Therefore, the most interesting reaction pathways for WTPO upgrading are hydrodesulfurization (HDS), hydrodearomatization (HDA) and hydrocracking (HC). It is a common industrial strategy to place different catalyst beds in series within a reactor in order to optimize catalyst and reactor performance according to the main hydroprocessing goal [17]. Great achievements can be obtained through a 2-stage hydroprocessing strategy regarding WTPO composition in terms of HDS, HAD and HC. The first hydroprocessing stage, using NiMo catalysts, has allowed for reducing the total amount of sulfur from an initial content of 11,800 ppm in WTPO to ca.2,000 ppm in hydro treated WT-PO(HT-WTPO), thanks to the high activity towards hydrogenation reactions of this type of catalysts. Furthermore, 13.2wt% less aromatics and 8wt% less gas oil were obtained working in mild hydrocracking conditions. However, greater achievements in terms of

HAD and HC have been obtained on the second hydroprocessing stage using a PtPd/SiO2-Al2O3 catalyst [17] due to both the higher hydrogenating activity of the metallic phase and cracking ability of the acidic support, which have allowed for further reduction of 18.6wt% of aromatics and almost complete removal of the gas oil lump in upgraded WTPO (Up-WTPO). Additionally, sulfur has reached levels below 100ppm. On the whole, global conversions of 99.2% in HDS, 99.7% in HC and 57% in HAD have been achieved. With very little amount of compounds with in the gas oil lump, and an aromatic content even lower than that of some diesel-type feedstock [39]. Up-WTPO comprises the required features for being co-fed with commercial diesel-type automotive fuels with promising performances in internal combustion engines. It is also to mention that the amount of remaining sulfur in Up-WTPO can be the limiting factor when determining the proportions in the diesel-WTPO blend to be used, in order to avoid excessive aromatic and particulate emissions and comply with the corresponding environmental policies [17].

#### **11. CONCLUSION**

Pyrolysis oil from waste tyres can be used as a substitute for diesel and as well as sources of raw materials and fuel to organic chemical industries. Also the oil can have a range of hydrocarbons depending on the composition of the feedstock which was used to undergo the pyrolysis this include aromatic hydrocarbons like benzene, toluene, and Xylene (BTX), as well as aliphatic hydrocarbons such as ethylene, propylene and butenes. Also Oxygenated compounds; compound that contains oxygen such aldehyde, ketones, acids, alcohols and furans. We can also get Polycyclic Aromatic hydro carbons (PAHs) example; Naphthalene, anthracene and phenanthrene. With this WTPO will serves as an alternative fuel instead of fully dependence to natural crude oil.

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## IZVOD

# PIROLIZNO ULJE IZ OTPADANIH GUMA (VTPO) KAO ALTERNATIVNI IZVOR GORIVA I HEMIKALIJA: PREGLED

Otpadne gume se odlažu i uobičajena je vrsta napuštanja čvrstog otpada. Skoro 3 milijarde guma se proizvede svake godine i svaka proizvedena guma će se na kraju pridružiti otpadnim proizvodima i ako se njima pravilno ne rukuje postaće zagađivač. U mnogim zemljama odlaganje otpadnih guma je zabranjeno; kao alternativu treba ih oporaviti i reciklirati. U ovom pregledu piroliza je predstavljena kao alternativni način reciklaže otpadnih guma. Piroliza omogućava rastvaranje otpada i takođe proizvodi korisne nusproizvode. Proizvodi dobijeni tokom procesa su pirolizno ulje, pirolizni uglien i kondenzabilni gas. Pirolizno ulje je glavni proizvod među njima i u ovom radu je dat pregled piroliznog ulia kao alternativnog izvora goriva za dizel motore i istaknute su hemikalije dobijene iz otpadnih guma od piroliznog ulia, koje uglavnom zavise od vrste sirovine, ti, vrste guma (npr. kamion, automobil, bicikl) koji se koriste u procesu pirolize. Većina dobijenih jedinjenja su alifatični i aromatični ugljovodonici (posebno policiklični aromatični ugljovodonici PAH) kao što su naftalen -NAP, acenaftilen – ACI, acenaften – ACE, fluoren – FLU, fenantren – PHE, antracen – ANT, Fluo – PIR, benzo[a]antracen – BAA, krizen – CRI, benzo[b]fluoranten – BBF, benzo[k[fluoranten – BKF, benzo[a]piren – BAP, dibenzo[a,h]antracen – DBA, benzo[g,h,i]perilen – BGP, Indeno[1,2,3-cd]piren – IND između ostalih. Shodno tome, dobijeno pirolizno ulje treba dalju nadogradnju putem reakcionih puteva: hidrodesulfurizacija (HDS), hidrodearomatizacija (HDA) i hidrokreking (HC) koji se mogu postići kroz 2-stepenu strategiju hidroobrade u pogledu sastava VTPO u smislu HDS, HAD i HC. Pirolizno ulje iz otpadnih guma može se koristiti kao zamena za dizel i kao izvor sirovina i goriva za organsku hemijsku industriju.

Ključne reči: otpadne gume, piroliza, pirolizno ulje, hemikalije, nadogradnja.

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Pregledni rad Rad primljen: 20.03.2024. Rad korigovan: 1.06.2024. Rad prihvaćen: 14.06.2024.-

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