



Effect of pre-devulcanization and temperature on physical and chemical properties of waste tire pyrolytic oil residue



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HIGHLIGHTS

- Half of pyrolysis time for RR compare to GTR observed at same temperatures.
- Pre-devulcanized nature of rubber gets important at lower temperatures (<600 °C).
- Parabolic relationship between pyrolysis temperature and time proposed.
- Alkanes/aromatics ratio decreased for HR and increased for HG by temperature.
- Aromatics have got larger Mw than aliphatics.

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ABSTRACT

The effect of pre-devulcanization and temperature in waste tire pyrolysis are investigated on pyrolysis time, yield and properties of residual Heavy Fraction Pyrolytic Oil (HFPO). A comparative pyrolysis of usual Ground Tire Rubber (GTR) and a commercial devulcanized ground tire rubber, (known as Reclaim Rubber-RR) is performed in a static-bed batch reactor at 400–600 °C and the oil is distilled to light and heavy fractions. Chemical composition studies show higher amounts of aromatics in HFPO than light fraction. As a novel approach, a relationship between isotherm at max temperature and pyrolysis temperature is presented in this work. Pyrolysis time for RR is approximately half of GTR at same temperatures due to RR devulcanized nature. The solid yield is larger for GTR than RR and decreases by temperature. The liquid yield for RR is larger than GTR. Pyrolysis time and liquid yields of GTR and RR approach to each other at higher temperatures. Kinematic viscosity and flash point are larger for GTR oils in comparison with RR. FTIR shows by increasing temperature the ratio of alkanes/aromatic (I_{2952}/I_{1456}) decreased for HR and increased for HG. So it can be said that both oil contain similar functional groups at different concentrations depending on temperature. ¹H NMR and ¹³C NMR spectra shows oils are a mixture of aromatics, alkanes, alkenes, alkynes and ethers or alcohols, which exist in different concentrations. Gel Permeation Chromatography (GPC) shows that pyrolysis of GTR produces oil which is heavier and broader in Mw distribution in comparison with pre-devulcanized sample (RR). Elemental analysis shows similar elemental composition of HFPOs.

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1. Introduction

The annual global production of waste tires is some 1.4 billion units (about 17 million tonnes) [1] and vast majority of them are easily being dumped in the open or in landfills [2]. This is environmentally and economically unacceptable. On the other hand, rubber recycling is exceedingly difficult due to the cross-linked structure of rubber (cannot be melted or solved) [1]. Product recycling [1,2], material recycling [2], energy recovery [3] and pyrolysis [4] are among the common rubber recycling methods.

In pyrolysis, the organic matter of tires (mainly the rubber polymers) is decomposed to lower molecular weight products including pyrolytic oil and non-condensable gas. The inorganic components (mainly steel) and mineral fillers remain as relatively unaltered solid residues which are referred as Pyrolytic Carbon Black (CBp) [4,5]. Pyrolysis can be done under atmospheric pressure or vacuum conditions (Table 1).

Tire pyrolysis gases are mainly composed of H₂ and C₁–C₄ hydrocarbons such as CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈ and rarely CO, CO₂, H₂S [8–10]. Non-condensable gas has a high gross calorific value of around 25.8–33 MJ m⁻³ with an average molecular weight of 28.3 g/mol [8,9,11]; so it can be used for pyrolysis energy requirements. In addition, from health aspects, most of the emissions are produced from the combustion of the

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Table 1

A short comparison between vacuum and atmospheric pyrolysis.

Property	Vacuum pyrolysis	Atmospheric pyrolysis
Temperature	Low temperature ($T = 400\text{--}500\text{ }^{\circ}\text{C}$) [7]	High temperature level ($T > 600\text{ }^{\circ}\text{C}$) [4]
Pressure	Low pressures ($P < 10\text{ kPa abs}$) [7]	Ambient pressure [4]
Secondary reactions	Minimize secondary reactions ^a [7]	Poor quality of solid and oil [4]
Economics	More oil yield due to less secondary reactions [7]	Weaker economics due to low quality CBp [6]
Carrier gas	No carrier gas [6]	Using carrier gas
Mw ^b of oil	Temperature does not affect on oil Mw [7]	Heavier oils by increasing temperature [4]
Residence time	Short residence time	Long residence time [6]
Environmental	No hazardous emission due to mild condition ^d [6]	Hazardous PAHs ^c via Diels–Alder type aromatization [6]

^a Secondary reaction such as thermal cracking, repolymerisation and recondensation.^b Molecular weight (Mw).^c Polyaromatic Hydrocarbons (PAHs).^d Such as low pyrolysis temperature and absence of a carrier gas.

tire pyrolysis gas are under the limits established by the Waste Incineration Directive [10,11].

Theoretically, CBp can be recycled in worthwhile applications such as carbon black, activated carbon or smokeless fuel. CBp can be activated by CO_2 [12] or steam which produces an activated carbon with a good surface area ($302\text{ m}^2\text{g}^{-1}$) [13] and properties close to commercially available activated carbons [14]; which can also be post-carbonized to gain excellent adsorption capacity for phenol and metals from solution [13]. It can be used also to rheologically modify road bitumen [15]. CBp as a solid fuel has a gross calorific value of around $33\text{--}35\text{ MJ kg}^{-1}$ [12,15–17].

The pyrolytic oils obtained in tire pyrolysis are dark brown-colored products, which resemble petroleum fractions [18]. Tire pyrolytic oil is a mixture of numerous $\text{C}_5\text{--C}_{20}$ hydrocarbons mainly Polyaromatic Hydrocarbons (PAHs), Polyaromatic Nitrogen Hydrocarbon (PANH) and Polyaromatic Sulfur Hydrocarbons (PASHs) [19]. The pyrolytic oil can be distilled into fractions. Its light fraction is a source of refined chemicals, such as BTX and styrene [13] and its heavy fraction is used to improve polymer modified asphalt properties [14]. As raw materials, these oils are interesting for petrochemical industry (mainly light olefins and aromatics) and for the synthesis of basic materials in tire manufacturing (isoprene and 1, 3-butadiene) [13,17]. Distillated pyrolytic oil presents specifications similar to commercial automotive and heating diesel oils [18]. Pyrolytic oil can be used as desulfurised fuel [11]. Researches show that the derived tire oils have gross calorific value of around 40 MJ kg^{-1} [20,22].

Here an experimental study on pyrolysis of two types of tire powder such as tire rubber (GTR) and pre-devulcanized tire rubber (RR) carried out in a laboratory installation at different temperatures. Liquid phase of whole pyrolysis runs is collected and thoroughly characterized. It should be emphasized that to the best of our knowledge this is the first time that RR, pre-devulcanized sample, has been pyrolysed at different temperatures and its pyrolysis yield/time and physical/chemical properties of its pyrolytic oil are compared with usual GTR. But primary the aim of the project was designed to produce a bitumen modifier for Pasargad Oil Company from two types of scarp tire exists in Iran and investigating on effect of feed type (as material parameter) and temperature (as process parameter) on yield and properties of produced bitumen modifier.

2. Experimental

2.1. Materials

Two types of commercial waste tire powders GTR and RR were supplied from Isatiss Tire Company, Yazd, Iran (Table 2). GTR was

converted to RR through a thermochemical devulcanization process. This process is basically a reclaim process. An autoclave, either steam or dry, or a kettle was used to carry out the process. Chemicals were used to soften or plasticize the crumb rubber. Temperatures ranged from $140\text{ to }200\text{ }^{\circ}\text{C}$. All were refined on a two-roll mill after the autoclaved treatment. The length of time was long up to 4 h [21]. The samples were kept in dry conditions prior to pyrolysis.

2.2. Pyrolysis experiments

Pyrolysis experiments were carried out at common studied temperatures: $400\text{ }^{\circ}\text{C}$, $500\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ [4,6,7,10,13,18–22], in vacuum conditions with a reduced pressure of approx 2.2 kPa abs .¹ The waste tire powders (GTR, RR) were pyrolysed in a static-bed batch reactor with an inner diameter of 11 cm and a depth of 27 cm, as shown in Fig. 1. The reactor was externally heated by an electrical furnace with a controlled heating regime. In a typical run, the sealed reactor was filled with 1000 g waste tire powder (GTR or RR) at room temperature. The system was heated at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ to the final selected temperature. At about $150\text{ }^{\circ}\text{C}$ white vapors was observed. The final temperature was held until no more pyrolysis gaseous products were formed (isotherm period). The hydrocarbon vapors were quickly removed from the reaction zone by a vacuum pump. The produced gases and vapors were cooled down in two series condensers. The vapors were cooled in a convecting manner with ambient air in the first condenser and subsequently with ethylene glycol (at $0\text{ }^{\circ}\text{C}$) in the second one. The oil collected from the first condenser was considered as major product, which were heated in a heater/stirrer by 200 rpm for 5 h at $120\text{ }^{\circ}\text{C}$ to remove any possible water, and then it was distilled at atmospheric pressure into two fractions: light fraction (bp $< 350\text{ }^{\circ}\text{C}$) and heavy fraction (bp $> 350\text{ }^{\circ}\text{C}$). The heavy fraction, final product, which called HFPOs, was collected for characterization purposes.

The abbreviations were used here for sample coding are: HG4 that stands for HFPO derived from pyrolysis of GTR at $400\text{ }^{\circ}\text{C}$; HR6 that stands for HFPO derived from pyrolysis of RR at $600\text{ }^{\circ}\text{C}$; HG (HR) oils that stands for HFPOs derived from pyrolysis of GTR (RR) at $400\text{--}600\text{ }^{\circ}\text{C}$ and finally UHG6 (UHR6) that stands for HG6 (HR6) oil which is experienced ultrasonic vibration.

The black residual char was removed from the reactor at the end of each experiment. Solid and liquid yields were evaluated in each experiment by weighing the amount of product and calculating the corresponding percentage to establish the mass balance and determine the products yields. The gas yields were calculated

¹ Absolute: abs.

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