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Chemical characteristics of oil-like products from hydrous pyrolysis of scrap tires at temperatures from 150 to 400 °C

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HIGHLIGHTS

- ▶ We used hydrous pyrolysis to study alteration products of scrap tire waste (STW).
- ▶ Two sets of experiments were conducted at T = 150–400 °C for 48 h.
- ▶ The first set included only STW and water and the second with oxalic acid (OA).
- ▶ The yields and alteration products increased with temperature and presence of OA.
- ▶ The results show that the yields are higher under reductive hydrous pyrolysis.

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ABSTRACT

Scrap tire waste consists of organic matter that is often commonly disposed in landfills, ultimately causing an environmental problem. Different pyrolysis techniques have been used to convert biomass into potential fuel products. Pyrolysis is considered a useful method for recycling scrap tires. These hydrous pyrolysis experiments were conducted to test the effects of water on product composition and yield from scrap tire rubber. The chemical compound compositions of the alteration products from two different pyrolysis conditions have been determined by gas chromatography–mass spectrometry. Two sets of experiments were conducted at temperatures ranging from 150 to 400 °C with contact periods of 48 h. The reaction mixtures of the first set included only shredded scrap tire rubber and water, whereas the second set also contained oxalic acid to provide excess hydrogen to enhance reduction of rubber pyrolysate. The yields of the total alteration products increased with temperature both in the presence and absence of oxalic acid, and were higher with oxalic acid. Hydrocarbon concentrations increased in the temperature range of 250–350 °C for both experiment sets and decreased noticeably at 400 °C due to cracking processes. The products confirm that alteration of scrap tire rubber in aqueous medium occurs rapidly and efficiently under reductive pyrolysis conditions above 150 °C. At temperatures above 350 °C cracking of organic products was the dominant reaction, and polycyclic aromatic hydrocarbons (PAHs) were the major products.

1. Introduction

Scrap tire disposal is one of the complex environmental problems. Currently, most of the scrap tire wastes are disposed in different sites of landfills. This is not a realistic solution, because of long term residence, and allied space limitation and health problems. The composition of passenger vehicle tires is approximately 85% carbon, 10–15% fabric materials and 0.9–1.25% sulfur [1]. The typical percentages of the rubber mix are 55% synthetic rubber (polybutadiene) and 45% natural rubber (latex) in passenger vehicle tires [1]. Thus, the abundant organic matter (OM) contents of tires can be converted into useful products for energy sources [1–3].

Various pyrolysis methods are common techniques that have been used to convert biomass into useful fuels for energy [3–12].

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Pyrolysis can be considered as a viable recycling technology for treatment of scrap tires [3,11–18]. It is a conversion process, where OM is heated at various elevated temperatures in an oxygen-free environment [19], and produces solid carbonaceous materials (char), liquid product (oil and tar), volatiles and gases. Previous pyrolysis experiments on scrap tires have been performed with different procedures, including thermogravimetric analysis [20,21], fixed bed reactors [22–25], fluidized bed pyrolysis units [4,7,10,26], spouted beds [8,9,11], rotary kiln [6,12] and vacuum pyrolysis units [27–32]. Those experiments were performed in laboratory and commercial scale plants. The pyrolysis studies of scrap tires have focused on different factors such as the products, temperature, time, size of the starting material, and sometimes the associated additives. Product characteristics and yields for pyrolysis depend on feedstock and operating conditions of the experiments as well as the size and the type of the reactor [14]. Therefore, results by different researchers are expected to vary. For example, de Marco et al. [23] and Roy et al. [32] found no influence of temperatures over 500 °C on pyrolysis yields. Other experiments demonstrated that oil yield decreased with temperature increases from 450 to 600 °C [22]. Williams et al. [25] reported that liquid yield increased in the temperature range from 300 to 720 °C and the effect of temperature was slight over 600 °C. Another study showed that oil yield decreased by raising the temperature from 640 to 840 °C [26]. It is obvious that the pyrolysis temperature and experimental conditions affect the yields and characteristics of the products, which vary from one experiment to another [4,6,14,22,31]. The variations in the resulting products by different researchers are likely due to the various experimental heating rates [7].

The role of water in pyrolysis experiments of OM has been demonstrated to be necessary for maximum formation of oil-like products under hydrous conditions [33]. The presence of water in catagenetic experiments is generally regarded as an important component of pyrolysis reactions, because it facilitates the ionic mineral reactions and regulates the Eh and pH of the aqueous system [34–37]. Therefore, the presence of water is essential during the thermal alteration of OM. Here we hypothesize that: (1) pyrolysis of tire organic matter can proceed in the presence of water, (2) the conversion yield maximizes under reductive hydrous pyrolysis conditions, and (3) lower temperatures are needed to convert tire OM under reductive hydrous pyrolysis conditions.

The main goal of this research is to study the effects of temperature and different experimental conditions in hydrous confinement pyrolysis on the chemical compound composition of the alteration products from vehicle tire rubber. Therefore, vehicle tire scrap was subjected to hydrous pyrolysis at different experimental conditions and including with additional hydrogen (reductive). The data and information obtained from this experimental approach are discussed to define yields, compound distributions, compound transformations and alteration processes.

2. Experimental procedures

Scrap passenger vehicle tires (Hankook 175/80 R14 Radial Tubeless) were collected from local puncher shops in the city of Riyadh, Saudi Arabia. The tire samples were cut into small pieces to remove threads and other non-rubber materials, shredded into small pieces, washed, dried and kept until experimental use. A sub-sample was analyzed using a CHN analyzer in the College of Sciences, King Saud University.

About 50 mg of the shredded scrap tire sample was extracted with dichloromethane and methanol mixture (3:1, v/v). The extract was filtered using glass fiber filter for the removal of suspended particles. The filtrate volume was adjusted to exactly 100 μL by addition of dichloromethane/methanol. The analysis of the derivatized extract was performed by gas chromatography–mass spectrometry (GC–MS). More information can be found in the appended Supplemental materials (SM).

We used 316 stainless steel vessels constructed with Sno-Trik high-pressure couplings [38–41] to study the alteration products of vehicle tire rubber under hydrous pyrolysis conditions. The description of the reactor is explained in SM-1.3. Two experimental sets were prepared for particular reaction conditions. Experiment set 1 was a mixture of doubly distilled water and about 30 mg of small pieces of scrap tire. The addition of pre-extracted solid oxalic acid dehydrate (99.5%, EM Science) to experiment set 1 gave experiment set 2. Aqueous oxalic acid ($C_2H_2O_4$) degrades to formic acid (CH_2O_2) and CO_2 at 160–230 °C following first order kinetics [42]. In the presence of excess water and at higher temperatures, formic acid decomposes to H_2, CO_2, CO and H_2O [43]. This decomposition provides hydrogen for reduction and the estimated pH of the aqueous oxalic acid at 25 °C is about 0.54 (acidic condition). The temperature settings were 150 °C, 250 °C, 300 °C, 350 °C and 400 °C for the two experiment sets. Upon removal from the oven, each sample was transferred to a glass vial after cooling to room temperature, where the vessel was rinsed with methylene chloride/methanol and added to the vial. Each extract was concentrated to approximately 50–100 μL. Aliquots of extracts were treated with silylating reagent [N,O-bis(trimethylsilyl)trifluoroacetamide, Pierce Chemical Co.] (BSTFA) before the GC–MS analysis.

The analysis of the alteration products and external standards was carried out with an Agilent GC–MS. The Agilent Chemstation software program was used to acquire and process the GC–MS data. The mass spectra of the fragmentation patterns were used to characterize and interpret the unknown compounds. The quantification of each compound was based on the compound area derived from total ion current (TIC) profile or key ion fragmentograms [44]. Detailed information is given in the SM-1.4.

3. Results and discussion

3.1. Nature of the starting OM

The elemental analysis of scrap tire showed that it contained 85.4% carbon, 7.7% hydrogen, 0.5% nitrogen, and 2.7% sulfur (Supplementary materials). The extract yield of the vehicle tire sample is found in Table 1 (Ambient column). The major components of the tire rubber extract were *n*-alkanes, *n*-alkanoic acids, methyl *n*-alkanoates, phenolic antioxidants, resin acids, hopane biomarkers (fossil fuel tracers, [45–47] and an unresolved complex mixture (UCM) of branched and cyclic compounds [48] (Fig. SM-2a). The vehicle tire is composed of a mixture of vulcanized synthetic and natural rubbers [49]. Synthetic rubber is a copolymer of styrene and butadiene (SBR), where primarily *cis*-butadiene is polymerized with styrene as terminator [3]. Natural rubber (NR) is mainly polyisoprene (latex). Vehicle tire rubber is usually a vulcanized mixture of SBR and NR, with antioxidants, antiozonants, and additives such as carbon black and fabric [50]. The major components of the extract from the starting tire sample were UCM, *n*-alkanes, *n*-alkanoic acids, methyl *n*-alkanoates, hopanes, and plasticizers (Fig. SM-2). The presence of hopane biomarkers, UCM and *n*-alkanes was likely from mainly additive components of petroleum tar/oil in the tire rubber, as well as from minor road asphalt and vehicle exhaust that were adsorbed on the tire surface with time. The *n*-alkanes in the initial sample extract ranged from C_{20} to C_{38}, with a carbon number predominance or carbon preference index (CPI, [48]) of 0.99 and carbon number maximum (C_{max}) at 32 (Table 1). This distribution indicates that they were from petroleum sources as part of the tire composition or adsorbed to the tire surface.