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Liquid fuels and chemicals from pyrolysis of motorcycle tire waste: Product yields, compositions and related properties

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ABSTRACT

In this study, experiments have been conducted on the sample of solid motorcycle tire wastes to determine particularly the effect of temperature, feed size, and apparent vapor residence time on the pyrolysis product yields and their compositions. The maximum liquid yield of 49 wt.% was obtained at a final pyrolysis temperature of 475 °C, feed size 4 cm^3, with a residence time of 5 s under N_2 atmosphere in a fixed-bed fire-tube heating reactor system. The pyrolysis liquid products were characterized by elemental analysis and various chromatographic and spectroscopic techniques. Chromatographic and spectroscopic studies on the liquids show that it can be used as liquid fuels and chemical feedstock, with a calorific value of 42.00 MJ/kg and empirical formula of $CH_{1.27}O_{0.025}N_{0.006}$.

1. Introduction

Bangladesh is one of the developing and most densely populated (914 persons/km^2) countries, with a total population of 135 million. About 77% people live in rural areas owing to its fertile land; agriculture is remaining as the major occupation. The road conditions in the rural areas are almost narrow and un-constructed, and hence more than 2% of adult (15–64 years old) male population (43 million) use motorcycle for their faster movement [1]. It is estimated that 1.72 million (5160 metric ton) of motorcycle tires become scrap every year and wait for disposal. The estimated value is about 6.16 wt.% of total tire waste generation in Bangladesh. Moreover, motorcycle is also a common carrier for faster movement all over the world.

The disposal of solid tire wastes from human activity is a growing environmental problem for the modern society, especially in developing countries. This organic solid waste is non-biodegradable. One common way of disposal is landfilling. Landfilling for disposal of used tires is connected with some problems: it needs a considerable amount of space because the volume of tires cannot be compacted. Dumped scrap tire in massive stockpiles is one of the possible causes of ideal breeding grounds for disease carrying mosquitoes and other vermin with the aid of rain water, which is deposited in the free space of the tire wall. Also, landfilling is a potential danger because of the possibility of accidental fires with high emissions of hazardous gases. Moreover, different alternatives are often used for tire recycling such as retreading, reclaiming, incineration, grinding, etc. with significant drawbacks and/or limitations [2].

Pyrolysis for energy recovery from organic solid wastes basically involves the decomposition of the wastes at high temperatures (300–900 °C) in an inert atmosphere. Three products are typically obtained from the organic solid wastes: liquids, solid char and gases. The pyrolysis of solid tire wastes has received increasing attention since the process conditions may be optimized to produce high energy density liquids, char, and gases. In addition, the liquid products can be stored until required or readily transportation to where it can be most efficiently utilized. Tire pyrolysis liquids (a mixture of paraffins, olefins, and aromatic compounds) have been found to have a high gross calorific value (GCV) of around 41–44 MJ/kg, which would encourage their use as replacements for conventional liquid fuels [2–10]. In addition to their use as fuels, the liquids have been shown to be a potential source of light aromatics such as benzene, toluene, and xylene, which command a higher market value than the raw oils [2–4,8,11,12]. Similarly, the liquids have been shown to contain monoterpene such as limonene [1-methyl-4-(1-methylethenyl)-cyclohexene], a high value light hydrocarbon. Limonene has extremely fast growing and wide industrial applications including formulation of industrial solvents, resins, and adhesives, as a dispersing agent for pigments, as a fragrance in cleaning products and as an environmentally acceptable solvent [7–9,13]. It is very common in cosmetic products and also used as flaming combustible liquid. Furthermore, the biological activity of limonene, such as its chemopreventive activity against rat mammary cancer, has been recently investigated [7]. In order to enhance the marketability of tire pyrolysis liquids, Stanciulescu and Ikura [14,15] separated

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limonene-enriched fraction using vacuum distillations and reacted with methanol to produce limonene ethers. Methyl limonene ether is a high value product and has a very pleasant fragrance. It can be used alone or as an odor-improving additive. The former researcher groups [7–9,13] extensively investigated separation of limonene from tire derived pyrolysis liquids using various techniques. Pyrolytic char may be used as a solid fuel or as a precursor for activated carbon manufacture [2,8,10,16]. Roy et al. [9] investigated that another potentially important end-use of the pyrolytic carbon black may be used as an additive for road bitumen. Furthermore, active carbons were prepared from used tires and their characteristics were investigated by Roy et al. [9], Zabaniotou and Stavropoulos [17], and Zabaniotou et al. [18]. They reported that active carbons, produced from tire chars, possess surface areas comparable with those of commercially available active carbons (areas around 1100 m^2/g). Some of the previous researcher groups [2,4,8,11,19] studied the composition of evolved pyrolysis gas fraction and reported that it contains high concentrations of methane, ethane, butadiene, and other hydrocarbon gases with a GCV of approximately 37 MJ/m^3, sufficient to provide the energy required by the pyrolysis process.

A variety of scrap tires are available in the modern society. These are bicycle and rickshaw tires, motorcycle and auto-rickshaw tires, car and taxi tires, microbus and jeep tires, tractor tires, bus and truck tires. Tires contain vulcanized rubber in addition to the rubberized fabric with reinforcing textile cords, steel or fabric belts, and steel-wire reinforcing beads [20]. Other components in the tire are: carbon black, extender oil, which is a mixture of aromatic hydrocarbons, sulphur, accelerator, typically an organo-sulphur compound, zinc oxide, and stearic acid [20–22]. There are many different manufacturers and countless different formulations available all over the world; the composition of the tire varies depending on the tire grade and manufacturers. Consequently, the tire pyrolysis products may also vary in terms of yield and chemical composition depending on the source and grade of the tires. Ucar et al. [23] determined the polymer types in rubber content of scrap truck and car tire wastes and reported that truck tire waste contained natural rubber (NR) 51 wt.%, styrene–butadiene rubber (SBR) 39 wt.%, and butadiene rubber (BR) 10 wt.% while car tire waste contained NR 35 wt.% and BR 65 wt.%. They also found significant variations in proximate and ultimate analyses of the two different solid tire wastes and variations in pyrolytic product yields and liquids and gaseous products compositions. Kyari et al. [24] studied pyrolysis analysis of seven different brands of used car tires from several countries throughout the world and characterized the product liquids obtained from individual and mixture of seven categories of tire wastes. They reported that there had been significant variation in concentration of different compounds presented in the derived liquids and gaseous products. Cypres and Bettens [21] have shown that pyrolysing different brands of automotive tires results in significant differences, of the order of 10%, in the yields of solid, liquid, and gaseous products. For the development of the pyrolysis processes, there is a need to understand the influence of different types of tire waste ranging from bicycle to truck tires available in different communities, on the yields and compositions of the derived products. There have been many pyrolysis woks [2–53] in international literature for automotive tire wastes but there is no work for the influence of rubber content of motorcycle tires on the product yields and compositions. Thus, it is crucial to investigate the pyrolysis behaviors of the motorcycle tire wastes including pyrolytic product yields and product characteristics.

Very different experimental procedures have been used to obtain liquid products from automotive tire wastes by pyrolysis technology including fixed-bed reactors [3,4,8,11,23–32,34], fluidized-bed pyrolysis units [6,33,35], vacuum pyrolysis units [7,9,36–39], spouted-bed reactors [40], etc., ranging from laboratory to commercial scale plants. Pyrolysis yields and characteristics of the products obtained from tire wastes depend on type and size of feedstock, size, and system configuration of reactor, efficiency of heat transfer, vapor residence time, etc. A fixed-bed consists of individual feed particles of different shapes and sizes, which are in contact with each other or with the void in between. Maximum liquid yields are obtained with high heating rate, at reaction temperature around 500 °C and with short vapor residence time. The heat transfer rate requirement imposes particle size limitations on the feed. The cost of size reduction in financial and energy terms have been clearly realized and similarly liquid yields from the very smaller size feed is low due to the fact that too quick devolatilization occurs and secondary reaction takes place in the reactor. Moreover, longer vapor residence time contributes to secondary reactions, which leads to less oil and more gas product. A number of research works [3,4,8,23,25,27,31,32,37,51–53] have been performed for the effect of reactor temperature on the product yields and product compositions but there have been very limited studies [6,10] in the international literature for the effect of feed size and vapor residence time in tire wastes pyrolysis regime. Dai et al. [6] and Barbooti et al. [10] investigated the effects of feed size and vapor residence time on product yields and compositions with respect to operating temperature for circulating fluidized-bed and fixed-bed reactor, respectively but poorly detailed. However, more understanding for optimum operating conditions in relation to the range of reactor temperature, larger feed size and vapor residence time, which make influence on the yields and composition of the derived products are essential to develop a more efficient pyrolysis unit.

In the present study, to provide a new approach in heating system for fixed-bed pyrolysis technology to the recovery of hydrocarbons from used tires, we have investigated fixed-bed pyrolysis with a fire-tube heating reactor. This process of heating has proved very effective in the technology for fire-tube steam boilers. The thermal recycling of motorcycle tire wastes by pyrolysis technology has been carried out in the internally heated fire-tube heating reactor system under N_2 atmosphere. The effects of operating temperature, feed size, and vapor residence time on the yields and compositions of product liquids were investigated. A detailed characterization of the whole pyrolysis liquids obtained at optimum operating conditions has been carried out including physical properties, elemental analyses, GCV, FT-IR, ^{1}H NMR, GC–MS analysis and distillation.

2. Materials and methods

2.1. Feed materials

The Indian made "MRF" brands of motorcycle tires, which are mostly consumed in Bangladesh, has been taken into consideration as feedstock throughout the experimental investigations and it was collected locally from a dumpsite of the Rajshahi City Corporation. The main components of tires such as rubber, fillers like carbon black, steel, sulfur, zinc oxide, processing oil, vulcanization accelerators, etc. are heterogeneously distributed over the cross-section. Therefore, in order to maintain uniformity of the components in the representative samples, very same tires were chopped cross-section wise into four different sizes of 8 cm × 1 cm × 0.25 cm = 2 cm^3; 8 cm × 1 cm × 0.50 cm = 4 cm^3; 8 cm × 1 cm × 1 cm = 8 cm^3 and 8 cm × 1 cm × 1.50 cm = 12 cm^3. The cross-section pieces, which were representative of the whole tire, contained no steel cords but the textile fabrics.

2.1.1. Major composition of motorcycle tire rubber

A representative sample of the whole tire waste has been prepared grinding the steel cords and textile fabrics free rubber for